Retro-Diels-Alder Reactions. III.[1] Kinetics of the Thermal Decompositions of *exo*- and *endo*-Dicyclopentadiene

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Both *exo*- and *endo*-dicyclopentadiene undergo thermal unimolecular reactions to yield cyclopentadiene monomer. Isomerization of *endo*-dicyclopentadiene to the *exo* isomer, or a change in the opposite sense, is not a detectable competing reaction. The first-order rate constants for gas phase decomposition in the Arrhenius form are $k(exo) = 10^{13.72} \exp(-38{,}490/RT)\ \text{sec}^{-1}$ and $k(endo) = 10^{13.01} \exp(-33{,}970/RT)\ \text{sec}^{-1}$. The difference in activation energies is shown to correspond to a difference in heat content for the activated complexes.

This paper describes the thermal Diels–Alder retrogressions of *exo*- and *endo*-dicyclopentadiene to cyclopentadiene monomer. The activation energies for these reactions are important parameters in the continuing discussion of the mechanism of the Diels–Alder reaction.[3] In particular, the activation parameters bear on the fact that dimerization of cyclopentadiene selectively gives rise to the *endo* isomer, as do the majority of other Diels–Alder reactions involving cyclopentadiene.[4]

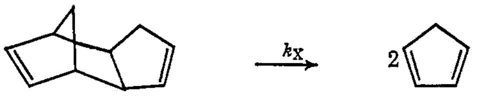
Studies of the thermal decomposition of the *endo* isomer have been reported by Harkness, Kistiakowsky, and Mears,[5] and by Khambata and Wassermann.[6] Alder and Stein[7] found that *exo*-dicyclopentadiene is formed from *endo*-dicyclopentadiene at temperatures (150–170°) which lie within the range of the kinetic studies just cited. Schröder has reported an intramolecular isomerization in the opposite sense (*exo* → *endo*).[8] Internal *endo*-*exo* isomerism is not unknown among Diels–Alder adducts,[9] but a recent study by Baldwin[10] with deuterium-labeled cyclopentadiene dimers strongly indicates dissociation to monomer as the critical step in the reactions reported by Alder and Stein[7] and Schröder.[8] Kinetic verifications of these points are possible (see below), and we have therefore undertaken a kinetic reinvestigation of the thermal reactions of *endo*-dicyclopentadiene. If thermal decomposition and isomerization are concurrent, the previously reported[5,6] activation parameters must be in error.

Some previous evidence indicates that *exo*-dicyclopentadiene is thermally more stable than the *endo* isomer.[8,10,11] *endo*-Dicyclopentadiene yields cyclopentadiene at only 140°; *exo*-Dicyclopentadiene is distilled unchanged at 170°.[11c] However, there are no previous kinetic studies of the thermal decomposition of the *exo* isomer.

Methods and Results

exo- and *endo*-dicyclopentadiene were obtained independently as described in the Experimental Section; the two isomers were separable by gas–liquid partition chromatography. For kinetic experiments, either pure *exo* isomer or *endo* isomer was allowed to flow in a stream of nitrogen through a gas phase, stirred flow reactor which has been described in detail previously.[1,12] This flow reactor is so constructed that the contents of the reactor are well mixed and uniform; time-invariant concentrations result.

The thermal decomposition of *exo*-dicyclopentadiene is depicted in eq 1. At the steady state which prevails in a stirred flow system, material balance eq 2 may be deduced. In this equation, V is the volume of the reactor, U is the flow rate, and k_X is the first-order rate constant.



X C (1)

$$2k_XV[\mathrm{X}] = U[\mathrm{C}] \qquad (2)$$

Rate constants at eight different temperatures are given in Table I. Each rate constant is the average of at least nine experiments, and the flow rate and partial pressures of the reactant *exo* isomer were varied in order to confirm the expected adherence to eq 2. Aging of the glass reaction vessels was not necessary for reproducible results, and the addition of propylene to the reacting stream of gas had no effect upon the reaction rate. The reaction was first order and presumably unimolecular.

No concurrent isomerization (*exo* to *endo*) was discernible. Since *exo*-dicyclopentadiene did prove to be much less reactive than *endo*-dicyclopentadiene (see below), this was not surprising. However, the isomerization (*endo* to *exo*), during thermal decomposi-

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(2) Inquiries should be addressed to W. C. Herndon at Texas Technological College, Lubbock, Texas. The support of the National Science Foundation through a grant (G.P. 247) and an undergraduate research participation program in which C. R. Grayson took part is gratefully acknowledged. J. M. Manion thanks the Department of Health, Education, and Welfare for a National Defense Education Act Fellowship (1962–1965).

(3) (a) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959); (b) M. J. S. Dewar, *Tetrahedron Letters*, No. 4, 16 (1959); (c) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961); (d) M. G. Ettlinger and E. S. Lewis, *Texas J. Science*, **14**, 58 (1962); (e) C. Walling and H. J. Schugar, *J. Am. Chem. Soc.*, **85**, 1360 (1963); (f) D. E. v. Sickle and J. O. Rodin, *ibid.*, **86**, 3091 (1964).

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(5) J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937).

(6) B. S. Khambata and A. Wassermann, *J. Chem. Soc.*, 375 (1939).

(7) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933).

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(9) (a) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951); (b) J. A. Berson, R. D. Reynolds, and W. M. Jones, *ibid.*, **78**, 6049 (1956); (c) J. A. Berson and W. A. Mueller, *ibid.*, **83**, 4940 (1961); (d) J. E. Baldwin and J. D. Roberts, *ibid.*, **85**, 115 (1963); (e) C. Ganter, U. Scheidegger, and J. D. Roberts [*ibid.*, **87**, 2771 (1965)] present almost conclusive evidence against an internal first-order isomerization of *endo*-maleic anhydride–cyclopentadiene adduct to *exo* adduct.

(10) J. E. Baldwin, *J. Org. Chem.*, **31**, 2441 (1966).

(11) (a) P. D. Bartlett and I. S. Goldstein, *J. Am. Chem. Soc.*, **69**, 2553 (1947); (b) A. A. Oswald and F. Noel, *J. Org. Chem.*, **26**, 3948 (1961); (c) R. C. Cookson, N. S. Isaacs, and M. Szelke, *Tetrahedron*, **20**, 717 (1964).

(12) W. C. Herndon, M. B. Henley, and J. M. Sullivan, *J. Phys. Chem.* **67**, 2843 (1963).

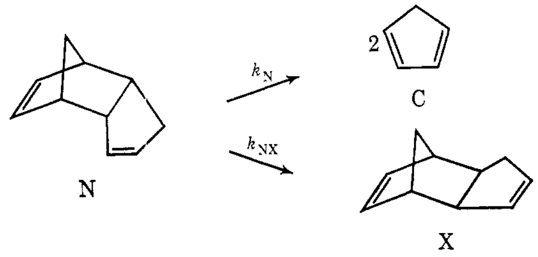
TABLE I

RATE CONSTANTS FOR THE GAS PHASE THERMAL DECOMPOSITION OF *exo*-DICYCLOPENTADIENE

Temp, °C	Rate constant × 10^4 sec^{-1}
200.5	0.947
210.5	2.05
221.6	4.50
229.2	9.28
243.0	27.2
254.5	70.7
263.3	116.0
271.8	186.0
327.1	5,640
340.3	9,510
351.9	17,430

tion of the *endo* isomer, would be distinguishable with our kinetic technique.

The reactions are assumed to be as shown in eq 3,



(3)

and at the steady-state material balance eq 4 and 5 are

$$2k_NV[N] = U[C] \tag{4}$$

$$k_{NX}V[N] = U[X] \tag{5}$$

inferred. These equations could be used to find the required rate constants, but for kinetic experiments the two isomers were only separable by gas chromatography at inconveniently long retention times However, eq 4 and 5 can be rearranged to give eq 6.[13]

$$2k_N([N] + [X])/[C] - k_{NX} = U/V \tag{6}$$

Then if experiments are performed at various flow rates, a plot of the ratio of dicyclopentadiene to cyclopentadiene *vs.* the flow rate divided by the volume will be a straight line with slope $2k_N$ and intercept $-k_{NX}$. One notes that no separation of the concurrently formed isomer is necessary.

Equation 6 is illustrated in Figure 1 for data obtained at eight different temperatures, at least three flow rates at each temperature. Some of the data are omitted from the figure for clarity of presentation. The zero intercept at each temperature demonstrates that isomerization of *endo*-dicyclopentadiene to the *exo* form does not occur in this temperature range. The slopes of the lines in Figure 1 are twice the first-order rate constants for conversion to cyclopentadiene. The numerical values of these rates are given in Table II.

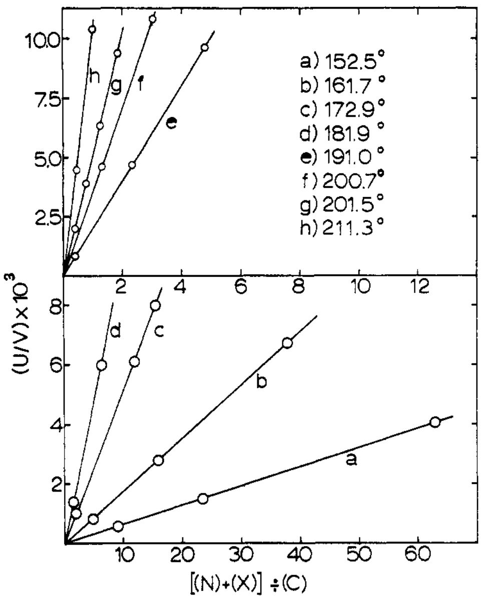


Figure 1.—Data plotted according to eq 6 for the thermal reactions of *endo*-dicyclopentadiene.

TABLE II

RATE CONSTANTS FOR GAS PHASE THERMAL DECOMPOSITION OF *endo*-DICYCLOPENTADIENE

Temp, °C	Rate constant × 10^4 sec^{-1}
152.5	0.353
161.7	0.892
172.9	2.58
181.9	4.79
191.0	10.7
200.7	19.6
201.5	24.5
211.3	50.4

The kinetic method outlined above is not too sensitive to values of the isomerization rate constant which are an order of magnitude or more smaller than the retro-Diels–Alder rate constant. Since the largest amount of *exo* isomer formed from *endo* isomer should be evident at long reaction times and large extent of retrogression to monomer, the products from the gas phase thermal reaction of *endo*-dicyclopentadiene were examined over the entire temperature range at more than 95% conversion to monomeric cyclopentadiene. Separate experiments showed that amounts of *exo* isomer smaller than 0.1% of the remaining dicyclopentadiene could have been detected. Since no *exo* isomer was detected, rate constants for isomerization must be smaller than those for thermal decomposition by at least a factor of 10^4.

Also, we qualitatively examined the thermal decomposition of pure liquid *endo*-dicyclopentadiene. The material was heated in an open system at 150 to 170° for 12 hr. At the end of that period approximately half of the liquid remained, the rest having distilled as monomeric cyclopentadiene. The remaining liquid was analyzed by gas chromatography and none of the *exo* form could be detected. We estimate that less than 0.05% was formed. Repetitions of this experiment gave the same results.

Some attempts were made to determine the difference in heats of formation of the *exo* and *endo* dimers. *endo*-Dicyclopentadiene or cyclopentadiene monomer was heated in sealed tubes at 205° for various long periods of time (12 to 24 hr). The tubes were opened after cooling, and the ratio of *endo* to *exo* dimer was determined by gas chromatography. Polymeric materials were formed to a large extent while the *exo* content in the dimeric mixture varied from 36 to 45%.

[13] Equation 4 divided by 5 gives $2k_N(X) = k_{NX}(C)$. Then, if one divides 4 by V, and adds $2k_N(X)$ to the left side and $k_{NX}(C)$ to the right side, and finally divides by (C), one obtains eq 6.

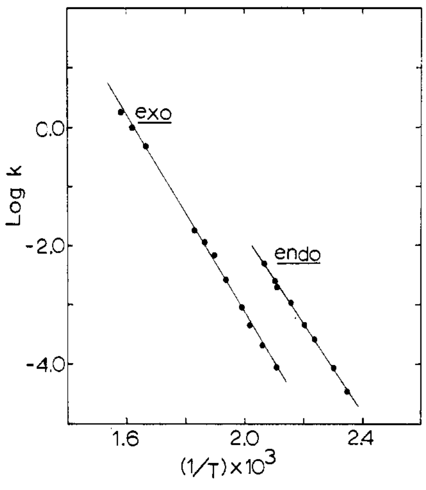


Figure 2.—Arrhenius plots for the thermal decompositions of *exo*- and *endo*-dicyclopentadiene.

Generally, longer periods of heating led to the larger fraction of *exo* dimer, but at periods of time longer than 24 hr the total dimer content decreased drastically to the point where determination of the *exo* and *endo* content was impractical.

Heats of combustion were determined for the chromatographically pure dimers. *exo*-Dicyclopentadiene was more stable than *endo*-dicyclopentadiene, but the results for duplicate analyses were very imprecise, and so these heats are of doubtful value.

Discussion

The nonoccurrence of concurrent isomerization during thermal decomposition of *endo*-dicyclopentadiene in the gas phase requires that previous observations of such isomerization[7] be the results of a dissociation–recombination mechanism, in complete agreement with the conclusions of Baldwin.[10] The nonoccurrence of isomerization in our liquid phase decomposition of *endo*-dicyclopentadiene is not inconsistent. The concentration of cyclopentadiene is never high enough for second-order recombination to become important and so no *exo* isomer is observed

The results reported here strengthen the statement of Berson and Mueller[9c] that such an internal isomerization "is not an invariable feature of the Diels–Alder reactions." It now seems more likely that such isomerizations may involve enolic intermediates,[14] especially since Baldwin and Roberts[9d] have shown that the dihydrocyclopentadiene–maleic anhydride adduct undergoes an internal *endo*-to-*exo* isomerization.

The data of Tables I and II yield the Arrhenius plots of Figure 2, and the respective Arrhenius equations are

$$k(endo) = 10^{13.01 \pm 0.27} \exp(-33{,}970 \pm 550/RT) \text{ sec}^{-1}$$

$$k(exo) = 10^{13.72 \pm 0.12} \exp(-38{,}490 \pm 290/RT) \text{ sec}^{-1}$$

Enthalpies and entropies of activation are

$\Delta H^‡(endo)$ 32,970 ± 540 cal/mole $\Delta S^‡(endo)$ $-$ 1.9 ± 1.0 e.u.

$\Delta H^‡(exo)$ 37,409 ± 290 cal/mole $\Delta S^‡(exo)$ $+$ 1.1 ± 0.6 e.u.

The indicated error limits are standard deviations from a least-squares regression line.

A comparison with previous Arrhenius parameters for the *endo* compound shows good agreement with the adduced values of Harkness, Kistiakowsky, and Mears[5] [$k = 1.0 \times 10^{13} \exp(-33{,}700/RT)$ sec^{-1}], but very poor agreement with a least-squares analysis of their data [$k = 10^{11.8 \pm 0.3} \exp(-31{,}400 \pm 600/RT)$ sec^{-1}]. A study by Khambata and Wassermann[6] in paraffin solution yielded the equation [$k = 10^{13.0 \pm 0.2} \exp(-34{,}200 \pm 400/RT)$ sec^{-1}]. Again, a least-squares analysis gives different values [$k = 10^{12.2 \pm 0.7} \exp(-32{,}850 \pm 1200/RT)$ sec^{-1}]. The reason for these discrepancies are not altogether clear. However, if one discounts the three smallest rates of Harkness, Kistiakowsky, and Mears,[5] the remaining data give $k = 10^{13.8 \pm 0.42} \exp(-34{,}450 \pm 910/RT)$ sec^{-1}, in good agreement with our values. Their smallest rates would probably be the least accurate.

Our attempts at equilibration of the two dimers and the heats of combustion, indicate that *endo*- and *exo*-dicyclopentadiene are of quite comparable stability. From our equilibration experiments and those of Alder and Stein,[7] one can calculate values for $\Delta\Delta G°$ which range from -1.2 to 0.0 kcal/mole, with the *endo*-dicyclopentadiene being the more stable. Although Diels–Alder additions with cyclopentadiene under equilibrating conditions are invariably reported to lead to comparable amounts of both *endo* and *exo* product,[15] the *exo* isomers are usually slightly more stable. It is possible that our dimer mixtures in the heated tubes were not at equilibrium. One or the other of the two dimers might be more reactive in the side reactions which lead to polymeric materials. Therefore, we crudely estimate a free-energy difference of 0.0 ± 1.0 kcal/mole.

Our experiments have shown that *endo* to *exo* isomerization is very unlikely. It should be noted that these data also strongly preclude the possibility of an isomerization of *exo* dimer to *endo* dimer prior to decomposition to monomer. The energy of activation for isomerization would then be 38.5 kcal/mole (in either direction) and detection of *exo* compound in the decomposing *endo* vapor would be possible. Assuming nearly equal rate constants for isomerization, the dimer remaining after 90% reaction at 210° would be approximately 30% *exo*.

Assuming microscopic reversibility, the difference in the height of the energy barrier for formation or retrogression of dimers is 4.5 kcal/mole, the *endo* addition or retrogression having the lower barrier. The exclusive formation of *endo*-dicyclopentadiene in the Diels–Alder reaction of cyclopentadiene is thus explained in terms of a lower heat of activation. A consideration of the various contributory terms to the entropies of activation[16] predicts that ΔS^* would actually be a little larger for the formation of *exo* dimers. (A first-order treatment predicts only a difference in the rotational partition function, owing to a larger moment of inertia for the *exo*-activated complex.)

A discussion of these results in terms of the proposed diradical (two-step) or four-center (one-step) mech-

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(14) J. A. Berson and R. D. Reynolds, *J. Am. Chem. Soc.*, **77**, 4434 (1955).

(15) See ref 4 for a general discussion. Some more specific references are K. Alder, H. Heimback, and R. Reubre, *Chem. Ber.*, **91**, 1516 (1958); J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957); M. Schwarz and M. Maienthal, *J. Org. Chem.*, **25**, 447 (1960); J. A. Berson and R. Swidler, *J. Am. Chem. Soc.*, **75**, 1921 (1953); A. C. Cope, E. Ciganek, and N. A. LeBel, *ibid.*, **81**, 2799 (1959).

(16) B. S. Khambata and A. Wassermann, *J. Chem. Soc.*, 371 (1939).

anisms for the Diels–Alder reaction[3] is not very profitable. Current viewpoints would postulate stabilizing overlap for the *endo* transition complex in either case. However, we do agree with Berson and Remanick[3c] that the question of the precise topography of the energy surface is not an irrelevant question.[3a,d] If one supposes that diradical intermediates could easily rotate before recombination or dissociation[17] a nonkinetic demonstration of the presence of diradical intermediates is possible.

In the *endo* dimer, breakage of one bond leads to a diallylic diradical intermediate which can reform the *endo* dimer by closure at either end of the two allylic systems, the product in either case being identical with the starting material. A reaction topologically equivalent to a degenerate Cope rearrangement[18] is possible. The *exo* compound is more interesting, in that it yields a diradical intermediate which after rotation can re-form *exo* dimer with configuration opposite to that of the starting material. We are presently studying the thermal decompositions of optically active *endo*- and *exo*-dicyclopentadiene in the hope of clarifying this problem.

Experimental Section

Materials.—*endo*-Dicyclopentadiene, mp 32.5°, was obtained commercially. *exo*-Dicyclopentadiene was prepared from the *endo* isomer using the procedure of Bartlett and Goldstein.[11a] The two isomers were separable by gas chromatography with a 6-ft, 5% SF96 oil on Chrom "W" column operating at room temperature and 14 psi. Retention times were 15.5 and 17.8 min for the *exo* and *endo* isomers, respectively. The commercial *endo*-dicyclopentadiene contained a very small amount (1%) of *exo*-dicyclopentadiene. Recrystallization removed the impurity. Our *exo* preparation was contaminated with 20% *endo* isomer. Because of the large difference in thermal reactivity for *exo*- and *endo*-dicyclopentadiene, pure *exo* isomer could be isolated by simply heating the mixture to 180° until all of the *endo* isomer had distilled as cyclopentadiene monomer.

Kinetic Experiments.—The stirred flow reactor system has been described in detail previously.[1,12] A controlled flow of inert gas is allowed to pass through a vaporizer containing the required isomer of dicyclopentadiene. Then the gas mixture flows into a spherical reactor, immersed in a constant temperature bath, and out through a soap-film flow meter. The gas stream can be sampled before and after the reactor, and the gas samples are analyzed by gas chromatography. At each temperature, three to five gas samples were analyzed at each of three to five flow rates. Known mixtures were used to calibrate the hydrogen flame detector and areas were determined with a mechanical integrator. Temperatures were measured with calibrated thermocouples and the electrical timer was checked against a calibrated stop watch.

Equilibration Studies.—One-gram samples of cyclopentadiene or *endo*-dicyclopentadiene were sealed into glass tubes and heated in an oil bath to 205°. The tubes were maintained at this temperature for periods of time ranging from 12 to 100 hr. The contents of the tubes were then analyzed for *exo*- and *endo*-dicyclopentadiene. In some cases a simple vacuum distillation was performed to separate dimeric and higher polymeric materials. Samples of the dimers were purified by gas chromatography, and submitted to E. W. Saybolt and Co., Inc., New Orleans, La., for determinations of heats of combustion. The results were imprecise.

Registry No.—*exo*-Dicyclopentadiene, 933-69-8; *endo*-dicyclopentadiene, 1755-01-7.

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(17) F. A. L. Anet, R. F. W. Bader, and A. r. d. Auwers, *J. Am. Chem. Soc.*, **82**, 3217 (1960).

(18) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

Preparation, Nuclear Magnetic Resonance Study, and Selective Dehydrohalogenations of 1-Bromo-2-trichloromethylcyclooctane[1]

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Photoinitiated addition of bromotrichloromethane to *cis*-cyclooctene gives 1-bromo-2-trichloromethylcyclooctane as the major addition product. Some 1-bromo-4-trichloromethylcyclooctane and appreciable amounts of 3-bromo-1-cyclooctene and trichloromethylcyclooctane are also formed. Nmr spectral studies have identified the major addition product (I) as a 50:50 mixture of *cis* and *trans* isomers. Solvent effects on the nmr spectra led to selective dehydrohalogenation experiments and the isolation of pure *trans* I.

As part of an investigation of radical rearrangements in medium-ring compounds, we have studied the radical addition of bromotrichloromethane to *cis*-cyclooctene. The major addition product is 1-bromo-2-trichloromethylcyclooctane (I); small amounts of the isomer, 1-bromo-4-trichloromethylcyclooctane (3–10% of the total addition product, depending on the mole ratio of the reactants), are also formed, apparently by a transannular radical rearrangement.[2] Nmr studies at 60 and 100 Mc, including decoupling experiments, clearly demonstrate that I is a 50:50 mixture of *cis* and *trans* isomers. While a mixture of geometric isomers is expected from a radical addition reaction,[3] formation of a 50:50 mixture from 2-trichloromethylcyclooctyl radical is surprising.

Bromotrichloromethane adds to olefins, under the influence of light, by a radical chain mechanism.[3] When a mixture of *cis*-cyclooctene and bromotrichloromethylcyclooctane is irradiated with 3500-A light, conversion of the olefin into reaction products is high. Besides the 1:1 addition products, 3-bromo-1-cyclooctene (II) and trichloromethylcyclooctane (III) are also formed in large and approximately equal amounts. Since 3-chloro-1-cyclooctene and trichloromethylcyclo-

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(2) See J. G. Traynham and T. M. Couvillon, *J. Am. Chem. Soc.*, **87**, 5806 (1965), and references cited there.

(3) C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963).