Pyrolysis of 1,1-Diphenyl-2-nitroethylene (3).—The pyrolysis of 1,1-diphenyl-2-nitroethylene (**3**) was effected at 600° (0.001 mm) with a head temperature of 75–78°. The pyrolysate was washed from the cold trap with carbon tetrachloride and gave the same white precipitate observed for **2**. Nmr analysis of the filtrate revealed the presence of benzophenone: nmr (CCl$_4$) δ 7.2–7.8 (m, C$_6$H$_5$). The pyrolysate obtained from the pyrolysis of **3** at 700° (0.002 mm) with a head temperature of 78–80° was identical with that obtained at 600°.

Pyrolysis of β-Methyl-β-nitrostyrene (4).—The pyrolysis of β-methyl-β-nitrostyrene was effected at 600° (0.001 mm) with a head temperature of 50–55°. Analysis of the pyrolysate by vpc indicated the presence of at least six components and the following peaks were observed in the mass spectrum (70 eV): *m/e* 106, 105, 78, 77, 76, 57, 52, 51, 50, 41, 40, and 39. The pyrolysate was shown to consist of acetonitrile, benzaldehyde, benzene, methyl isocyanate, and methylphenylacetylene by comparison of vpc retention times and spectral data with those of authentic samples. The following were recorded for the pyrolysate: ir (CCl$_4$) 4.25–4.55 (broad band) and 5.85 μ (CO); nmr(CCl$_4$) δ 1.9 (s, CH$_3$CN), 2.02 (s, C$_6$H$_5$CCCH$_3$), 2.1 (s, unknown), 3.0 (s, CH$_3$NCO), 7.15–7.3 (m, C$_6$H$_5$CCCH$_3$), 7.27 (s, C$_6$H$_6$), 7.4–7.8 (m, C$_6$H$_5$CHO), and 9.92 (s, C$_6$H$_5$CHO). A sixth minor product was not identified. The product ratios were determined by nmr. The pyrolysis of **4** at 500° (0.250 mm) with a head temperature of 60–70° was shown to give starting material and the aforementioned products by nmr analysis. Pyrolysis of **4** at 400° (0.100 mm) with a head temperature of 65–70° returned starting material only.

Pyrolysis of 1-(α-Naphthyl)-2-nitropropene (5).—The pyrolysis of 1-(α-naphthyl)-2-nitropropene (**5**) was accomplished at 600° (0.001 mm) with a head temperature of 52–53°. Nmr analysis of the pyrolysate indicated the presence of acetonitrile, methyl isocyanate, and naphthaldehyde. Vpc analysis of the pyrolysate (BDS, 175°) established the presence of naphthalene. Vpc data also suggested the presence of methyl-α-naphthylacetylene, which was confirmed by an ir absorption at 4.5 μ (C$\equiv$C) in the absence of acetonitrile and methyl isocyanate. A minor component of the pyrolysate was not identified. The following nmr data were obtained for the pyrolysate: nmr (CCl$_4$) δ 1.9 (s, CH$_3$CN), 2.15 (s, C$_{10}$H$_7$CCCH$_3$), 2.2 (s, unknown), 7.2–8.2 (m, C$_{10}$H$_7$CHO and C$_{10}$H$_8$), and 10.33 (s, C$_{10}$H$_7$CHO).

Pyrolysis of 1,1-Diphenyl-2-nitropropene (6).—Pyrolysis of 1,1-diphenyl-2-nitropropene (**6**) was carried out at 700° (0.001 mm) with a head temperature of 50–51°. Nmr and vpc analyses of the pyrolysate indicated the presence of acetonitrile, benzene, benzophenone, methyl isocyanate, and an unidentified product: nmr (CCl$_4$) δ 1.9 (s, CH$_3$CN), 2.1 (s, unknown), 3.0 (s, CH$_3$NCO), 7.28 (s, C$_6$H$_6$), and 7.2–7.9 [m, (C$_6$H$_5$)$_2$CO].

Pyrolysis of Nitrotriphenylethylene (8).—Pyrolysis of nitrotriphenylethylene was accomplished at 600° (0.001 mm) with a head temperature of 101–105°. Vpc analysis of the pyrolysate demonstrated the presence of benzene, benzonitrile, benzophenone, and phenyl isocyanate. The presence of benzonitrile, phenyl isocyanate, and benzophenone was further confirmed by ir data: ir (CCl$_4$) 4.35–4.60 (nitrile–isocyanate) and 6.02 μ (CO). A considerable portion of the pyrolysate solidified before reaching the cold trap. Analysis of this material by mass spectrometry revealed the presence of 2,3-diphenylbenzofuran (*m/e* 270) and a C$_{20}$H$_{24}$ hydrocarbon (*m/e* 254).

Registry No.—**2,** 102-96-5; **3,** 5670-69-9; **4,** 705-60-2; **5,** 23854-03-7; **6,** 15795-69-4; **8,** 5670-70-2.

Acknowledgment.—The authors gratefully acknowledge the financial support supplied by grants from Eli Lilly & Co. and the Petroleum Research Fund administered by the American Chemical Society.

Photochemical Oxidations. III. Photochemical and Thermal Behavior of α-Hydroperoxytetrahydrofuran and Its Implications Concerning the Mechanism of Photooxidation of Ethers[1a]

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The suspected intermediate peroxide in the photooxidation reaction of tetrahydrofuran (THF) was synthesized, and its thermal and photochemical behavior was studied. Liquid-phase thermal decomposition of a dilute peroxide solution gives rise to α-hydroxytetrahydrofuran, whereas vpc decomposition produces α-hydroxytetrahydrofuran and butyrolactone. Photochemically, the peroxide yields only α-hydroxytetrahydrofuran and the rate of production follows first-order kinetics. Using ir analysis and iodimetry, the rates of formation of the products in the photooxidation of THF were determined, and a modified mechanism was proposed for this reaction.

In previous papers of this series it was postulated that the photooxidation of ethers proceeds through the α-hydroperoxides of ethers.[2,3] In order to obtain further experimental data on the role of peroxides in these reactions, the thermal and photochemical behavior of α-hydroperoxytetrahydrofuran (I) has been studied. It was hoped that the hydroperoxide of diethyl ether could also be studied, but this was not possible, since the compound is too unstable to be prepared. In our previous work,[3] the rate of accumulation for the two products formed in the photooxidation of tetrahydrofuran (THF), *i.e.*, butyrolactone (II) and α-hydroxytetrahydrofuran (III), had been followed by vpc. However, since peroxides were also found in the reaction mixture, there was the possibility that thermal decomposition of these peroxides may have occurred during the vpc analysis and given rise to a portion of the products found. Therefore, it was necessary that the thermal decomposition of α-hydroperoxytetrahydrofuran, the postulated peroxide, be studied.

Compound I was prepared and a solution of it in THF was injected into a gas chromatograph with the injection chamber at 100°. It was found that both II and III were produced under these conditions. Also no trace of I could be detected in the vpc spectrum. The molar ratio of products obtained (II to III) was *ca.* 3:1, with the exact ratio depending on the experimental conditions and techniques. Therefore, it is obvious that the vpc results for rates of product accumulation during the photooxidation contain an

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[1] (a) Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; (b) Taken in part from the Ph.D. thesis of C. T. Wang, University of North Dakota, June 1969.

[2] V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **32**, 3227 (1967).

[3] N. Kulevsky, C. T. Wang, and V. I. Stenberg, *ibid.*, **34**, 1345 (1969).

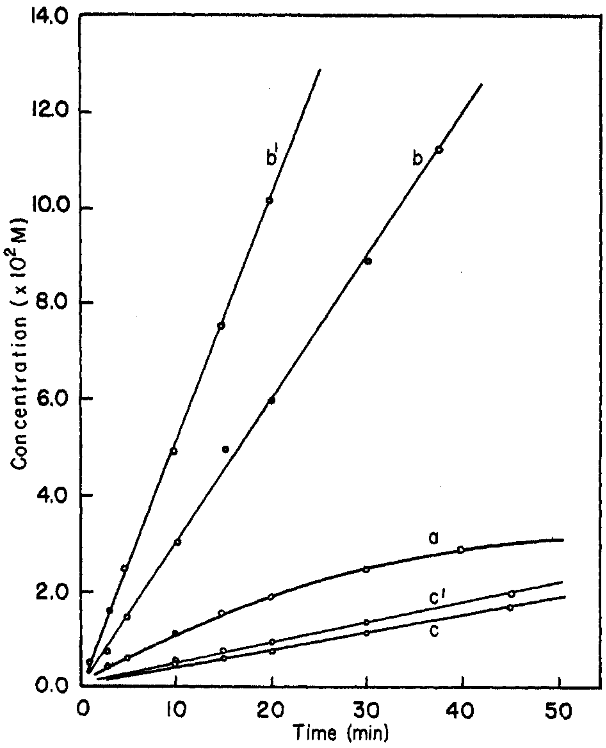


Figure 1.—Rates of product formation during photooxidation of tetrahydrofuran: (a) α-hydroperoxytetrahydrofuran; (b) α-hydroxytetrahydrofuran; (c) butyrolactone; (b' and c') α-hydroxytetrahydrofuran and butyrolactone, respectively, in the same process with the addition of 9.14×10^{-2} *M* α-hydroperoxytetrahydrofuran prior to the start of the irradiation.

inherent error which is proportional to the amount of hydroperoxide present.

There remained the possibility that the thermal decomposition of I in solution could play a significant role in the photooxidation of THF. As a consequence, the thermal decomposition of a THF solution of I in a sealed tube at 100° was studied. As opposed to the vpc results, only III is produced. At room temperature or lower the thermal reaction of I is very slow and, for the time period of the irradiation, it is not likely to be the source of III in the photooxidation of THF, since this reaction is also run at low temperatures. Furthermore, the pyrolysis of I in the injection chamber or column of the vpc is more complex than the liquid-phase pyrolysis. Apparently, the decomposition in the chamber may occur wholly in the vapor state or in a combination of liquid and vapor states, and this probably accounts for the variable ratio of products in the vpc work.

To obtain more accurate rates of product-accumulation data for the photochemical oxidation of THF, an analytical method which would not decompose the hydroperoxide in the reaction mixture was necessary. Accordingly, infrared spectrometry was utilized to follow concentrations of the products, II and III, directly on the reaction mixture, while iodimetric titrations were used for the peroxide I. The rates of product accumulation obtained in this way are shown in Figure 1. These demonstrate that even for very short irradiation times all products I–III are formed, III is formed at a faster rate than II, and the hydroperoxide I attains what appears to be a steady-state concentration on prolonged irradiation.

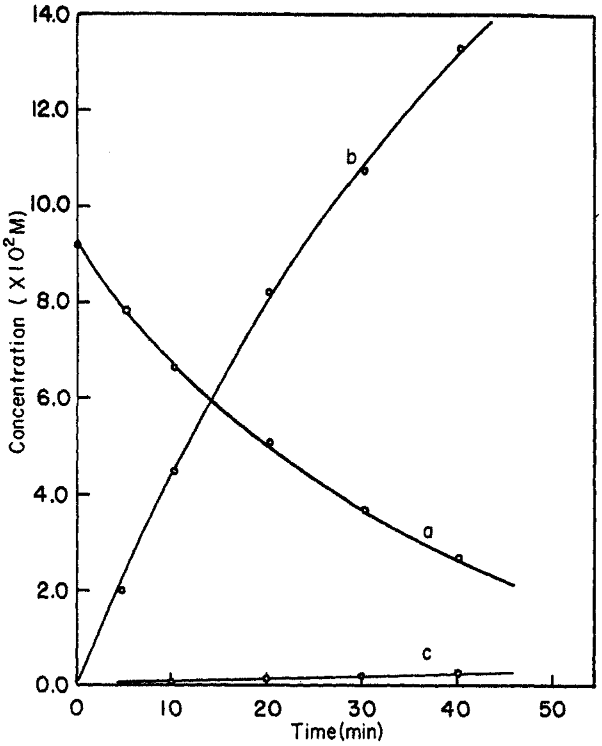


Figure 2.—Plots of the concentrations of (a) α-hydroperoxytetrahydrofuran, (b) α-hydroxytetrahydrofuran, and (c) butyrolactone *vs.* time for the photodecomposition of β-hydroperoxytetrahydrofuran.

With the data described above, it still was not possible to determine if the peroxide in the reaction solution, presumably the hydroperoxide I, serves as a precursor of II and III or if II and/or III are generated by an independent pathway. With this question in mind, a study of the photochemical behavior of the peroxide I in THF was done at about the concentration it has in the photooxidation reactions. In these experiments, the peroxide I degrades rapidly in a nitrogen atmosphere upon irradiation (Figure 2), yielding one major product, the hydroxy ether III, with only a trace of the lactone II (see Figure 2). A further observation is that *ca.* 2 mol of III are formed from every mole of I decomposed. The kinetics of the reaction are first order with respect to the peroxide concentration, as shown in Figure 3. It is noteworthy that this reaction is the best and neatest method of preparing III.

From the above data the decomposition of I in THF solution is most likely to be a bimolecular reaction of I with THF. Since THF is present in excess as a solvent whose concentration will not change very much during the course of the reaction, it may be regarded as a constant, and the reaction will be pseudo first order. Furthermore, the data implies that chain processes are not involved in the initial stages of the reaction, possibly owing to the low concentration of reactants. Also it is clear that the lactone II formed in the photooxidation of THF is not formed directly from the peroxide. Presumably the association of I with THF *via* hydrogen bonding results in a bimolecular photodecomposition.

There remained the possibility that I in the presence of oxygen may photochemically yield II. However, when a dilute THF solution of I is irradiated under oxygen, the evidence does not support this possibility. The data shown in Figure 1 as curve c' indicate that

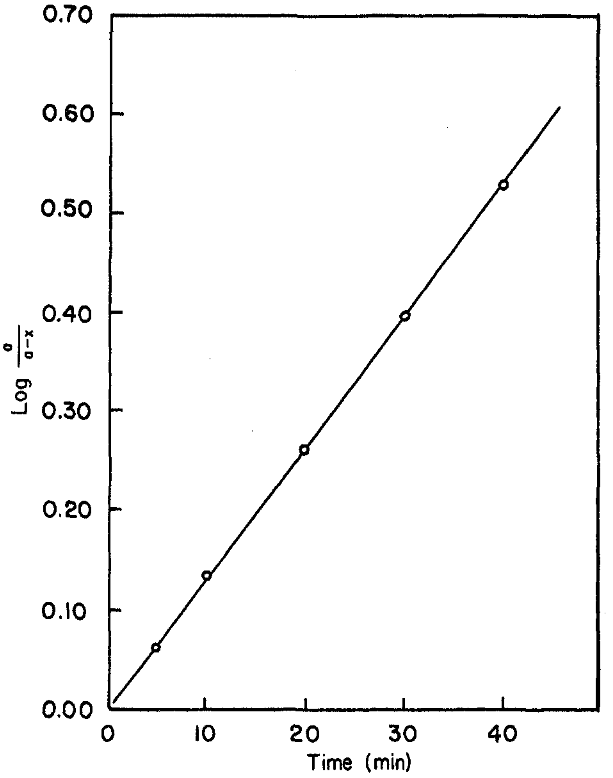
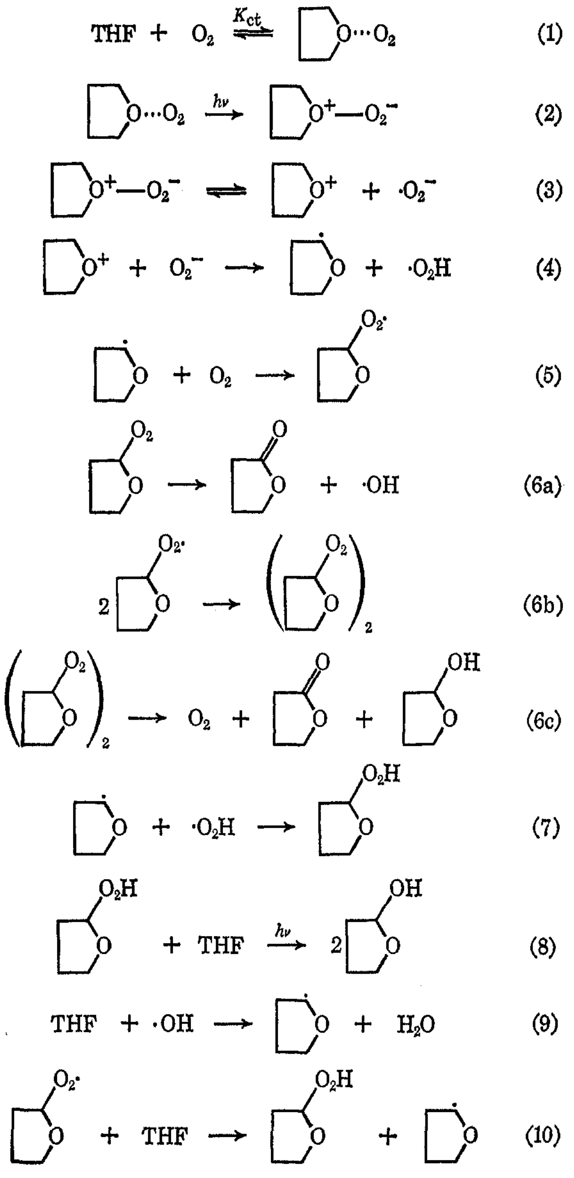


Figure 3.—First-order plot of the photodecomposition of α-hydroperoxytetrahydrofuran.

the rate of formation of II is only slightly faster than without the added peroxide, whereas the rate of formation of III (curve b′) is considerably increased. Thus the observed results can be accounted for simply by an addition of the photooxidation of tetrahydrofuran and the photochemical conversion of the hydroperoxide.

With the data presented above and that presented in previous papers,[1-3] a more detailed mechanism can now be presented for the photooxidation of ethers (Scheme I). Step 1 is the formation of the charge-transfer complex and step 2 is the excitation of this complex by the light, for which the evidence was given in the previous paper. Step 3, a new feature of the mechanism, is the dissociation of the excited-state complex, which is analogous to that proposed for other complexes.[4] For those cases, esr evidence for radical formation was taken as proof of the dissociation. Previously we had suggested that the excited state of the charge-transfer complex underwent a proton shift and then gave the hydroperoxide directly.[3] However, it is now necessary to postulate this dissociation (step 3), since the work presented here demonstrates that the hydroperoxide is not the precursor of the lactone. Steps 4–6a are then postulated as the route for the generation of lactone without going through the hydroperoxide. Step 6a is analogous to one suggested to occur in the oxidation of cyclohexane.[5] Steps 6b and 6c also lead to the formation of the lactone.[4] However, step 6b is not very likely under the conditions of these reactions (solution in THF and low concentration of radicals), as combination of peroxy radicals would be precluded by the ability of THF to trap free radicals. Steps 4, 7, and 10 produce hydroperoxide and take into account the photochemical decomposition of the hydroperoxide shown in this work.

SCHEME I



Experimental Section

Materials.—Tetrahydrofuran (Fisher reagent grade) was purified as described previously.[2,3] α-Hydroperoxytetrahydrofuran was prepared by the method of Grosborne and de Roch[6] and was obtained 95.3% pure. The purity was determined by iodimetric titrations.[7]

Determination of Rates.—The apparatus and procedure were essentially the same as described previously[3] except that, instead of gas chromatography, infrared spectrometry was used in the quantitative determination of products. The same process was also repeated with the addition of I prior to the start of the THF photooxidation. The ir spectra of the reaction mixtures with THF as a reference were monitored over the initial 50 min. The path length of the matched ir cells was 0.2 mm. A Beckman Model IR-12 spectrophotometer was used. Quantitative measurements were made by comparing the absorbance of irradiated products with that of a mixture of known concentrations of reactant and products. The bands used to follow the concentration of II and III were 1789 and 1735 cm^{-1}, respectively. The peroxide concentration was determined by iodimetric titration.[7]

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[4] K. U. Ingold, *Accounts Chem. Res.*, **2**, 1 (1969).

[5] R. Guedj and J. Jullien, *Bull. Soc. Chem. Fr.*, 1501 (1964).

[6] P. Grosborne and I. S. de Roch, *ibid.*, 2260 (1967).

[7] C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

Thermal Decomposition of α-Hydroperoxytetrahydrofuran (I). A. Pyrolysis in the Gas Chromatograph.—A 1-μl sample of a 4.3×10^{-2} *M* solution of I in THF was injected into a Beckman GC-5 gas chromatograph equipped with a flame ionization detector and a 6 ft × 0.125 in. Carbowax column on Chromosorb W. The gas chromatogram showed two major peaks for butyrolactone and α-hydroxytetrahydrofuran in a ratio of *ca.* 1:3.

B. Pyrolysis in a Sealed Tube.—A 5-ml solution of 8.6×10^{-2} *M* I in THF was placed in a glass reaction tube which was connected to a vacuum line. The solution was thoroughly outgassed by conventional freeze-pump-thaw techniques. After a final check for noncondensable gases, the glass reaction tube was isolated by sealing off from the line and then allowed to reach room temperature. The sealed tube was then heated in a furnace at 100° for 30 min. The reaction mixture was analyzed and found to contain III as the only major products.

Photodecomposition of α-Hydroperoxytetrahydrofuran.—A solution of 9.1×10^{-2} *M* I in THF was placed in a 3-ml uv spectrophotometric cell. The irradiation procedure used was identical with that described before[8] except that, instead of bubbling oxygen through the solution, a slow stream of nitrogen was maintained. The products were identified by ir and vpc and the progress of the reaction was followed as described above. For each set of data, five or more experiments were required for the points on the curve for the range of 0 to 65% decomposition of I. The irradiation of I under oxygen was performed and analyzed in a similar manner.

Registry No.—I, 4676-82-8; THF, 109-99-9.

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Electronic Effects in Solvolysis Reactions. III. Solvolysis of Allyl-Substituted Cumyl Derivatives[1]

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Synthetic procedures are described for *p*-γ,γ-dimethylallyl-, *p*-α,α-dimethylallyl-, *p*-3-butenyl-, *m*-allyl, *p*-allyl-, and *p*-γ,γ-dideuterioallylcumyl *p*-nitrobenzoates. The possibility of allylic participation during the solvolysis of these compounds in aqueous mixtures was investigated. Substituent constants (σ^+), skeletal rearrangement studies, and kinetic isotope effect measurements were employed to determine the nature and extent of such participation. These data, coupled with the uniformity of activation parameters and the absence of skeletal isomerizations, suggest that inductive effects by the allylic double bond are the major influence in the solvolytic behavior of these esters.

Much interest and experimental work has centered around the stabilizing influence of cyclopropyl and allyl substituents in solvolytic reactions. Both functional groups provide stabilization for developing carbonium ions and, hence, rate enhancements are frequently observed.[3] As a quantitative measure of the electronic effects of the cyclopropyl substituent in carbonium ion reactions, the substituent constant σ^+ was determined from solvolytic studies of substituted cumyl derivatives.[4-6] These data indicated that the *p*-cyclopropyl group (relative to other alkyl groups) exhibited an abnormally large (negative) σ^+ value and that the ability of the substituent to supply electron density was conformationally dependent.[5] It was considered, therefore, of general interest to prepare a number of allyl-substituted cumyl derivatives in order to assess, in more quantitative terms, the stabilizing influence of *m*- and *p*-allyl substituents on developing carbonium ions.

Results

Substituted cumyl *p*-nitrobenzoates were chosen for this investigation and were synthesized, for the most part, by conventional procedures. All esters gave satisfactory elemental analyses.

Water-acetone mixtures were selected as solvolytic media, and rate constants for solvolysis were determined at several temperatures for each of several solvent compositions. Detailed product studies indicated that *p*-nitrobenzoic acid and substituted cumyl alcohols were the only products produced during solvolysis. Under these reaction conditions, isomerization of the double bond in the allyl substituents into conjugation with aromatic ring could not be detected. Similarly, deuterium labeling in the allyl group indicated that carbon skeletal rearrangement did not occur during solvolysis.

Table I summarizes the solvolytic rate data for the substituted cumyl *p*-nitrobenzoates at various temperatures and solvent compositions. In all cases the kinetic runs were followed to at least 70% completion. Agreement between most runs was ±1%.

The standard substituents methyl, *t*-butyl, hydrogen, and chlorine were used to obtain Hammett ρ values under each set of conditions. Good linear correlations were observed in each case ($r = 0.994$). At 46.4° in 60% aqueous acetone, the reaction constant (using Brown σ^+ values) was found to be -4.55, and in 50% aqueous acetone at the same temperature the ρ value was found to be -4.38. A reaction constant of -4.70 was observed in 50% aqueous acetone at 38.0°. These ρ values were then employed to determine σ^+ values of each allyl and butenyl substituent. These data are tabulated in Table II. Values for several other substituents are included for reference.

Table III lists activation parameters for solvolysis of the allyl-substituted esters. Within experimental error, all of the esters have the same energy of activa-

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[1] For part II, see L. B. Jones and S. S. Eng, *Tetrahedron Lett.*, 1431 (1968).

[2] Phillips Petroleum Co. Fellow, 1966–1968.

[3] See, for example, J. D. Roberts, R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, and M. S. Silver, *J. Amer. Chem. Soc.*, **81**, 4390 (1959); J. D. Roberts and K. L. Servis, *ibid.*, **86**, 3773 (1964).

[4] L. B. Jones and V. K. Jones, *Tetrahedron Lett.*, 1493 (1966).

[5] H. C. Brown and J. D. Cleveland, *J. Amer. Chem. Soc.*, **88**, 2051 (1966).

[6] R. C. Hahn, T. F. Corbin, and H. Shechter, *ibid.*, **90**, 3404 (1968).