SYNTHESIS AND REACTIVITY OF CYCLIC, TRISUBSTITUTED OLEFINS

by

James Wesley Rhoades

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by James Wesley Rhoades

entitled Synthesis and Reactivity of Cyclic, Trisubstituted Olefins

be accepted as fulfilling the dissertation requirement for the degree of Doctor of Philosophy

H. K. Hall, Jr. — Dissertation Director — 6/24/78 — Date

As members of the Final Examination Committee, we certify that we have read this dissertation and agree that it may be presented for final defense.

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SIGNED: James W. Rhoades

TO MY WIFE, KATE

ACKNOWLEDGMENTS

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ABSTRACT

The first maleic anhydride containing a single strongly electron-withdrawing substituent, carbomethoxymaleic anhydride was synthesized and its cycloaddition and polymerization reactions were explored.

Carbomethoxymaleic anhydride was found to be a more reactive dienophile than either maleic anhydride or tetracyanoethylene in Diels-Alder reactions. Diels-Alder adducts were prepared with cyclopentadiene, anthracene, furan, butadiene, isoprene and chloroprene. Carbomethoxymaleic anhydride reacted with anethole and with p-methoxystyrene to give double Diels-Alder adducts.

Carbomethoxymaleic anhydride could be homopolymerized with either free radical or anionic initiation and it polymerized without initiation on heating or exposure to UV radiation. Carbomethoxymaleic anhydride spontaneously copolymerized without initiation with a number of electron-rich olefins, including styrene, p-methoxystyrene, 2,5-dichlorostyrene, isobutyl vinyl ether and vinyl acetate. These polymerizations occurred when the monomers were mixed neat or in solution. The formation of a charge-transfer complex was suspected in these polymerizations. In addition, free radical copolymers were prepared with methyl methacrylate, acrylonitrile and

tricarbomethoxyethylene. In no case was the formation of any cyclobutanes observed.

Attempts were also made to synthesize cyanomaleic anhydride, acetylmaleic anhydride and N-phenylcarbomethoxy-maleimide.

INTRODUCTION

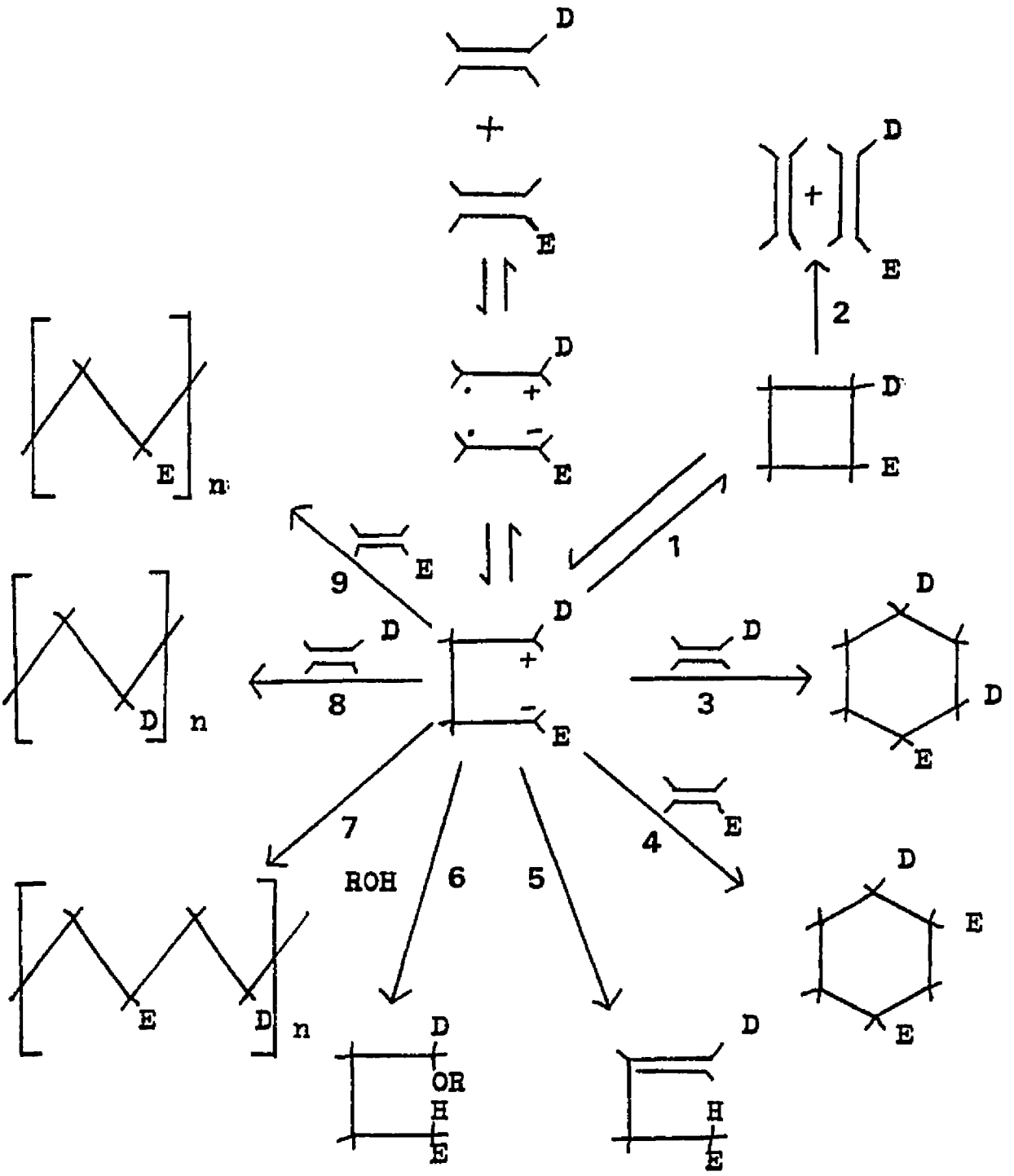
An area of organic chemistry in which there has been growing interest is the reactions and interactions between electron-rich and electron-poor olefins, that is between olefins containing one or more electron-donating groups and those with one or more electron-withdrawing substituents. The work reported here represents part of an on-going investivation into the chemistry of trisubstituted electron-poor olefins. These compounds are of interest for a number of reasons.

First of all, although much work has been done on the polymerization of mono-and disubstituted olefins, until recently little has been reported on the polymerizations of trisubsti uted olefins. This is probably because these olefins do not homopolymerize, a fact which is generally attributed to steric hindrance caused by the β-substituent. They do copolymerize, however. One might expect the reactivity of trisubstituted olefins to be similar to that of monosubstituted ones because, while the β-substituent decreases reactivity sterically, the second α-substituent should increase reactivity due to added stabilization of the growing radical. In recent investivations (Noren and Hall 1972, Hall and Daly 1975) the polymerizations of several trisubstituted olefins containing strongly

electron-withdrawing substituents, specifically tricyanoethylene, ethyl 2,3-dicyanoacrylate, dimethyl cyanofumarate and tricarbomethoxyethylene were examined. Although these compounds failed to homopolymerize, they readily copolymerized with a number of electron-rich monomers (various styrenes, vinyl ethers, vinylcarbazole, etc.) to give 1:1 alternating copolymers.

A second reason for interest in trisubstituted olefins is that they might prove to be useful cycloaddition partners, thus paving the way to some new and interesting cyclobutanes or cyclohexanes. Hall and Ykman (1975) examined the four electron-poor olefins mentioned earlier and studied their cycloaddition reactions with electron-rich olefins such as enamines, vinyl ethers and vinyl sulfides. In these cases, as in others, it has been shown that under the right conditions electron-rich and electron-poor olefins can react to form a number of interesting compounds (Figure 1). The initial formation, perhaps via a charge-transfer complex, of a cation radical-anion radical pair, followed by coupling to produce the zwitterion has been proposed. Depending again on the olefins involved, the solvent etc., a number of final products can be produced.

Coupling can produce the cyclobutane (1) which may be stable or may open up, giving either the original reactants or the olefin metathesis products (2), or the zwitterion can add a second molecule of either donor (3) or



D = Electron-Donating Substituent

E = Electron-Withdrawing Substituent

Fig. 1. Possible Donor-Acceptor Reactions

acceptor (4) to produce a cyclohexane. In cases where a β-hydrogen is present, rearrangement to an alkene (5) is possible and in protic solvents the zwitterion may be trapped (6). Polymerization to produce a 1:1 alternating copolymer (7) or zwitterion initiated homopolymerization of either donor (8) or acceptor (9) is also possible. The exact mechanisms involved and the exact effects of various substituents and/or reaction conditions has only recently begun to be investigated.

In light of what has been said above, a particularly interesting class of compounds to study would be cyclic electron-poor trisubstituted olefins, such as substituted maleic anhydrides or maleimides. Such compounds should be as reactive toward polymerization as those studied by Hall and Daly, and perhaps more reactive since the β-substituent is confined by the ring, thus decreasing steric hindrance and allowing effective resonance. Homopolymerization might even be possible since the parent maleic anhydride is known to polymerize to some extent (Gaylord 1975) and the presence of an added α-substituent should enhance reactivity. The cycloadditions of such cyclic olefins might offer a route to new and unusual bicyclic compounds.

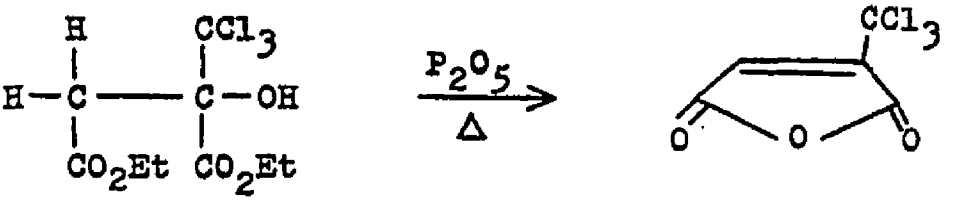
Interestingly, a search of the literature showed that, although a number of substituted maleic anhydrides and maleimides with weakly electron-withdrawing

substituents (e.g., F, Cl, CF_3, SO_3H) are known, none is known with a strongly electron-withdrawing substituent (e.g., CN, CO_2R, $COCH_3$). Initial attempts to synthesize cyanomaleic anhydride, acetylmaleic anhydride and the corresponding N-phenylmaleimides (Wai 1976) unfortunately, all proved unsuccessful. The research reported here deals with the first successful synthesis of a maleic anhydride containing a single strongly electron-withdrawing substituent, namely carbomethoxymaleic anhydride, and the subsequent cycloadditions and polymerizations of this unusual compound. In addition, several other attempted syntheses of cyclic trisubstituted olefins are reported.

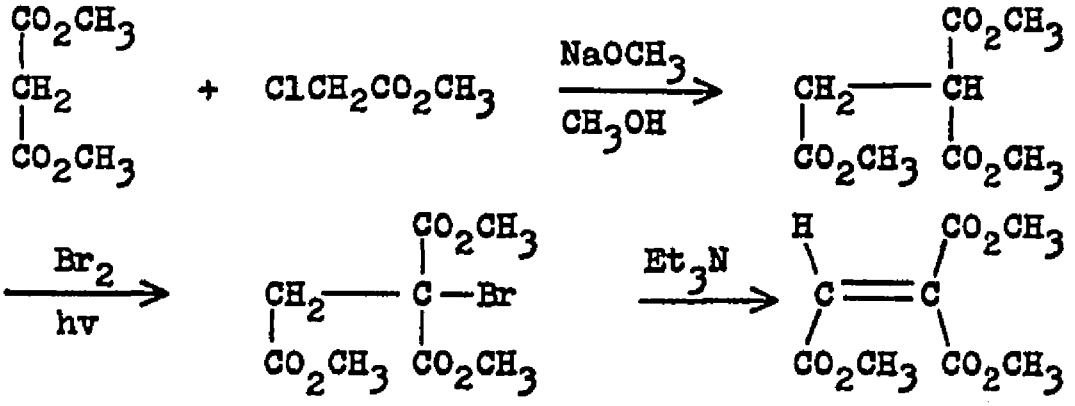
RESULTS

Synthesis of Carbomethoxymaleic Anhydride

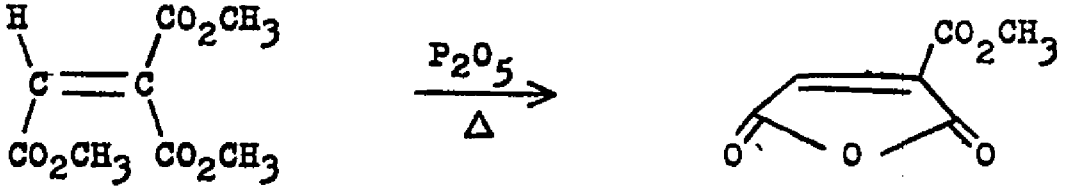
The synthesis of carbomethoxymaleic anhydride was modeled after a reaction reported by Bowman, Closier and Islip (1964) in which they made trichloromethylmaleic anhydride from diethyl α-hydroxy-α-trichloromethylsuccinate by heating with phosphorus pentoxide.



Tricarbomethoxyethylene was available from the work of Hall and Daly (1975) via malonic ester alkylation.



Heating it with two equivalents of phosphorus pentoxide to 180° for one hour and distilling under vacuum gave carbomethoxymaleic anhydride.

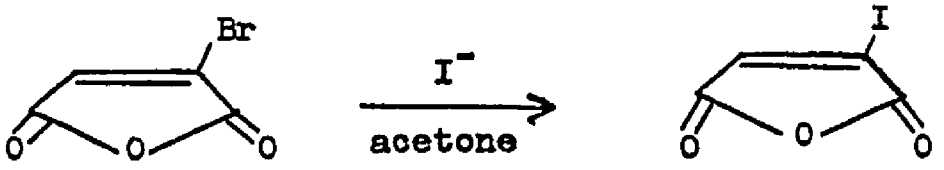


A white powder found in the dry ice trap consisted mostly of dimethyl fumarate plus some other unidentified olefin. The product was somewhat contaminated with unreacted tricarbomethoxyethylene, but could be purified by recrystallization from diethyl ether (yield 66%). Carbomethoxymaleic anhydride is a white solid, mp 37-38°, soluble in chloroform, acetone and water.

Attempted Synthesis of Cyanomaleic Anhydride

Via Substitution Reactions

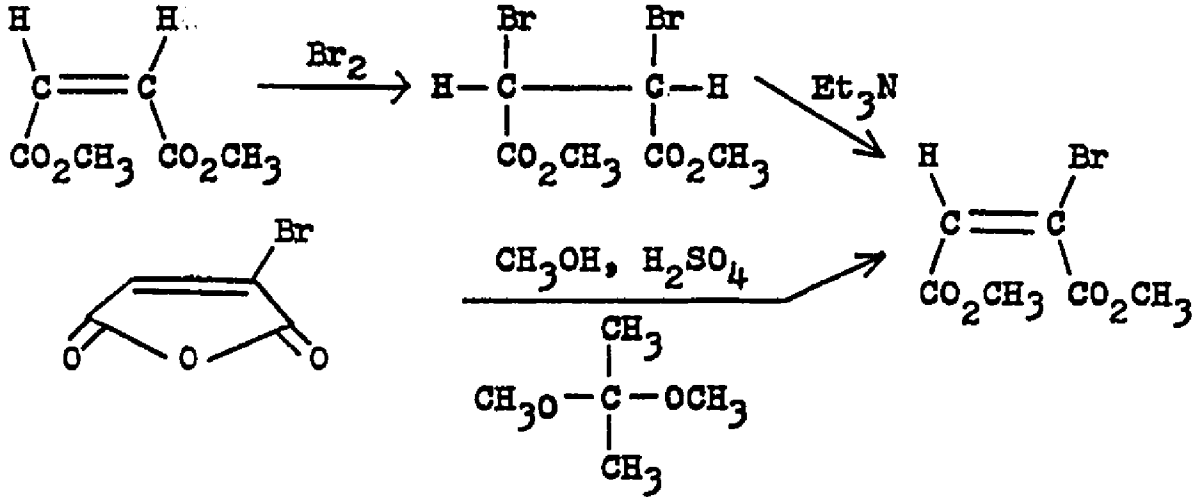
Several attempts had been made previously by Wai (1976) to synthesize cyanomaleic anhydride by nucleophilic substitution of bromide in bromomaleic anhydride with cyanide. All were unsuccessful. Since iodide is a better leaving group than bromide, it seemed logical to try the same substitution on iodomaleic anhydride. A search of the literature revealed that, although diiodomaleic anhydride is known (Diels and Reinbeck 1910), apparently the monosubstituted anhydride is not. It was easily synthesized from bromomaleic anhydride, however, by iodide exchange in acetone.



Unfortunately treatment with either silver cyanide or cuprous cyanide in acetonitrile at reflux for 20 - 45

minutes failed to convert the iodide to cyanide as it had failed for bromomaleic anhydride.

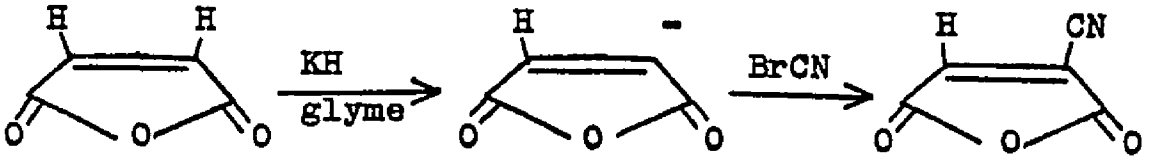
Even though cyanide would not replace bromide or iodide in the halomaleic anhydride, it might replace it in dimethyl bromomaleate, which could then be cyclized with phosphorus pentoxide. Dimethyl bromomaleate was prepared by two different methods. Bromination and dehydrobromination of dimethyl maleate gave the desired compound, as did treatment of bromomaleic anhydride with methanol.



Various conditions were tried in order to replace the bromide with cyanide. Heating dimethyl bromomaleate with silver cyanide in N-methyl pyrrolidone for two hours at reflux gave only starting material. With cuprous cyanide in N-methyl pyrrolidone under the same conditions, gas chromatography showed the starting material had reacted. The presence of a nitrile was apparent in the ir spectrum, but attempts to isolate the material failed. Likewise, heating dimethyl bromomaleate and cuprous cyanide without

solvent to 200° for two to four hours produced small amounts of the same unknown product. Some of it was distilled. Spectral analysis showed a weak CN absorption at 2250 cm^{-1} in the ir, and a vinyl H at δ6.9 and a methoxyl at δ3.8, integration 1:6 in the nmr. Heating dimethyl bromomaleate to reflux with cuprous cyanide and sodium cyanide in N,N-dimethylformamide afforded homogeneous conditions. Extraction with benzene yielded an oil with CN absorption at 2250 cm^{-1} in the ir, but only in very small yield. Treatment of dimethyl bromomaleate with potassium cyanide and dibenzo-18-crown-6 in acetonitrile yielded only starting material after refluxing for three hours. When this reaction was repeated with sulfolane as the solvent at reflux for 4½ hours, ether extraction produced an oil which showed a CN absorption in the ir, but again the yield was very small. Reaction with sodium cyanide or potassium cyanide in aqueous N,N-dimethylformamide, aqueous ethanol or anhydrous methanol all failed to produce the desired substitution. Reaction did happen, but nmr showed in each case the disappearance of the double bond. Trimethylsilyl cyanide, synthesized by the method of Zubrick, Dunbar and Durst (1975), and a catalytic amount of potassium cyanide and 18-crown-6 neat at 112° for 12 hours gave no reaction.

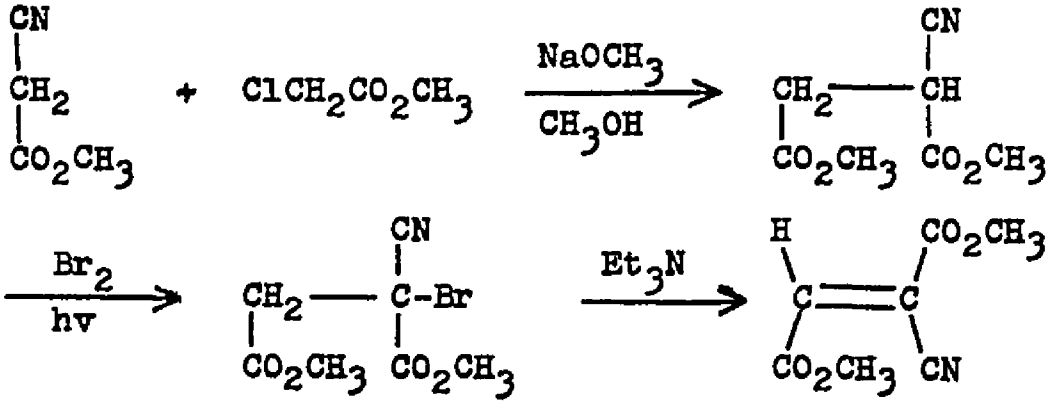
An attempt was made to synthesize cyanomaleic anhydride by the following sequence.



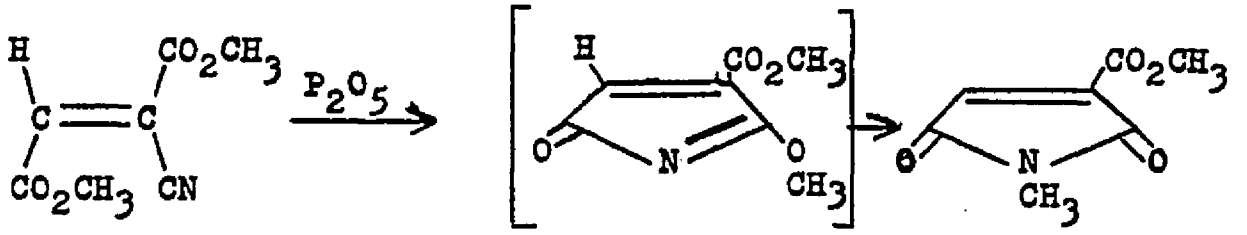
However, addition of maleic anhydride to potassium hydride in glyme failed to liberate any gas (monitored by a wet test meter). The slurry did turn pink in color but there was no other indication of reaction. Addition of N-methylpyrrolidone also failed to initiate reaction. Trimethylchlorosilane was added to trap any anions, but work-up of the mixture produced nothing but starting materials and maleic acid. The reaction was repeated, heating to 80° for one day, but still there was no evidence of reaction.

Via Isomerization

Once carbomethoxymaleic anhydride had been prepared from tricarbomethoxyethylene, it seemed logical to attempt the same reaction on dimethyl cyanomaleate. Unfortunately, although dimethyl cyanofumarate has been made (Hall and Daly 1975), the maleate has not.



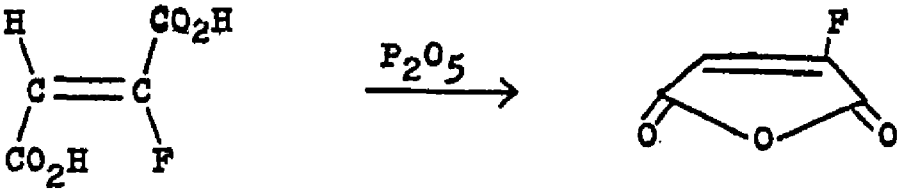
Heating dimethyl cyanofumarate with phosphorus pentoxide under the same conditions as used with the triester, resulted in a mixture of starting material and N-methylcarbomethoxymaleimide.[1]



Yield of the maleimide was poor though, and this would not seem to be a very good method for preparing maleimides.

Several attempts were made to photoisomerize dimethyl cyanofumarate to dimethyl cyanomaleate. The fumarate was irradiated with UV light in deuterobenzene with benzophenone, and in tetrahydrofuran, and in acetonitrile. In none of these cases was any of the maleate observed. Dimethyl cyanofumarate was also irradiated in the presence of 1,3,5-trimethoxybenzene in deuterochloroform and in deuteroacetone. In neither case was any of the maleate observed by nmr.

Raasch, Miegel and Castle (1959) reported that phosphorus pentoxide would convert fluorofumaric acid to fluoromaleic anhydride.



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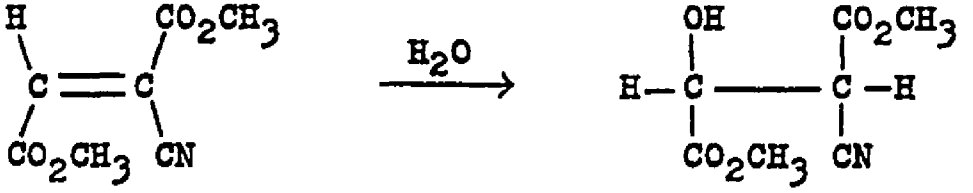
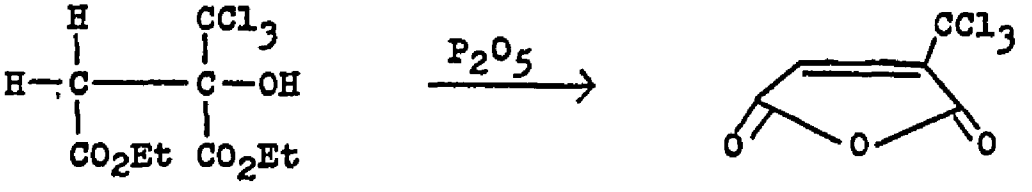
1. nmr ($CDCl_3$) δ: 3.1 (s, 1H); 3.9 (s, 3H); 7.2 (s, 1H).

If cyanofumaric acid would undergo the same reaction, an easy route to cyanomaleic anhydride would be at hand. Hydrolysis of dimethyl cyanofumarate was attempted under basic conditions (Na_2CO_3), acidic conditions (H_2SO_4) and neutral conditions (H_2O/tetra-n-propyl titanate or tetra-isopropyl titanate). In every case, the first reaction to take place was addition of water across the double bond.

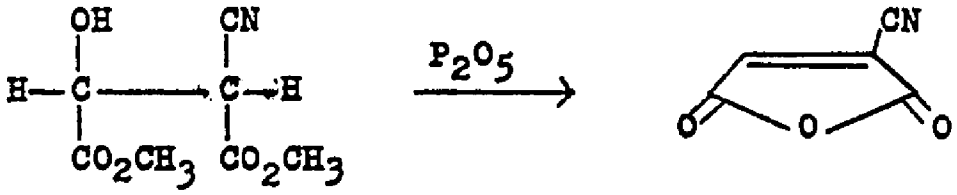


Depending on conditions used, further reactions took place. For example, with sodium carbonate some hydrolysis of ester to acid was observed, but there was also evidence of hydrolysis of the nitrile to amide and always some unreacted ester.

In this particular case, the addition of water across the double bond was not actually disappointing since, by allowing free rotation around the central C-C bond, the cyclization to anhydride and reintroduction of the double bond might be carried out in a single step. The original synthesis of carbomethoxymaleic anhydride, after all, had been modeled after the synthesis by Bowman et al. (1964) of trichloromethylmaleic anhydride.



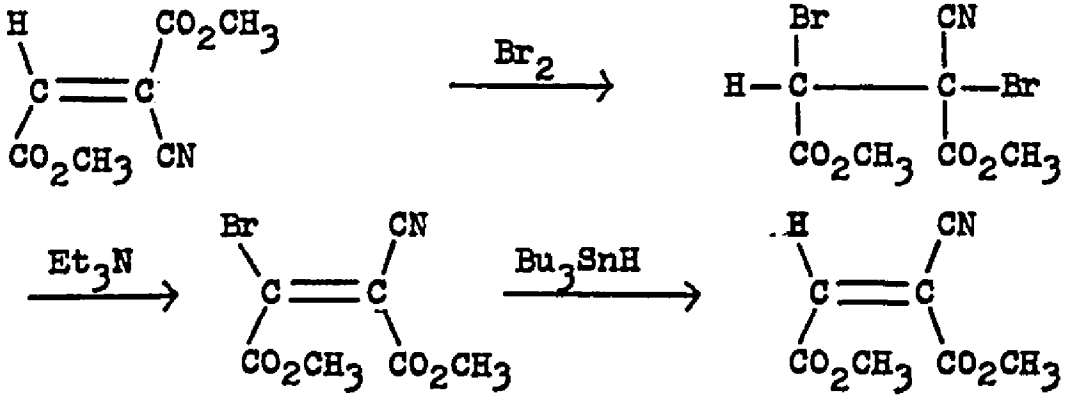
It seemed reasonable that our hydroxy compound might behave similarly.



Unfortunately, in our case the loss of water to regenerate the double bond happened more readily than cyclization. Heating the alcohol with phosphorus pentoxide simply regenerated the dimethyl cyanofumarate which was then distilled. There was also some evidence for the formation of N-methylcarbomethoxymaleimide as had been observed before on heating dimethyl cyanofumarate with phosphorus pentoxide. Attempts to hydrolyze the ester under nonaqueous conditions with lithium iodide in collidine or with triethylenediamine (DABCO), neat were also unsuccessful.

Via Bromination and Dehydrobromination

Conversion of dimethyl cyanofumarate to the maleate was attempted by the following reaction sequence.

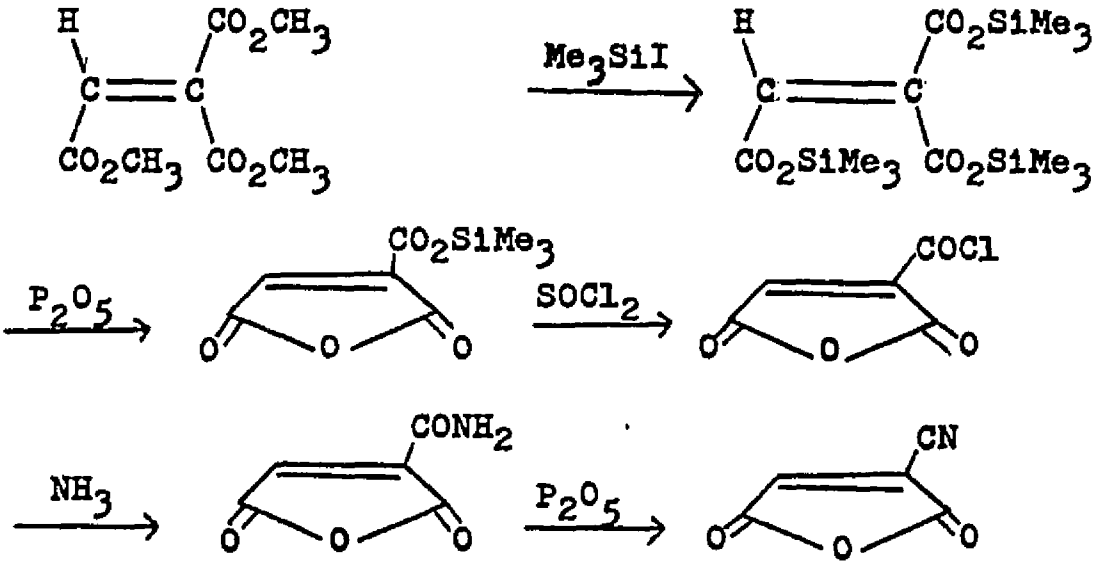


Dimethyl cyanofumarate, however, failed to decolorize

bromine. NMR showed the disappearance of the vinyl H and addition of triethylamine produced a white precipitate, but elemental analysis showed only half enough bromine.[2]

Via Tricarbomethoxyethylene

Jung and Lyster (1977) have reported the use of trimethylsilyl iodide to convert esters to trimethylsilyl esters which are then easily hydrolyzed or otherwise transformed. This could offer a route to cyanomaleic anhydride as follows.



However, when trimethylsilyl iodide was added to tricarbomethoxyethylene in chloroform under nitrogen, the solution immediately turned dark brown (probably I_2). After heating overnight to 55° in the absence of light, nmr showed some evidence for $CO_2Si(CH_3)_3$, but also lots of unreacted ester,

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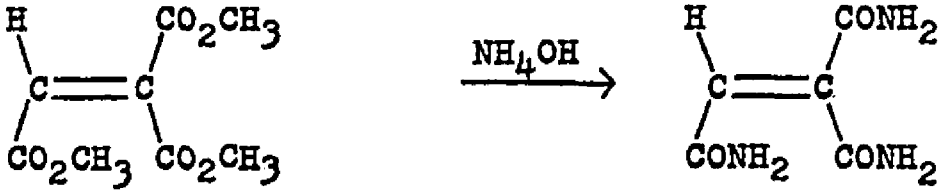
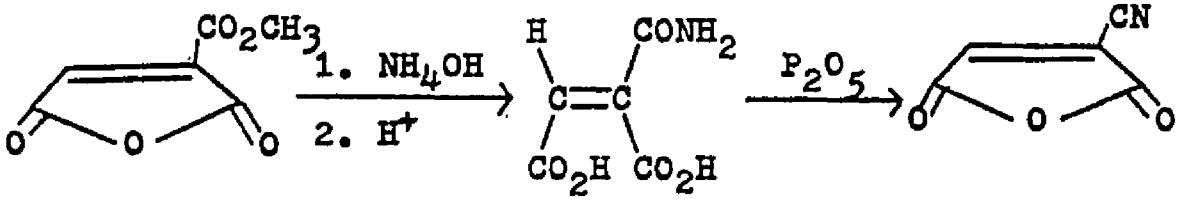
2. Anal. calcd. for $C_7H_6O_4NBr$: C, 33.89; H, 2.44; N, 5.65; Br, 32.26. Found: C, 38.21; H, 3.83; N, 3.56; Br, 19.07.

some free acid and almost no vinyl H. Apparently the reactivity of the double bond has interfered with the silylation.

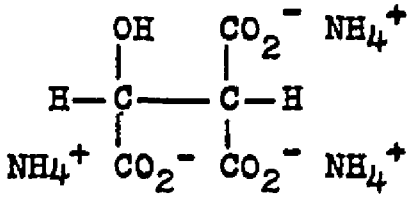
A brief attempt was made to convert tricarbomethoxyethylene to ethylenetricarboxamide.



If this could be accomplished without affecting the double bond, the following route might give the desired cyanomaleic anhydride.



With slight heating tricarbomethoxyethylene dissolved in concentrated ammonium hydroxide. Evaporation produced a yellow solid (mp 172-185° dec). The absence of a vinyl H in the nmr, however, indicated water had again added across the double bond. Since addition of potassium hydroxide to a water solution of this compound liberated ammonia, it was assumed to be the following ammonium salt.



This seemed to be consistant with an nmr (D_2O) which was featureless except for some small peaks δ3.6 - 4.8.

However, elemental analysis failed to support this structure.[3] Mass spectrum and ir spectrum of this compound were useless and attempts to acidify and extract the free acid into an organic phase failed.

Carbomethoxymaleic anhydride reacted exothermicly with ammonium hydroxide, producing a red solution. Pouring it through a Dowex (H) 50W-X8 (20-50 mesh) sulfonic acid cation exchanger to replace NH_4^+ ions with H^+ produced a yellow solution. Evaporation produced a yellow water-soluble solid, similar to that found with tricarbomethoxyethylene and ammonia except that nmr showed the presence of CO_2CH_3. Again there was no vinyl H in the nmr spectrum. Again an attempt to modify substituents appears to have been thwarted by the reactive double bond.

Via Cyanosuccinic Anhydride

One way to minimize the problem of the double bond reactivity would be to generate it in the last step. Previous attempts by Wai (1976) to dehydrogenate cyanosuccinic anhydride or dehydrohalogenate chlorocyanosuccinic anhydride had all failed. Another possible way to generate the double bond is the thermolysis of cyanobenzoyloxysuccinic anhydride. Acidic hydrogens can be replaced with a benzoyloxy group by generating the carbanion in the

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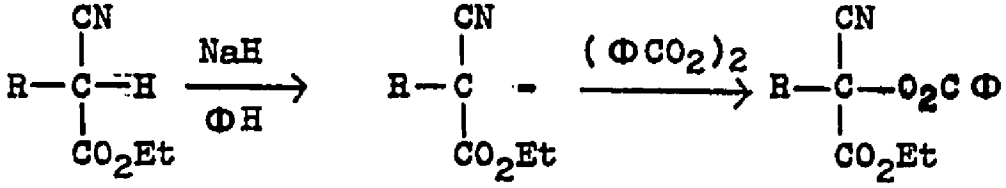
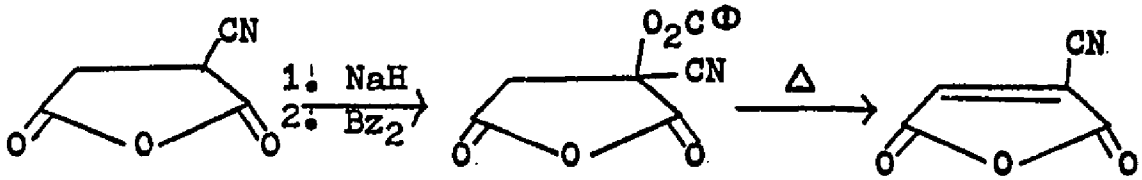
3. Anal. calcd. for $C_5H_{1.5}N_3O_7$: C, 26.20; H, 6.60; N, 18.36. Found: C, 38.34; H, 4.48; N, 22.74.

presence of benzoyl peroxide (Lawesson and Frisell 1961). For example:



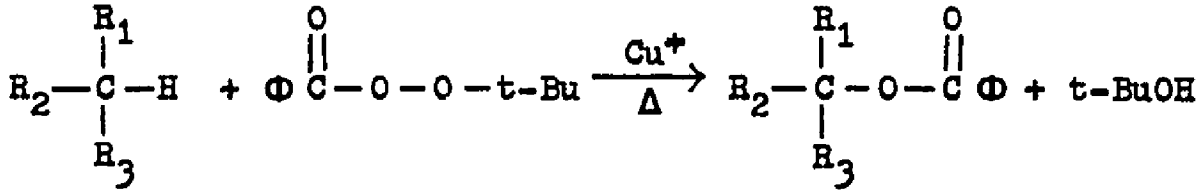
In our case the following reaction sequence might be possible.



An attempt to generate cyanosuccinic anhydride directly from dimethyl cyanosuccinate by heating with phosphorus pentoxide failed. It was synthesized, though, by the method of Wai (1976) involving hydrolysis of the ester in aqueous potassium hydroxide followed by treatment with acetic anhydride. However, treatment with sodium hydride in benzene liberated only a small fraction of the expected gas (monitored by a wet test meter). The benzoyl peroxide was added anyway. Work-up produced a brown viscous oil from which some white crystals sublimed. The white crystals proved to be biphenyl. There was evidence from nmr that the brown oil also contained benzoic acid, but there was no evidence of the desired product. The reaction was repeated in tetrahydrofuran. Again very little gas was evolved even in the presence of N-methylpyrrolidone as a catalyst. Treating dimethyl cyanosuccinate with potassium

hydride in tetrahydrofuran under similar conditions did liberate gas, but attempts to isolate the product failed.

A similar reaction for replacing an active hydrogen with a benzoyloxy group has been used by Rowlinson and Sosnovsky (1972).

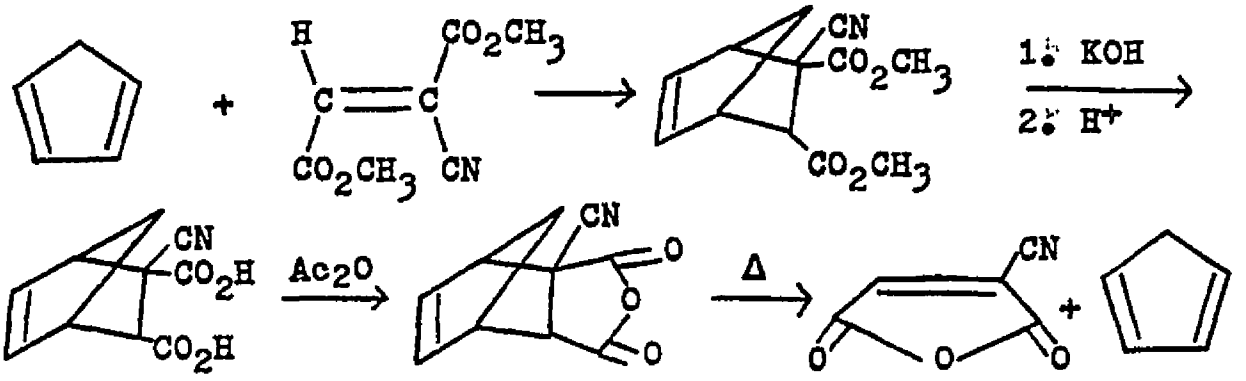


Treatment of dimethyl cyanosuccinate with t-butyl peroxybenzoate in benzene with cuprous chloride catalyst under nitrogen gave, after heating to 65-80° over a weekend, only unreacted starting material.

Via Diels-Alder Adducts

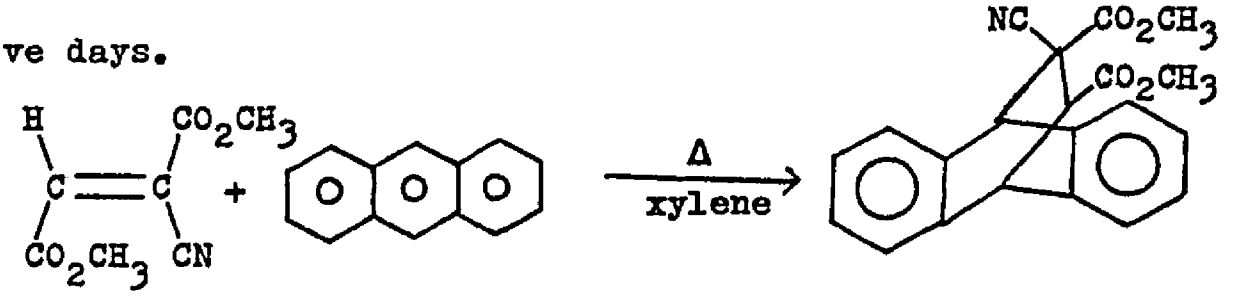
Since the reactivity of the double bond had interfered with several otherwise promising syntheses, it was decided to protect the double bond by a Diels-Alder reaction, and then to regenerate it via a retro-Diels-Alder reaction. Furan failed to give any Diels-Alder adduct with dimethyl cyanofumarate even at 55° for five days in a sealed tube. With butadiene and dimethyl cyanofumarate, the Diels-Alder adduct formed in appreciable yield only after heating the reagents neat in a sealed tube to 55° for 24 hours. Cyclopentadiene, on the other hand, reacted essentially instantaneously with dimethyl cyanofumarate in solution at room temperature. This appeared to open the

way for the following approach.



Saponification of the Diels-Alder adduct readily gave the acid, which was a crystalline solid, and treatment with acetic anhydride produced the anhydride, but attempts to crack it to cyanomaleic anhydride were unsuccessful.

The dimethyl cyanofumarate-anthracene adduct was also synthesized by refluxing the reactants in xylene for five days.

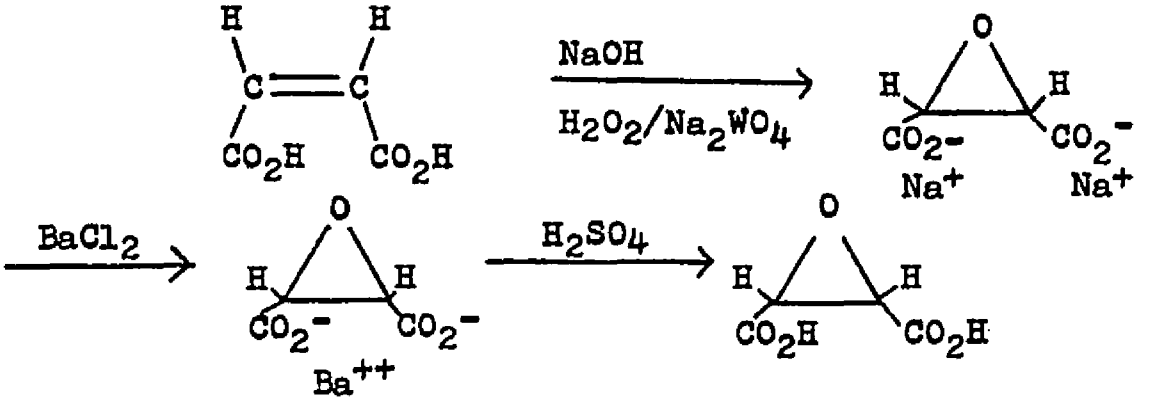


An attempt to cyclize and crack this adduct in one step by heating with phosphorus pentoxide failed, although the adduct did undergo the retro-Diels-Alder reaction liberating dimethyl cyanofumarate. Saponification to the diacid was attempted, but failed due to the insolubility of the adduct in refluxing potassium hydroxide even in the presence of methyltricaprylylammonium chloride as a phase-transfer catalyst. Non-aqueous hydrolysis with

triethylenediamine (DABCO) likewise failed, giving the monohydrolyzed product after 24 hours at 110°.

Via Epoxides

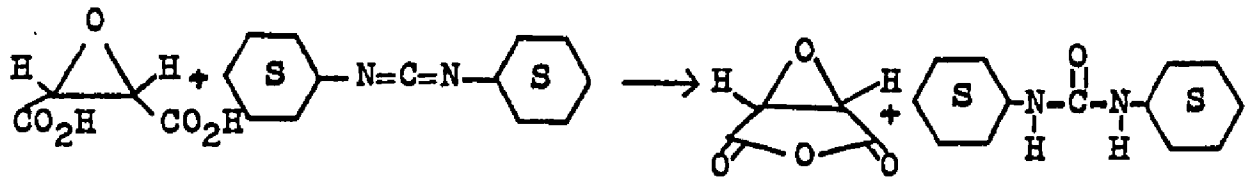
Another intriguing route to cyanomaleic anhydride was via the epoxysuccinate. Cis-epoxysuccinic acid was synthesized by the method of Payne and Williams (1959) from maleic acid.



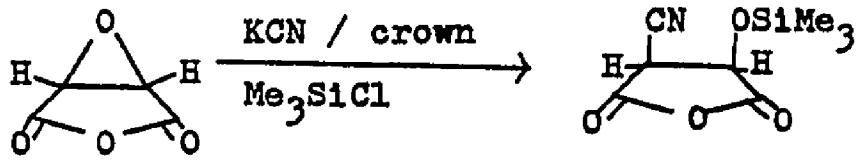
Attempts to open the epoxide with cyanide were made under both acidic and basic conditions. Treatment of cis-epoxysuccinic acid with sodium cyanide or potassium cyanide in water (pH=3) gave only starting material even when heated to 60° overnight in a sealed tube to prevent escape of hydrogen cyanide. Heating the disodium salt with potassium cyanide (pH=12) to 70° overnight produced on work-up epoxysuccinic acid and tartaric acid. Repeating with magnesium sulfate present as a buffer (pH=9) at 45-55° for one hour gave only unreacted epoxysuccinic acid.

Attempts were also made to generate cyanohydroxymaleic anhydride by addition of cyanide to cis-epoxysuccinic

anhydride, which was made from epoxysuccinic acid by the method of Creighton and Mitchell (1967).

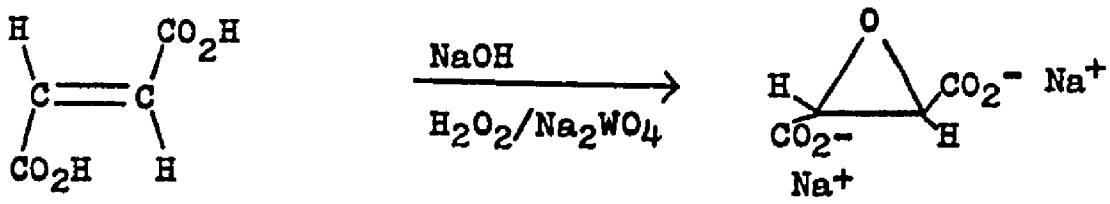


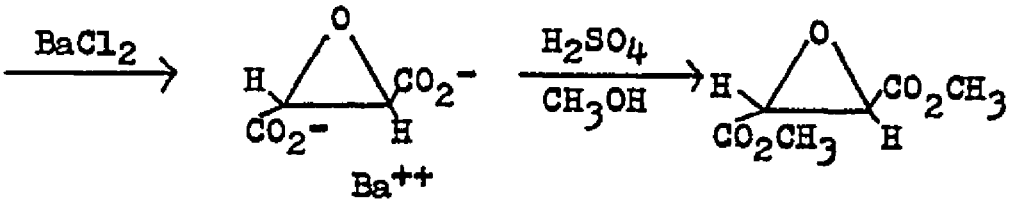
The following reaction was attempted.



Reaction did take place, but the only compounds which could be positively identified by nmr were trimethylsilyl cyanide and hexamethyldisiloxane. Several attempts were made to react trimethylsilyl cyanide directly with epoxysuccinic anhydride. Again reaction did take place, but nmr was not consistant with that expected. Distillation of the product partially regenerated epoxysuccinic anhydride. It is possible that the trimethylsilyl cyanide opened the anhydride ring rather than the epoxide to produce the acyl cyanide-TMS ester.

To avoid the problem of the reactive anhydride, the same reactions were conducted on dimethyl trans-epoxysuccinate which was synthesized from fumaric acid in a manner analogous to the previous synthesis.

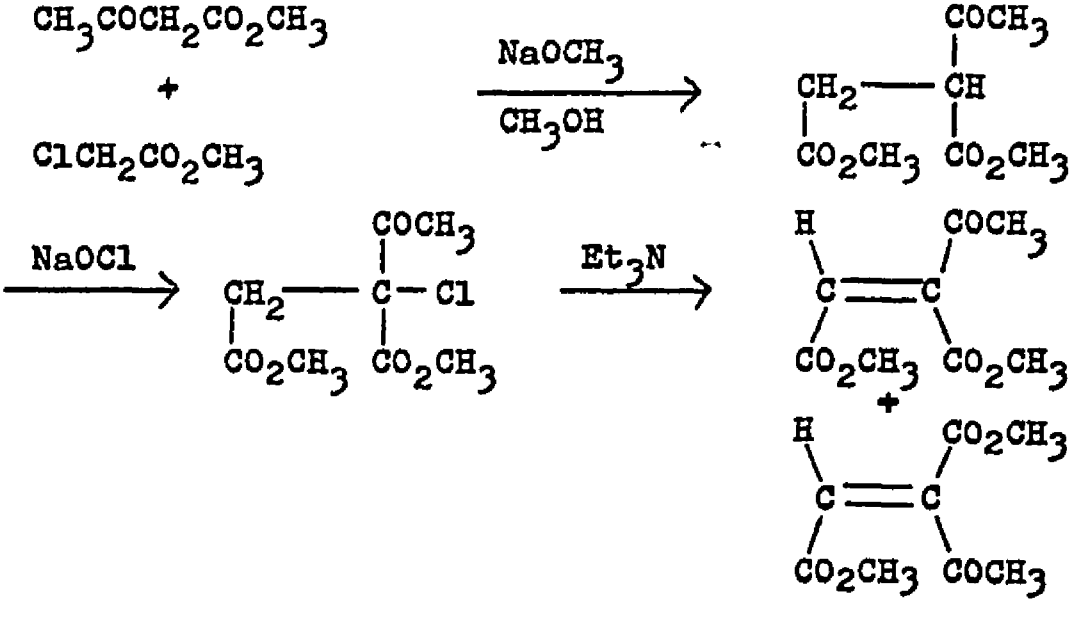




All attempts to react dimethyl trans-epoxysuccinate with trimethylsilyl cyanide failed, even when heated to 135° for three days, giving added evidence that any reaction with epoxysuccinic anhydride must have been with the anhydride functionality, rather than the epoxide. The trans ester did react with trimethylsilyl iodide. The products, however, were iodine, hexamethyldisiloxane and dimethyl fumarate.

Attempted Synthesis of Acetylmaleic Anhydride

In addition to the previous attempts to make cyanomaleic anhydride, an attempt was made to synthesize acetylmaleic anhydride. The synthesis of dimethyl acetylethylenedicarboxylate results in a 50/50 mixture of the cis and trans isomers (Wai 1976).



Heating this mixture with phosphorus pentoxide, in hopes of distilling out acetylmaleic anhydride from the dimethyl acetylmaleate, was unsuccessful, resulting in decomposition even at temperatures as low as 100°.

Attempted Synthesis of N-Phenylcarbomethoxymaleimide

An attempt was also made to synthesize N-phenylcarbomethoxymaleimide by reaction of carbomethoxymaleic anhydride with aniline in tetrahydrofuran. Under various conditions reaction produced a yellow solid (mp 54-60°). NMR of this solid showed very little CO_2H and mass spectrum indicated it was probably oligomeric, giving peaks well above the expected parent.

Reactions of Carbomethoxymaleic Anhydride

Hydrolysis

Carbomethoxymaleic anhydride is hygroscopic. On standing at room temperature in an open vial it absorbed water from the air, becoming a semisolid, chloroform-insoluble gel. Spectral analysis of this product indicated that the initial reaction with water was opening of the anhydride ring to form carbomethoxymaleic acid.[4] However, if allowed to stand, more than one equivalent of water was absorbed and the olefinic proton resonance

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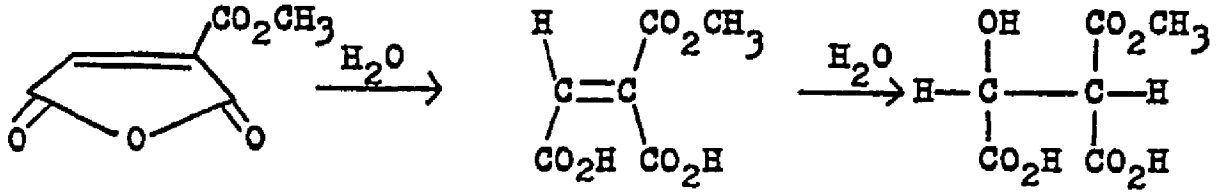
4. nmr (acetone-d6) δ: 3.7 (s, 3H); 6.8 (s, 1H); 10.2 (s, 2H), ir (acetone-d6): C=O, 1650, 1800 cm^{-1},s; OH, 3000 cm^{-1}, s (broad).

disappeared from the nmr, indicating a nucleophilic attack on the double bond by water.



This reaction could be followed in the nmr by dissolving the anhydride in D_2O. There was a small quantity of gas evolution observed when the anhydride was placed in water, but measurements of the amount indicated that it was not a significant quantity.

For comparison, tricarbomethoxyethylene was also reacted with water in acetone. Although it was slower, reaction did take place. Addition of triethylamine as a catalyst did not seem to significantly affect the rate of this hydrolysis reaction.

Ethanol also reacted with carbomethoxymaleic anhydride in deuterochloroform. Initially the half acid ester was formed, but when an excess of the alcohol was used, it also attacked the double bond.

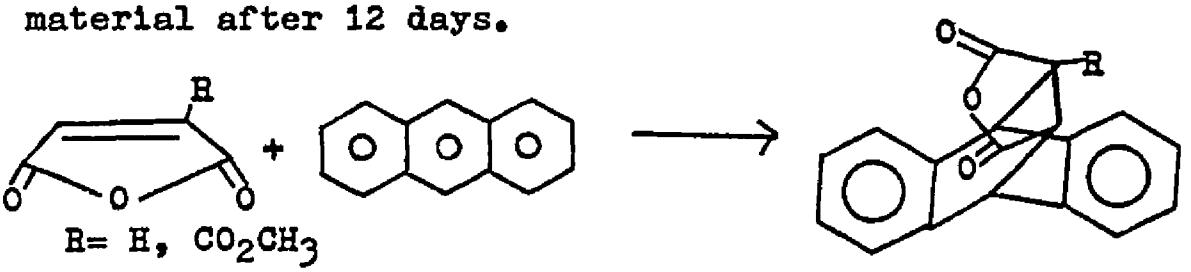
Cycloadditions

Diels-Alder Adducts. Several 4+2 cycloadducts of carbomethoxymaleic anhydride (CMA) and maleic anhydride (MA) were prepared. CMA and MA both reacted rapidly with cyclopentadiene to form the corresponding bicyclo[2.2.1]hep-2-ene-5,6-dicarboxylic anhydrides.

R= H, CO_2CH_3

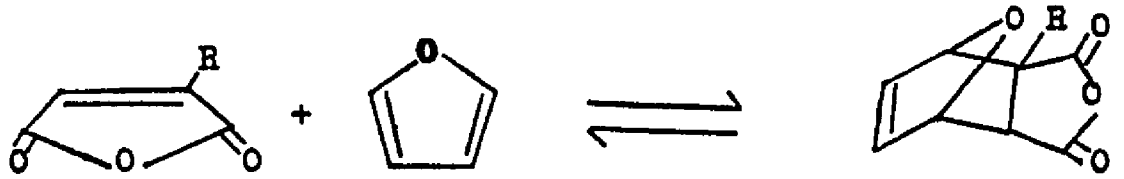
When the reactions were carried out in ether, the MA cyclo-adduct precipitated out while the CMA adduct was soluble. When the reactions were carried out in deuterochloroform in order to follow them by nmr, in both cases, reaction was complete before the spectrum could be taken.

With anthracene CMA reacted within 15 minutes while MA still showed a mixture of adduct and starting material after 12 days.



R= H, CO_2CH_3

The reaction in chloroform with furan for both MA and CMA was an equilibrium reaction.



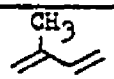
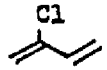
R= H, CO_2CH_3

Equilibrium could be shifted for MA and furam by running the reaction in a poor solvent such as ether. The adduct precipitated out as it formed. When the adduct was dissolved in chloroform, it slowly (2 weeks) reverted to the equilibrium mixture. The CMA-Furan adduct likewise could be precipitated out as an oil from ether, but on dissolving in chloroform equilibrium was rapidly reestablished. In

both cases equilibrium could be shifted to the adducts by running the reaction in an excess of furan.

In order to better determine the relative reactivity of carbomethoxymaleic anhydride as a dienophile, it was reacted with butadiene, chloroprene and isoprene. The rates of these reactions were compared to the rates with the parent maleic anhydride and with tetracyanoethylene (TCNE) which is known to be a very reactive dienophile. Reactions were run with equimolar amounts of diene and dienophile in deuteroacetone and monitored by nmr. The half-life for each reaction was measured and the results are listed in Table 1.

Table 1. Half-Lives in Diels-Alder Reactions

Diene	Concentration	TCNE	CMA	MA
	0.83 M	<5 min	<5 min	4 hr
	0.83 M	15 min	<5 min	9 hr
	0.83 M	equilib.	1½ hr	5 da
	0.24 M	1 hr	15 min	2 da

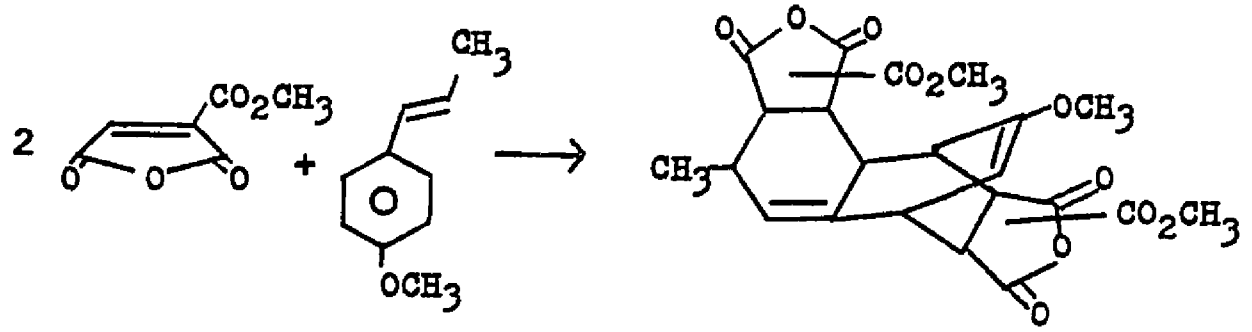
Unfortunately chloroprene and TCNE gave a slowly forming 4:1 (chloroprene : adduct) equilibrium. Since chloroprene and TCNE had produced an equilibrium mixture in acetone, two mixed solvents were tried: acetone-d6/

chloroform-d (1:1) and acetone-d6/benzene-d6 (1:1). In both cases the same equilibrium seemed to establish itself, but a fine precipitate slowly formed as well.

Since it was rather unexpected that CMA should prove more reactive with butadiene than TCNE, the reactions were repeated at a different concentration as a check. The reaction rates observed for MA and TCNE are in satisfactory agreement with those reported by Huisgen, Grashey and Sauer (1964).

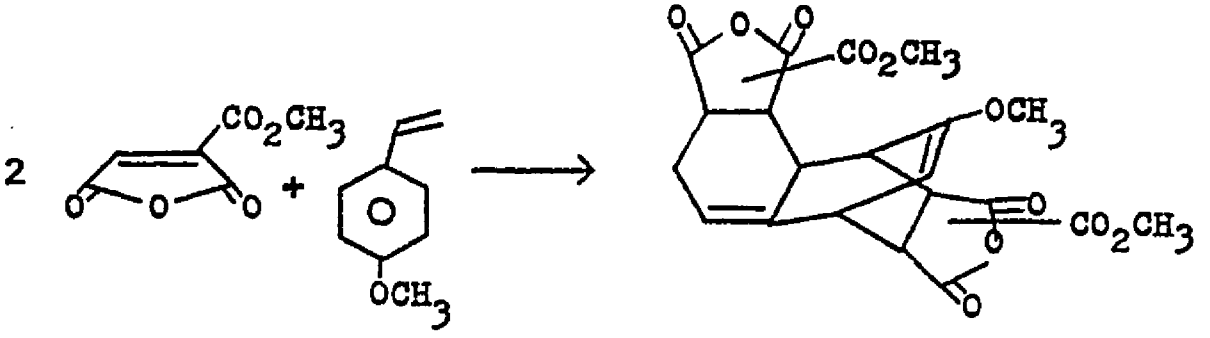
An attempt was made to carry out a Diels-Alder reaction between tricarbomethoxyethylene and butadiene under the same conditions, but no adduct was obtained.

Double Diels-Alder Adducts. Carbomethoxymaleic anhydride was found to form double Diels-Alder adducts with certain styrenes. Mixing CMA and anethole in ether resulted in a yellow solution, from which a white solid precipitated as the color faded. This solid proved to be the double Diels-Alder adduct analogous to that reported by Bruckner, Kovacs and Huhn (1951) for maleic anhydride.



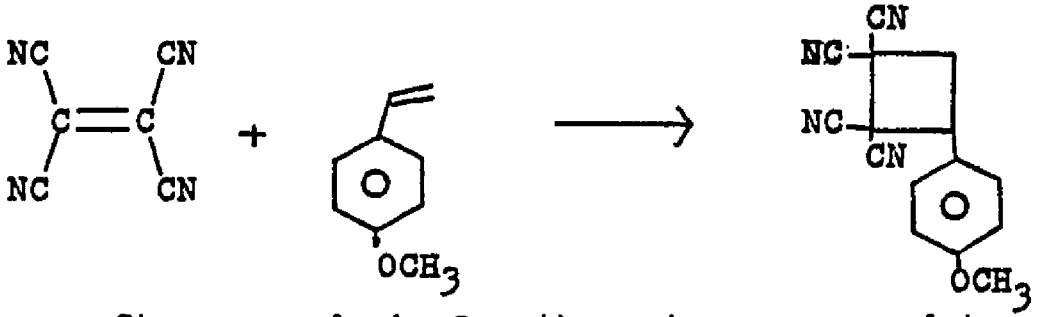
Unlike maleic anhydride, CMA also formed a double Diels-Alder adduct with p-methoxystyrene. Again mixing in

ether produced a yellow solution from which the white adduct precipitated.



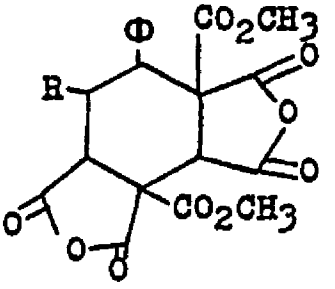
In both cases it is uncertain which isomer was produced. When maleic anhydride and p-methoxystyrene were mixed in ether, a yellow color was observed, but no precipitate formed. In deuterochloroform or deuteroacetone, these two compounds polymerized after a few days at room temperature. The polymer was insoluble in acetone, chloroform and benzene, but did dissolve in dimethyl sulfoxide.

TCNE reacted with p-methoxystyrene in deuteroacetone, giving a purple color, which faded as the 2+2 cyclobutane adduct formed.



Styrene and cis-β-methoxystyrene seemed to also form adducts with CMA in ether. Unfortunately, although elemental analysis of these solids indicated approximately 1:2 composition, nmr in both cases gave broad peaks, and the mass spectrum showed small peaks above the expected

parent peak. The presence of aromatic resonance in the nmr indicated that these solids could not be Diels-Alder adducts and so they were assumed to be cyclohexanes.



R= H, OCH_3

Such 1:2 cyclohexane adducts are known. (cf. N,N-dimethyl-isobutenylamine and 1,1-dicarbomethoxyethylene, Brannock et al. 1964). For more definitive evidence, samples of these two "adducts" were submitted for osmometry molecular weight determinations. The results (styrene adduct -- 895 and β-methoxystyrene adduct -- 1326) clearly show that these are oligomers rather than cycloadducts. CMA and styrene reacted in ether, even in the presence of 3-t-butyl-4-hydroxy-5-methylphenyl sulfide as a free radical inhibitor, indicating the oligomer produced is formed by an ionic mechanism. Even though the monomers were mixed 1:1, the ratio of CMA to styrene in the polymer in this case was 6:1. Maleic anhydride also gave a slow-forming oligomeric solid when treated with one equivalent of β-methoxystyrene in ether.

Maleic anhydride has been reported (Bergmann, Szmuszkowicz and Fawaz 1947) to form a double Diels-Alder adduct with 1,1-diphenylethylene, although under rather rigorous conditions (140-160° for three hours).

Treating CMA with 1,1-diphenylethylene in ether did not produce a precipitate as it had with anethole or p-methoxystyrene. Repeating the reaction in deuteroacetone in order to follow it by nmr resulted not in the formation of the double Diels-Alder adduct, but rather in the polymerization of the CMA.

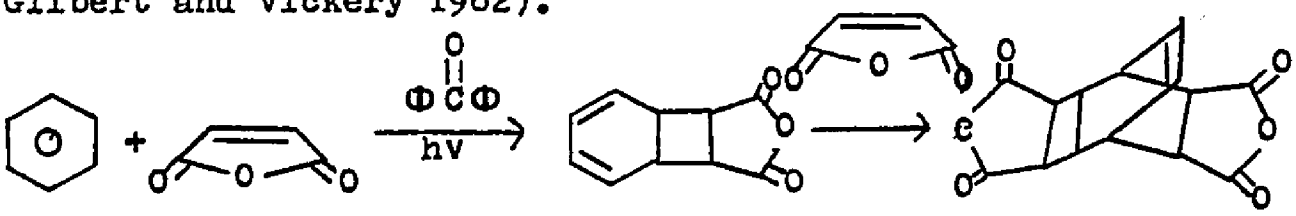
Attempted Cyclobutane Adducts. Less success has been obtained in attempted 2+2 cycloadditions, polymerization being favored over cycloaddition in all cases. Mixing CMA with styrene, p-methoxystyrene, 2,5-dichlorostyrene, 2,6-dichlorostyrene, n-butyl vinyl ether or vinyl acetate neat all resulted in spontaneous polymerization, even in the presence of hydroquinone as a free radical inhibitor. In the case of 2,6-dichlorostyrene, sulfolane was added as a solvent due to the immiscibility of the anhydride and the styrene. In this case polymerization took two weeks, whereas 24 hours or less was sufficient where no solvent was used.

Cycloadditions of CMA and vinyl bromide in acetonitrile and of CMA and vinylidene chloride in acetonitrile were attempted both thermally and photolytically with benzophenone as a sensitizer. With vinyl bromide, no reaction occured with photoinitiation after 60 hours. Thermally, after 60 hours at 65°, nmr showed the disappearance of the vinyl H in the anhydride, but no change in the vinyl bromide. With vinylidene chloride, no reaction

was observed after 24 hours of photoirradiation, but after 48 hours, the vinyl H resonance of the anhydride was almost gone in the nmr. The vinylidene chloride was unaffected. Thermally, after 24 hours, the vinyl H resonance was gone and again the vinylidene resonance was unchanged.

Steinmetz, Hartmann and Schrenck (1965) have reported the photochemical cycloaddition of maleic anhydride with either cis-or trans-1,2-dichloroethylene in various solvents in the presence of benzophenone as a sensitizer. An attempt to carry out the same reaction with CMA and trans-1,2-dichloroethylene in deuteroacetonitrile produced after four days only unreacted CMA and poly-CMA.

Maleic anhydride reacts with benzene in the presence of benzophenone and uv light as follows (Bryce-Smith, Gilbert and Vickery 1962).



An attempt to carry out the analogous reaction with CMA failed, producing only starting materials after one week of irradiation.

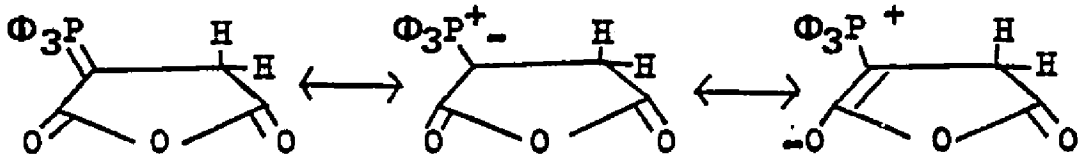
Several cycloadditions were also attempted between maleic anhydride or carbomethoxymaleic anhydride and vinyl ethers in solution. MA did not react with methyl vinyl ether in chloroform. CMA did react under the same conditions, but as more CMA was added, it was gradually consumed,

leading to polymer. As with methyl vinyl ether, there was no reaction after five days between equivalent amounts of isobutyl vinyl ether (BVE) and maleic anhydride. Heating MA and BVE to 100°, however, produced a copolymer.

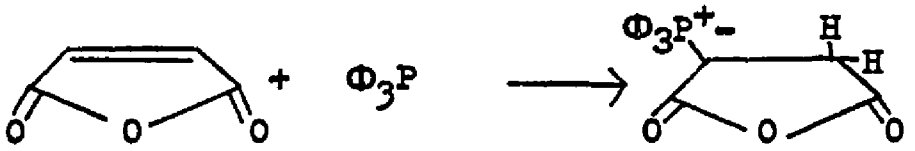
Carbomethoxymaleic anhydride did react with BVE in either chloroform or acetone. Mixing CMA and BVE 1:1 in deuterochloroform resulted in immediate reaction. NMR showed BVE to be in excess. If more CMA was added, BVE disappeared and CMA appeared in excess, but on standing the olefin peak of CMA disappeared. When BVE was added dropwise to excess CMA, following the reaction by nmr, CMA was gone when 1/4 to 1/3 of an equivalent of BVE had been added. When a catalytic amount of BVE was added to CMA in deuteroacetone and allowed to stand overnight, the CMA polymerized. However, a catalytic amount of CMA under the same conditions was incapable of polymerizing BVE.

Ylids

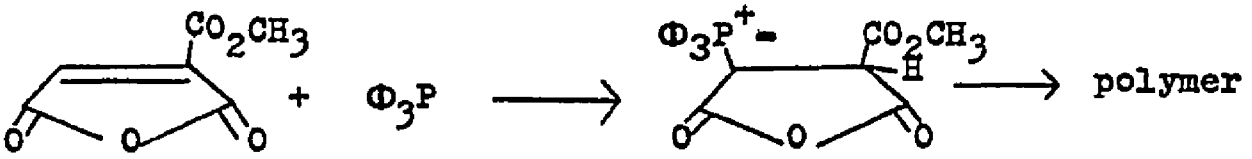
Triethylamine and triphenylphosphine are known to add to some olefins to produce ylids. For example, triphenylphosphine reacts with maleic anhydride to produce the following ylid (Hudson and Chopard 1963).



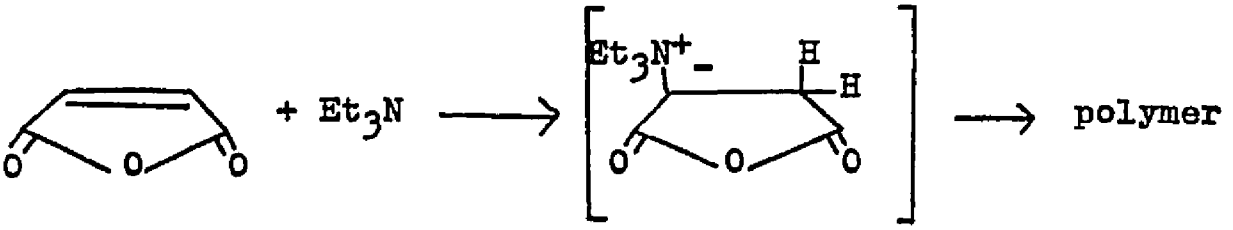
When triphenylphosphine and maleic anhydride were mixed (1:1) in deuterochloroform, a red solution was produced, which was attributed to the ylid. No polymerization was observed.



Triphenylphosphine and carbomethoxymaleic anhydride (1:1) in deuterochloroform produced a yellow solution which gradually darkened. There was evidence in the nmr for both ylid and polymer. When allowed to stand overnight, the amount of polymer and unreacted triphenylphosphine increased relative to the ylid. Use of a catalytic amount of triphenylphosphine slowly polymerized CMA as well.

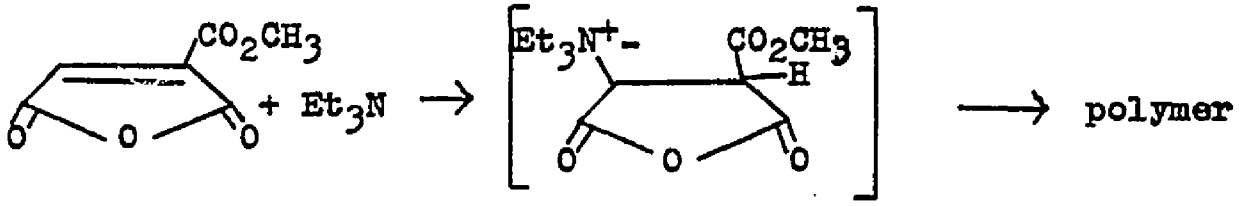


Addition of triethylamine to maleic anhydride (1:1) in deuterochloroform produced a reddish-brown solution with formation of considerable dark insoluble material. There was no evidence for maleic anhydride in the nmr while triethylamine was still present. Apparently polymerization had taken place.



A catalytic amount of triethylamine also induced the polymerization of MA when allowed to stand overnight.

Addition of an equivalent of triethylamine to CMA in deuterochloroform produced an orange solution with formation of insoluble material. It was apparent from the nmr spectrum that polymerization had occured.



Likewise, a catalytic amount of triethylamine induced the polymerization of CMA.

Charge-Transfer Complexes

Since colors were often observed when mixing CMA with electron donors, such as p-methoxystyrene, presumably a charge-transfer complex is initially formed. When CMA or MA was mixed with either p-dimethoxybenzene or 1,3,5-trimethoxybenzene, similar yellow colors were observed. When CMA and p-dimethoxybenzene were mixed together as solids, a red color was produced. When these were dissolved in acetone, the color was yellow and the CMA gradually polymerized. When CMA and 1,3,5-trimethoxybenzene (TMB) were mixed neat, they turned yellow. Mixing CMA and TMB in acetone produced a yellow color which gradually faded as the CMA polymerized. When each was first dissolved in ether, mixing resulted in an immediate yellow solution and

precipitation of yellow needles which were partially ether soluble. On standing a few days in a closed vial or on heating to 65-70°, these yellow crystals turned white. It was apparent from the ir spectrum as well as the melting point (140-142°) that this was a compound and not merely a mixture of CMA and TMB, but its exact structure has not been determined.

Polymerizations

Homopolymerizations. Carbomethoxymaleic anhydride has been homopolymerized with azobisisobutyronitrile (AIBN) or benzoyl peroxide initiation and heat (65°) and with AIBN initiation and UV light. Heating CMA without initiator or solvent also resulted in polymerization although at a slower rate. In deuteroacetone CMA was completely polymerized by heating to 60° overnight either with or without AIBN. Likewise irradiation with UV light overnight either with or without AIBN resulted in complete conversion to polymer. Irradiating CMA in the presence of t-butyl hydroperoxide without solvent produced a mixture of monomer, polymer and the hydrolysis product carbomethoxymaleic acid. During homopolymerizations a small amount of gas evolution has occassionally been observed, but it is uncertain whether this is due merely to the decomposition of the initiator or to some decarboxylation as has been noted for the polymerization of maleic anhydride (Gaylord 1975).

The ability of CMA to be homopolymerized by catalytic amounts of electron-rich monomers (e.g., isobutyl vinyl ether) suggested a possible anionic mechanism. To test this, CMA was dissolved in THF with a catalytic amount of potassium cyanide and dibenzo-18-crown-6. After two days the solvent was evaporated off and the resulting polymer triturated with ether. Drying left a 56% yield of brown powder (η_{inh} 0.014). This polymerization was repeated at -70° yielding 42% of the same brown powder (η_{inh} 0.028). When this experiment was repeated at -70° without the potassium cyanide or crown ether, however, polymer was also obtained, perhaps via a donor-acceptor complex between the CMA and the tetrahydrofuran. Maleic anhydride is known to form such a complex with tetrahydrofuran on irradiation (Bawn, Ledwith and Parry 1965).

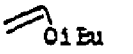
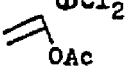
Since the solvent had apparently participated in these reactions, the polymerization was repeated in deuteroacetonitrile. Either potassium cyanide or tetraethylammonium chloride was capable of initiating the polymerization in this solvent at room temperature. In the absence of initiator, CMA did not polymerize.

Copolymerizations. Carbomethoxymaleic anhydride copolymerized readily with a number of monomers. When mixed with various electron-rich monomers, polymerization occurred spontaneously without initiation even in solution. Mixing CMA neat with either isobutyl vinyl ether or

p-methoxystyrene resulted in an immediate exothermic polymerization. From the nmr it could be seen that the copolymer obtained between CMA and BVE was essentially 1:1. With p-methoxystyrene a mixture of copolymer and the previously discussed double Diels-Alder adduct was obtained. The reaction between CMA and styrene was somewhat slower, taking approximately two minutes to polymerize to a viscous gel. Again nmr indicated an essentially 1:1 composition. With 2,5-dichlorostyrene or vinyl acetate the spontaneous copolymerization was much slower, but in both cases a copolymer was obtained after standing overnight. NMR indicated again a 1:1 composition for the dichlorostyrene, but with vinyl acetate, there seemed to be an excess of CMA in the final product.

When these spontaneous polymerizations were repeated in deuteroacetone, the reaction rates were slower although the same relative rates were observed. Results of these polymerizations are listed in Table 2.

Table 2. Spontaneous Solution Polymerizations

Comonomer	% Unreacted CMA after 5 hours	% Unreacted CMA after 14½ hours	% Comonomer Consumed
	0	0	60
	35	0	30
	50	10	0
	45	25	0

In these solution polymerizations the polymer formed consistently contained an excess of CMA, even when the monomers were mixed in equimolar amounts.

Free radical copolymerizations of CMA and methyl methacrylate (MMA), acrylonitrile (AN) and tricarbomethoxyethylene(TCE) were also carried out. In each case the monomers were mixed neat with AIBN as an initiator and heated to 65-80°. The CMA-MMA polymer was dissolved in acetone and precipitated in ether. It was established from ir, nmr and elemental analysis that it was a copolymer containing an excess of MMA. The polymer from the CMA-AN reaction was insoluble in chloroform and acetone, but did dissolve in acetonitrile. It was then precipitated in ether. IR and nmr failed to establish unambiguously the presence of acrylonitrile in the polymer. Only a small CN peak was observed in the ir spectrum. However, elemental analysis confirmed the presence of some AN in the polymer. Polymer from the CMA-TCE reaction was dissolved in chloroform and precipitated in ether. Whether this was a true copolymer or merely a homopolymer of CMA was unclear from the nmr and ir spectra. The fact that white crystals of tricarbomethoxyethylene sublimed out of the reaction mixture implied the polymer might merely be homopoly-CMA. Elemental analysis though, again confirmed that this was indeed a copolymer.

The reaction of CMA with isobutyl vinyl ether was further examined to determine the effect of solvent. In previous experiments mixing CMA and BVE had led to polymer rather than cycloadduct, but the mechanism of polymerization was unknown. Here CMA and BVE were stirred 1:1 in various solvents for several days, after which time the solvent was pumped off and the polymer examined by nmr. In THF, which should favor anionic polymerization, both monomers were immediately soluble. The polymer produced appeared from nmr to be slightly richer in CMA than BVE. When the reaction was run in methylene chloride, which should favor cationic polymerizations, CMA was initially insoluble. However, on addition of BVE, solution was affected. NMR of the polymer produced showed it to be close to 1:1. With acetonitrile as solvent, nmr showed again a slight excess of CMA, while with benzene composition was 1:1. In benzene, as with methylene chloride, the presence of BVE was necessary to affect total solubility of the CMA. The slight excess of CMA in some cases is not surprising in view of the previous findings that catalytic amounts of BVE could polymerize CMA while catalytic amounts of CMA were incapable of polymerizing BVE.

In an attempt to better understand the mechanism of CMA polymerizations, a number of experiments were conducted using catalytic amounts of one monomer. In acetone or or acetonitrile, CMA was polymerized by a catalytic amount

of styrene. A catalytic amount of CMA, however, was unable to polymerize styrene in these solvents. In chloroform or benzene, a catalytic amount of styrene initiated the polymerization of CMA, but the polymer precipitated from solution, leaving unreacted CMA in the solution. A catalytic amount of CMA did not polymerize styrene in chloroform. As in the styrene case, CMA could be polymerized by a catalytic amount of p-methoxystyrene in acetone, but p-methoxystyrene could not be polymerized by CMA.

These experiments and the fact that solution copolymerizations of CMA with electron-rich olefins always resulted in an excess of CMA units in the polymer suggested a mixture of free radical initiated 1:1 alternating copolymer and anionic homopolymer. A number of experiments were conducted in an attempt to favor either the free radical copolymerization or the anionic homopolymerization. When copolymerization of CMA and styrene was carried out in deuteroacetone or deuteroacetonitrile, standard free radical inhibitors such as 2,2-diphenyl-1-picrylhydrazyl (DPPH) or 3-t-butyl-4-hydroxy-5-methylphenyl sulfide (S inhib.) decreased the amount of styrene incorporated into the polymer, while the presence of a free radical initiator, AIBN, accompanied by UV irradiation increased the amount of styrene incorporated.

When CMA and styrene were copolymerized neat, the presence of 3-t-butyl-4-hydroxy-5-methylphenyl sulfide slowed the reaction rate and greatly reduced the amount of styrene in the final product.

An attempt was also made to inhibit the anionic homopolymerization by addition of various acids or methylating agents. Acetic acid, trifluoroacetic acid, methyl iodide, methyl sulfate, methyl tosylate and trimethylchlorosilane, however, all failed to affect the amount of styrene incorporated into the polymer. These results are summarized in Table 3.

Table 3. Solution Polymerizations with Additives*

Additive	% Styrene consumed
none	30
DPPH	10
S inhib.	0
AIBN + hv	45
CH_3I	30
$(CH_3)_2SO_4$	30
CH_3OTs	20
CH_3CO_2H	40
F_3CCO_2H	40
$(CH_3)_3SiCl$	40

*These reactions were run in deuteroacetonitrile.

DISCUSSION

Carbomethoxymaleic anhydride is the first maleic anhydride containing a single strongly electron-withdrawing substituent to be synthesized. As expected, it has proved to be a very interesting compound. Although the synthesis of other members of this family, most notably cyanomaleic anhydride, has so far been unsuccessful, there is as yet no reason to believe they cannot be made. The preparation of carbomethoxymaleic anhydride by heating tricarbomethoxyethylene with phosphorus pentoxide should be a general method for other maleic anhydrides, provided the appropriate maleates can be made.

The vulnerability to nucleophilic attack of the double bond in the trisubstituted olefins used as starting materials has ruled out many otherwise promising syntheses. Although this double bond reactivity has been a problem in the synthesis of other substituted maleic anhydrides, it is undoubtedly the most interesting aspect of the chemistry of the one maleic anhydride successfully synthesized.

The susceptibility of the double bond in carbomethoxymaleic anhydride to nucleophilic attack is attested to by its ability to react even with such weak nucleophiles as water and ethanol. Although the parent olefin,

tricarbomethoxyethylene also adds water across its double bond, the reaction is much slower than with CMA.

The main reason for synthesizing CMA was to study its reactivity in cycloaddition and polymerization reactions. It seemed logical to compare it to maleic anhydride itself. In cycloaddition reactions, CMA behaved chemically similarly to maleic anhydride, except that it was much more reactive. With cyclopentadiene, anthracene, butadiene, isoprene and chloroprene both CMA and MA gave the expected Diels-Alder adducts, although in each case CMA reacted much faster. With furan, both compounds gave an equilibrium mixture of reactants and adduct. This equilibrium could be shifted in favor of products by the usual methods, i.e., running the reaction in an excess of furan or in a poor solvent so as to precipitate out the adduct as formed. Again reaction rates were much faster for CMA than for MA. When the maleic anhydride adduct was dissolved in chloroform, two weeks were required to reestablish the equilibrium mixture, while the CMA adduct under the same conditions, reverted immediately on dissolving to the equilibrium composition.

The fact that CMA was an even more reactive dienophile than tetracyanoethylene was somewhat surprising, and it would be interesting to have a series of substituted maleic anhydrides in order to compare the effect of substituents on rates in these reactions.

CMA followed MA in its ability to form a double Diels-Alder adduct with anethole. Again the reaction rate was much faster for CMA. It reacted spontaneously at room temperature with anethole in solution while the corresponding maleic anhydride adduct has been produced in significant yield only after heating the reactants together neat for four hours at 80° (Bruckner and Kovacs 1947). The greater reactivity of CMA is also seen by the fact that it reacted with p-methoxystyrene to give an analogous double Diels-Alder adduct, while no such adduct is known for maleic anhydride.

CMA seems to also follow MA in its reluctance to form 2+2 cycloadducts, preferring instead to polymerize. I am not aware of any thermal 2+2 cycloadditions of maleic anhydride although numerous photochemical 2+2 cycloadditions have been reported. Several attempts were made to cycloadd CMA to various vinyl compounds, either thermally or photochemically, but none was successful.

The ability of MA to form an ylid with triphenylphosphine was also mimicked by CMA, although the reactivity of CMA toward polymerization ultimately led to polymer after initial formation of the ylid, presumably via an anionic mechanism.

Homopolymerization of trisubstituted olefins is uncommon. CMA, however, readily polymerized under either free radical or anionic conditions. Although inherent

viscosity measurements indicate a rather low molecular weight, the fact that any homopolymer at all formed is unusual. Its ability to polymerize can perhaps best be understood by examining its structure. The presence of two α-substituents, both of which are capable of stabilizing either a free radical or anion via resonance, favors polymerization. In addition, the cyclic nature of this compound helps to reduce steric hindrance at the β-carbon and the planar nature of the ring allows effective overlap with the growing polymer chain. The fact that CMA homopolymerizes, while similar trisubstituted olefins such as tricarbomethoxyethylene do not, is added evidence that steric hindrance at the β-carbon is the major obstacle to polymerization of trisubstituted ethylenes.

Carbomethoxymaleic anhydride also readily copolymerized. A unique aspect of these copolymerizations was that many were spontaneous, requiring no initiation. Spontaneous copolymerization was obtained with styrene, p-methoxystyrene, 2,5-dichlorostyrene, 2,6-dichlorostyrene, methyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether and vinyl acetate. Such polymerizations, although not unheard of, are rare for similar non-cyclic trisubstituted electron-poor olefins. Although the properties of these copolymers were not extensively examined, they did appear to be of high molecular weight. The CMA-styrene copolymer, for example, could be cast into a film.

The mechanism of these polymerizations appears to be rather complicated, but some conclusions can be drawn from the experiments conducted. Copolymerizations of CMA and styrene in deuteroacetone or deuteroacetonitrile followed by nmr indicated that the polymer produced is not a simple 1:1 alternating copolymer, as was the case for previously examined trisubstituted electron-poor olefins (Hall and Daly 1975). Even when mixed 3:1 (CMA:styrene) in deuteroacetone, nmr indicated the presence of a small amount of unreacted styrene after all the CMA had been consumed. The fact that a catalytic amount of styrene was capable of initiating the polymerization of CMA in a number of solvents, while a catalytic amount of CMA did not initiate the polymerization of styrene, suggests that the spontaneous copolymerization of CMA and styrene may involve both 1:1 alternating copolymer and a CMA homopolymer. Such mixtures of homopolymer and alternating copolymer have been found by Stille and Chung 1975, Stille et al. 1975 for vinylidene cyanide and various vinyl ethers.

When mixed neat, CMA and various electron rich monomers (isobutyl vinyl ether, styrene, 2,5-dichlorostyrene) produced copolymers which were essentially 1:1. However, as Table 2 indicates, when these reactions were repeated in solution, an excess of CMA was usually obtained and in the case of the least electron rich monomers

(2,5-dichlorostyrene and vinyl acetate), only homopoly-CMA was obtained. The reaction rates were as expected with the more electron-rich monomers reacting more rapidly than the less electron-rich.

Some further evidence for the idea of a mixture of 1:1 copolymer and CMA homopolymer was found in polymerizations conducted in the presence of a free radical inhibitor. CMA and styrene polymerized in ether to produce a product which elemental analysis showed to contain a ratio of CMA:styrene of 2:1. Mass spectrum of this polymer gave substantial peaks at 312 and 468 corresponding to two and three CMA units respectively. When the experiment was repeated with 3-t-butyl-4-hydroxy-5-methylphenyl sulfide as a free radical inhibitor, polymer was still obtained, but from nmr it was apparent that the CMA:styrene ratio was now close to 6:1. Likewise in deuteroacetone or deuteroacetonitrile, free radical inhibitors reduced the amount of styrene incorporated into the polymer, while AIBN and UV light increased the incorporation of styrene (Table 3).

Since addition of CMA to styrene even in solution produces a yellow color which fades as polymerization takes place, the presence of a charge-transfer complex is suspected. It seems reasonable that formation of a cation radical-anion radical pair could follow. From here two modes of polymerization could take place: free radical

copolymerization to produce the 1:1 alternating copolymer and/or anionic homopolymerization of the carbomethoxymaleic anhydride. The presence of a free radical inhibitor would be expected to inhibit the former polymerization while allowing the latter to proceed.

Polymerizations of isobutyl vinyl ether and CMA were much more rapid than the styrene-CMA polymerizations. In methylene chloride and benzene, CMA and BVE gave a copolymer which appeared from nmr to be 1:1. In tetrahydrofuran or acetonitrile, however, there seemed to be a slight excess of CMA in the resultant polymer. Tetrahydrofuran and acetonitrile are good solvents for anionic polymerizations, which could explain the slight excess of CMA when polymerizations were conducted in these solvents. When polymerization was carried out in deuteroacetone in order to follow it via nmr, mixing the monomers 1:1 resulted in a small amount of unreacted isobutyl vinyl ether, while mixing in a 2:1 ratio showed neither monomer to be in excess. As in the styrene case, CMA was polymerized by a catalytic amount of BVE, but BVE could not be polymerized by a catalytic amount of CMA. Again there may be a competition between anionic homopolymerization and free radical copolymerization. The fact that the CMA-BVE polymers were always close to 1:1 in composition may reflect the fact that the copolymerization reaction was much faster in the CMA-BVE case than in the CMA-styrene case.

Although a preliminary study of the reactivity of carbomethoxymaleic anhydride has been made here, a better understanding of the factors which affect the formation of cycloadduct, homopolymer or copolymer must await the synthesis of more monosubstituted electron-poor maleic anhydrides.

EXPERIMENTAL

Instrumentation

All melting points were determined in a Thomas-Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance (nmr) spectra were determined on a Varian model T-60 spectrometer at 60 MHz. Infrared (ir) spectra were obtained with a Perkin-Elmer 337 grating infrared spectrophotometer. Mass spectra were determined on a Hewlett-Packard 5930A quadrapole mass spectrometer. Gas chromatograms were obtained on a Varian Aerograph 1700 using a five foot x $\frac{1}{4}$ inch column packed with 3% S.E. 30 on 80-100 mesh chromosorb W AW/DMCS HP. Inherent viscosities were determined with an Ostwald-Fenske viscometer.

Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. Osmometric molecular weights were determined by Huffman Laboratories, Inc., Wheatridge, Colorado.

Chemicals

Styrene (Aldrich), p-methoxystyrene (Aldrich), methyl methacrylate (Eastman), acrylonitrile (Eastman), isoprene (Aldrich), and vinyl acetate(MCB) were freed of inhibitors by distillation and stored in a cold box under nitrogen. Chloroprene (50% in xylene, Polysciences) was

distilled and stored in a cold box. Cyclopentadiene was prepared by cracking 3a,4,7,7a-tetrahydro-4,7-methanoindene (MCB) and stored in a cold box. Anthracene (Baker) was recrystallized twice from benzene. All other chemicals were used without further purification, unless otherwise noted.

1,1,2-Tricarbomethoxyethane

Sodium (28.8 g, 1.25 mol) was dissolved in 1.25 l of absolute methanol in a round-bottom flask equipped with a mechanical stirrer. The solution was cooled in an ice bath and 286 ml (330 g, 2.5 mol) of dimethyl malonate (MCB) was added. To this solution, 110 ml (136 g, 1.25 mol) of methyl chloroacetate (Aldrich) was added dropwise at 0° with stirring over a period of 90 minutes. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The mixture, including precipitated NaCl was rotoevaporated down at 60° under apirator, and then poured into 400 ml of water. The water solution was extracted with three 200 ml portions of ether. The combined ether layers were dried over anhydrous K_2CO_3, and the ether rotoevaporated off. Fractional distillation on a spinning band column gave fraction 1 (bp 40-60°/0.5 torr) which was unreacted dimethyl malonate, and fraction 2 (bp 100-110°/1.5 torr) which was the desired product. Yield: 162.21 g (64%). nmr(neat) δ: 3.3 (m, 2H); 4.1 (m, 10H).

1-Bromo-1,1,2-tricarbomethoxyethane

Tricarbomethoxyethane (162.21 g, 0.80 mol) was dissolved in 750 ml of CCl_4. Bromine (45.5 ml, 141 g, 0.88 mol) was added dropwise with UV irradiation and stirred overnight. The solution was rotoevaporated down at 50° under aspirator. Yield of crude product: 238.34 g.

Tricarbomethoxyethylene

The residue (238.34 g) from the previous synthesis was dissolved in 750 ml of ether and 116 ml (84.8 g, 0.84 mol) of triethylamine was added dropwise with stirring. The precipitated triethylamine hydrobromide was filtered off, washed with ether and the ether rotoevaporated off. The product was then distilled (bp 105°/0.7 torr). Yield: 139.25 g (86%); mp 39-40° (lit. mp 40-41°, Hall and Daly 1975).

nmr ($CDCl_3$) δ: 3.8 (t, 9H); 6.9 (s, 1H).

ir (neat): C=O, 1750 cm^{-1},s; CH, 2950 cm^{-1}, s.

Carbomethoxymaleic Anhydride

Tricarbomethoxyethylene (20.2 g, 0.10 mol) was mixed with 28.4 g (0.20 mol) of P_2O_5 in a small distillation apparatus with water cooled condenser. The mixture was heated to 180° in an oil bath for one hour. The product was then distilled from the black mass at full vacuum (bp 50-60°/0.2 torr). The product was a liquid which solidified on cooling. NMR showed the product to be

contaminated with tricarbomethoxyethylene. Recrystallization from ether gave the pure anhydride. Yield: 10.24 g (66%); mp 37-38°.

nmr (neat) δ: 4.0 (s, 3H); 7.7 (s, 1H).

ir (neat): C=O, 1770, 1800 cm^{-1},s; CH, 2950, 3100 cm^{-1}, s.

mass spec. (70 Ev): molecular ion 156 m/e.

calcd: 156 m/e.

anal. calcd. for $C_6H_4O_5$: C, 46.16; H, 2.59.

Found: C, 46.09; H, 2.81.

Iodomaleic Anhydride

Bromomaleic anhydride (Aldrich) (3.2 g, 18 mmol) was added to a solution of 4.0 g (27 mmol) of NaI in 15 ml of acetone. The solution turned red and a precipitate of NaBr formed. The precipitate was removed by filtration. Yield: 1.95 g (theoretical yield: 1.85 g). The acetone was rotoevaporated away at 50° under aspirator leaving an oil.

nmr (acetone) δ: 7.7 (s).

ir (neat): C=O, 1800 cm^{-1}, s; CH, 3100 cm^{-1}, m.

Dimethyl Bromomaleate: Method I

Dimethyl maleate (124 ml, 144 g, 1.0 mol) was dissolved in 500 ml of methylene chloride with 1.65 g (1 mol %) of tetraethylammonium chloride as a catalyst. Bromine (53 ml, 165 g, 1.0 mol) was added with stirring and uv irradiation. The solution was stirred overnight. The solvent was rotoevaporated off and the resulting

orange-red oil dissolved in 400 ml of tetrahydrofuran. Triethylamine (138 ml, 111 g, 1.0 mol) was added dropwise while cooling in an ice bath. The mixture was allowed to warm to room temperature and stirred overnight. The solution was filtered and the solvent distilled off under vacuum. Yield: 204.26 g (92%). The product was slightly contaminated with dimethyl maleate and dimethyl bromofumarate.

Dimethyl Bromomaleate: Method II

Bromomaleic anhydride (17.7 g, 0.1 mol) was refluxed with 20 ml of methanol and 1 ml of sulfuric acid for two hours. At this point, gas chromatography showed the reaction to be >90% complete. Dimethoxypropane (15.6 g, 0.15 mol) was added to remove water and shift the equilibrium. After one more hour the reaction was essentially complete. The solution was rotoevaporated down, leaving a brown liquid. This liquid was dissolved in 30 ml of ether and extracted with four 20 ml portions of a saturated Na_2CO_3 solution. The combined aqueous layers were back-extracted with three 20 ml portions of ether and the combined ether layers were dried over anhydrous $MgSO_4$, filtered and rotoevaporated down. Distillation (bp 60°/0.1 torr) gave the desired product. Yield: 19.55 g (88%).
nmr ($CDCl_3$) δ: 3.7 (s, 3H); 3.9 (s, 3H); 6.5 (s, 1H).
ir (neat): C=O, 1630, 1740 cm^{-1}, s; CH, 2950 cm^{-1}, s.

Dimethyl Cyanosuccinate

Sodium (46 g, 2.0 mol) was dissolved in 1.8 l of anhydrous methanol in a round-bottom flask equipped with a mechanical stirrer. The solution was cooled in an ice bath and 178 ml (198 g, 2.0 mol) of methyl cyanoacetate (Aldrich) was added. To this solution was added a solution of 88 ml (110 g, 1.0 mol) of methyl chloroacetate (Aldrich) in 200 ml of methanol dropwise at 0° with stirring over a period of two hours. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The NaCl precipitate was filtered off and the solvent rotoevaporated away. The remaining tar was poured into 1.5 l of ice water, acidified with 100 ml of concentrated HCl and extracted with four 100 ml portions of methylene chloride. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent rotoevaporated off, leaving a purple oil. Distillation gave fraction 1 (bp 40-50°/0.3 torr) which was unreacted methyl cyanoacetate and fraction 2 (bp 55°/0.3 torr) which was the desired product. Yield: 73.7 g (43%).

nmr ($CDCl_3$) δ: 3.0 (d, 2H); 3.7 (s, 3H); 3.8 (s, 3H); 4.0 (t, 1H).

Dimethyl α-Bromo-α-cyanosuccinate

Dimethyl cyanosuccinate (26.5 g, 0.15 mol) and 0.1 g of AIBN were dissolved in 250 ml of methylene

chloride. To this solution, 8.3 ml (24 g, 0.15 mol) of bromine was added dropwise with stirring and UV irradiation. After three hours the red color of bromine had disappeared. The solvent was rotoevaporated off, leaving a brown oil.

Dimethyl Cyanofumarate

The brown oil from the previous synthesis was dissolved in 250 ml of ether and stirred in an ice bath while 20.8 ml (0.15 mol) of triethylamine was added dropwise. After ½ hour, the mixture was warmed to room temperature and stirred for 45 minutes. The precipitate of triethylamine hydrobromide was filtered off, washed with ether, and the ether rotoevaporated down leaving an orange-red solid. Distillation of this solid under vacuum gave 16.51 g of the crude product. Recrystallization from ether gave the pure dimethyl cyanofumarate. Yield: 13.35 g (53%).

nmr ($CDCl_3$) δ: 3.9 (d, 6H); 7.5 (s, 1H).

ir (neat): C=O, 1725 cm^{-1}, s; CN, 2240 cm^{-1}, w; CH, 2950, 3050 cm^{-1}, s.

Trimethylsilyl Iodide

Hexamethyldisiloxane (16.2 g, 0.1 mol) and 5.4 g (0.2 mol) of aluminum powder were stirred in a round-bottom flask under nitrogen and heated to 60°. Iodine (25.4 g, 0.1 mol) was added slowly with stirring. The

mixture was refluxed for 1½ hours and the product distilled out (bp 110-115°). Yield: 7.25 g (18%).
nmr (neat) δ: 1.4 (s).

Trimethylsilyl Cyanide

In a dry round-bottom flask were mixed 13.2 g (0.2 mol) of potassium cyanide, 40 ml of methylene chloride, 0.2 g (0.8 mmol) of 18-crown-6 and 28 ml (24 g, 0.22 mol) of trimethylchlorosilane (distilled from CaH_2). The mixture was refluxed 24 hours with stirring and protected from water in the atmosphere with a $CaSO_4$ drying tube. Distillation through a Vigreaux column gave methylene chloride in the first fraction and trimethylsilyl cyanide in the second. Yield: 7.04 g (36%).
nmr (neat) δ: 0.5 (s).

Cyanosuccinic Acid

In a round-bottom flask was placed 10.2 g (0.16 mol) of 85% KOH and 20 ml of water and the solution was cooled in an ice bath. To this solution, 13.15 g (77 mmol) of dimethyl cyanosuccinate was added dropwise. The mixture was stirred two hours and then acidified with HCl. The white precipitate of KCl which formed was removed by filtration and the filtrate extracted with six 20 ml portions of ether. The combined ether layers were dried over anhydrous $MgSO_4$, filtered and evaporated down, leaving a white solid.

nmr (acetone-d6) δ: 3.0 (d, 2H); 4.2 (t, 1H); 9.5 (s, 2H).

Cyanosuccinic Anhydride

The white solid from the previous synthesis was stirred for two hours at 55° with 10 ml of acetic anhydride. The liquid was pumped off leaving a brownish solid. Attempts to recrystallize the crude product or to sublime it failed, but trituration with ether finally resulted in a clean product (mp 95-98° dec.).

nmr (acetone-d6) δ: 3.6 (d, 2H); 4.9 (t, 1H).

Dimethyl 4-Cyano-4,5-cyclohexanedicarboxylate

Dimethyl cyanofumarate (0.50 g, 3.0 mmol) was dissolved in 5 ml of liquid butadiene with a small amount of 3-t-butyl-4-hydroxy-5-methylphenyl sulfide as a free radical inhibitor in a glass tube, which was then sealed. The solution was stirred and heated to 55° for 24 hours. The product was washed with pentane to remove butadiene dimers and pumped dry.

nmr ($CDCl_3$) δ: 2.6 (broad s, 4H); 3.2 (broad s, 1H); 3.7 (s, 3H); 3.9 (s, 3H); 5.7 (broad s, 2H).

Dimethyl 2-Cyanobicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate

Dimethyl cyanofumarate (1.69 g, 10 mmol) was dissolved in 20 ml of methylene chloride. To this solution 0.66 g (10 mmol) of cyclopentadiene was added dropwise.

The solution was stirred for 10 minutes and the solvent was pumped off, leaving a slightly yellow oil.
nmr ($CDCl_3$) δ: 2.0 (q, 2H); 3.3 (m, 3H); 3.9 (t, 6H); 6.0 (broad s, 1H); 6.4 (broad s, 1H).

5-Cyanobicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Acid

The yellow oil from the previous synthesis was added dropwise with stirring to 1.45 g (22 mmol) of 85% KOH in 5 ml of water in an ice bath. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was acidified with HCl and extracted with six 20 ml portions of ether. The combined ether layers were dried over anhydrous $MgSO_4$, filtered and rotoevaporated down, leaving a white solid. Yield: 0.94 g (40%), mp 83-85° dec.
anal. calcd. for $C_{10}H_8NO_4$: C, 57.97; H, 4.38; N, 6.76.
Found: C, 57.78; H, 4.54; N, 6.57.

5-Cyanobicyclo[2.2.1.]hept-2-ene-5,6-dicarboxylic Anhydride

The white solid (0.25 g, 1.2 mmol) was stirred at 55° for two hours with 5 ml of acetic anhydride. Pumping removed most of the acetic anhydride leaving a brown oil, but nmr indicated the presence of some acetic acid even after pumping for three days.

Dimethyl 11-Cyano-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate

Dimethyl cyanofumarate (1.86 g, 11 mmol) and 1.95 g (11 mmol) of anthracene were refluxed in 25 ml of xylene for five days. The solvent was stripped off and the remaining tar stirred overnight with pentane. It was then washed with two 10 ml portions of ether and dried under vacuum. The product was still somewhat contaminated with anthracene. Yield: 1.60 g; mp 152-154°.
nmr ($CDCl_3$) δ: 3.6 (s, 3H); 3.7 (s, 1H); 3.8 (s, 3H); 4.7 (m, 1H); 4.8 (broad s, 1H); 7.2 (m, 8H).

Sodium Cis-epoxysuccinate

In a round-bottom flask with thermometer and mechanical stirrer were mixed 116 g (1.0 mol) of maleic acid (practical) and 300 ml of water. To this was added 60 g (1.5 mol) of sodium hydroxide in 100 ml of water. The temperature rose to 70°. To the warm solution was added 5.9 g (20 mmol) of sodium tungstate, followed by 133 ml (1.2 mol) of 30% hydrogen peroxide. The temperature was maintained at 55-60° with an ice bath and the pH maintained above 4 by adding a solution of 20 g (0.5 mol) of sodium hydroxide in 100 ml of water dropwise as needed. After one hour, the remainder of the NaOH solution was added. At this point the temperature was 50° and the pH approximately 6. The solution was stirred for another hour as the temperature dropped to room temperature. The volume was then

reduced at 40° under vacuum to approximately 300 ml. At this point some solid had begun to precipitate from the solution. This mixture was poured into 1.5 l of acetone and the white sodium salt filtered off, washed with acetone and dried under vacuum. Yield was quantitative.

Barium Cis-epoxysuccinate Dihydrate

One half of the sodium cis-epoxysuccinate prepared above (0.5 mol) was dissolved in 300 ml of water, filtered and added to a warm solution of 222 g (0.5 mol) of barium chloride dihydrate in 370 ml of water. Within one minute a white precipitate of the barium salt formed. It was filtered off and dried under vacuum. Again yield was quantitative.

Cis-epoxysuccinic Acid

One half of the barium cis-epoxysuccinate prepared above (0.25 mol) was stirred in a round-bottom flask with 15 g of anhydrous $MgSO_4$ and 375 ml of ether at 0° in an ice bath. To this was added dropwise 24.5 g (0.25 mol) of concentrated H_2SO_4 in 100 ml of ether over a one hour period. The mixture was allowed to slowly warm to room temperature and stirred overnight. Barium sulfate was filtered off and the ether was stripped away leaving a white solid. Yield: 25.64 g (72%).

nmr (acetone-d6) δ: 3.8 (s, 2H), 10.5 (s, 2H).

Epoxysuccinic Anhydride

Dicyclohexylcarbodiimide (13.85 g, 68 mmol) in 200 ml of ether was added rapidly to 8.3 g (63 mmol) of epoxysuccinic acid in 300 ml of ether. An immediate precipitate of N,N-dicyclohexylurea formed. After one hour, the urea was filtered off and the ether stripped away, leaving a yellow solid. Yield: 7.65 g.

nmr (acetonitrile-d3) δ: 4.4 (s).

Dimethyl Trans-epoxysuccinate

Sodium trans-epoxysuccinate was prepared from fumaric acid (116 g, 1.0 mol) exactly as the cis-epoxysuccinate had been from maleic acid. Yield: 161.7 g (92%). Treatment of 88 g (0.5 mol) of this sodium salt with barium chloride dihydrate gave the barium salt. Yield: 149.3 g (98%). The barium salt (100g, 0.33 mol) was stirred at 0° with 300 ml of dry methanol as 22.6 ml (41.6 g, 0.425 mol) of concentrated H_2SO_4 was added dropwise. The mixture was then stirred at room temperature over a weekend. Anhydrous $MgSO_4$ (12 g, 0.1 mol) was added and the mixture refluxed with stirring for five hours. Then 9.35 g (90 mmol) of $CaCO_3$ was added and the mixture was suction filtered while hot and the solid washed with methanol. The methanol was rotoevaporated off and the crude product pumped dry. Recyrstallization from either chloroform or 1,2-dichloroethane gave pure product.

nmr($CDCl_3$) δ: 3.6 (s, 2H), 3.8 (s, 6H).

Dimethyl Acetylsuccinate

Sodium (38.6 g, 1.68 mol) was dissolved in 1.2 l of absolute methanol in a round-bottom flask equipped with mechanical stirrer. The solution was cooled in an ice bath and 180 ml (194.3 g, 1.68 mol) of methyl acetoacetate (Aldrich) was added. To this solution, 81 ml (100g, 0.92 mol) of methyl chloroacetate (Aldrich) was added dropwise at 0° with stirring. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The NaCl was filtered off and the solvent rotoevaporated away. The remaining slurry was poured into 600 ml of ice water, acidified with 50 ml of concentrated HCl and extracted with five 100 ml portions of ether. The combined organic layers were back-extracted with 100 ml of saturated KCl, dried over anhydrous $MgSO_4$, filtered, washed with ether, and the ether rotoevaporated off leaving a yellow liquid. Fractional distillation on a spinning band column gave fraction 1 (bp 32-50°/0.3 torr) which was unreacted methyl acetoacetate and fraction 2 (bp 72-80°/0.3 torr) which was the desired product. Yield: 79.70 g (46%).

nmr ($CDCl_3$) δ: 2.3 (s, 3H); 2.8 (d, 2H); 3.6 (s, 3H); 3.7 (s, 3H); 4.0 (t, 1H).

Dimethyl α-Acetyl-α-chlorosuccinate

Dimethyl acetylsuccinate (36.4 g, 0.19 mol) and 12 g of acetic acid were dissolved in 20 ml of water. The

solution was cooled in an ice bath and 285 ml (0.20 mol) of 5.25% NaOCl was added dropwise. The mixture was stirred for one hour, then acidified with HCl and extracted with four 100 ml portions of ether. The combined ether layers were dried over anhydrous $MgSO_4$, filtered and the ether rotoevaporated off. The mixture was then dried under vacuum. Yield: 40.8 g (97%).

nmr ($CDCl_3$) δ: 2.4 (s, 3H); 3.3 (s, 2H); 3.7 (s, 3H); 3.9 (s, 3H).

Dimethyl Acetylethylene-1,2-dicarboxylate

Dimethyl α-acetyl-α-chlorosuccinate (40.8 g, 0.184 mol) was dissolved in 240 ml of anhydrous ether and cooled in an ice bath. Triethylamine (25.5 ml, 18.6 g, 0.184 mol) was added dropwise with mechanical stirring. After four hours, the solid triethylamine hydrochloride was filtered off and washed with ether. The ether solution was back-extracted with 120 ml of water and then dried over anhydrous $MgSO_4$. The solvent was rotoevaporated off and the crude product distilled through a short spinning band column (bp 80-90°/0.5 torr). The product was a mixture of cis and trans isomers. Yield: 24.08 g (70%).

nmr ($CDCl_3$) δ: 2.4 (d, 3H); 3.7 (d, 3H); 3.8 (d, 3H); 6.7 (d, 1H).

Bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Anhydride

Maleic anhydride (100 mg, 1 mmol) was dissolved in 2 ml of ether and 70 mg (1mmol) of cyclopentadiene was added. Within 15 minutes, a white precipitate had formed. The ether was pumped off.

nmr ($CDCl_3$) δ: 1.7 (q, 2H); 3.6 (m, 4H); 6.3 (d, 2H).

5-Carbomethoxybicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Anhydride

Carbomethoxymaleic anhydride (160 mg, 1 mmol) was dissolved in 2 ml of ether and 70 mg (1 mmol) of cyclopentadiene was added. The solution was allowed to stand overnight and then the ether was pumped off leaving a colorless oil.

nmr ($CDCl_3$) δ: 1.8 (m, 2H); 3.1-3.8 (m, 3H); 3.9 (s, 3H); 6.3 (d, 2H).

9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Anhydride

Maleic anhydride (5 mg, 0.05 mmol) was dissolved in 0.1 ml of $CDCl_3$ and 9 mg (0.05 mmol) of anthracene was dissolved in 0.5 ml of $CDCl_3$. The two solutions were mixed in an nmr tube. An immediate yellow color was observed, but nmr indicated that even after 12 days, starting materials were still present.

nmr ($CDCl_3$) δ: 3.5 (t, 2H); 4.8 (t, 2H); 7.2 (m, 8H).

11-Carbomethoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Anhydride

Carbomethoxymaleic anhydride (8 mg, 0.05 mmol) was dissolved in 0.1 ml of $CDCl_3$ and 9 mg (0.05 mmol) of anthracene was dissolved in 0.5 ml of $CDCl_3$. On mixing in an nmr tube, the solution turned orange. This color gradually faded.

nmr ($CDCl_3$) δ: 2.8 (broad s, 1H); 3.7 (s, 3H); 4.8 (d, 1H); 5.1 (s, 1H); 7.2 (m, 8H).

7-Oxabicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Anhydride

Maleic anhydride (20 mg, 0.25 mmol) was dissolved in 0.3 ml of $CDCl_3$ in an nmr tube and 20 mg (0.25 mmol) of furan was added. The solution was monitored by nmr for two weeks, after which time starting materials were still present, but crystals of the adduct were growing on the sides of the nmr tube. The adduct was also prepared in diethyl ether. Maleic anhydride (100 mg, 1 mmol) was dissolved in 1 ml of ether and 70 mg (1 mmol) of furan was added and allowed to stand overnight. White crystals formed. The solution was decanted off and the crystals washed with ether.

nmr ($CDCl_3$) δ: 3.1 (s, 2H); 5.4 (d, 2H); 6.5 (d, 2H).

5-Carbomethoxy-7-oxabicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Anhydride

Carbomethoxymaleic anhydride (40 mg, 0.25 mmol) was dissolved in 0.3 ml of $CDCl_3$ in an nmr tube and 20 mg

(0.25 mmol) of furan was added. This produced an equilibrium mixture of starting materials and product.
nmr ($CDCl_3$) δ: 3.4 (s, 1H); 3.8 (s, 3H); 5.5 (d, 2H); 6.6 (s, 2H).

1-Methylcyclohexene-4,5-dicarboxylic Anhydride

Maleic anhydride (25 mg, 0.25 mmol) was dissolved in 300 µl of acetone-d6 in an nmr tube. Isoprene (25 µl, 17 mg, 0.25 mmol) was added. No color was observed. The reaction was followed by nmr. Half-life was four hours. After two days, the reaction was essentially complete.
nmr (acetone-d6) δ: 1.8 (s, 3H); 2.4 (m, 4H); 3.5 (m, 2H); 5.6 (m, 1H).

Carbomethoxy-1-methylcyclohexene-4,5-dicarboxylic Anhydride

Carbomethoxymaleic anhydride (39 mg, 0.25 mmol) was dissolved in 300 µl of acetone-d6 in an nmr tube. Isoprene (25 µl, 17 mg, 0.25 mmol) was added. No color was observed, but an nmr spectrum taken immediately showed the reaction was already over 90% complete.
nmr (acetone-d6) δ: 1.8 (s, 3H); 2.6 (m, 4H); 3.9 (s, 3H); 4.1 (m, 1H); 5.7 (m, 1H).

1-Methyl-4,4,5,5-tetracyanocyclohexene

Tetracyanoethylene (32 mg, 0.25 mmol) was dissolved in 300 µl of acetone-d6 in an nmr tube. Isoprene (25 µl, 17 mg, 0.25 mmol) was added. The solution turned

yellow. An nmr spectrum taken immediately showed the reaction was already over 90% complete.
nmr (acetone-d6) δ: 2.0 (s, 3H); 3.4 (m, 4H); 5.8 (m, 1H).

1-Chlorocyclohexene-4,5-dicarboxylic Anhydride

Maleic anhydride (25 mg, 0.25 mmol) was dissolved in 300 µl of acetone-d6. The solution was colorless. Chloroprene (23 µl, 22 mg, 0.25 mmol) was added. The solution turned slightly milky. The reaction was followed by nmr. The half-life was 5 days.
nmr (acetone-d6) δ: 2.7 (m, 4H); 3.7 (m, 2H); 6.0 (m, 1H).

Carbomethoxy-1-chlorocyclohexene-4,5-dicarboxylic Anhydride

Carbomethoxymaleic anhydride (39 mg, 0.25 mmol) was dissolved in 300 µl of acetone-d6. The solution was colorless. Chloroprene (23 µl, 22 mg, 0.25 mmol) was added. The solution turned slightly milky. The reaction was followed by nmr. The half-life was 1¼ hours. After 24 hours all of the CMA was gone.
nmr (acetone-d6) δ: 2.9 (d, 4H); 3.8 (s, 3H); 4.2 (t, 1H); 6.0 (m, 1H).

1-Chloro-4,4,5,5-tetracyanocyclohexene

Tetracyanoethylene (32 mg, 0.25 mmol) was dissolved in 300 µl of acetone-d6. The solution was slightly yellow. Chloroprene (23 µl, 22mg, 0.25 mmol) was added. The solution turned bright yellow. The reaction was

followed by nmr. After nine days, the ratio of chloroprene to product was 4.3:1.

nmr (acetone-d6) δ: 3.6 (m, 2H); 3.8 (m, 2H); 6.2 (m, 1H).

Cyclohexene-4,5-dicarboxylic Anhydride

Butadiene (200 µl) was liquified and dissolved in acetone-d6 to a total volume of 2.0 ml. Maleic anhydride (25 mg, 0.25 mmol) was dissolved in 100 µl of acetone-d6 in an nmr tube. To this solution was added 200 µl (0.25 mmol) of the 10% butadiene solution. No color was observed. The reaction was followed by nmr. The half-life was 9 hours. After 22 hours, the ratio of butadiene to adduct was about 1:4.

nmr (acetone-d6) δ: 2.4 (m, 4H); 3.6 (m, 2H); 5.9 (m, 2H).

4-Carbomethoxycyclohexene-4,5-dicarboxylic Anhydride

Carbomethoxymaleic anhydride (39 mg, 0.25 mmol) was dissolved in 100 µl of acetone-d6 in an nmr tube. To this solution was added 200 µl (0.25 mmol) of the 10% butadiene solution. No color was observed. The reaction was followed by nmr. The half-life was less than 5 minutes. The reaction was essentially complete in one hour.

nmr (acetone-d6) δ: 2.7 (m, 4H); 3.8 (s, 3H); 4.0 (m, 1H); 6.1 (m, 2H).

4,4,5,5-Tetracyanocyclohexene

Tetracyanoethylene (32 mg, 0.25 mmol) was dissolved in 100 µl of acetone-d6 in an nmr tube. The

solution was slightly yellow. To this solution was added 200 µl (0.25 mmol) of the 10% butadiene solution. The solution turned darker yellow. The reaction was followed by nmr. The half-life was 15 minutes. After six hours, the reaction had gone to completion.

nmr (acetone-d6) δ: 3.4 (d, 4H); 6.0 (m, 2H).

Dicarbomethoxy-1,4,4a,5,6,7-hexahydro-3-methoxy-7-methyl-1,4-ethanonaphthalene-5,6,9,10-tetracarboxylic Dianhydride

Carbomethoxymaleic anhydride (156 mg, 1 mmol) was dissolved in 5 ml of ether in a vial. To this was added 149 µl (148 mg, 1 mmol) of anethole. Immediately the solution turned yellow. Within a few minutes, a white precipitate had formed and the color of the solution had begun to fade. After five hours the color was gone, but the vial was allowed to stand overnight. The ether was decanted off and the solid washed three times with ether and dried under vacuum. Yield: 155 mg (67%), mp 178-182 dec.

nmr (acetonitrile-d3) δ: 1.4 (d, 3H); 2.3 (m, 1H); 2.9 (broad s, 1H); 3.4 (s, 3H); 3.6 (s, 1H); 3.7 (s, 3H); 3.9 (s, 3H); 4.0 (m, 3H); 5.0 (q, 1H); 5.7 (t, 1H).

mass spec. (10 Ev): molecular ion 460 m/e.

Calcd: 460 m/e.

anal. calcd. for $C_{22}H_{20}O_{11}$: C, 57.39; H, 4.38.

Found: C, 57.21; H, 4.50.

Dicarbomethoxy-1,4,4a,5,6,7-hexahydro-3-methoxy-1,4-ethano-naphthalene-5,6,9,10-tetracarboxylic Dianhydride

Carbomethoxymaleic anhydride (47 mg, 0.30 mmol) was dissolved in ether in a vial. To this was added 46 µl (46 mg, 0.34 mmol) of p-methoxystyrene. The solution turned yellow, but the yellow color gradually faded and a white precipitate formed. The ether was decanted off and the precipitate washed three times with ether and dried under vacuum. Yield: 48 mg (72%), mp 207-212 dec.

nmr (acetone-d6) δ: 2.3 (m, 1H); 2.7 (m, 1H); 3.0 (m, 1H); 3.5 (s, 3H); 3.7 (s, 3H); 3.9 (s, 3H); 4.1 (m, 4H); 5.2 (m, 1H); 6.0 (m, 1H).

mass spec. (10 Ev): molecular ion 446 m/e.

Found: 446 m/e.

anal. calcd. for $C_{21}H_{18}O_{11}$: C, 56.50; H, 4.06

Found: C, 56.47; H, 4:19

1,1,2,2-Tetracyano-3-(4'-methoxyphenyl)-cyclobutane

Tetracyanoethylene (33.5 mg, 0.26 mmol) was mixed with 35 µl (35 mg, 0.26 mmol) of p-methoxystyrene in acetone-d6 in an nmr tube. The solution turned purple, but the color gradually faded to yellow.

nmr (acetone-d6) δ: 3.7 (m, 2H); 3.8 (s, 3H); 4.9 (t, 1H); 7.1 (d, 2H); 7.6 (d, 2H).

Maleic Anhydride and Triphenylphosphine

Maleic anhydride (46 mg, 0.41 mmol) and 106 mg (0.40 mmol) of triphenylphosphine were placed in an nmr tube and dissolved in $CDCl_3$. The solution was dark red. NMR showed no starting material, only product.

nmr ($CDCl_3$) δ: 3.2 (s, 2H); 7.6 (m, 15H).

ir (neat): C=O, 1720, 1800 cm^{-1}, s; CH, 2910, 3060 cm^{-1}, s.

Carbomethoxymaleic Anhydride and Triphenylphosphine

Carbomethoxymaleic anhydride (23 mg, 0.15 mmol) and 32 mg (0.12 mmol) of triphenylphosphine were placed in an nmr tube and dissolved in $CDCl_3$. The solution was yellow initially, but gradually turned orange. NMR showed the presence of triphenylphosphine, polymer and ylid.

nmr ($CDCl_3$) δ: 7.3 (d),(Φ_3P); 3.6 (broad m),(polymer); 3.3 (s, 3H); 4.3 (s, 1H); 7.6 (m, 15H),(ylid).

Maleic Anhydride and Triethylamine

Maleic anhydride (36 mg, 0.37 mmol) was dissolved in $CDCl_3$ in an nmr tube and 42.7 mg (0.42 mmol) of triethylamine was added. The solution turned reddish-brown with formation of considerable insoluble material. The experiment was repeated using only a catalytic amount of triethylamine. After sitting overnight it polymerized to a solid purple mass.

Carbomethoxymaleic Anhydride and Triethylamine

Carbomethoxymaleic anhydride (21 mg, 0.13 mmol) was dissolved in $CDCl_3$ in an nmr tube and 12.8 mg (0.13 mmol) of triethylamine was added. The solution turned orange-brown with formation of some insoluble material. The experiment was repeated using only a catalytic amount of triethylamine.

Carbomethoxymaleic anhydride (53 mg, 0.34 mmol) was dissolved in 2 ml of chloroform. Triethylamine (2 µl) was added. The solution turned slightly yellow. After 15 minutes the solution was poured into several ml of ether. A white-yellow precipitate formed which was filtered, washed with ether and dried under vacuum. η_{inh} (acetone) 0.15.

Photopolymerization of Carbomethoxymaleic Anhydride

A catalytic amount of AIBN was added to carbomethoxymaleic anhydride in a small vial and irradiated with uv light for one day. This resulted in a very viscous solid. η_{inh} (acetone) 0.10.

anal. calcd. for $C_6H_4O_5$: C, 46.16; H, 2.59

Found: C, 45.99; H, 2.85

Thermopolymerization of Carbomethoxymaleic Anhydride

A catalytic amount of AIBN was added to carbomethoxymaleic anhydride in a small vial and it was heated

to 65° for one day. This resulted in a very viscous solid. η_{inh} (acetone) 0.09, mp 208-210°.

Copolymerization of Carbomethoxymaleic Anhydride and Styrene

Carbomethoxymaleic anhydride (156 mg, 1.0 mmol) was placed in a vial, swept with nitrogen and covered with a rubber septum. The CMA was warmed to melt and 114 µl (104 mg, 1.0 mmol) of styrene was injected. The solution turned yellow, became hot and set up to a viscous gel as the color faded. The reaction was complete within five minutes. After 24 hours, the polymer was dissolved in acetone and precipitated in ether. The solid was washed three times with ether and dried under vacuum. Yield: 89.6 mg (34%). η_{inh} (acetone) 0.35.

Copolymerization of Carbomethoxymaleic Anhydride and Methyl Methacrylate

Carbomethoxymaleic anhydride (156 mg, 1.0 mmol) and 106 µl (100 mg, 1.0 mmol) of methyl methacrylate were mixed in a vial. The CMA dissolved. A catalytic amount of AIBN was added, the vial was swept with nitrogen, sealed and irradiated with uv light overnight. By the next morning, a solid plug of polymer had formed. It was dissolved in acetone and precipitated in ether. The polymer was washed with ether and dried under vacuum.

It was evident from nmr and ir that this was a copolymer. Yield: 118.4 mg (46%). η_{inh} (acetone) 0.33.
anal. found: C, 54.37; H, 5.93.

Copolymerization of Carbomethoxymaleic Anhydride and Acrylonitrile

Carbomethoxymaleic anhydride (100 mg, 0.64 mmol) and 44 µl (34 mg, 0.64 mmol) of acrylonitrile were mixed in a vial. A catalytic amount of AIBN was added, the vial was swept with dry nitrogen, sealed and heated to 65-70°. After three days, the yellow polymer which had formed was dissolved in acetonitrile and precipitated in ether as a fluffy yellowish powder. The polymer was washed three times with ether and then dried under vacuum. The ir spectrum showed only a small CN peak at 2260 cm^{-1}. Yield: 12.8 mg (10%).
anal. found: C, 47.82; H, 4.04; N, 2.96.

Copolymerization of Carbomethoxymaleic Anhydride and Tricarbomethoxyethylene

Carbomethoxymaleic anhydride (100 mg, 0.64 mmol) and 129 mg (0.64 mmol) of tricarbomethoxyethylene were mixed in a vial. These were melted together and a catalytic amount of AIBN was added. The vial was swept with dry nitrogen and heated to 65°. After three days a brown oily solid had formed and white crystals had sublimed around the top of the vial. The white crystals proved to be tricarbomethoxyethylene. The brown solid was dissolved

in acetone, precipitated in ether, washed three times with ether and dried under vacuum. Yield: 35 mg (15%).
anal. found: C, 46.84; H, 3.68.

Copolymerization of Carbomethoxymaleic Anhydride and Isobutyl Vinyl Ether

Carbomethoxymaleic anhydride (156 mg, 1 mmol) was placed in a five ml round-bottom flask with approximately 3 ml of solvent (THF, CH_2Cl_2, CH_3CN or C_6H_6) and stirred as 130 µl (100 mg, 1 mmol) of isobutyl vinyl ether was added. The flask was then swept with nitrogen, capped and stirred for four days. The solvent was then pumped off and the polymer examined by nmr. When THF was the solvent the polymer was a white solid whereas with the other three solvents a brownish tar was obtained. The polymer from the THF run was submitted for elemental analysis.
anal. calcd. for 1:1: C, 56.24; H, 6.29.
Found: C, 52.38; H, 6.51.

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