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PART I: NUCLEOPHILICITY OF CHLORIDE ION TOWARD A CARBONYL CARBON

PART II: ALLYLIC PARTICIPATION IN THE SOLVOLYSIS OF ALLYL CUMYL p-NITROBENZOATES

by

James Perry Foster

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GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by James Perry Foster

entitled I: Nucleophilicity of Chloride Ion Toward a Carbonyl Carbon

II: Allylic Participation in the Solvolysis of Allyl Cumyl p-Nitrobenzoates

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

Lee B. Jones — Dissertation Director — Date 4/23/68

After inspection of the final copy of the dissertation, the following members of the Final Examination Committee concur in its approval and recommend its acceptance:*

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SIGNED: James P. Foster

TO MARY ANN

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ABSTRACT

Part 1

Nucleophilicity of Chloride Ion Toward a Carbonyl Carbon

The relative rates of addition of chloride ion and water to a carbonyl group have been measured. Comparison was made between solvolysis and symmetrical chloride exchange reactions of ethyl chloroformate in aqueous acetonitrile mixtures at 30.1°. Contrary to recent suggestions, chloride ion does react at a measurable rate although its reactivity is somewhat diminished when compared to saturated systems. Rate ratios (chloride ion relative to water) for addition to carbonyl carbon were found to be 45, 19 and 18 for 40, 60 and 85% aqueous acetonitrile, respectively.

Part 2

Participation in the Solvolysis of Allyl Cumyl-p-Nitrobenzoate

Synthetic procedures, physical constants and spectral properties are described for p-γ, γ-dimethylallyl-, p-3-butenyl-, m-allyl-, and p-allylcumyl p-nitrobenzoates. The possibility of allylic participation during the solvolysis of these compounds in aqueous

mixtures was considered. Both substituent constants (σ^+) and skeletal rearrangement studies were used to determine the nature and extent of the interaction. The following σ^+ values were obtained: p- γ, γ -dimethylallyl, -0.262; p-3-butenyl, -0.262; p-allyl, -0.221 and m-allyl, -0.023. These data, coupled with the uniformity of activation parameters and absence of skeletal isomerization, suggest that inductive effects by the allylic double bond are the major influence in the behavior of these esters.

PART I

NUCLEOPHILICITY OF CHLORIDE ION TOWARD A CARBONYL CARBON

INTRODUCTION

Nucleophilic displacements are among the most common reactions encountered in organic chemistry. Their number as well as their tremendous synthetic utility, has prompted a great deal of effort to more fully delineate the mechanistic details involved in these reactions. From the available data one can draw reasonable conclusions as to the variables that are important in any given reaction, especially with respect to variations in the solvent, the leaving group ability and the nucleophilicity of the incoming reagent.

A linear free energy relationship has been used by Swain and Scott (1953) to define a nucleophilic constant $\underline{n}$ which is a measure of relative nucleophilicities of various groups. This equation is designed to correlate direct displacement reactions and has the form

$$\log (k/k_o) = S\underline{n}$$

where k_o is a rate constant for reaction with water, k is the corresponding rate constant for reaction with another nucleophile, S is a substrate constant defined as 1.00 for methyl bromide in water at 25^o and $\underline{n}$ is a constant characteristic of the nucleophile. Values of $\underline{n}$ for several nucleophiles are listed in Table I.1.

TABLE I.1 -- Nucleophilic Constants of Several Nucleophiles.[a]

Nucleophile	n
Water	0
Hydroxide Ion	4.2
Chloride Ion	3.0
Acetate Ion	2.7
Aniline	4.5

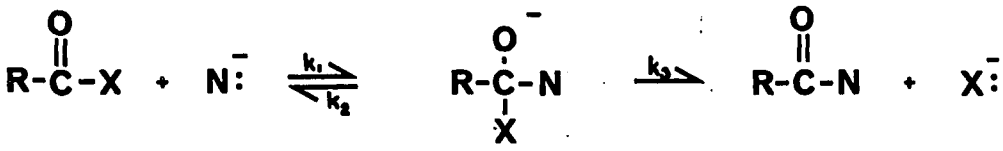
C. G. Swain and C. B. Scott, J. Amer. Chem. Soc., 75, 141(1953)

Other types of correlations have been attempted (Edwards and Pearson, 1962). Their success, however, is not much greater on a quantitative basis. Green and Hudson (1959) noted that the nucleophilicities of various species toward ethyl chloroformate were quite different from their nucleophilicities in the S_n2 attack on saturated carbon.

This immediately poses the question as to the importance of the hybridization of the reacting carbon in determining relative nucleophilicities of various species in solution. Although many nucleophilic displacement reactions are known to take place on unsaturated carbon atoms, these reactions are not completely understood.

In large part, this is due to the difficulty brought about by the mechanistic pathways usually associated with these systems.

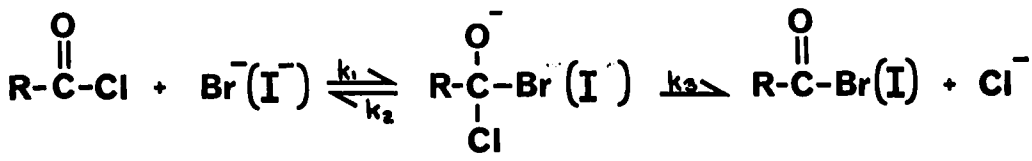
The general problem of assessing quantitatively the nucleophilic reactivity of various species toward unsaturated carbon atoms is complicated by the fact that most displacement reactions on such carbon atoms take place by an addition-elimination mechanism. Thus, under normal conditions the rate is dependent upon the addition step (k_1), as well as the ratio of rate constants for the two possible elimination steps (k_2) and (k_3).



The observed rate constant for the above reaction, assuming steady state kinetics are obeyed, is $k_1/[(k_2/k_3) + 1]$. As a result, most studies involving displacements at unsaturated centers indicate only gross effects and provide no quantitative measure of the rate of addition (k_1) of the nucleophile to an unsaturated carbon.

Hudson and Green (1962) have reported that bromide and iodide ions do not add to the carbonyl carbon of ethyl chloroformate at a measurable rate. These conclusions were based on the absence of any

rate effect of these halide ions on the rate of hydrolysis of ethyl chloroformate in aqueous acetone solution. These observations may, however, be rationalized in either of two ways: 1) the rate of addition (k_1) of halide ion to form the tetrahedral intermediate is too slow to be of any significance; 2) the addition intermediate 1 reverts to starting material faster than it proceeds to products ($k_2/k_3 \gg 1$).



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In order to be meaningful, any quantitative study of nucleophilic reactivity toward a carbonyl carbon should be capable of measuring the rate of addition (k_1) alone. By employing the technique of symmetrical exchange, information concerning the rate of addition is readily available. This study was initiated to determine the relative rates of addition of chloride ion and water to the carbonyl carbon of ethyl chloroformate.

EXPERIMENTAL

Materials -- Eastman practical grade acetonitrile was purified by primary distillation from sodium hydroxide followed by distillation from phosphorus pentoxide to yield material having bp 80-81°. Matheson technical grade n-hexane was stirred over concentrated sulfuric acid, washed with water, dried over sodium hydride, and distilled to give material having bp 68-69°. Eastman White Label ethyl chloroformate was filtered to remove the calcium carbonate stabilizer and distilled through a short Vigreux column to give material having bp 93.5-94.5°. Dioxane and tetrahydrofuran were purified by standard procedures (Fieser, 1957).

Tetra-n-Butylammonium Chloride-^{36}Cl -- Tri-n-butylamine (43 g, 0.23 mole) and n-butyl bromide (32 g, 0.23 mole) were refluxed for 2 days in 250 ml of dry acetonitrile. The pale yellow solution was poured into 700 ml of dry ether and the resultant crystalline precipitate was filtered. The tetra-n-butylammonium bromide was dissolved in 100 ml of water and the solution was passed through a Dowex 1-X8 anion-exchange resin in the chloride form enriched with chlorine-36. The water was removed under reduced pressure and the viscous solution was dried in a vacuum desiccator over phosphorus pentoxide

to yield 38 g of a white powder. This compound was extremely hygroscopic and had to be stored in a dry atmosphere.

Scintillation Solution -- To 750 g of dioxane and 250 g of tetrahydrofuran was added 4 g of 2,5-diphenyloxazole (PPO) and 0.2 g of 1,4-bis(4-methyl-5-phenyloxazolyl) benzene (POPOP). PPO and POPOP were obtained from Packard Instrument Co.

Exchange Measurements -- A reaction flask containing the aqueous acetonitrile solvent and the desired quantity of tetra-n-butylammonium chloride -^{36}Cl was allowed to reach thermal equilibrium in a constant temperature bath maintained at 30.1 ± 0.05°. The required amount of ethyl chloroformate was added and aliquots of the reaction mixture were removed at various time intervals and extracted with n-hexane. Experiments indicated that equilibrium of the ethyl chloroformate between the aqueous and n-hexane layers was rapid and required less than two minutes. The ionic chloride remained in the aqueous layer. A 1 ml sample of the n-hexane layer was then placed in a counting vial containing 15 ml of scintillation solution and the radiochloride concentration was determined by counting with a Nuclear Chicago Mark I liquid scintillation counter. High specific activities of the enriched salt were employed to increase the sensitivity of the measurements. Product studies by Hudson and Green (1962) indicate

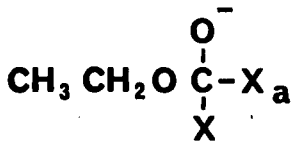
that the activity in the n-hexane layer must be due to labeled ethyl chloroformate and not ethyl chloride.

Solvolytic Measurements -- For internal consistency a kinetic technique analogous to that employed for the chloride exchange measurements was followed except that unlabeled tetra-n-butylammonium chloride was used. In a few instances lithium chloride was used. This, however, had no gross effects upon the rates. Samples taken from the extracted n-hexane phase were analyzed for ethyl chloroformate according to the procedure of Kivinen (1965).

Kinetic Treatment -- The kinetic analysis of the solvolytic reactions has been described elsewhere (Kivinen, 1965) and was used without modification. The kinetic treatment for the chloride exchange rates was similar to that used by McCleary and Hammett (1941). See Appendix A for further explanation.

RESULTS AND DISCUSSION

Symmetrical exchange studies have the advantage that the addition intermediate 2, excluding the small isotope effects, has an equal probability of partitioning between reactant and product ($k_2/k_3 = 1$).



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As a result, the rate of incorporation of some species, X_a, chemically equivalent to the group being displaced, is one-half its rate of addition to the carbonyl carbon ($k_1 = 2\ k_{obs.}$). This results in a considerable simplification of the kinetic expressions and allows a direct measurement of the rate constant for the addition step.

The method chosen consisted of studying the symmetrical chloride exchange and solvolysis reactions in aqueous acetonitrile solution of ethyl chloroformate and tetra-n-butylammonium chloride-^{36}Cl, a chloride salt known to be dissociated in solvents of this nature (Winstein, et al, 1960). There are several advantages associated with this system. The rate of addition of water to the carbonyl carbon (k_1) may be approximated by the rate of hydrolysis of

the acid chloride since acid chlorides show little or no oxygen-18 exchange during hydrolysis (Bunton, Lewis, and Llewellyn, 1954). Further, evidence for the presence of a tetrahedral intermediate in the hydrolysis of ethyl chloroformate, a critical requirement in symmetrical exchange studies, has been presented by Hudson and Green (1962) and Kivinen (1965). Consistent with this suggestion is our observation that hydrolysis of this acid chloride shows no electrophilic catalysis when studied in the presence of silver perchlorate.

The rates of nucleophilic chloride exchange and solvolysis are listed in Table I.2. The ratio $2k_e/k_s$ where k_e and k_s are the second order rate constants for exchange and solvolysis, respectively, is a measure of the rate of addition of chloride ion relative to water to the carbonyl carbon of ethyl chloroformate.

TABLE I.2 -- Rates of Chloride Exchange and Solvolysis for Ethyl Chloroformate in Water - Acetonitrile Mixtures at 30.1°.

% H_2O	$k_e \times 10^6$ liter/mole-sec	$k_s \times 10^6$ [a] liter/mole-sec	2 k_e/k_s
40	12.1 ± 1.3	5.35 ± 0.12	45
60	6.32 ± 0.22	6.74 ± 0.13	19
85	6.71 ± 0.10	7.31 ± 0.10	18

[a]Second-order rate constants for solvolysis were obtained by dividing the observed first-order rate constant by the water concentration.

Since the exchange measurements were made concurrently with solvolysis, the experimental error tends to be somewhat high. This is to be expected because solvolysis is fast with respect to exchange. Consequently, precise data for the solvolysis reaction is required in order to back calculate the exchange rate (see Appendix A).

The data presented in Table I.2 can be somewhat misleading if attempts are made to generalize. A comparison of these data with those obtained for saturated systems should be made with caution because the mechanisms are different and little is known about the effects of changes in hybridization on nucleophilicity. Also, the carbonyl group used here is not necessarily a good model for other carbonyl containing compounds such as aldehydes and ketones.

The data clearly indicate, however, that at least in this system, chloride ion in aqueous solution is a more reactive nucleophile toward the carbonyl carbon than is water. Its reactivity appears to be somewhat less (relative to water) than that observed for displacements on saturated carbon atoms where chlorine is observed to be more reactive than water by a factor of approximately one thousand (Table I.1). Conversely, although Hudson and Green (1962) suggested that chloride ion was unreactive toward ethyl chloroformate, it is obvious that this is not the case. It is felt that this discrepancy arises from the increased sensitivity of the measurements made in this work.

Rationalization of the observed reactivities are difficult since there have been so few studies of this nature. Bender and Glasson (1959) have postulated that nucleophile basicity (proton affinity) may be of much greater importance in substitution on unsaturated than saturated carbon atoms. In addition, Hine and Weimar (1965) have pointed out that it is possible that the order of nucleophilicities toward ethyl chloroformate observed by Hudson and Green (1962) may be the same as the order of basicities (affinity for a carbonyl carbon). The trend observed here is qualitatively similar to that expected on the basis of these workers' suggestions, but quantitatively the ratios seem low. It is not unreasonable to assume that the transition state occurs late in both the exchange and solvolysis reactions, i.e. tetrahedral intermediate

formation is well under way at the transition state, (Bender and Glasson, 1959; Jones and Sloane, 1966). This implies a rather close approach by both the water molecule and chloride ion to the carbonyl carbon during bond formation. This would decrease the reactivity of chloride ion relative to water, since the former would suffer more from electrostatic repulsion by the flanking chlorine and oxygen atoms (Jencks and Carriuolo, 1960).

Carbon basicity (which may or may not parallel proton affinity) could be a factor of overriding importance. Unfortunately, the variables which control this effect are not well enough understood to discuss its ramifications on this study.

Exchange reactions of substituted aromatic acid chlorides were studied briefly. Both the complexity of the exchange data and the disagreement as to the mechanism of their solvolysis (Swain and Langsdorf, 1951; Hudson and Saville, 1955; Bender and Ginger, 1960) led to the abandonment of these compounds in favor of ethyl chloroformate.

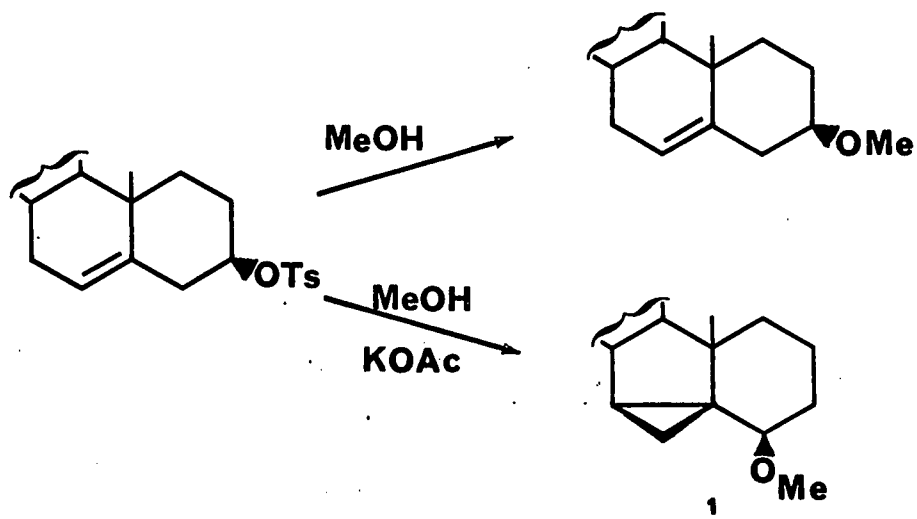
PART II

ALLYLIC PARTICIPATION IN THE SOLVOLYSIS OF ALLYL CUMYL p-NITROBENZOATES

INTRODUCTION

The question of carbon-carbon sigma and pi bond participation in solvolysis reactions has been intimately associated with allylcarbinyl, cyclopropylcarbinyl and cyclobutyl compounds. The solvolytic rate enhancements, skeletal isomerizations, and isotopic scrambling of these compounds (collectively referred to as homoallylic) have held the interest of organic chemists for twenty years (Bartlett, 1965; Breslow, 1963; Brown, 1966; Hanack and Schneider, 1967; Schleyer and van Dine, 1966; Sargent, 1966; Vogel and Roberts, 1966).

Participation of a double bond in a solvolysis reaction was first suggested in the i-steroid reaction (Shoppee, 1946; Winstein and Adams, 1948). It was found that nucleophilic displacements at C_3 in



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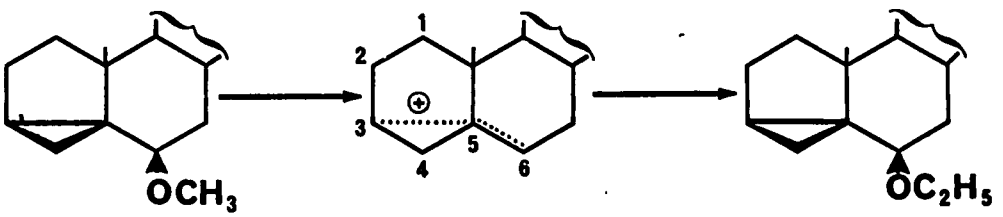
Δ^5 - cholestene derivatives led to an overall retention of configuration. In addition, the hundred-fold solvolysis rate enhancement of this compound over saturated analogs, isolation of a cyclopropyl structure 1, and the stereospecific ether exchange at the 6-position of i- cholesteryl methyl ether, 2 → 4, led to the proposal of an intermediate ion 3,



2 3 4

which has the cationic charge distributed between positions 3 and 6 (Winstein and Schlesinger, 1948).

The relationship of intermediate(s) between cyclobutyl, cyclopropylcarbinyl and allylcarbinyl compounds is very striking in the simplest homoallyl derivatives. Deamination of cyclopropylcarbinyl- and cyclobutylamine, hydrolysis of cyclopropylcarbinyl and cyclobutyl chloride (Roberts and Mazur, 1951), and the formolysis of allylcarbinyl tosylate (Roberts and Servis, 1964) all yielded the same products and in approximately the same proportion as seen in Figure II.1. In addition, carbon-14 studies show extensive but incomplete scrambling of the carbon atoms during reaction.

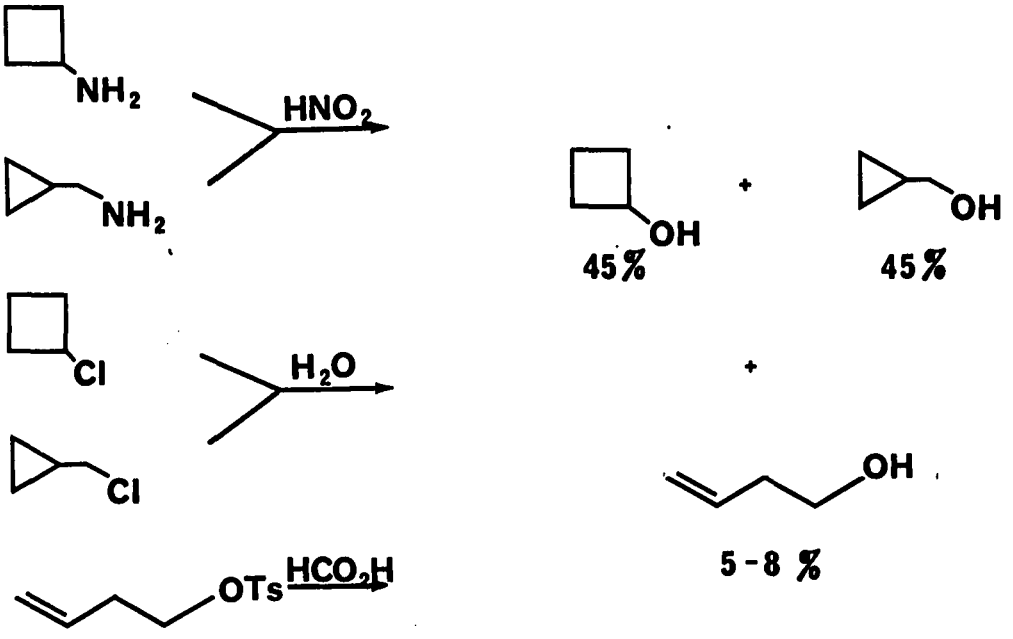
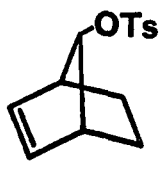


Figure II.1 - Products & Product Distribution for Representative Homoallylic Reactions

Rigid bicyclic compounds have also been used to determine the effectiveness of carbonium ion stabilization by a neighboring small ring or double bond. The most familiar example is the comparison of the solvolysis reactions of anti-7-norbornenyl tosylate 5 and 7-norbornyl tosylate 6. It was observed that the



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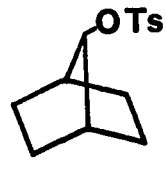

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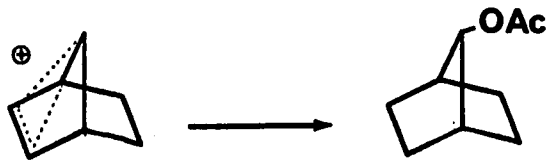
acetolysis of 5 was 10^{11} times as fast as 6. The high reactivity of 5 was attributed to anchimeric assistance to ionization by the π cloud yielding the 7-norbornenyl cation 7. In addition, 7 reacts with the solvent stereospecifically with overall retention of configuration (Winstein, et al, 1955).



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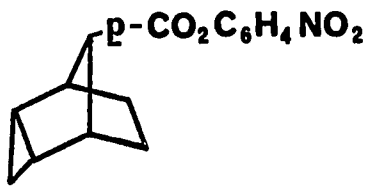
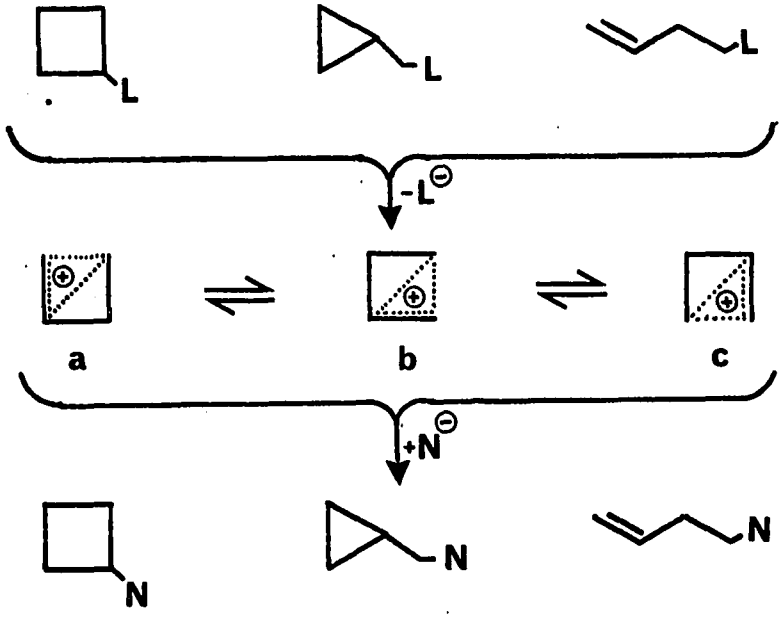
Later, nmr spectroscopic investigation showed that the charge was located mainly on C-5 and C-6 and less on C-7 (Brookhart, Diaz and Winstein, 1966; Richey and Lustgarten, 1966). Quite similar behavior has been observed for endo-anti-8-tricyclo $[3.2.1.0^{2,4}]$ octyl p-nitrobenzoate 8. The cyclopropyl group



8

enhances the 8 solvolysis rate by a factor of 10^{14} over the unsubstituted ester (Tinida, Tsuji and Irie, 1967; Deyrup, et al, 1967).

In an attempt to rationalize the solvolytic rate enhancements, skeletal rearrangements, and isotope scrambling found in these compounds, Roberts, et al, (1959) proposed the formation of an intermediate bicyclobutonium ion 9 a-c. To account for the non-random scrambling of the skeletal carbon atoms, each of these species was assumed to be rapidly but not instantly interconverted. Also, each

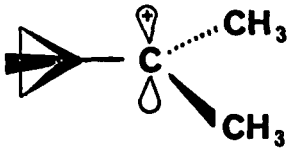


gave the same product mixture upon reaction with a nucleophilic reagent.

With one notable exception (Brown, 1962; 1966) this suggestion served as a basis for discussion in most studies of

homoallylic systems. Some results indicate, however, that the generality, if not the existence, of the bicyclobutonium ion as envisioned by Roberts may be limited.

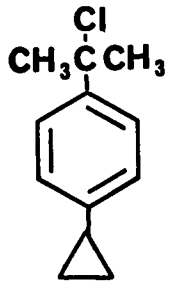
The direct observation of cyclopropylcarbinyl cations in strong acid solution provided evidence that stabilization effects of the cyclopropyl group involve considerable charge dispersal through the cyclopropyl ring but no extensive skeletal rearrangements (Deno, et al, 1962; Pittman and Olah, 1965). The cyclopropylcarbinyl carbonium ion generated by addition of dimethylcyclopropylcarbinol to FSO_3H-SO_2-SbF_5 at -78° is especially interesting. Nmr spectra indicate that the methyl groups in the ion are not equivalent, being separated by 0.54 ppm. In addition, no rotation of the cyclopropyl group was observed because the methyl peaks did not coalesce upon warming to -35° at which temperature the ion was destroyed. It was suggested that the cyclopropyl ring lies in a plane perpendicular to the plane of the gem-dimethyl group 10 in a fixed bisected form. The cyclopropyl



10

ring was assumed to be utilizing its "banana" bonds in this fashion to obtain maximum overlap with the electron deficient site.

The bisected form has also found support in solvolytic studies. Brown and Cleveland (1966) studied the rates of solvolysis for methyl substituted derivatives of p-cyclopropylcumyl chloride 11, 12, 13.



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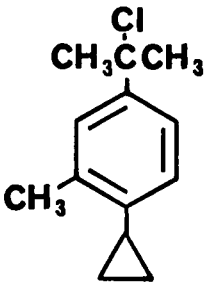

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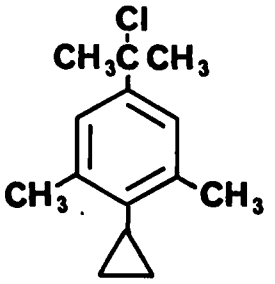
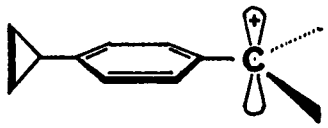


13

It was found that after correction for the presence of the methyl group, 12 was only slightly less reactive than 11. The cyclopropyl group still possesses the conformational freedom to stabilize the carbonium ion in a bisected form similar to 10. The cyclopropyl group in 13 shows none of the reactivity found in 11 and 12 after a similar substituent correction. In this case the cyclopropyl ring is forced into a conformation not suitable for participation. Also, the high ρ value (-0.410) for the cyclopropyl group and high entropy of activation in the solvolysis of 9 relative to other para substituted alkyl groups (Jones and Jones, 1966) suggest that if there is no large charge dispersal in the transition state,

the cyclopropyl ring can stabilize a carbonium ion to a considerable extent provided the proper conformation can be attained. This again is consistent with a bisected cyclopropyl ring conformation 14.



14

Work in aliphatic cyclopropyl derivatives yields similar conclusions. Schleyer and van Dine (1966) have found that methyl groups on cyclopropylcarbinyl p-nitrobenzoates increase the rate of hydrolysis, even when they are attached to the carbon atom that is supposedly uncharged in the unsymmetrical bicyclobutonium ion model. This suggests that the charge is distributed over all the carbon atoms in the ring as in the symmetrical bisected ion.

The nature and extent of allylcarbinyl participation in compounds such as 11 is unknown. Such data would provide information as to the capability of an allyl group to participate via resonance with an electron deficient site. The purpose of this study is to provide such data on allyl and substituted allyl cumyl p-nitrobenzoates.

EXPERIMENTAL

General -- Melting points were determined with a Mel-Temp capillary apparatus and are uncorrected. Nmr spectra were determined in CCl_4 solution with Varian A-60 and HA-100 spectrometers using external and internal tetramethylsilane respectively as standards. Infrared spectra were determined with a Perkin-Elmer Model 337 using neat samples between sodium chloride plates. Ultraviolet spectra were obtained on a Cary Model 14 spectrometer. Gas chromatography was performed on a Wilkins Model A-90, P-3 chromatograph. The columns used were a 5 foot, 5% FFAP on 60/80 Chromsorb P, and an 8 foot, 18% GE-SE-30 on base washed Chromsorb P. Microanalyses were performed by Huffman Laboratories, Inc., Wheatridge, Colorado.

Materials -- Mallinckrodt A. R. acetone was refluxed with potassium permanganate until the color persisted and was then distilled. Magnesium turnings and dry ether were both Mallinckrodt A. R. The p-dibromobenzene, p-bromoanisole, p-bromotoluene, and bromobenzene were Matheson A. R. p-Bromochlorobenzene, t-butylbenzene and p-chlorobenzyl chloride were obtained from Aldrich Chemical Co. All were used as received. Eastman practical grade allyl bromide was

stirred over calcium chloride and distilled before use. Drying was done with magnesium sulfate unless otherwise noted.

p-t-Butylbromobenzene -- t-Butylbenzene (100 g, 0.745 moles) and 6.1 g of iron filings were placed in a 500 ml round bottom flask equipped with a magnetic stirrer, thermometer, addition funnel and condenser fitted with a hydrogen bromide trap. Bromine (131 g, 0.820 moles) was then added dropwise over a two hour interval during which time the temperature was maintained at 30°. The solution was then stirred overnight at room temperature. An equal volume of ether was added and the mixture was extracted with successive portions of sodium bisulfite, sodium bicarbonate and water. The solution was dried (K_2CO_3), concentrated, and distilled, giving 87 g of p-t-butylbromobenzene: bp 130-133° (20 mm); n_D^{27} 1.5300; lit. bp 101-103.5° (11 mm); n_D^{27} 1.534 (Boocock and Hickinbottom, 1961).

γ, γ-Dimethylallyl Chloride -- The procedure was as previously described (Ultée, 1948). A solution of 477 g (7.0 moles) of isoprene (Eastman White Label) and 100 ml of dry ether was cooled to -70°. Dry HCl was then bubbled into the solution until 170 g had been added. The reaction mixture was allowed to stand overnight at Dry Ice temperature. The solution was then neutralized with anhydrous potassium

carbonate, dried ($CaCl_2$) and distilled through a four foot Widmer column, yielding 220 g of γ,γ-dimethylallyl chloride, bp 45-60° (150 mm); lit. bp 67.2° (167 mm) (Young, Winstein and Goering, 1951).

1-(p-Chlorophenyl)-3-methyl-2-butene -- The Grignard reagent from 103.0 g (0.54 moles) of p-bromochlorobenzene and 13.1 g of magnesium turnings was prepared in 200 ml of dry ether by conventional techniques. The solution was cooled to 0° and 57.0 g (0.54 moles) of γ,γ-dimethylallyl chloride in 100 ml of ether was added over fifteen minutes. A two phase system gradually developed and after an hour of stirring the inorganic salts were granulated by dropwise addition of saturated aqueous ammonium chloride. The slurry was filtered and the solids were washed with 2 - 100 ml portions of ether. The washings and filtrate were combined, dried, concentrated and distilled, yielding 40.8 g (42%) of 1-(p-chlorophenyl)-3-methyl-2-butene: bp 84-88° (1.5 mm); n_D^{27} 1.5303; nmr (CCl_4) δ 1.54 (d, 6H, J = 4Hz further split, J = 1Hz $-CH_3$), 3.08 (d, 2H, J = 8Hz, $-CH_2-$) 4.95-5.37 (t, 1H, J = 8Hz, further split into multiplet, J = 1Hz = CH-), 6.93 (m, 4H, Aromatic H).

This reaction, as well as other coupling reactions to be described subsequently, has an induction period of one to five minutes. Some care must therefore be taken during the initial addition

of the halide to keep its concentration at a minimum or some of the material will be lost from vigorous boiling.

p-Bromoallylbenzene -- The Grignard reagent from 354 g (1.5 moles) of p-dibromobenzene and 40 g of magnesium turnings in 900 ml of ether was prepared by conventional techniques. A solution of 200 g (1.65 moles) of allyl bromide in 100 ml of ether was then added. Work-up as above with ammonium chloride followed by distillation of the concentrate yielded 193 g (65%) of p-bromoallylbenzene: bp 117-122° (19 mm); n_D^{27} 1.5507; lit. bp 95-96° (12 mm); n_D^{20} 1.520 (Frisch, 1959); nmr (CCl_4) δ 3.01 (d, 2H, J = 6Hz, $-CH_2-$), 4.63-5.10 (m, 2H, $=CH_2$), 5.35-6.20 (m, 1H, -CH =), 6.50-7.45 (m, 4H, Aromatic H). Vpc analysis (GE-SE-30) of the product indicated a 4% contamination with p-dibromobenzene.

3-(p-Chlorophenyl)-1-butene -- Using the previously described procedures, the Grignard reagent from 125 g (0.778 moles) of p-chlorobenzyl chloride and 19 g of magnesium turnings in 500 ml of ether was coupled with a solution of 97 g (0.8 moles) of allyl bromide in 100 ml of ether. Distillation yielded 77.6 g (60%) of 3-(p-chlorophenyl)-1-butene; bp 59-61° (1.4 mm); n_D^{27} 1.5234 nmr (CCl_4) δ 1.82-2.63 (m, 4H, $-CH_2CH_2-$), 4.53 (m, 1H), 4.75 (m, 1H) 5.11-5.80 (m, 1H), 6.47-6.91 (m, 4H, Aromatic H).

m-Chloroallylbenzene -- Using the previously described procedures, the Grignard reagent from 100 g (0.68 moles) 0f m-dichlorobenzene and 16.5 g of magnesium turnings in 110 ml of tetrahydrofuran (THF) (Ramsden, et al, 1957) was coupled with a solution of 84.8 g (0.70 moles) of allyl bromide in 30 ml of THF. Since magnesium halides are somewhat soluble in THF, 500 ml of pentane was added to precipitate them prior to adding the saturated ammonium chloride solution. Distillation of the concentrate yielded 26 g (25%) of m-allylchlorobenzene: bp 60-65° (3 mm); n_D^{27} 1.5321; nmr (CCl_4) δ 2.65 (d, 2H, J = 7Hz, $-CH_2-$), 4.27 (m, 1H), 4.50 (m, 1H), 4.82-5.42 (m, 1H), 6.09-6.58 (m, 4H, Aromatic H).

2-Phenyl-2-propanol -- The Grignard reagent from 157.0 g (1.0 moles) of bromobenzene and 24.3 g of magnesium in 500 ml of ether was prepared by conventional techniques. A solution of 58 g (1.0 mole) of acetone in 100 ml of ether was added with cooling. After a short period of stirring, the alkoxide salts were destroyed by adding a saturated ammonium chloride solution until a heavy granular precipitate formed. The solution was filtered, the salts washed with 2 - 100 ml portions of ether and the washings and filtrate were combined, dried and concentrated. Distillation of the residual oil

from potassium carbonate in base-washed glassware yielded 67 g (50%) of 2-phenyl-2-propanol: bp 60-65° (4mm).

The same general procedure was employed in the synthesis of the other substituted phenyldimethylcarbinols. Tetrahydrofuran was used when it was necessary to generate an aryl chloro-Grignard. Table II.1 lists the starting aryl compound as well as the physical constants of these alcohols. Nmr spectra of all the alcohols were consistent with structure and where available, the physical constants were in agreement with those obtained by Brown and Okamoto (1957), Brown, Okamoto, and Ham (1957), and Brown, et al (1957).

TABLE II.1 -- Physical Constants and Starting Halides of p-Substituted 2-Phenyl-2-Propanols

Substituent	Parent Compound	mp	bp	mm	n_D^{27}
p-Hydrogen	Bromobenzene		60-65°	4.0	1.5102
p-Methyl	p-Bromotoluene		76-78°	2.0	1.5128
p-t-Butyl	p-Bromo-t-butyl-benzene	76-78°			
p-Methoxy	p-Bromoanisole		85-90°	0.5	1.5263
p-Allyl	p-Bromoallylbenzene		70-75°	0.2	1.5217
p-Chloro	p-Bromochlorobenzene	42-43°	98-103°	4.0	1.5339
p-γ,γ-Dimethyl allyl	p-γ,γ-Dimethylallyl-chlorobenzene		85-95°	0.5	1.5247
m-Allyl	m-Allylchlorobenzene		74-77°	3.0	1.5186
p-3-Butenyl	p-3-Butenyl-bromobenzene		104-107°	0.45	1.5184

Conversion of Alcohols to p-Nitrobenzoates

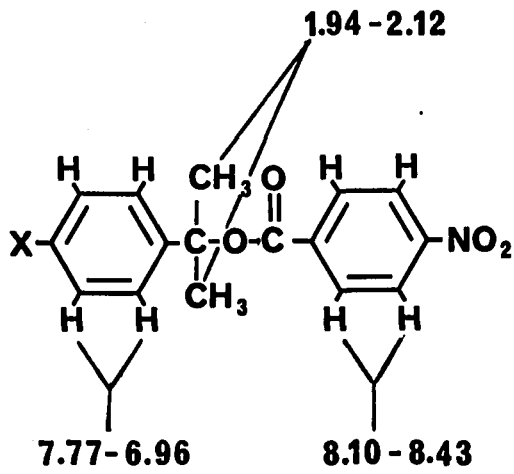
Although minor variations were used from alcohol to alcohol, the following procedure for 2-(p-chlorophenyl)-2-propyl p-nitrobenzoates is a typical example. Hereafter the alcohol portion of the esters will be named according to the cumyl system. Thus the above becomes p-chlorocumyl p-nitrobenzoate.

A solution of 17.0 g (0.1 mole) of p-chlorocumyl alcohol in 100 ml of dry pyridine was cooled to 0^{o} and 18.6 g (0.1 mole) of p-nitrobenzoyl chloride (freshly recrystallized from CCl_4) was added in portions. After stirring for 24 hours at 0^{o} the solution was poured into a cold mixture of 200 ml of 3 N hydrochloric acid and 200 ml of pentane. The solution was filtered, the organic layer of the filtrate was separated and the aqueous layer was extracted with 2 - 100 ml portions of pentane. The pentane solutions were combined, washed with successive 100 portions of cold 3 N hydrochloric acid, saturated sodium bicarbonate and water. Drying and concentrating yielded an oil which was crystallized by trituration with cold pentane. Recrystallization from hexane yielded 18.1 g (57%) of p-chlorocumyl p-nitrobenzoate: mp 133-134.5^{o}; λ max (C_2H_5OH) 259 m, (log ϵ = 3.108); nmr (CCl_4) δ 2.08 (s, 6H, CH_3 - C - CH_3), 7.44 (s, 4H, cumyl ring aromatic H), 8.39 (s, 4H, p-nitrobenzoyl H).

Table II.2 lists the melting points and ultraviolet absorbances for all the esters synthesized and elemental analysis of the olefinic esters used in this study. The uniformity of the ultraviolet spectra are also found in the nmr spectra. Figure II.2 indicates the regions in the spectrum where absorbances occur. For reference purposes the nmr spectrum of each olefinic ester has been included separately (Figures II.3 - II.6).

TABLE II.2 -- Melting points, Absorbances and Chemical Analysis of Cumyl p-Nitrobenzoates Synthesized

p-Substituent	mp	λ max (log ε)	C(calc.)	H(calc.)	C(found)	H(found)
Hydrogen	132.5-133.5°	259 (3.102)				
Methyl	105-107°	259 (3.105)				
Methoxyl	88-91° (167-175)					
t-Butyl	114-116°	260 (3.114)				
Chloro	133-134.5°	259 (3.108)				
p-Allyl	45.4-46.1°	260 (3.109)	70.14	5.89	70.04	5.91
m-Allyl	66-67°	260 (3.110)	70.14	5.89	69.94	5.83
p-3-Butenyl	69-69.5°	260 (3.107)	70.78	6.24	70.63	6.22
γ,γ-Dimethylallyl	71.0-71.8°	258 (3.102)	71.37	6.56	71.53	6.65



X = H, Cl, OCH_3, t-Bu, CH_3

Figure II.2 Regions of Nmr absorption (δ) for the p-Nitrobenzoates Indicated

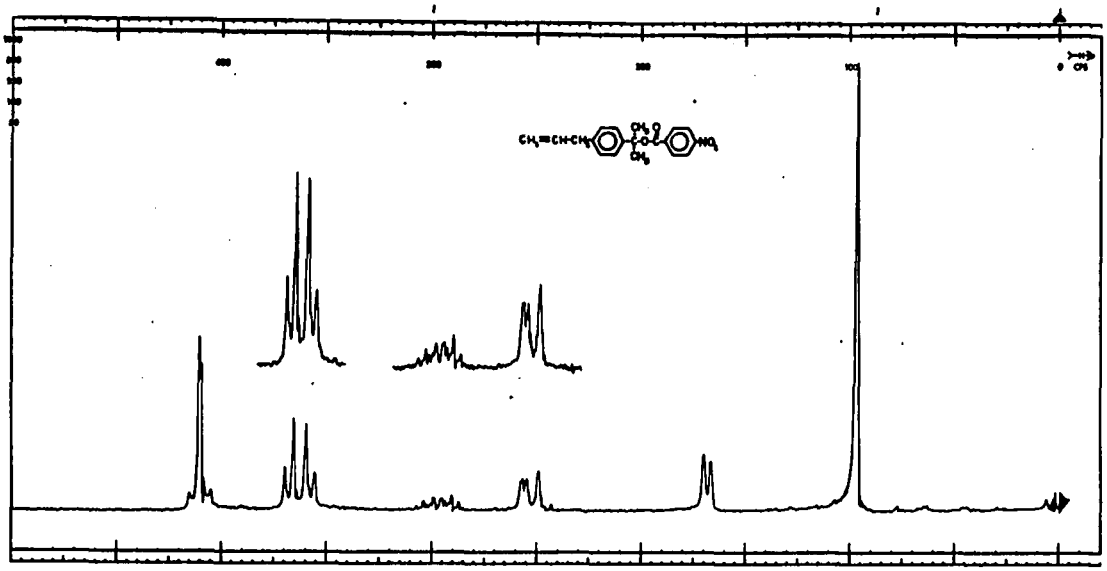


Figure II. 3 -- 100 MHz Nmr Spectrum of p-Allylcumyl p-Nitrobenzoate

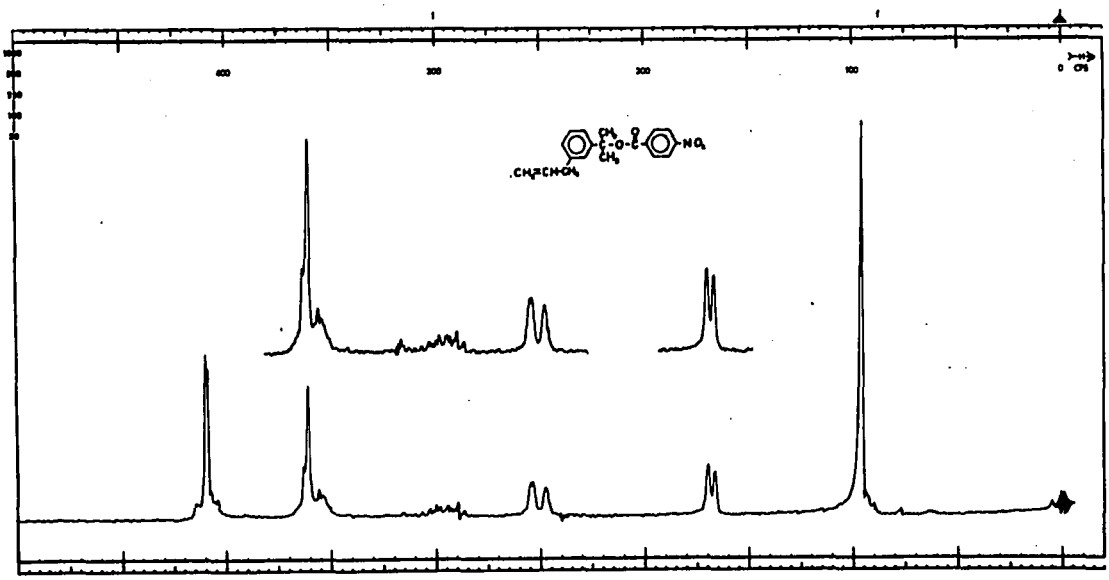


Figure II. 4 -- 100 MHz Nmr Spectrum of m -Allylcumyl p-Nitrobenzoate

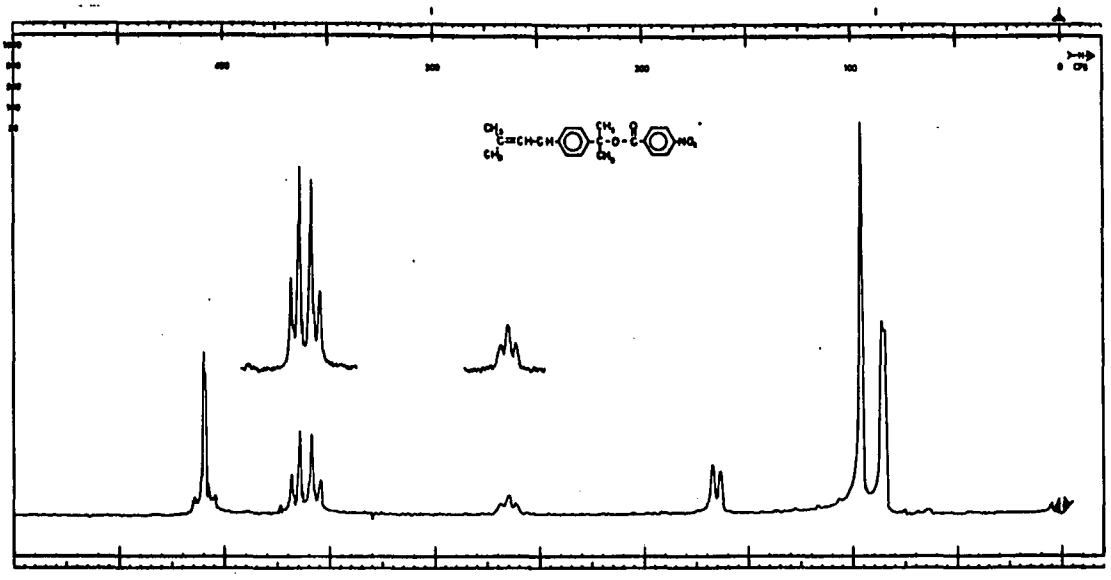


Figure II. 5 -- 100 MHz Nmr Spectrum of p-γ,γ- Dimethylallylcumyl p- Nitrobenzoate

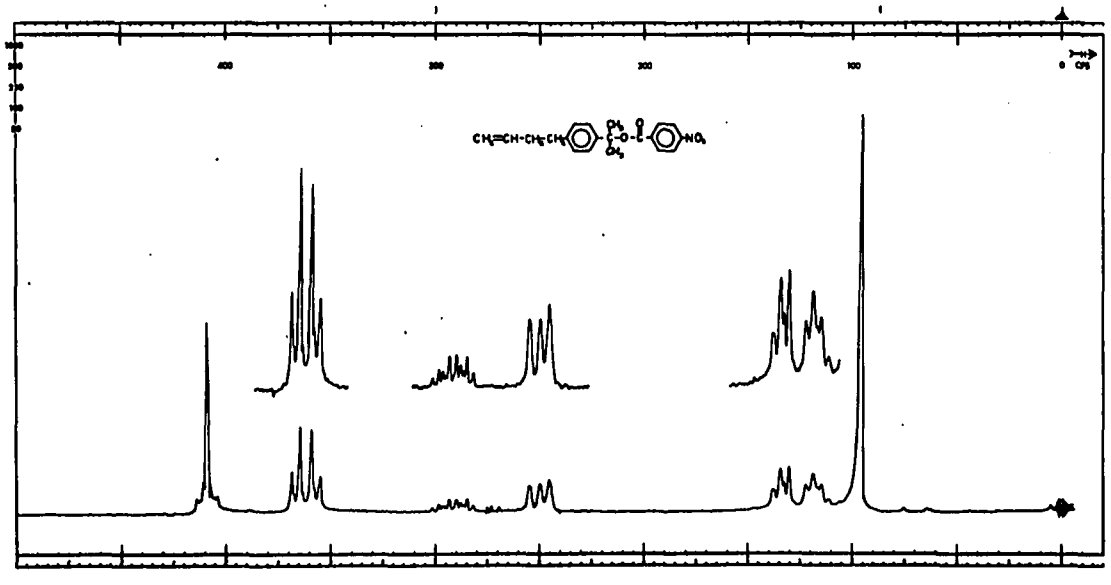


Figure II. 6 -- 100 MHz Nmr Spectrum of p-3 - Butenylcumyl p- Nitrobenzoate

Kinetic Procedure -- The desired amount of ester was dissolved in a preweighed quantity of acetone in a 100 ml volumetric flask and the required weight of distilled, carbonate free water was then added with shaking. The flask was placed in a thermostated bath and allowed to equilibrate for fifteen minutes. In those cases where the half-life was less than thirty minutes, the solvents were pre-equilibrated at the bath temperature before mixing. At appropriate time intervals, 9 ml samples were removed, quenched with 10 ml of acetone at 0^{o} and the free p-nitrobenzoic acid was titrated with approximately 0.02 N sodium hydroxide using bromthymol blue as the indicator. Infinity titers were taken after at least ten times the estimated half life. Temperatures in all cases were controlled to at least $\pm 0.03^{o}$. Appendix C contains experimental data for individual rate constants.

Product Studies -- A solution of 0.3070 g of p-allylcumyl p-nitrobenzoate in 100 ml of 50% w/w aqueous acetone was allowed to stand for twe weeks at room temperature. After removing the acetone under reduced pressure the aqueous residue containing some solid was made basic with sodium bicarbonate and the resultant solution was extracted with three 20 ml portions of ether. The extracts were combined, washed once with water, dried and concentrated. The small quantity of residual oil which remained (ca. 50 μl) was distilled

in a Hickmann still. Capillary nmr spectra (Varian HA-100 spectrometer) of the distillate proved to be identical with that of p-allylcumyl alcohol. Infrared spectra were also identical as were vapor phase chromatograms using GE-SE-30 and FFAP liquid phases. No other components were detectable in the distillate. The pot residue had a melting point of 235-240°, undepressed on mixing with an authentic sample of p-nitrobenzoic acid.

In similar experiments, p- γ,γ-dimethylallyl-, m-allyl-, p-3-butenyl-, and p- α,α-dimethylallylcumyl[1] p-nitrobenzoates were solvolyzed in an identical manner. Isolation of the product alcohols again proved no rearrangement took place by virtue of nmr, infrared and gas chromatographic comparisons with authentic samples.

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1. The author wishes to thank Vera K. Jones for the generous sample of p- α,α-dimethylallylcumyl p-nitrobenzoate, and information concerning its solvolysis rates.

RESULTS

The esters used in this study were synthesized with little difficulty using well known procedures. Esterification of the tertiary alcohols proved to be the most troublesome step. The procedure outlined by Dauben and Wiseman (1967) gave the best results and with slight modifications in reaction conditions and work-up, yields of 50-65% were obtained. In all cases, the products were highly crystalline with a pale yellow color. The olefinic esters gave satisfactory elemental analyses.

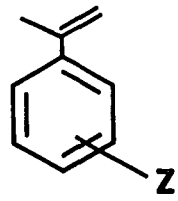
Several trial kinetic runs were required to select a solvolytic media. Rates in glacial acetic acid and ethanol were extremely slow even for the more reactive esters at elevated temperatures. In contrast, rates in formic acid were far too fast at 10^{o}. Formic and possibly acetic acids also have the disadvantage that the acidic conditions favor elimination of p-nitrobenzoic acid from the esters and rearrangement of the allylic double bonds. Either or both of these reactions would produce excessive complication in the kinetic analysis.

Water-acetone mixtures were selected for a number of reasons. The solvent properties could be altered readily by varying

the ratio of acetone to water. The solutions were neutral which minimized the above side reactions. Sharp end-points were obtained when the liberated p-nitrobenzoic acid was titrated with aqueous sodium hydroxide. Also, Brown and Okamoto (1957) used water-acetone mixtures in determining the σ^+ values for the substituents used as standards in this study. Although it is assumed that σ^+ is invariant with solvent, it was thought best to maintain conditions as close as possible to those used by Brown.

Solubility of the esters presented some difficulty especially in mixtures of high water content. The p-γ,γ-dimethylallyl, and p-t-butyl esters were the most insoluble, maximum concentration being ca 0.01 M in 50% aqueous acetone at 38°. As a result, it was necessary to dissolve the ester in the acetone and then add the water: had this order not been followed, in some cases several half-lives would have passed before all of the ester dissolved. A 50-50 w/w water-acetone mixture was the maximum water concentration that would dissolve enough ester to give good titrimetric end-points.

Detailed product studies on the olefinic esters showed that the double bond maintained its position during solvolysis and also that solvolysis products were p-nitrobenzoic acid and corresponding tertiary alcohol. No evidence of a styryl derivative was found.(15).



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The α,α and γ,γ-dimethylallyl rearrangement studies have particular significance and will be discussed later.

Table II.3 summarizes the solvolysis rates of the substituted cumyl p-nitrobenzoates at various temperatures and solvent compositions. In all cases the kinetic runs were followed to at least 70% completion. Rate constants were determined with a standard first-order rate expression except in the slower reactions where the method of Guggenheim was used. Agreement between most runs was ±1%. Several attempts were made to determine the rate constant for the methoxyl substituent. This compound solvolyzed very rapidly and could not be followed with accuracy.

TABLE II.3 -- Solvolysis Rates of Substituted Cumyl p-Nitrobenzoates at Various Temperatures and Solvent Compositions.

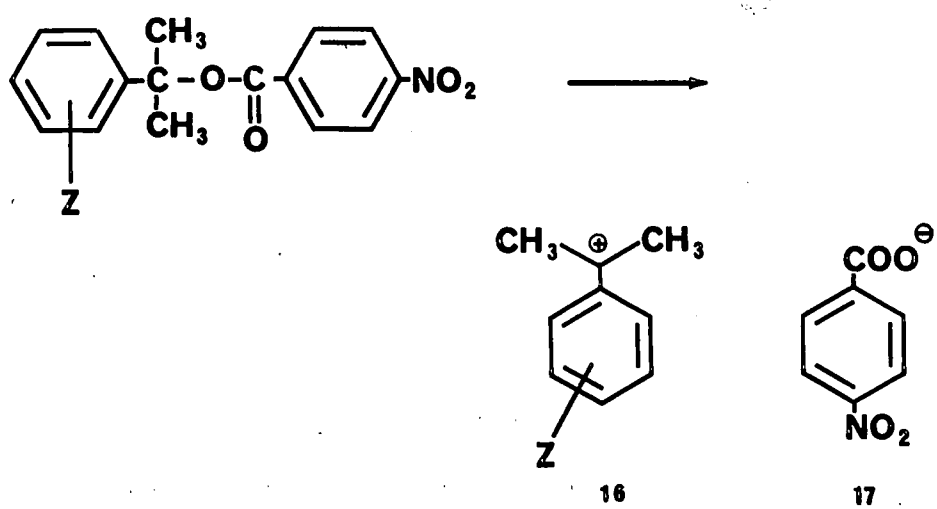
Substituent	Solvent Composition w/w	Temp.	$k_1 \times 10^5$ sec^{-1}	
p-Methyl	60% Aq. Acetone	32.0	3.31	± 0.05
p-Methyl	"	46.4	1.84	± 0.04
p-Hydrogen	"	"	0.746	± 0.007
p-Allyl	"	"	7.49	± 0.06
p-t-Butyl	"	"	11.8	± 0.2
p-Chlorine	"	"	0.220	± 0.004
p-γ,γ-Dimethylallyl	"	"	11.8	± 0.1
m-Allyl	"	"	0.858	± 0.005
p-3-Butenyl	"	"	12.7	± 0.3
p-Methyl	50% Aq. Acetone	"	61.4	± 0.2
p-Hydrogen	"	"	2.63	± 0.03
p-Allyl	"	"	24.7	± 0.1
p-t-Butyl	"	"	36.1	± 0.3
p-γ,γ-Dimethylallyl	"	"	39.0	± 0.5
m-Allyl	"	"	2.65	± 0.02
p-3-Butenyl	"	"	38.7	± 0.3
p-Methyl	"	38.0	24.6	± 0.4

TABLE II.3 -- Continued

Substituent	Solvent Composition w/w	Temp.	$k_1 \times 10^5$ sec^{-1}
p-Hydrogen	50 % Aq. Acetone	38.0	0.879 ± 0.018
p-Allyl	"	"	9.72 ± 0.10
p-t-Butyl	"	"	15.0 ± 0.1
p-γ, γ-Dimethylallyl	"	"	15.4 ± 0.2
m-Allyl	"	"	1.20 ± 0.01
p-3-Butenyl	"	"	15.6 ± 0.2
p-Allyl	"	30.0	3.87 ± 0.01
p-γ, γ-Dimethylallyl	"	"	6.15 ± 0.06
p-3-Butenyl	"	"	5.92 ± 0.06
m-Allyl	"	55.0	8.15 ± 0.06

Figures II.7, II.8 and II.9 are Hammett plots for the solvolysis of the esters under the conditions indicated. The standard substituents methyl, t-butyl, hydrogen and chlorine show good linearity (r = 0.994). The σ^+ values determined for the allylic substituents are listed in the discussion section.

These figures provide insight into the mechanism for these reactions. The linearity observed by using σ^+ substituent constants (rather than σ as seen in Figure II.10), coupled with the large ρ values ca. -4.6 indicates that a carbonium ion is being developed which allows direct conjugation between substituent and reacting carbon (Brown and Okamoto, 1957). This is consistent with an alkyl-oxygen cleavage mechanism yielding the carbonium ion 16 and p-nitrobenzoate anion 17.



16 17

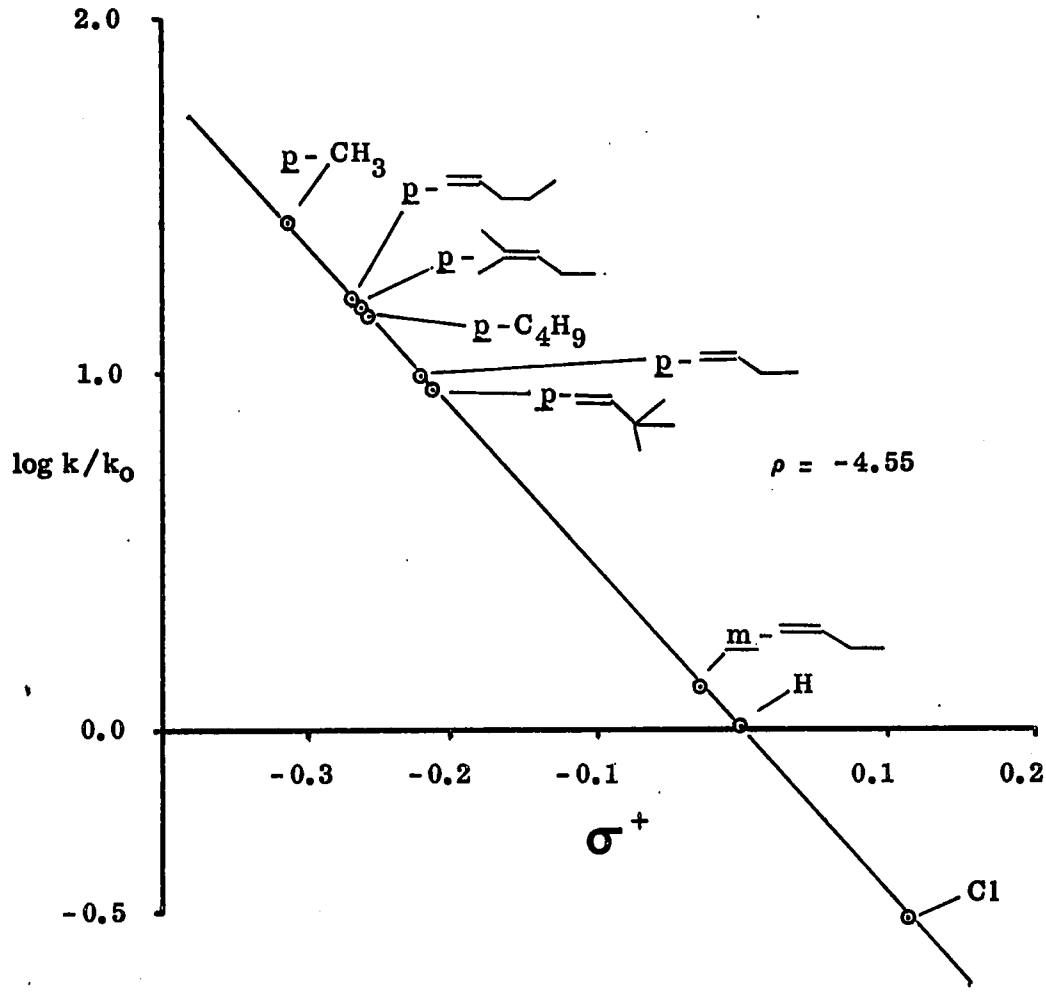


Figure II.7 -- Hammett Plot for the Solvolysis of p-Substituted Cumyl p-Nitrobenzoates at 46.4° in 60% Aqueous Acetone.

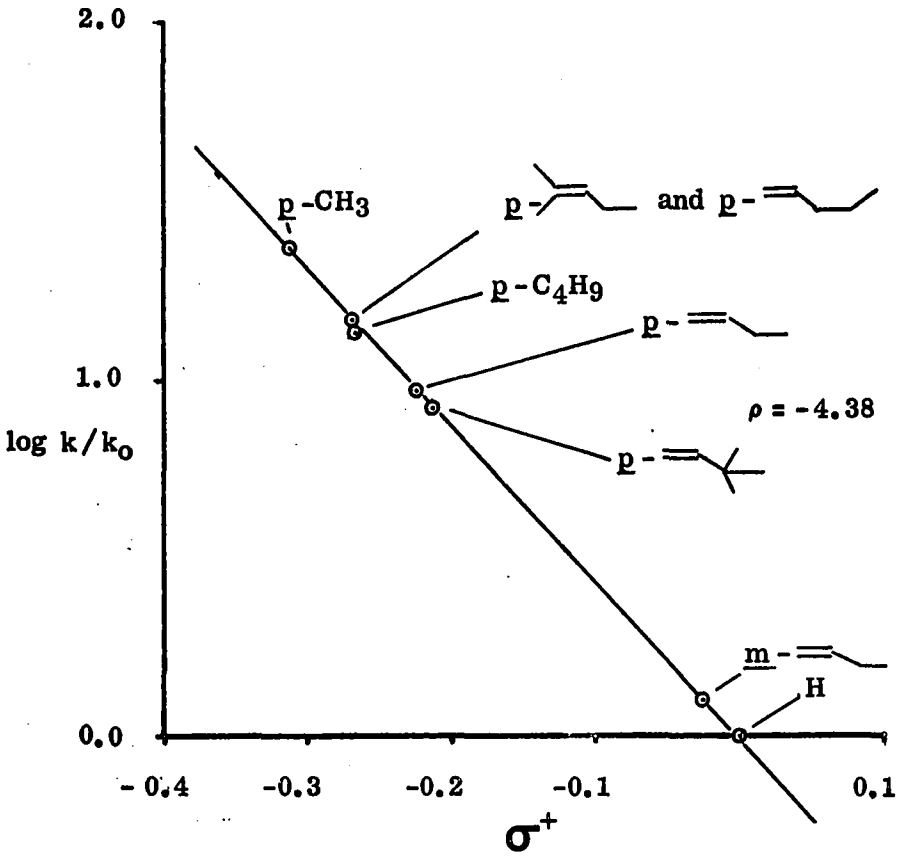


Figure II.8 -- Hammett Plot for the Solvolysis of p-Substituted Cumyl p-Nitrobenzoates at 46.4^0 in 50% Aqueous Acetone.

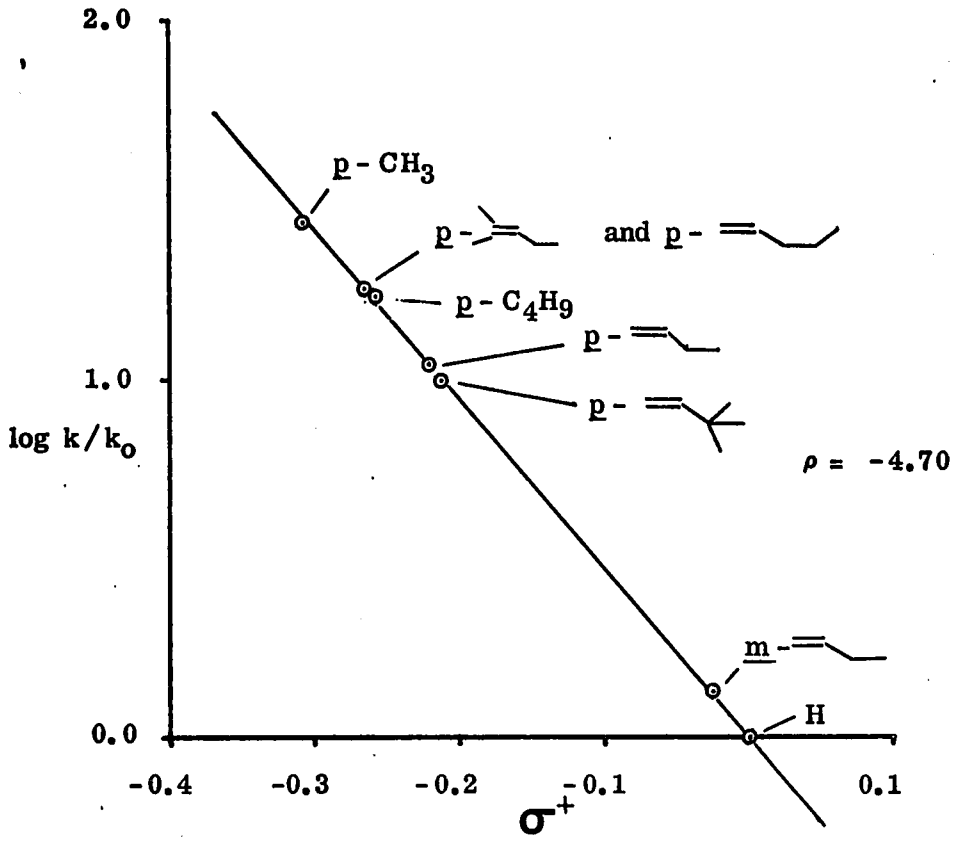


Figure II.9 -- Hammett Plot for the Solvolysis of p-Substituted Cumyl p-Nitrobenzoates at 38.0° in 50% Aqueous Acetone.

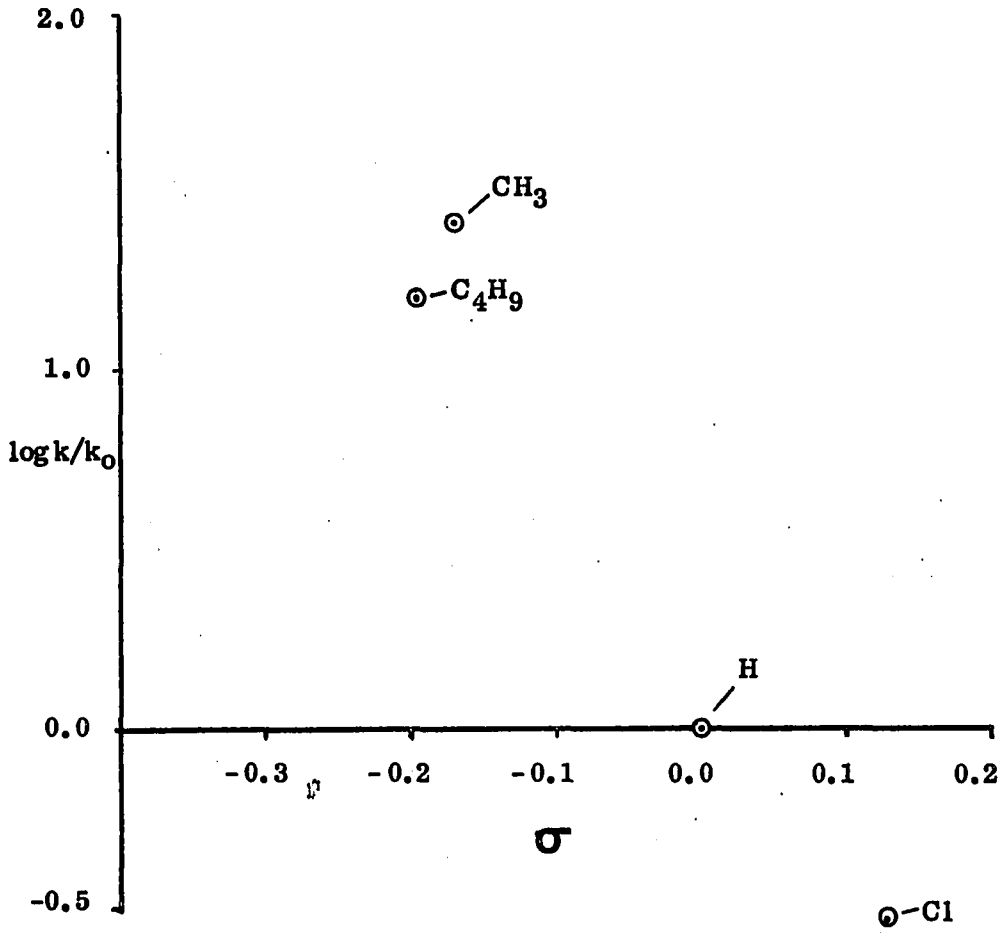


Figure II.10 -- Plot of log k/k_o versus σ as a Check for an Acyl-Oxygen Cleavage Mechanism.

Figure II.11 is an Arrhenius plot for the allylic and the p-methyl esters. The linearity is good for all of the compounds except m-allyl ester whose low solubility at the lower temperatures made rate measurements difficult due to extreme dilution. Consequently, the scatter for this compound is more pronounced.

Table II.4 lists the activation parameters derived from Figure II.11. Within experimental error, all of the esters have the same energy of activation. The p-methyl group is included for comparative purposes.

TABLE II.4 -- Activation Parameters for the Solvolysis of Methyl, Allyl, and Substituted Allyl Cumyl p-nitrobenzoates in 50% Aqueous Acetone at 30.0°.

Substituent	E_{act} kcal/mole	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ e.u.
p-Methyl	20.2	19.6	-18.2
p-Allyl	21.2	20.6	-20.1
p-γ,γ-Dimethyl	20.6	20.0	-19.3
p-3-Butenyl	20.6	20.0	-19.2
m-Allyl	23.1	22.6	-24.4

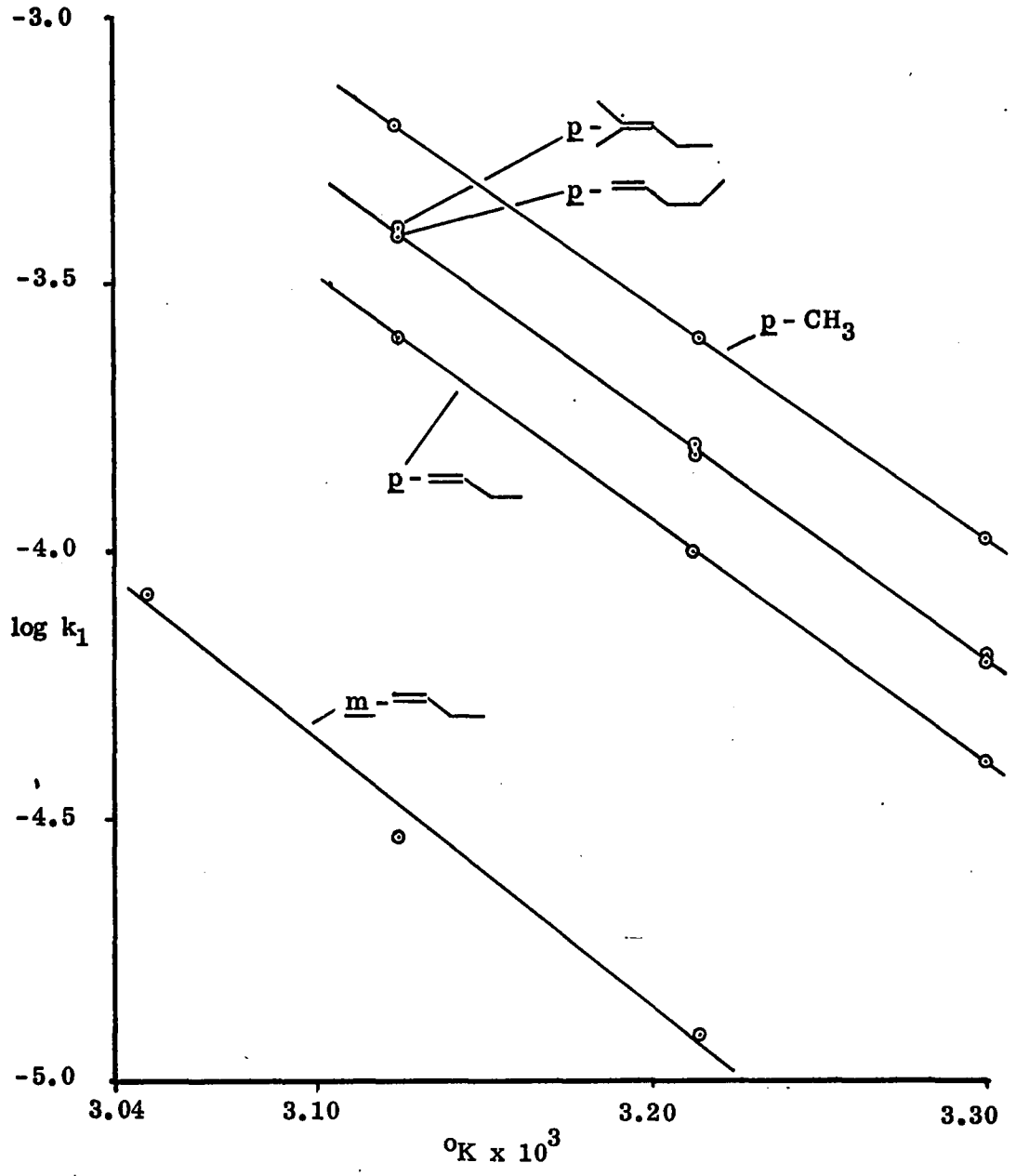


Figure II.11 Arrhenius Plots for p-Methyl, p-Allyl, m-Allyl, p-3-Butenyl, and p-γ, γ-Dimethylallylcumyl p-Nitrobenzoates.

DISCUSSION

Many free energy relationships have been developed in an attempt to correlate kinetic data. The σ^+ relationship defined by Brown and Okamoto (1957) provides a sensitive probe for measuring electronic changes in a carbonium ion reaction as a function of substituents suitably located to allow for conjugative interaction. The magnitude of the σ^+ constant for any given substituent is proportional to its ability to interact with a positive charge. In addition, the sign of σ^+ also indicates whether the substituent will stabilize (-) or destabilize (+) a positive charge by electron donation or withdrawal. For example, the sign and magnitude of the σ^+ constant for a cyclopropyl group, -0.410, indicates that this substituent, relative to the other alkyl substituents listed in Table V, is very effective in stabilizing carbonium ions.

Table II.5 lists the σ^+ constants determined for the allyl groups used in this study, as well as values for other substituents selected for reference purposes. The allyl σ^+ constants are the average of those obtained in two solvent compositions and two temperatures and are accurate to ± 0.006 σ^+ units.

TABLE II.5 -- Substituent Constants for Allylic and Several Reference Substituents

Substituent	σ^+
H	0.00[a]
p - Ethyl	-0.291[b]
m - Ethyl	-0.063[b]
p - Allyl	-0.221[c]
m - Allyl	-0.023[c]
p - γ, γ - Dimethylallyl	-0.262[c]
p - 3 - Butenyl	-0.262[c]
p - t - Butyl	-0.256[b]
p - α, α - Dimethylallyl	-0.212[d]

[a] By definition
[b] Okamoto and Brown, 1957
[c] Determined in this study
[d] Jones, April, 1968

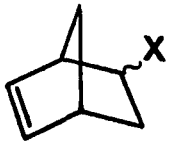
The trends observed in the σ^+ constants for the allylic substituents are consistent with their structure and isomeric differences. The reduced reactivity relative to alkyl substituents is also consistent and reflects the inductive electron withdrawal of the carbon-carbon unsaturation. Every substituent having a double bond is less reactive than a corresponding saturated derivative. For example, the p-ethyl group is more electron donating than either the p-allyl or p-γ,γ-dimethylallyl groups.

Although a rate enhancement may be taken as evidence for neighboring group participation, the reverse does not necessarily follow. The difficulty lies in selecting a proper model for comparison. Significant participation (participation being defined here as any interaction between the allylic double bond and the adjacent phenyl ring), may be present but masked by the inductive effects of the double bond. This type of situation is easily seen in the hydration studies of divinyl benzenes (Eng, 1967). The σ_m^+ value for a vinyl group is +0.146 whereas σ_p^+ is -0.152. This change indicates that relative to hydrogen, the vinyl group changes from an electron withdrawing to an electron donating substituent. Although the reactivity of a p-vinyl substituent is lower than an ethyl group ($\sigma_p^+ = -0.291$), the stabilizing capability is difficult to rationalize without invoking a resonance stabilization mechanism.

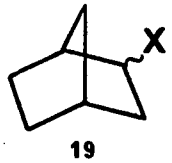
Support for the conclusion that the allylic double bond does not interact via neighboring group participation is found in the activation parameters listed in Table IV. All of the compounds show similar enthalpies and entropies of activation. This implies that the solvolysis mechanism remains unchanged when the substituents are varied. Such is not the case in the solvolysis of p-cyclopropyldimethylcarbinyl chloride 11, where a change of 10 e.u. was found when compared to other alkyl substituents.

Kinetic data can relate only to processes which are occurring during the rate limiting step. Although examples are few, some allylic systems undergo structural isomerization indicating allylic participation without showing significant rate acceleration.

Such behavior was found in the solvolysis of exo- and endo-dehydronorbornyl halides 18, when compared with the corresponding exo- and endo- norbornyl halides 19.

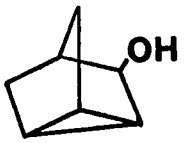


18



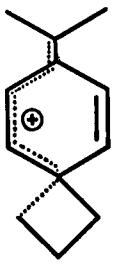
19

Although the dehydronorbornyl halides solvolyzed at the same or slightly slower rates than their saturated counterparts, 90% of the product was 3-hydroxynortricycline 20.(Roberts, Bennett, and Armstrong, 1950).



20

In view of this, detailed product studies were carried out on the α , α - and γ, γ -dimethylallylcumyl p-nitrobenzoates. In both cases, the alcohol recovered from the solvolytic mixture was identical to that in the starting ester. Indications here are that no significant sigma bond development is occurring between the terminal carbon atom and the adjacent phenyl ring as illustrated.



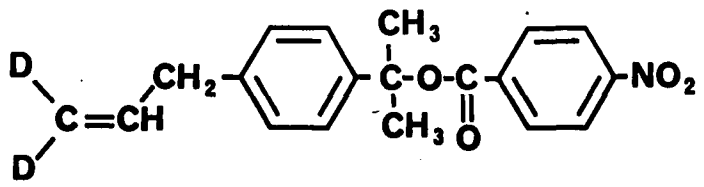
This is not unexpected because the development of a sigma bond in this fashion would destroy the aromaticity of the phenyl ring.

In some systems, the absence of significant allylic participation is due to solvent effects. Solvolysis of allylcarbinyl benzene sulfonates (Bergstrom and Siegel, 1952), β -naphthalenesulfonates

(Hanack and Schneider, 1964) and various substituted derivatives showed no rate enhancement with respect to saturated analogs. In contrast, Roberts and Servis (1964) found that in 98% formic acid allylcarbinyl tosylate solvolyzes 3.7 times faster than n-butyl tosylate. In 80% formic acid - water, the ratio is decreased to 1.3.

These differences have been suggested to arise from a mechanistic change which occurs upon changing solvent (Hanack and Schneider, 1967). Bimolecular displacements in simple allylcarbinyl compounds are predominant in nucleophilic solvents such as ethanol or formic acid - water mixtures, while a unimolecular process, generally accompanied by participation, is favored in powerfully ionizing but weakly nucleophilic media such as formic acid. Since an S_n1 mechanism is operative in the p-nitrobenzoates, their behavior should be similar to that of allylcarbinyl compounds in formic acid rather than solvents such as ethanol.

In the absence of any gross kinetic evidence, skeletal isomerizations or variations in activation parameters, it may be cautiously concluded that allyl substituents interact mainly by inductive rather than resonance effects. This conclusion would be strengthened by determining the deuterium isotope effects of p-γ,γ-dideutereoallylcumyl p-nitrobenzoate 21.



21

This compound, however, is difficult to synthesize and will require a good deal of further work.

APPENDIX A

Procedure for Calculating Exchange Rate Constants in Part I.

Since exchange reactions are concurrent with solvolysis, the kinetic treatment used must be able to account for the reduction in acid chloride concentration with time. The easiest way to do this is to correct the observed activity of a sample to that which would be present if no solvolysis had taken place. For example, if a sample was removed at a time corresponding to one solvolytic half-life and the activity was X CPM, then the activity would be 2X CPM if no solvolysis had occurred.

$$\text{Thus:} \qquad (\text{CPM})_t = \frac{(\text{CPM})_{obs} - \text{Background}}{\text{Fraction of acid chloride remaining at time t.}}$$

The problem of determining the activity at infinite time may be solved by assuming random distribution of the chloride ion between the acid chloride and tetra-n-butylammonium chloride-^{36}Cl. This yields the activity of the acid chloride in the aqueous phase which in turn may be converted to activity in the n-hexane phase by use of the distribution coefficient.

$$(\text{CPM})_\infty = \frac{(\text{CPM})_{initial} \times (\text{Fraction of total chlorine in acid chloride})}{(\text{Fraction of acid chloride in n-hexane phase})}$$

These two figures allow one to calculate the pseudo first order rate constant from the following standard expression.

$$k_1 = \frac{2.303}{t} \log \frac{(CPM)_\infty - (CPM)_0}{(CPM)_\infty - (CPM)_t}$$

APPENDIX B

Tables of Experimental Data from Part I

TABLE Ib -- Chloride Exchange of 0.105 M Ethyl Chloroformate and 0.0660 M n-Bu_4N^+ Cl^- in 40% Aqueous Acetonitrile

Time, min	CPM
0	47 Background
0	247, 337 Aqueous Phase
20	1451
40	2470
62	2121
80	3623
104	4028
125	3809
175	3690

$k_2 = 1.55 \times 10^{-4}$ liter / mole - sec

TABLE IIb -- Chloride Exchange of 0.0840 M Ethyl Chloroformate and 0.0351 M n-Bu_4N^+ Cl^- in 40% Aqueous Acetonitrile

Time, min	CPM
0	52 Background
0	462, 871 Aqueous Phase
20	2145
40	3965
60	4692
93	5536
110	6451
152	5665
181	5442

$k_2 = 1.20 \times 10^{-4}$ liter / mole - sec

TABLE IIIb-- Hydrolysis of 0.0628 M Ethyl Chloroformate in 85% Aqueous Acetonitrile containing 0.212 M LiCl.

Time, min	ml HCl	k_1, $min^{-1} \times 10^2$
0	6.22	-
5	8.30	2.63
10	9.87	2.40
18	11.25	1.95
38	15.14	1.95
46.5	16.21	1.90
55	17.25	1.89
67	18.53	1.92
85	19.87	1.90
105	20.78	1.83
∞	23.27	-

$k_1 = 3.40 \times 10^{-4}$ sec^{-1}
$k_2 = 7.20 \times 10^{-6}$ liters/mole-sec

TABLE IVb-- Hydrolysis of 0.0628 M Ethyl Chloroformate in 85% Aqueous Acetonitrile containing 0.0296 M LiCl.

Time, min	ml HCl	k_1, $min^{-1} \times 10^2$
0	7.25	-
5	9.10	2.49
15	11.85	2.30
20	13.05	2.30
36	15.05	1.91
45	16.88	2.11
55	17.97	2.09
65	18.70	2.02
80	20.00	2.09
100	20.90	2.04
130	21.70	1.98
170	22.37	1.93
∞	22.96	-

$k_1 = 3.51 \times 10^{-4}$ sec^{-1}
$k_2 = 7.41 \times 10^{-6}$ liters/mole-sec

TABLE Vb-- Exchange of 0.0631 M Ethyl Chloroformate and 0.0925 M $\underline{n}$-$Bu_4N^+ Cl^-$ in 85% Aqueous Acetonitrile.

Time, min	CPM
0	34 Background
0	350, 517 Aqueous Phase
10	462
20	794
30	983
40	1017
50	992
65	871

$k_2 = 6.65 \times 10^{-5}$ liters/mole-sec.

TABLE VIb-- Exchange of 0.0631 M Ethyl Chloroformate and 0.1525 M $\underline{n}$-$Bu_4N^+ Cl^-$ in 85% Aqueous Acetonitrile.

Time, min	CPM
0	43 Background
0	567, 104 Aqueous Phase
10	939
20	1456
31	1691
40	1681
53	1844
60	1752

$k_2 = 6.77 \times 10^{-5}$ liters/mole-sec.

TABLE VIIb-- Hydrolysis of 0.210 M Ethyl Chloroformate in 60% Aqueous Acetonitrile containing 0.0600 M LiCl.

Time, min	ml HCl	$k_1 \times 10^2$ min^{-1}
0	3.85	-
5	5.10	1.26
17	8.08	1.37
25	9.86	1.40
35	11.38	1.32
45	13.07	1.34
60	15.35	1.37
80	16.90	1.28
100	18.92	1.34
130	20.63	1.33
∞	24.25	-

$k_1 = 2.22 \times 10^{-4}$ sec^{-1}
$k_2 = 6.67 \times 10^{-6}$ liter/mole-sec

TABLE VIIIb-Hydrolysis of 0.0116 M Ethyl Chloroformate in 60% Aqueous Acetonitrile containing 0.380 M LiCl.

Time, min	ml HCl	$k_1 \times 10^2$ min^{-1}
0	1.55	-
20	7.35	1.33
30	9.97	1.38
42	12.70	1.41
54	14.55	1.36
68	16.90	1.40
88	18.98	1.36
110	21.32	1.43
∞	26.52	-

$k_1 = 2.31 \times 10^{-4}$ sec^{-1}
$k_2 = 6.94 \times 10^{-6}$ liter/mole-sec

TABLE IXb-- Hydrolysis of 0.1047 M Ethyl Chloroformate in 60% Aqueous Acetonitrile containing 0.063 M $\underline{n}$-$Bu_4N^+ Cl^-$.

Time, min	ml HCl	$k_1 \times 10^2$ min^{-1}
0	2.27	-
8	4.12	1.25
16	5.97	1.33
25	7.73	1.33
35	9.46	1.32
50	11.66	1.33
70	14.38	1.40
84	14.89	1.25
120	17.79	1.34
150	19.21	1.38
∞	21.66	-

$k_1 = 2.20 \times 10^{-4}$ sec^{-1}
$k_2 = 6.61 \times 10^{-6}$ liter/mole-sec

TABLE Xb-- Chloride Exchange of 0.096 M Ethyl Chloroformate and 0.212 M $\underline{n}$-$Bu_4N^+ Cl^-$ in 60% Aqueous Acetonitrile.

Time, min	CPM
0	37 Background
0	386, 421 Aqueous phase
25	2119
51	2501
98	2123
146	1807

$k_2 = 6.56 \times 10^{-5}$ liter/mole-sec

TABLE XIb-- Chloride Exchange of 0.0838 M Ethyl Chloroformate and 0.271 M n-$Bu_4N^+ Cl^-$ Aqueous Acetonitrile.

Time, min	CPM
0	46 Background
0	493, 945 Aqueous phase
15	2913
30	4199
45	5140
83	4638
100	5096

$k_2 = 6.12 \times 10^{-5}$ liter/mole-sec

TABLE XIIb-- Chloride Exchange of 0.0126 M Ethyl Chloroformate and 0.190 M n-$Bu_4N^+ Cl^-$ in 60% Aqueous Acetonitrile.

Time, min	CPM
0	51 Background
0	358, 209 Aqueous phase
15	1858
31	2920
45	3498
59	3786
75	3712
90	3593
118	3432

$k_2 = 6.26 \times 10^{-5}$ liter/mole-sec

TABLE XIIIb-- Hydrolysis of 0.0419 M Ethyl Chloroformate in 40% Aqueous Acetonitrile containing 0.0295 M LiCl.

Time, min	ml HCl	$k_1 \times 10^3$ min^{-1}
0	3.05	-
20.5	6.25	7.29
50	10.08	7.15
64	12.00	7.44
100	15.33	7.43
150	18.47	7.30
180	20.04	7.30
∞	26.30	-

$k_1 = 1.22 \times 10^{-4}$ sec^{-1}
$k_2 = 5.52 \times 10^{-6}$ liter/mole-sec

TABLE XIVb-- Hydrolysis of 0.0419 M Ethyl Chloroformate in 40% Aqueous Acetonitrile containing 0.0239 M LiCl.

Time, min	ml HCl	$k_1 \times 10^3$ min^{-1}
0	2.83	-
10	4.56	7.50
20	6.02	7.22
50	9.75	6.89
65	11.61	7.10
100	14.77	7.03
150	18.48	7.19
180	19.82	7.00
∞	26.54	-

$k_1 = 1.19 \times 10^{-4}$ sec^{-1}
$k_2 = 5.36 \times 10^{-6}$ liter/mole-sec

TABLE XVb-- Hydrolysis of 0.1047 M Ethyl Chloroformate in 40% Aqueous Acetonitrile No Added Salts.

Time, min	ml HCl	$k_1 \times 10^3$ min^{-1}
0	5.52	-
20	11.42	6.60
40	16.54	6.59
60	21.64	6.89
90	27.16	6.78
130	32.86	6.61
160	36.42	6.59
200	40.94	6.88
∞	52.86	-

$k_1 = 1.13 \times 10^{-4}$ sec^{-1}
$k_2 = 5.17 \times 10^{-6}$ liter/mole-sec

TABLE XVIb-- Chloride Exchange of 0.210 M Ethyl Chloroformate and 0.0525 M $\underline{n}$-$Bu_4N^+ Cl^-$ in 40% Aqueous Acetonitrile

Time, min	CPM
0	61 Background
0	197, 122 Aqueous phase
15	555
25	869
50	1443
75	1270
100	1764
128	1852
176	1778

$k_2 = 0.86 \times 10^{-4}$ liter/mole-sec

APPENDIX C

Tables of Experimental Data from Part II

TABLE Ic-- Solvolysis of 0.0630 M p-Methylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.53	-
13.9	1.21	1.73
28.8	1.84	1.73
42.7	2.33	1.72
56.9	2.84	1.80
77.4	3.38	1.78
102.3	3.89	1.78
143.0	4.49	1.78
188.9	4.89	1.77
∞	5.58	-

$k_1 = 1.76 \times 10^{-4}$ sec^{-1}

TABLE IIc -- Solvolysis of 0.0591 M p-Methylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.61	-
13.2	1.21	1.80
27.8	1.85	1.92
43.0	2.35	1.88
56.7	2.77	1.92
77.6	3.31	1.95
102.4	3.75	1.93
143.4	4.25	1.90
∞	5.13	-

$k_1 = 1.90 \times 10^{-4}$ sec^{-1}

TABLE IIIc-- Solvolysis of 0.0614 M p-Methylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.84	-
15.0	1.49	1.70
29.3	2.09	1.83
43.8	2.57	1.82
57.0	3.01	1.90
77.9	3.58	1.98
102.9	3.99	1.92
144.1	4.52	1.93
∞	5.38	

$k_1 = 1.87 \times 10^{-4}$ sec^{-1}

TABLE IVc-- Solvolysis of 0.0671 M Cumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^6$ sec^{-1}
0	0.259	-
488.4	1.459	7.53
683.9	1.883	7.62
875.2	2.303	7.83
1518.3	3.271	7.55
1976.1	3.760	7.28
2957.8	4.561	6.98
∞	6.310	-

$k_1 = 7.47 \times 10^{-6}$ sec^{-1}

TABLE Vc-- Solvolysis of 0.0639 M Cumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^6$ sec^{-1}
0	0.321	-
165.8	0.738	7.53
324.0	1.098	7.45
488.8	1.453	7.47
683.2	1.890	7.77
874.1	2.154	7.31
1517.6	3.103	7.26
1975.8	3.632	7.24
2957.1	4.418	7.00
∞	6.071	-

$k_1 = 7.38 \times 10^{-6}$ sec^{-1}

TABLE VIc-- Solvolysis of 0.0763 M Cumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^6$ sec^{-1}
0	0.335	-
166.4	0.849	7.78
323.7	1.315	7.90
489.5	1.712	7.58
684.1	2.099	7.22
873.9	2.591	7.55
1518.3	3.729	7.45
1976.2	4.373	7.43
2957.8	5.328	7.27
∞	7.219	-

$k_1 = 7.52 \times 10^{-6}$ sec^{-1}

TABLE VIIc-- Solvolysis of 0.0914 M p-Allylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.213	-
17.7	0.487	7.60
45.9	0.866	7.40
80.6	1.252	7.17
120.1	1.686	7.45
183.2	2.203	7.48
245.6	2.572	7.42
322.6	2.905	7.35
512.5	3.402	7.45
∞	3.761	-

$k_1 = 7.42 \times 10^{-5}$ sec^{-1}

TABLE VIIIc-- Solvolysis of 0.0965 M p-Allylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.232	-
45.1	0.976	8.05
80.8	1.407	7.62
121.3	1.850	7.62
186.2	2.387	7.48
245.7	2.751	7.37
322.1	3.094	7.22
∞	4.037	-

$k_1 = 7.49 \times 10^{-5}$ sec^{-1}

TABLE IXc-- Solvolysis of 0.0865 M p-t-Butylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.196	-
21.3	0.682	1.14
53.9	1.324	1.18
78.5	1.730	1.19
111.0	2.153	1.19
176.3	2.758	1.19
299.2	3.304	1.14
408.8	3.517	1.08
479.5	3.609	1.08
∞	3.768	-

$k_1 = 1.15 \times 10^{-4}$ sec^{-1}

TABLE Xc-- Solvolysis of 0.0915 M p-t-Butylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.262	-
21.0	0.768	1.17
53.4	1.440	1.19
78.5	1.849	1.19
111.9	2.339	1.23
176.7	2.939	1.21
304.0	3.552	1.20
409.5	3.776	1.21
480.5	3.837	1.17
∞	3.964	-

$k_1 = 1.20 \times 10^{-4}$ sec^{-1}

TABLE XIc -- Solvolysis of 0.00888 M p- γ , γ -Dimethylallylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.225	-
25.6	0.540	1.15
54.3	0.847	1.18
97.6	1.218	1.22
239.0	1.824	1.20
337.3	1.967	1.11
414.4	2.067	1.17
∞	2.174	-

$k_1 = 1.17 \times 10^{-4}$ sec^{-1}

TABLE XIIc -- Solvolysis of 0.00779 M p- γ , γ -Dimethylallylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.473	-
42.8	1.261	1.21
63.1	1.540	1.18
96.5	1.981	1.23
158.4	2.442	1.15
210.0	2.726	1.14
262.5	2.922	1.12
315.3	3.081	1.13
∞	3.432	-

$k_1 = 1.18 \times 10^{-4}$ sec^{-1}

TABLE XIIIc - Solvolysis of 0.00956 M p-Chlorocumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, hours	ml NaOH
0	0.077
11.43	0.490
20.12	0.768
35.97	1.267
50.14	1.661
71.51	2.148
114.51	2.929
171.80	3.708

Guggenheim Treatment : $k_1 = 2.24 \times 10^{-6}$ sec^{-1}

TABLE XIVc - Solvolysis of 0.00985 M p-Chlorocumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, hours	ml NaOH
0	0.080
11.43	0.510
20.12	0.807
35.97	1.311
50.14	1.740
71.51	2.284
114.51	3.156
171.80	4.036

Guggenheim Treatment : $k_1 = 2.16 \times 10^{-6}$ sec^{-1}

TABLE XVc -- Solvolysis of 0.0795 M p-3-Butenylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.545	-
29.2	1.120	1.22
44.7	1.442	1.33
64.2	1.729	1.37
83.8	2.014	1.34
104.4	2.239	1.33
136.5	2.506	1.30
165.6	2.730	1.32
206.3	2.944	1.30
∞	3.541	

$k_1 = 1.31 \times 10^{-4}$ sec^{-1}

TABLE XVIc - Solvolysis of 0.0781 M p-3-Butenylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.226	-
13.2	0.560	1.31
28.2	0.865	1.24
47.9	1.217	1.20
67.4	1.529	1.20
89.1	1.854	1.22
108.4	2.042	1.18
142.7	2.449	1.24
∞	3.619	

$k_1 = 1.23 \times 10^{-4}$ sec^{-1}

TABLE XVIIc - Solvolysis of 0.00690 M p-3-Butenylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.222	-
23.5	0.650	1.32
45.8	0.971	1.28
71.8	1.301	1.30
100.5	1.603	1.31
125.4	1.786	1.29
177.9	2.095	1.27
248.4	2.390	1.32
344.1	2.562	1.27
	2.746	-

$k_1 = 1.30 \times 10^{-4}$ sec^{-1}

TABLE XVIIIc - Solvolysis of 0.00683 M p-3-Butenylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.208	-
23.4	0.610	1.22
45.5	0.954	1.27
71.7	1.263	1.24
100.6	1.570	1.27
125.6	1.760	1.24
178.0	2.093	1.26
246.6	2.351	1.24
344.0	2.544	1.20
	2.760	-

$k_1 = 1.24 \times 10^{-4}$ sec^{-1}

TABLE XIXc - Solvolysis of 0.00778 M m-Allylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.124	-
117.3	0.300	8.55
300.8	0.552	8.51
443.3	0.740	8.60
658.5	0.999	8.68
916.6	1.267	8.66
1400.0	1.697	8.78
2056.0	2.106	8.68
2974.0	2.483	8.56
∞	3.137	-

$k_1 = 8.63 \times 10^{-6}$ sec^{-1}

TABLE XXc - Solvolysis of 0.00795 M m-Allylcumyl-p-nitrobenzoate in 60% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.133	-
300.9	0.550	8.13
443.7	0.755	8.56
658.8	0.999	8.46
917.1	1.284	8.61
1400.0	1.724	8.78
2057.0	2.111	8.48
2974.0	2.539	8.71
∞	3.182	-

$k_1 = 8.53 \times 10^{-6}$ sec^{-1}

TABLE XXIc - Solvolysis of 0.0785 M p-Methylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.568	-
4.58	1.017	6.31
8.86	1.371	6.03
14.13	1.733	6.12
20.10	2.111	6.07
27.77	2.418	6.22
40.39	2.813	6.02
∞	3.506	

$k_1 = 6.13 \times 10^{-4}$ sec^{-1}

TABLE XXIIc - Solvolysis of 0.0824 M p-Methylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.824	-
4.43	1.268	6.32
9.09	1.628	6.01
15.70	2.080	6.12
21.57	2.386	6.07
28.96	2.720	6.22
42.19	3.068	6.02
∞	3.694	-

$k_1 = 6.14 \times 10^{-4}$ sec^{-1}

TABLE XXIIIc -Solvolysis of 0.00765 M Cumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.316	-
31.4	0.552	2.43
71.4	0.877	2.58
144.7	1.408	2.63
209.0	1.804	2.60
298.3	2.310	2.62
434.0	2.963	2.63
658.2	3.772	2.63
∞	5.661	-

$k_1 = 2.59 \times 10^{-5}$ sec^{-1}

TABLE XXIVc - Solvolysis of 0.00713 M Cumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.267	-
31.9	0.507	2.65
70.7	0.791	2.60
145.0	1.314	2.70
209.0	1.666	2.63
298.3	2.147	2.65
435.1	2.777	2.68
664.0	3.535	2.68
∞	5.249	-

$k_1 = 2.66 \times 10^{-5}$ sec^{-1}

TABLE XXVc - Solvolysis of 0.00761 M p-Allylcumyl p-nitrobenzoate in 50 % Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.625	-
14.7	1.154	2.59
25.5	1.462	2.55
39.0	1.772	2.50
54.7	2.057	2.42
82.0	2.442	2.40
121.6	2.753	2.35
	3.219	-

$k_1 = 2.47 \times 10^{-4}$ sec^{-1}

TABLE XXVIc - Solvolysis of 0.00734 M p-Allylcumyl p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.660	-
14.8	1.155	2.53
25.7	1.469	2.60
39.1	1.747	2.50
55.0	2.023	2.47
87.1	2.378	2.33
121.2	2.662	2.37
	3.094	-

$k_1 = 2.47 \times 10^{-4}$ sec^{-1}

TABLE XXVIIc - Solvolysis of 0.00810 M p-t-Butylcumyl p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	1.845	-
10.06	2.141	3.31
17.72	2.325	3.66
31.51	2.543	3.56
44.62	2.741	3.83
61.77	2.847	3.45
81.72	2.994	3.67
	3.210	-

$k_1 = 3.58 \times 10^{-4}$ sec^{-1}

TABLE XXVIIIc - Solvolysis of 0.00772 M p-t-Butylcumyl p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	1.533	-
9.43	1.898	3.70
30.97	2.483	3.65
45.10	2.774	3.81
62.29	2.973	3.67
119.90	3.297	3.43
185.62	3.461	3.43
	3.550	-

$k_1 = 3.64 \times 10^{-4}$ sec^{-1}

TABLEXXIXc- Solvolysis of 0.00791 M p- γ , γ -Dimethylallylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	1.020	-
7.00	1.426	4.05
14.11	1.771	4.22
24.19	2.177	4.28
34.09	2.369	3.80
52.20	2.761	3.80
65.50	2.965	3.83
85.73	3.142	3.67
∞	3.520	-

$k_1 = 3.95 \times 10^{-4}$ sec^{-1}

TABLE XXXc- Solvolysis of o.00788 M p- γ , γ -Dimethylallylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.504	-
7.40	0.872	3.65
14.96	1.260	4.08
25.81	1.659	4.08
53.18	2.255	3.88
64.20	2.385	3.73
85.92	2.593	3.65
∞	2.970	-

$k_1 = 3.85 \times 10^{-4}$ sec^{-1}

TABLE XXXIc-Solvolysis of 0.00741 M p-3-Butenylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.504	-
5.09	0.835	3.87
10.23	1.142	3.92
18.05	1.521	3.85
31.02	2.038	3.88
42.16	2.355	3.83
52.16	2.646	4.03
64.28	2.829	3.92
76.60	2.995	3.92
∞	3.489	-

$k_1 = 3.90 \times 10^{-4}$ sec^{-1}

TABLE XXXIIc-Solvolysis of 0.00773 M p-3-Butenylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.495	-
6.43	0.919	3.74
10.93	1.171	3.67
18.06	1.561	3.80
25.07	1.875	3.82
33.15	2.235	4.02
44.16	2.554	3.96
56.15	2.793	3.85
72.96	3.082	3.88
∞	3.659	-

$k_1 = 3.84 \times 10^{-4}$ sec^{-1}

TABLE XXXIIIc - Solvolysis of 0.00815 M m-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.211	-
117.9	0.764	2.63
218.2	1.163	2.63
301.2	1.445	2.63
385.1	1.716	2.68
444.1	1.856	2.63
600.0	2.190	2.60
∞	3.470	-

$k_1 = 2.63 \times 10^{-5}$ sec^{-1}

TABLE XXXIVc - Solvolysis of 0.00763 M m-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 46.4°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.203	-
117.8	0.678	2.60
218.0	1.037	2.67
301.0	1.316	2.76
385.1	1.509	2.68
444.0	1.630	2.63
599.8	1.941	2.65
∞	3.033	-

$k_1 = 2.67 \times 10^{-5}$ sec^{-1}

TABLE XXXVc - Solvolysis of 0.00638 M p-Methylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.690	-
8.4	1.153	2.64
17.3	1.637	2.46
27.2	2.008	2.48
40.4	2.490	2.50
55.8	2.931	2.48
71.1	3.268	2.47
91.2	3.618	2.45
120.6	4.012	2.52
∞	4.655	-

$k_1 = 2.50 \times 10^{-4}$ sec^{-1}

TABLE XXXVIc - Solvolysis of 0.00654 M p-Methylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.855	-
8.6	1.328	2.50
16.6	1.665	2.33
27.1	2.135	2.43
41.0	2.603	2.40
56.4	3.047	2.42
71.1	3.391	2.45
91.5	3.702	2.37
120.9	2.056	2.35
∞	4.770	-

$k_1 = 2.41 \times 10^{-4}$ sec^{-1}

TABLE XXXVIIc - Solvolysis of 0.00517 M Cumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^6$ sec^{-1}
0	0.327	-
241.1	0.762	8.77
342.1	0.953	9.08
493.0	1.211	9.27
1323.0	2.215	9.05
1730.0	2.559	8.96
2122.0	2.810	8.80
∞	4.014	-

$k_1 = 8.98 \times 10^{-6}$ sec^{-1}

TABLE XXXVIIIc - Solvolysis of 0.00621 M Cumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^6$ sec^{-1}
0	0.349	-
241.5	0.869	8.45
339.7	1.080	8.58
493.0	1.409	8.95
1322.0	2.582	8.50
1728.0	3.044	8.67
2120.0	3.337	8.42
∞	4.897	-

$k_1 = 8.60 \times 10^{-6}$ sec^{-1}

TABLE XXXIXc - Solvolysis of 0.00494 M p-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.252	-
35.4	0.840	9.87
59.3	1.180	10.00
88.6	1.509	9.78
112.0	1.736	9.70
154.5	2.084	9.67
225.6	2.540	9.91
330.7	2.908	9.82
∞	3.350	-

$k_1 = 9.82 \times 10^{-5}$ sec^{-1}

TABLE XLc-- Solvolysis of 0.00537 M p-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.287	-
22.8	0.702	9.45
43.0	1.025	9.47
60.7	1.317	9.87
85.4	1.608	9.58
115.4	1.939	9.58
194.3	2.668	10.03
254.5	2.888	9.42
∞	3.699	-

$k_1 = 9.63 \times 10^{-5}$ sec^{-1}

TABLE XLIc -- Solvolysis of 0.00642 M p-t-Butylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	1.994	-
34.7	2.543	1.55
77.2	3.004	1.57
106.8	3.213	1.53
136.5	3.373	1.49
178.9	3.573	1.53
230.2	3.669	1.41
272.8	3.765	1.44
∞	3.951	-

$k_1 = 1.50 \times 10^{-4}$ sec^{-1}

TABLE XLIIc -- Solvolysis of 0.00593 M p-t-Butylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	2.065	-
13.1	2.290	1.58
36.0	2.597	1.49
78.2	3.070	1.56
107.8	3.258	1.48
137.9	3.422	1.46
179.6	3.621	1.51
273.5	3.798	1.38
∞	4.000	-

$k_1 = 1.49 \times 10^{-4}$ sec^{-1}

TABLE XLIIIc -- Solvolysis of 0.00439 M p- γ , γ -Dimethylallylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.400	-
19.3	0.846	1.57
45.5	1.326	1.55
61.3	1.577	1.57
81.5	1.833	1.56
112.6	2.157	1.58
155.5	2.420	1.50
225.8	2.731	1.50
∞	3.083	-

$k_1 = 1.55 \times 10^{-4}$ sec^{-1}

TABLE XLIVc -- Solvolysis of 0.00487 M p- γ , γ -Dimethylallylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.405	-
16.8	0.852	1.55
28.7	1.089	1.46
46.3	1.445	1.49
61.0	1.719	1.52
74.8	1.915	1.50
100.9	2.269	1.54
180.0	2.927	1.59
∞	3.480	-

$k_1 = 1.52 \times 10^{-4}$ sec^{-1}

TABLE XLVc -- Solvolysis of 0.00711 M p-3-Butenylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.220	-
31.2	0.932	1.62
40.6	1.092	1.59
57.5	1.366	1.59
70.2	1.530	1.56
91.7	1.797	1.58
111.4	1.986	1.57
137.6	2.198	1.58
166.9	2.366	1.56
∞	2.940	-

$k_1 = 1.58 \times 10^{-4}$ sec^{-1}

TABLE XLVIc -- Solvolysis of 0.00750 M p-3-Butenylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.306	-
31.2	1.001	1.54
40.4	1.181	1.56
57.4	1.452	1.54
70.1	1.632	1.54
91.8	1.877	1.51
111.2	2.086	1.53
137.5	2.290	1.52
166.7	2.479	1.52
∞	3.085	-

$k_1 = 1.53 \times 10^{-4}$ sec^{-1}

TABLE XLVIIc -- Solvolysis of 0.00770 M m-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.139	-
105	0.311	0.95
287	0.626	1.05
436	0.836	1.03
586	1.029	1.02
901	1.405	1.03
1394	1.869	1.05
2050	2.272	1.04
2957	2.630	1.04
∞	3.098	-

$k_1 = 1.03 \times 10^{-5}$ sec^{-1}

TABLE XLVIIIc -Solvolysis of 0.00796 M m-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 38.0°.

Time, min	ml NaOH	$k_1 \times 10^4$ sec^{-1}
0	0.130	-
110	0.337	1.04
294	0.646	1.02
440	0.849	0.99
655	1.153	1.01
902	1.439	1.00
1394	1.918	1.01
2050	2.340	1.00
2957	2.717	0.99
∞	3.260	-

$k_1 = 1.01 \times 10^{-5}$ sec^{-1}

TABLE XLIXc -- Solvolysis of 0.00627 M p-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 30.0°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.308	-
70.7	0.637	3.87
171.3	1.009	3.78
272.1	1.324	3.85
352.7	1.531	3.90
435.9	1.700	3.90
519.4	1.830	3.85
601.3	1.946	3.87
∞	2.486	-

$k_1 = 3.86 \times 10^5$ sec^{-1}

TABLE Lc -- Solvolysis of 0.00637 M p-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 30.0°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.295	-
70.4	0.646	4.02
170.7	1.020	3.80
271.7	1.339	3.82
352.1	1.544	3.83
435.5	1.734	3.90
518.7	1.880	3.92
600.7	1.976	3.80
∞	2.547	-

$k_1 = 3.87 \times 10^{-5}$ sec^{-1}

TABLE LIc -- Solvolysis of 0.00624 M p- γ , γ -Dimethylallylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 30.0°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.781	-
98.6	1.341	6.32
167.4	1.637	6.45
279.4	1.934	6.13
363.5	2.107	6.15
446.1	2.236	6.22
528.0	2.309	6.02
∞	2.577	-

$k_1 = 6.22 \times 10^{-5}$ sec^{-1}

TABLE LIIc - Solvolysis of 0.00579 M p- γ , γ -Dimethylallylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 30.0°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.740	-
98.3	1.240	5.97
167.1	1.508	6.07
237.3	1.733	6.25
279.1	1.805	5.97
363.4	1.980	6.10
445.7	2.098	6.12
527.5	2.170	5.97
∞	2.426	-

$k_1 = 6.07 \times 10^{-5}$ sec^{-1}

TABLE LIIIc -- Solvolysis of 0.00582 M p-3-Butenylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 30.0°.

Time, min	ml NaOH	$k_1 \times 10^{-5}$ sec^{-1}
0	0.318	-
170.2	1.288	6.08
271.7	1.638	6.10
351.5	1.836	6.11
435.1	1.991	6.13
518.3	2.092	6.02
600.2	2.177	6.05
∞	2.414	-

$k_1 = 6.07 \times 10^{-5}$ sec^{-1}

TABLE LIVc -- Solvolysis of 0.00615 M p-Butenylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 30.0°.

Time, min	ml NaOH	$k_1 \times 10^{5}$ sec^{-1}
0	0.328	-
170.0	1.320	5.62
271.7	1.699	5.65
351.4	1.938	5.83
435.2	2.113	5.87
518.0	2.224	5.75
600.0	2.318	5.75
∞	2.605	-

$k_1 = 5.74 \times 10^{-5}$ sec^{-1}

TABLE LVc -- Solvolysis of 0.00620 M m-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 30.0°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.436	-
55.2	0.932	8.38
163.2	1.552	8.05
231.6	1.818	8.10
305.6	2.030	8.23
427.6	2.221	8.02
511.1	2.293	7.75
∞	2.483	-

$k_1 = 8.09 \times 10^{-5}$ sec^{-1}

TABLE LVIc -- Solvolysis of 0.00666 M m-Allylcumyl-p-nitrobenzoate in 50% Aqueous Acetone at 30.0°.

Time, min	ml NaOH	$k_1 \times 10^5$ sec^{-1}
0	0.463	-
55.2	0.980	8.48
163.3	1.668	8.12
231.7	1.950	8.13
305.4	2.171	8.22
427.5	2.380	8.05
511.3	2.483	8.25
∞	2.659	-

$k_1 = 8.21 \times 10^{-5}$ sec^{-1}

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