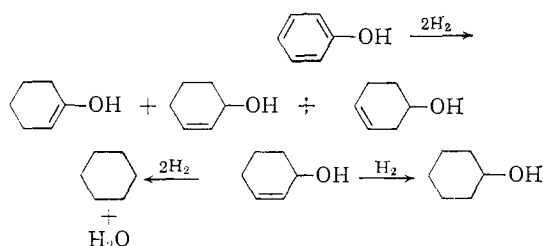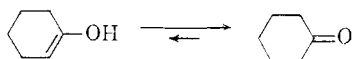give cyclohexanol. The reactions probably occur simultaneously until the double-bonded molecules are saturated.


Three hydroxycyclohexene intermediates are possible, and these are shown above. The 1-hydroxy-cyclohexene-1 is the tautomeric form of cyclohexanone.

This tautomerization would be expected to take place since the keto form is more stable than the enol form by about 18 kcal. mole^{-1}.[3] This could account for the presence of ketones in the reaction mixture without claiming that cyclohexanone is a reaction intermediate in the usual sense.

Similar reaction routes for the dihydroxybenzenes can be shown to explain the results obtained in the course of this study. Consider as an example the reaction route for the hydrogenation of catechol
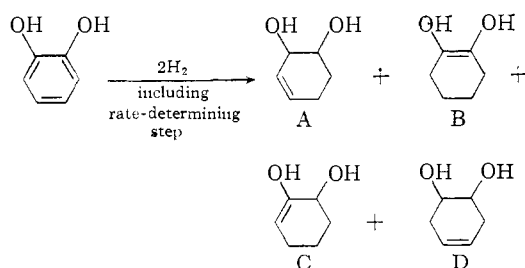
Intermediates B and C undergo tautomerization to 2-hydroxycyclohexanone

when desorbed from the catalyst into the reaction mixture. Experiments performed during this research have shown that 2-hydroxycyclohexanone is formed during the hydrogenation of catechol. Intermediate A has a double-bond β-γ to a hydroxyl group and renders this group labile to hydrogenolysis. Intermediate D makes the least contribution to the over-all reaction. If steric factors are important at all in determining the course of the reaction, intermediate B would be expected to predominate. This would account for the fact that catechol cleaves less rapidly than do resorcinol and hydroquinone.
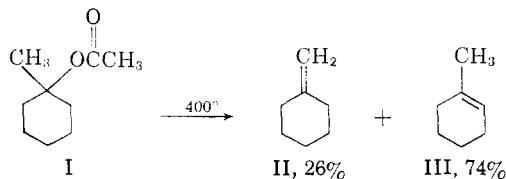

Pyrolytic *cis* Eliminations. II. Eliminations of Axial and Equatorial Acetates[1]

BY C. H. DEPUY AND R. W. KING

cis- and *trans*-1-methyl-4-*t*-butylcyclohexyl acetates have been prepared and a study made of the relative amounts of *exo* and *endo* olefin formed in the pyrolyses of these conformationally pure esters. It was shown that *there are no conformational effects on the direction of elimination in the pyrolysis of these esters*, both isomers giving the same *exo/endo* product ratio as was found in the pyrolysis of 1-methylcyclohexyl acetate. Relative rate studies on these same two acetates and on *cis*- and *trans*-4-*t*-butylcyclohexyl acetate showed that the ease of pyrolysis depends mainly on the ground state energy of the acetates, since with the 1-methyl-4-*t*-butylcyclohexyl acetates the equatorial ester undergoes elimination more readily, while the axial ester is the more reactive of the 4-*t*-butylcyclohexyl acetates.

When 1-methylcyclohexyl acetate (I) is pyrolyzed at 400°, it is smoothly converted into a mixture of methylenecyclohexane (II) and 1-methylcyclohexene (III). Although it was at first thought that the former of these olefins was the predominant product of this elimination, more recent studies

I II, 26% III, 74%

have shown that the internal olefin III makes up 74% of the olefinic product.[2] The preponderance of 1-methylcyclohexene has been ascribed to the fact that pyrolytic eliminations from esters have transition states with appreciable double bond character[3] and that the well-known greater stability of internal over external olefins in the cyclohexane series[4] accounts for its ease of formation. Nevertheless, in more complicated systems *exo* olefin has been reported to be the major product of elimination. Thus Maali acetate (IV) decomposes

(1) Part I, C. H. DePuy, C. A. Bishop and C. N. Goeders, *J. Am. Chem. Soc.*, **83**, 2151 (1961). This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.
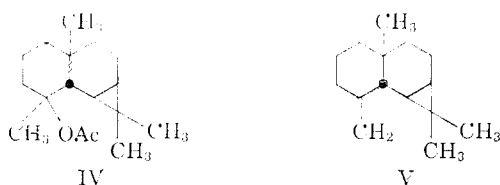
(2) (a) D. H. Froemsdorf. C. H. Collins, G. S. Hammond and C. H. DePuy, *ibid.*, **81**, 643 (1959); (b) W. J. Bailey and W. F. Hale, *ibid.*, **81**, 651 (1959); (c) R. A. Benkeser and J. J. Hazdra, *ibid.*, **81**, 228 (1959).

(3) C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

(4) H. C. Brown, J. H. Brewster and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

mainly to α-maaliene (V) on heating,[5] and similar results in other systems have been reported in the literature.[6,7]

IV   V

It has been known for some time that conformational effects may have a profound effect on the ease and direction of elimination in cyclohexyl compounds. In fused polycyclic systems it has been shown that, as an example, axial and equatorial alcohols give widely different ratios of *exo* and *endo* olefins when dehydrated with phosphorus oxychloride in pyridine.[8,9] No similar study of pyrolytic eliminations has been reported, and it appeared possible that at least part of the driving force for the larger than normal amount of exocyclic olefin formed from maali acetate and other esters might be due to the conformationally pure equatorial nature of the acetoxy group.

It has now become standard to use the 4-*t*-butyl group as a conformational anchor for the cyclohexane ring.[10] At the time we began this work, the necessary alcohols, *cis-* and *trans-*4-*t*-butylcyclohexanol (VI and VII),[11] had not been previously prepared. Since the completion of this work, Cross and Whitham have described these compounds.[12] Our observations of these alcohols differ enough from theirs that we feel justified in discussing them briefly.
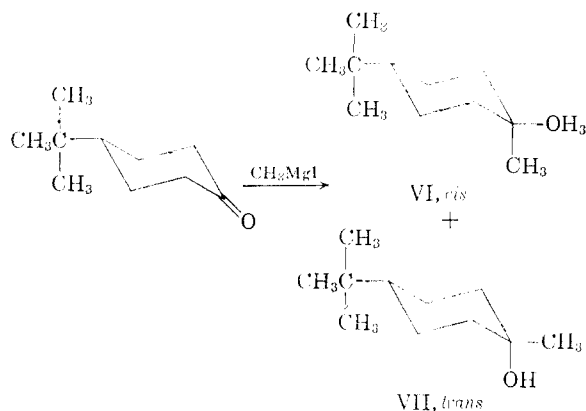
A mixture of the two isomeric alcohols was obtained from the reaction of 4-*t*-butylcyclohexanone with methylmagnesium iodide. Gas chromato-

(5) G. Büchi, M. S. v. Wittenau and D. M. White, *J. Am. Chem. Soc.*, **81**, 1968 (1959).

(6) G. Ohloff and G. Schade, *Chem. Ber.*, **91**, 2017 (1958).

(7) A. Breuner and H. Schinz, *Helv. Chim. Acta*, **35**, 1333 (1952).

(8) D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951).

(9) (a) H. Heusser, N. Wahba and F. Winternitz, *Helv. Chim. Acta*, **37**, 1052 (1954); (b) D. H. R. Barton, A. da S. Campos-Neves and R. C. Cookson, *J. Chem. Soc.*, 3500 (1956); (c) E. J. Corey and R. R. Sauers, *J. Am. Chem. Soc.*, **81**, 1739 (1959).

(10) (a) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955); (b) E. L. Eliel and R. S. Ro, *ibid.*, **79**, 5992 (1957).

(11) *Cis* refers to the relationship of the methyl and *t*-butyl groups.

(12) B. Cross and G. H. Whitham, *J. Chem. Soc.*, 3892 (1960).

graphic analysis showed the two alcohols to be formed in nearly equal amounts. Careful chromatography of 12.4 g. of the mixed alcohols on alumina isomer, 4.4 g., and the more tightly bound *cis* isomer, 5.4 g., the remainder being a mixture of the two alcohols. The *trans*-alcohol melted at 70.5–71°, and the *cis* at 97.5–98°.[13] This system therefore shows substantially no conformational preference for attack by the Grignard reagent.[5] On the other hand, lithium aluminum hydride reduction of the same ketone gives mainly (>90%) product with equatorial hydroxyl.[10b]

Cross and Whitham[12] studied the phosphorus oxychloride–pyridine dehydration of these two alcohols and reported that by infrared analysis the *trans* isomer VII gave exclusively 1-methyl-4-*t*-butylcyclohexene (IX). We also examined this elimination and are in substantial agreement with these results. We used gas chromatography to determine the olefin ratios and were able to detect 1.3% *exo* olefin in the product from the *trans*-alcohol and 12% *exo* olefin in the product from the *cis*-alcohol. Equilibration of the *exo* and *endo* olefins by heating under reflux with *p*-toluenesulfonic acid gave a product with 0.8% *exo* olefin. Since at a somewhat lower temperature an equilibrium mixture of methylenecyclohexane and 1-methylcyclohexene contains 0.4% *exo* olefin,[14] it is clear that the 4-*t*-butyl group exerts no profound effect on stability in these cyclohexene systems.

VIII   IX
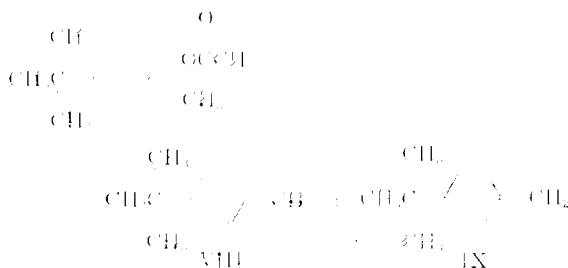
Each pure alcohol was converted to its acetate with acetyl chloride in dimethylaniline. The acetates were shown to be conformationally pure by gas chromatography. Each was pyrolyzed at 400 ± 3° at a rate of 3–4 ml./min. as previously described.[2a,3] The results of these pyrolyses are recorded in Table I, along with results of a similar pyrolysis of 1-methylcyclohexyl acetate. It is clear that *conformational effects have no effect on the direction of pyrolysis* in this system. Both *equatorial* and *axial* esters give identical product ratios on pyrolysis and this ratio is identical with that obtained from 1-methylcyclohexyl acetate.

TABLE I

Cyclohexyl acetate	exo olefin, %	endo olefin, %
1-Methyl-[2]	24	76
cis-1-Methyl-4-*t*-butyl-	23	77
trans-1-Methyl-4-*t*-butyl-	23	77

(13) Cross and Whitham[12] report melting points of 66–67° and 89–90°, respectively, for these alcohols. However their *trans* isomer could not be obtained analytically pure and was described as hygroscopic. We did not experience this difficulty in obtaining an analytical sample.

(14) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell and Z. Jacura, *J. Am. Chem. Soc.*, **81**, 3153 (1959).

We next turned our attention to the relative rates of pyrolysis of axial and equatorial acetates. In the first place, we felt these studies would shed additional light on the transition state of ester eliminations. In the second place, these data were necessary to rule out the possibility that the absence of conformational effects on the direction of elimination, observed above, was due to the fact that all reactions took place preferentially from either the axial or equatorial conformation. If that were so, there should be a large difference in rate of pyrolysis between *cis*- and *trans*-4-*t*-butyl acetate, since in the transition state of one of them the *t*-butyl group would have to be axial.

The relative rates of pyrolysis of *cis*- and *trans*-1-methyl-4-*t*-butylcyclohexyl acetate and of *cis*- and *trans*-4-*t*-butylcyclohexyl acetate[15] were determined by the competitive pyrolysis of a mixture of two acetates containing an internal standard. The results for these two systems are summarized in Table II.

TABLE II

RELATIVE RATES OF PYROLYSIS OF AXIAL AND EQUATORIAL ACETATES

Cyclohexyl acetate	Rate ratio, k axial/k equat.	Temp., °C.
cis and *trans*-4-*t*-Butyl-	1.69, 1.63	450
cis and *trans*-1-Methyl-4-*t*-butyl-	0.70, 0.71	325

The data are not consistent with the view that only one conformer is undergoing elimination, for the differences in the rates are too small and the inversion in the order of greatest reactivity cannot be accounted for by that mechanism. In fact, the data seem consistent only with the view that *the relative rates are determined mainly by differences in ground state energy of the acetates.* In the case of *cis*- and *trans*-4-*t*-butylcyclohexyl acetates, the *cis* compound with the axial acetate group is at a higher energy than the *trans* compound. Since the products of elimination from both molecules are the same, and assuming that the transition state is closer to products than reactants, it would be expected that the axial acetate would undergo elimination more rapidly than its equatorial isomer. With the 1-methyl-4-*t*-butylcyclohexyl acetates the ground state energies are reversed. Here the methyl group is more bulky than the acetoxyl group[16] and so the *cis* isomer, with the equatorial acetate, has the higher ground state energy. Again the products of elimination are identical from the two isomers and the relative rates are determined by differences in ground state energy. As a consequence, the more strained equatorial acetate undergoes elimination more rapidly then the axial acetate.

In summary, these results show that conformational effects *per se* do not affect the direction of elimination in the pyrolysis of esters, and that the greater amounts of *exo* olefin observed in more com-

plicated systems must be due to other effects. They also lend support to previous arguments that the transition state in these pyrolyses resembles products more than it does reactants. The synthetic work also suggests that the addition of Grignard reagents to unhindered cyclohexanones is not stereospecific.

Experimental

Melting points are corrected; boiling points are uncorrected. Microanalyses are by Weiler and Strauss, Oxford, England, and Midwest Microlabs, Inc., Indianapolis, Ind.

cis- and *trans*-1-Methyl-4-*t*-butylcyclohexanol.—A solution of crude 4-*t*-butylcyclohexanone [10a] (20 g., 0.13 mole) in 50 ml. of dry ether was added dropwise to the Grignard reagent from methyl iodide (21.3 g., 0.15 mole) in 100 ml. of dry ether. After addition was complete, the solution was heated at reflux for 1 hour and worked up in the usual way with saturated ammonium chloride solution. Removal of solvent gave 20.4 g. (93% yield) of crude mixed alcohols.

Separation of the mixed alcohols (12.4 g.) was effected on a column of 200 g. of activated alumina. Elution was started with hexane, and the progress of the chromatography was followed by the injection of a 50-μl. sample of each 100-ml. fraction of eluent onto a g.p.c. column of Theed (tetra-(hydroxyethyl)-ethylenediamine) on Celite. The first 13 fractions contained 4.4 g. of pure *trans*-alcohol. Elution with increasing amounts of benzene in hexane and ether in benzene gave 5.4 g. of pure *cis*-alcohol in fractions 35–54. Intermediate fractions contained mixtures of the two alcohols.

The *trans*-alcohol VII was sublimed for analysis, m.p. 70.5–71°. *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.28; H, 13.10.

The *cis*-alcohol VI was recrystallized from hexane, m.p. 97.5–98°. *Anal.* Found: C, 77.41; H, 12.72.

trans-1-Methyl-4-*t*-butylcyclohexyl Acetate.—To the *trans*-alcohol (1.34 g.) in 10 ml. of dimethylaniline was added acetyl chloride (1.68 ml., 3 equiv.), dropwise, with cooling and stirring. After standing overnight at room temperature, the solution was heated on the steam-bath for 1 hour. The reaction mixture was poured into water, the acetate extracted into hexane and the hexane solution washed with acid and bicarbonate solutions. Removal of the solvent gave a liquid which was purified by distillation, b.p. 106–107° (14 mm.). Gas chromatographic analysis showed it to be free from the *cis*-acetate and from unreacted alcohol. Less vigorous conditions gave much unreacted alcohol.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 74.04; H, 11.09.

cis-1-Methyl-4-*t*-butylcyclohexyl acetate was prepared by the same method as for the *trans* isomer above. Removal of the solvent gave a solid which, after sublimation, melted at 48–48.5°.

Anal. Found: C, 73.70; H, 11.43.

Dehydration of *cis*- and *trans*-1-Methyl-4-*t*-butylcyclohexanol by Phosphorus Oxychloride.—To 1 g. of *cis*- or *trans*-alcohol, free from its epimer by g.p.c., dissolved in 10 ml. of dry pyridine was added POCl₃ (1.1 ml., 2 equiv.) dropwise, with stirring and ice cooling. The mixture was stirred in an ice-bath for 2 hours and at room temperature for an additional 2 hours. The excess POCl₃ was destroyed by the addition of ice and the mixture acidified to congo red with HCl. The olefins were extracted into 2 ml. of pentane, dried over anhydrous K_2CO_3 and analyzed by g.p.c. on a 3-meter column of Ucon LB 550X on Celite. Control experiments showed that there was no fractionation of the olefins during the work-up.

The olefinic products were identified by their infrared spectra after separation by gas chromatography. The 4-*t*-butylmethylenecyclohexane (lower retention time) showed peaks at 3.275, 6.08 (exocyclic methylene) and 11.26 μ which were absent in the spectrum of the other olefin, assumed to be 1-methyl-4-*t*-butylcyclohexene.

Equilibration of *exo* and *endo* Olefins.—A small amount of the olefin mixture from the acetate pyrolysis (see below) was heated at reflux for 0.5 hour with a trace of *p*-toluenesulfonic acid, washed, dried and analyzed by g.p.c. About 0.8% *exo* olefin was found to be present.

(15) *cis* refers to the relationship between the *t*-butyl group and the hydroxyl group. It should be noted that *cis*-1-methyl-4-*t*-butylcyclohexyl acetate and *trans*-4-*t*-butylcyclohexyl acetate have *equatorial* ester groups while *trans*-1-methyl-4-*t*-butylcyclohexyl acetate and *cis*-4-*t*-butylcyclohexyl acetate have *axial* ester groups.

(16) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 54.

cis- and *trans*-4-*t*-Butylcyclohexyl Acetates.—The commercially available mixture of *cis*- and *trans*-4-*t*-butyl-cyclohexanol (Matheson Chemical Co.) containing about 75% *trans*-alcohol was esterified by acetyl chloride in benzene–pyridine to give a mixture of *cis*- and *trans*-acetates, b.p. 104–105° (15 mm.).

Relative Rates of Pyrolysis.—The results for one run on *cis*- and *trans*-4-*t*-butylcyclohexyl acetate are typical of the method.

A mixture of approximately 70% of the acetates and 30% tetralin was made and analyzed by g.p.c. A peak area ratio of 3.13 was found for *trans* and *cis* esters and one of 2.27 for total esters and tetralin. One ml. of this mixture was pyrolyzed at 450° and the column cooled and washed with hexane. The products were similarly analyzed, giving ratios of 4.94 and 1.07, respectively. From the initial and final ester/tetralin ratios the conversion, 52.9%, could be calculated.

It may be shown that if the initial and final mole ratios of reactants, a_0/b_0 and a/b, respectively, and the conversion fraction, C, are known, then the ratio of the two first-order rate constants is given by

$$\frac{k_1}{k_2} = \frac{\log\left(\dfrac{1}{1-c} \times \dfrac{1+b_0/a_0}{1+b/a}\right)}{\log\left(\dfrac{1}{1-c} \times \dfrac{1+a_0/b_0}{1+a/b}\right)}$$

Substitution of the above values gives a value for k_{cis}/k_{trans} of 1.69.

Pyrolysis of *cis*- and *trans*-1-Methyl-4-*t*-butylcyclohexyl Acetates.—The *cis* ester (0.25 ml.) or melted *trans* ester (0.25 ml.) was passed at the rate of 0.3–0.4 ml./min. in a slow stream of nitrogen through the pyrolysis column at 400 ± 3°. The products were collected in a Dry Ice trap and the column was cooled and washed with 2 ml. of hexane. The crude pyrolysis mixture was analyzed by gas chromatography on a 3-meter column of Ucon LB 550X on Celite.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE, NEWARK, DEL.]

Studies on the Mechanism of Peroxide Cleavage of Benzils[1a,b]

BY HAROLD KWART AND NORMAN J. WEGEMER

RECEIVED AUGUST 19, 1960

The kinetics of the cleavage of various substituted benzils were studied in 35% *t*-butyl alcohol–65% water at three different temperatures over a wide range of *p*H value. The reaction was found to be first order in each of the components, benzil and hydrogen peroxide, but its dependence on hydroxyl ion concentration was cleanly first order only in the *p*H range 7.4 to 10.7. Outside this range the rate of cleavage showed a much smaller variation with *p*H change. The cleavage of benzil with *t*-butyl hydroperoxide was also investigated. No upper *p*H limit to the range of hydroxyl ion dependence could be established in this case. Furthermore, the rate of cleavage with the alkyl hydroperoxide was only approximately one-ninetieth as great as with hydrogen peroxide. Peracetic acid, on the other hand, was almost two thousand times faster in the cleavage of benzil. Rate constants for the reaction of hydrogen peroxide with various *p*-substituted benzils could be correlated with Hammett σ-values but not with Brown σ^+-values. The activation parameters of benzil cleavage and the substituent effects on the rates of cleavage were shown to be comparable to the related cases of cyanide ion-catalyzed cleavage and hydroxide ion-catalyzed rearrangement of benzils. The mechanism of cleavage under all these circumstances has been discussed and related to other observations in the literature.

Introduction

The reaction of simple ketones with hydrogen peroxide and hydroperoxide derivatives is the well known Baeyer–Villiger oxidation. The product of this oxidation is an ester (or lactone, in the case of cyclic ketones), the structure of which has been reported to depend on the relative migratory abilities of the substituent groups attached to the carbonyl group[2] or, when the substituent groups differ significantly in bulk, on conformational effects as well.[3] The over-all pattern of these and related reactions, where a peroxyester intermediate is clearly indicated, has been followed in a number of cases using labeled oxygen.[4−6] The results of these and other experiments reported[7−9]

strongly suggest a reaction transition state involving an ion pair intermediate in which the anion remains associated with the two cationic reaction centers (oxygen and carbon) during the entire course of rearrangement. Essentially, the rate-determining step in all these cases is the heterolytic breaking of the –O–O– bond in a peroxy intermediate[10] and the transition state,[3b] as illustrated for an aromatic ketone reaction, resembles a heterocyclic "phenonium ion."
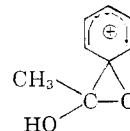
Transition State in Baeyer–Villiger and Related Reactions.—The transition state of the corresponding reaction where R is the oxygen of a carbonyl group, *viz.*, the cleavage of α-diketones with hydroperoxides, has received comparatively less attention. A number of authors have pointed out the analogy to the Baeyer–Villiger reaction and have on this basis postulated that the immediate reaction product is the anhydride, which then undergoes further solvolytic reaction in the medium to give the observed products.[11−14]

(1) (a) Presented in part before 138th A.C.S. Meeting, New York, N. Y., Sept., 1960. (b) Part of this work has been abstracted from the thesis of Norman J. Wegemer submitted in partial fulfillment of the requirements for the degree of Master of Science at the University of Delaware.

(2) W. von E. Doering and L. Speers, *J. Am. Chem. Soc.*, **72**, 5515 (1950).

(3) (a) S. L. Friess and N. Farnham, *ibid.*, **72**, 5518 (1950); (b) M. F. Hawthorne, W. D. Emmons and K. S. McCullum, *ibid.*, **80**, 6393 (1958).

(4) W. von E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953).

(5) D. B. Denny and D. G. Denny, *ibid.*, **77**, 1706 (1955); **79**, 4806 (1957).

(6) C. A. Bunton, T. A. Lewis and D. R. Llewellyn, *J. Chem. Soc.*, 1226 (1956).

(7) R. Criegee, R. Kaspar and W. Dietrich, *Ann.*, **560**, 127, 135 (1948).

(8) P. D. Bartlett and J. L. Kice, *J. Am. Chem. Soc.*, **75**, 5591 (1953).

(9) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

(10) The corresponding homolytic reaction has been discussed in several review articles: (a) J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949); (b) C. H. Hassall in R. Adams, *et al.*, *Organic Reactions*, Vol. IX, John Wiley and Sons, Inc., New York, 1957, p. 73.