7.05 ppm confirming the presence of a dideuteriomethylene moiety.

Pyrolysis of 7,7-Dideuteriobenzonorcaradiene (1).—In a partial rearrangement reaction 100 μl of 1 was sealed in an evacuated 50-ml Pyrex vessel, heated at 260–270° for 2 hr (40% rearrangement), and cooled; it was then opened. Preparative vlpc[16] afforded a pure sample of **2**. Nmr analysis provided this ratio for the hydrogens at positions 3–7, respectively: 0.73:0.59:1.0:0.59:1.46. In the same reaction, recovery of unreacted 1 allowed an nmr demonstration that no deuterium scrambling occurred in the starting material.

Pyrolysis of 5,6-Dideuterio-2,3-benzonorbornadiene (7).—In typical reactions to completion, 100–200 mg of **7** was sealed in an evacuated 50-ml glass vessel and heated at 370–390° for 50–70 min. Nmr data were in some cases obtained directly from the crude reaction mixture. Alternatively, purification was achieved by preparative vlpc.[16] In either case, nmr analysis showed that the ratio of hydrogens at positions 3–7, respectively, was 0.83:0.81:0.10:0.81:1.65.

A partial completion reaction (375°, 30 min, 70% rearrangement) showed that deuterium scrambling into positions 3 and 7 lagged considerably behind rearrangement. The ratio of hydrogens at positions 3–7, respectively, was 0.94:0.65:0.10:0.64:1.87. Starting material recovered from this reaction was shown by nmr analysis to have undergone no deuterium scrambling.

Pyrolysis of 3,5,7,7-Tetradeuterio-1,2-benzotropilidene (11).—In a typical run, 30 μl of **11** was sealed in an evacuated 50-ml glass vessel and heated at 380–400° for 80 min. The vessel was then cooled and opened. Pure 1,2-benzotropilidene-d_4 was then obtained by preparative vlpc.[16] An nmr spectrum (CCl_4 solution) afforded the following protium ratio for positions 3–7, respectively: 0.40:0.40:0.03:0.40:0.80.

Surface Catalysis Experiments.—Samples of **1**, **7**, and **11** were partially pyrolyzed in the presence of powdered glass, simultaneously with samples without added glass. Gas chromatography revealed that the ratio of reactant to product in the pyrolysis of **1** and **7** was the same with and without the powdered glass. Preparative vlpc[16] afforded pure samples in each case, which by nmr analysis were shown to have scrambled, within experimental error, the same amount of deuterium (Table I).

Table I

Compound	Temp, °C	Time, min	Extent of reaction, %	1,2-Benzotropilidene nmr ratios by position 3	4	5	6	7
1[a]	400	5	80	0.69	0.65	1.0	0.65	1.38
1 + powdered glass[a]	400	5	80	0.68	0.66	1.0	0.68	1.36
7	400	14	89	0.87	0.75	0.1	0.75	1.74
7 + powdered glass	400	14	87	0.87	0.75	0.1	0.75	1.74
11	380–400	20		0.10	0.85	0.0	0.85	0.20
11 + powdered glass	380–400	20		0.11	0.83	0.0	0.83	0.22

[a] Since these reactions were run at 400° partial equilibration of positions 4 and 6 with 3 and 7 occurred by the same mechanism which accounts for deuterium scrambling observed in **7** and **11**.

Registry Nos.—**1**, 17790-63-5; **7**, 17818-07-4; **11**, 17790-64-6; benzonorcaradiene, 3463-79-4; benzonorbornadiene, 4453-90-1; 1,2-benzotropilidene, 264-08-4.

Retro Diels–Alder Reactions. IV.[1]

Kinetics of the Thermal Decomposition of Bornylene and the Thermal Rearrangement of 1,5,5-Trimethylcyclopentadiene[2]

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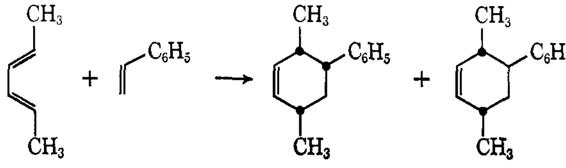
The temperature dependence of the gas phase rate of decomposition of bornylene to produce 1,5,5-trimethylcyclopentadiene and ethylene has been determined. The rate equation for this homogeneous first-order reaction is $\log k = 14.1 - (46{,}000/2.3RT)$. Comparisons are made with other retro Diels–Alder reactions, and the results are considered to support a concerted cycloaddition mechanism. The thermal rearrangement of 1,5,5-trimethylcyclopentadiene is interpreted as involving a rate-determining 1,5-sigmatropic methyl shift. This reaction is also first order and homogeneous; the rate equation is $\log k = 13.7 - (45{,}100/2.3RT)$.

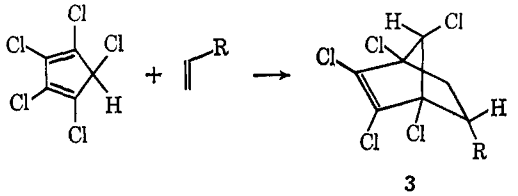
Over 30 years have elapsed since the classic paper by Alder and Stein on the mechanism of the Diels–Alder reaction.[5] Hundreds of Diels–Alder reactions have been carried out in the laboratory since that time; yet the precise details of the mechanism are still obscure, and the lack of detail still continues to beguile the organic chemist.

One of the perplexing features is the effect of substituent groups on the course of the reaction. The specific problem that we refer to is evident in two recently reported investigations. Korver, *et al.*,[6] found that the reaction of styrene with *trans,trans*-2,4-hexadiene (eq 1) gave the all-*cis* adduct **1** and the *trans* adduct **2** in an 8:5 ratio, respectively, and Williamson, *et al.*,[7] reported that pentachlorocyclopentadiene undergoes reactions with various dienophiles (eq 2), in most cases



(1)

1 **2**



(2)

3

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[1] Previous papers: (a) W. C. Herndon and L. L. Lowry, *J. Amer. Chem. Soc.*, **86**, 1922 (1964); (b) W. C. Herndon, W. B. Cooper, and M. J. Chambers, *J. Phys. Chem.*, **68**, 2016 (1964); (c) W. C. Herndon, C. R. Grayson, and J. M. Manion, *J. Org. Chem.*, **32**, 526 (1967).

[2] Taken in part from a dissertation by J. M. Manion submitted to the faculty of the University of Mississippi in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Author to whom inquiries should be addressed at Texas Technological College.

[4] National Defense Education Act Fellow, 1962–1965.

[5] K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

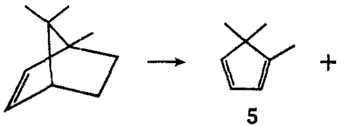
[6] O. Korver, T. L. Kwa, and C. Boelhouwer, *Tetrahedron*, **24**, 1025 (1968).

[7] K. L. Williamson, Y.-F. Hsu, and R. E. Lacko, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P-45.

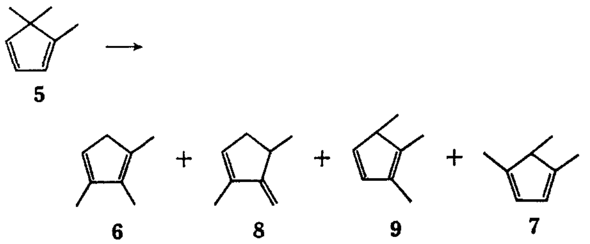
to yield a preponderance of the *anti*-7-chloro adduct **3**. In both cases the predominant product is that which would be formed *via* the more sterically crowded transition complex. These kinds of results are general; both Titov[8] and Sauer[9] cite numerous examples in their respective review articles.

We are interested in obtaining quantitative measures of substituent effects like those described above. Accordingly, we will now describe a kinetic study of the gas phase retro Diels–Alder reaction of bornylene (1,7,7-trimethylbicyclo[2.2.1]heptene-2), and the results will be compared with our previous study[1b] of the thermal decomposition of the unsubstituted norbornylene (bicyclo[2.2.1]heptene). In principle, studies of retro Diels–Alder reactions can reveal information about the forward reactions. In the present case, kinetic investigation of the forward reaction was not even feasible, since the cyclopentadiene moiety undergoes self-condensation much more easily than it undergoes reaction with dienophilic ethylene.

Anticipating the results, we found that bornylene undergoes a clean decomposition in the gas phase to yield ethylene and 1,5,5-trimethylcyclopentadiene (eq 3). The trimethylcyclopentadiene which is produced then undergoes further reactions (eq 4), and the kinetics of this secondary process were also investigated.



4 **5** (3)



5 **6** **8** **9** **7** (4)

Experimental Section

Kinetic Experiments.—Bornylene, prepared from borneol by a Chugaeff reaction,[10] was allowed to flow in a stream of nitrogen through a gas phase, stirred flow reactor which has been described in detail previously.[1a,11] A Pyrex flow reactor with a volume of 60.06 ml was used in this work. At least four flow rates and two partial pressures of reactant were studied at each temperature. Flow rates varied from 0.1 ml/sec at lower temperatures to a maximum flow rate of 3.4 ml/sec at the highest temperature investigated. The reactions are investigated under the conditions (relatively slow flow rate, high temperature) where the contents of the reactor are well mixed and time invariant concentrations result. The reactor was immersed in a molten lead bath constructed from a stainless steel beaker. The major part of the heat required for the reaction temperature was provided by a heating mantle and variable transformer. Fine temperature control was maintained by a proportional temperature controller (Bailey Model 104) and a cartridge heater. The temperature of the reactor was constant to within ±0.05° as determined with a Bureau of Standards calibrated Chromel–Alumel thermocouple inserted in the reactor.

Quantitative product analyses were carried out by gas chromatography. An Aerograph Hy-Fi gas chromatograph with hydrogen flame detector, fitted with a 1-m column packed with 5% SF-96 silicon oil on Chromosorb W support was used. The detector was calibrated with known samples synthesized by independent methods. Peak areas were integrated with a Disc integrator.

Product Isolation and Identifications.—The primary products of the pyrolysis of bornylene were isolated by running the reaction at low conversion and separating the products by gas chromatography (Aerograph Autoprep) using a 25-ft column of 25% butanediol succinate on Chromosorb maintained at 95°. One of the primary products was identified as 1,5,5-trimethylcyclopentadiene from its uv, ir, and nmr spectra. The other primary product was confirmed as ethylene by comparing the retention times of the product and an authentic sample of ethylene.

The rearrangement products of 1,5,5-trimethylcyclopentadiene were obtained by carrying out the pyrolysis of bornylene to very high extents of conversion and trapping the products in liquid nitrogen. The product mixture was then separated into three fractions by preparative gas chromatography using a 12-ft silicon oil (SF-96) column at room temperature. The two major products were identified as 1,2,3-trimethylcyclopentadiene and 3-methylene-2,4-dimethylcyclopentene by comparing their respective ir and uv spectra with those of authentic samples, synthesized in the manner described by Mironov, *et al.*[12] The small third fraction had a uv spectrum consistent with a tentative identification as a mixture of 1,2,5-trimethylcyclopentadiene and 1,4,5-trimethylcyclopentadiene. A sufficient quantity for positive identification was not obtained.

It should be noted that during the kinetic analysis it was necessary to analyze gas samples taken directly from the hot reactor in order to obtain consistent and precise results.

Results

The thermal decomposition of bornylene and the subsequent rearrangement of 1,5,5-trimethylcyclopentadiene were investigated over the temperature range 328.7–429.1°. Preliminary experiments indicated that at least two consecutive unimolecular reactions were taking place as indicated in eq 5. In our stirred flow

$$\mathbf{4} \xrightarrow{k_1} \text{ethylene} + \mathbf{5} \qquad (5)$$
$$\mathbf{5} \xrightarrow{k_2} \mathbf{6} - \mathbf{9}$$

reactor system the kinetic equations are simple algebraic expressions which can be derived from material balance equations;[13] for the present system a material balance equation for product **5** leads to the kinetic expression (eq 6) where k_1 and k_2 are first-order rate con-

$$k_1[(\mathbf{4})/(\mathbf{5})] - k_2 = \frac{u}{v} \qquad (6)$$

stants, and u and v are the flow rate of the gas and the volume of the reactor, respectively. An excellent adherence of the rate data at each temperature to this kinetic expression confirmed the postulated reaction scheme. The rate constant for the first reaction (bornylene decomposition) could also be calculated by determining the fraction of bornylene which underwent reaction at a particular flow rate and reactor volume. In the same manner, a determination of the mole ratio of all rearrangement products to 1,5,5-trimethylcyclopentadiene can yield the rate constant for the second reaction. Rate constants determined in this way are in satisfactory agreement with those determined by using eq 6.

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[8] Yu. A. Titov, *Russ. Chem. Rev.*, **31**, 267 (1962).

[9] J. Sauer, *Angew. Chem. Intern. Ed. Eng.*, **6**, 16 (1967).

[10] H. R. Nace, *Org. Reactions*, **12**, 87 (1962).

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

[12] V. A. Mironov, E. V. Sobolev, A. N. Elizaro, *Tetrahedron*, **19**, 1939 (1963).

[13] W. C. Herndon, *J. Chem. Educ.*, **41**, 425 (1964).

More than one series of experiments was carried out, some ascending in temperature, some descending in temperature, and in two experiments the reactor was packed with Pyrex tubing in order to ascertain the effect of a different surface to volume ratio. The first-order rate constants, from eq 6, are given in Table I. In a few earlier experiments only one of the two consecutive reasons was quantitatively analyzed.

Table I
Rate Constants for Gas Phase Thermal Decomposition of Bornylene (k_1) and Thermal Rearrangement of 1,5,5-Trimethylcyclopentadiene (k_2)

Temp. °K	$k_1 \times 10^2$, sec^{-1}	$k_2 \times 10^2$, sec^{-1}
608.2	0.378	0.314
611.3	0.361	0.372
614.6	0.482	
617.7	0.578	0.709
623.5		0.906
626.0	1.16	1.11
632.0	1.17	1.00
634.3	1.93	1.50
640.1	2.01	2.41
640.4[a]	2.83	2.29
641.1	2.28	2.34
647.0	4.23	3.10
651.3	3.56	3.37
653.7		4.90
655.7	4.90	3.96
664.0	8.44	5.92
669.0	11.7	
670.3[a]	12.0	9.57
670.4	10.8	13.4
679.8	17.7	
680.2	24.4	17.0
681.6	18.3	23.0
692.8	31.3	30.7
693.2	37.2	
702.1	56.9	

[a] Reactor packed with glass tubing.

Imprecise and erratic results were obtained at temperatures higher than those listed in Table I. Above about 710°K a surface catalysis of both reactions was evident; so we have not included such results. In the temperature range of Table I, the reported reactions were not affected to a significant degree (over 10% variation) by seasoning of the reaction vessels or by a tenfold change in the partial pressure of introduced reactant bornylene. However, the precision of the data, especially the variation with temperature of the ratio of k_1 to k_2, is not so good as those results which we have reported in earlier papers.[1] Even so, by carrying out the large number of experiments summarized in Table I, we were then able to obtain activation parameters with reasonably small error limits. In Table II the activation parameters are listed. The error limits are standard deviations from a least-squares regression line.

Table II
Activation Parameters for Thermal Decomposition of Bornylene (k_1) and Rearrangement of 1,5,5-Trimethylcyclopentadiene (k_2)

	k_1	k_2
Preexponential factor	$10^{14.1 \pm 0.3}$	$10^{13.7 \pm 0.4}$
Energy of activation	46.0 ± 0.9 kcal/mol	45.1 ± 1.2 kcal/mol
Entropy of activation	2.3 ± 1.3 eu	0.7 ± 1.9 eu
Enthalpy of activation	44.7 ± 0.9 kcal/mol	43.8 ± 1.2 kcal/mol

One other experimental result is of interest. The relative ratios of the rearrangement products of 1,5,5-trimethylcyclopentadiene were found to be flow rate independent at each temperature, and also to be temperature independent. The approximate yields are **6**, 83%; **7**, 13%; and **8** and **9**, 4%.

Discussion

The two reactions which we are reporting on in this paper are separate and distinct even though they are studied simultaneously in the same system. We will therefore discuss each reaction in a separate section. The kinetic parameters for the thermal decomposition of bornylene also raise a question about the so-called "quasi-heterolytic" gas phase pyrolyses[14] of bornyl and isobornyl halides and esters. This question is discussed briefly in a separate paper.[15]

Retro Diels–Alder Reaction of Bornylene.—Bornylene undergoes the retro Diels–Alder reaction at a slower rate than does norbornylene. Rate constants at 350° are, for bornylene, 8.51×10^{-3} and, for norbornylene, 66.1×10^{-3} sec^{-1}.[1b] The order of magnitude difference in rate is primarily due to a 3-kcal/mol difference in energy of activation, the Arrhenius equation for norbornylene being $\log k = 13.78 - (42{,}750/2.3RT)$.[1b]

Straightforwardly we might assign this 3-kcal/mol difference to a steric factor which increases the activation energy in the methyl substituted bornylene. We take as our model for the transition state the model which was described by Herndon and Hall,[16] which has recently received some additional support.[17] The electronic nature of the transition state corresponds to that of the separated diene and dienophile but the two molecules are oriented in a state closely resembling the gross skeleton of the adduct. The rationale for this picture of the activated complex is described in the earlier paper.[16]

Now, as the bornylene molecule begins to dissociate, flattening of the cyclopentadiene and ethylene moiety must occur. The *anti*-methyl group at C-7 would then be much closer to the departing ethylene molecule than it is in the ground state. Assuming bond distances and bond angles for the bicycloheptane system reported by Wilcox[18] and Kitaygordsky,[19] the distance from the center of the methyl group to the center of the double bond is approximately 3 Å. Assuming a transition state in which the diene portion is planar and breaking bonds have been extended 10% (longer extensions are not likely since entropies of activation for retro Diels–Alder reactions are close to zero), the methyl group-double-bond distance is shortened to 2 Å. The calculation is very crude, but it does indicate an increase of steric interference of the methyl group as progress is made along the reaction coordinate.

Our original expectation was that the methyl group might have an accelerating effect upon the retro Diels–Alder reaction, analogous to that found by Williamson,

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(14) For the most recent review, see A. Maccoll and P. J. Thomas, "Progress in Reaction Kinetics," Vol. 4, C. Porter, Ed., Pergamon Press, Oxford, 1967, p 119.

(15) W. C. Herndon and J. M. Manion, *Tetrahedron Lett.*, in press.

(16) W. C. Herndon and L. H. Hall, *ibid.*, 3095 (1967).

(17) D. C. F. Law and S. W. Tobey, *J. Amer. Chem. Soc.*, **90**, 2376 (1968).

(18) C. F. Wilcox, Jr., *ibid.*, **82**, 414 (1960).

(19) A. I. Kitaygordsky, *Tetrahedron*, **14**, 230 (1961).

et al.,[7] for the chlorine atom at position 5, in the reaction of pentachlorocyclopentadiene with ethylenic dienophiles (eq 2). The effect in that case is ascribed to stabilizing dispersion interactions between the closely held partners in the transition state. However, the effect of the methyl group is destabilizing rather than stabilizing. One possible explanation is related to the relative van der Waals sizes of the substituent chlorine atom and methyl group (1.8 and 2.0 Å, respectively).[20] It is possible that, in the transition state, the methyl group position may be close enough to the dienophilic ethylene moiety to be in the repulsive part of the van der Waals potential. The chlorine atom, being smaller, could still be in the attractive part of the potential. If the role of dispersion forces is a major one in stabilizing the transition complex, the distance from the C-7 substituent to ethylenic moiety might be delineated within 0.2 Å. More experimental measurements with substituents in various positions will be useful in this regard.

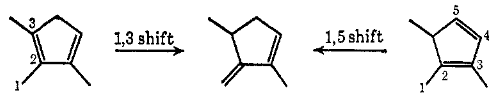
The discussion till now has assumed a concerted cycloaddition mechanism for the Diels–Alder reaction and its inverse. We believe that our results support the concerted cycloaddition mechanism. If only one carbon–carbon single bond were severed in the rate-determining step, and if a diradical intermediate were formed, such a diradical could become free of steric interaction with substituents at C-7 by rotation around carbon–carbon single bonds. A substituent at the 7 position might even be expected to accelerate the reaction if such a mechanism is functioning. The observation of the steric effect seems more consistent with a transition state in which both dienophile–diene bonds are partially broken.

In summary, *anti*-methyl substituents at C-7 in the bicyclo[2.2.1]heptane series destabilize the transition state for the Diels–Alder reaction. *anti*-7-Chloro substituent seems to stabilize the transition state.[7] Both of these effects are probably steric in origin, and concerted cycloaddition mechanisms are thereby supported.

Rearrangement of 1,5,5-Trimethylcyclopentadiene (5).—The thermal lability of **5** was noted by Alder and Muders in 1958,[21] and they reported rearrangement to **6** at 400°. De Haan and Kloosterziel[22] later reported a kinetic study of the thermal isomerization with results differing from ours in some respects. They do not report the obtention of **7**, and their activation parameters, $\Delta H^{\ddagger} = 40.3$ kcal/mol, $\Delta S^{\ddagger} = -4$ eu, are much different from those which we find, $\Delta H^{\ddagger} = 43.8$ kcal/mol and $\Delta S^{\ddagger} = 0.7$ eu. However we do note that these two different sets of activation parameters give very similar rate constants over a large range of temperature. The more positive enthalpy of activation in our results is compensated for by the more positive entropy for activation. De Haan and Kloosterziel did not publish the details of their kinetic work;[22] so it is difficult to resolve the discrepancy. They also studied the thermal rearrangements of 2,5,5-trimethylcyclopentadiene,[22] reactions very similar to the reactions of **5**. In this case they found activation enthalpies of 44.4 and 44.2 kcal/mol (for methyl shift in the two different possible directions). These figures could be construed as supporting our results.

The rearrangement reactions of **5** can be formulated as a rate-determining allowed suprafacial 1,5-sigmatropic methyl shift[23,24] to produce 1,2,5-trimethylcyclopentadiene. At the elevated temperatures required for the rate-determining step, further allowed 1,5-sigmatropic shifts of hydrogen atoms would occur immediately to produce the other cyclopentadiene molecules which are observed. 1,5-Sigmatropic hydrogen shifts have been studied extensively,[12,25] and activation energies are on the order of 20 kcal/mol. The magnitude of the activation energy for rearrangement of **5** seems quite reasonable, and is comparable with the increased activation energy found for carbon shifts *vs.* hydrogen shifts in the tropilidene series.[24]

The formation of the exocyclic isomer **7** is more difficult to explain. Superficially, **7** can arise from either **6** or **8** (eq 7). However, the 1,3 shift is not a suprafacially allowed reaction, and is inconceivable in an antarafacial manner. The allowed 1,5-shift **8** → **7** also does not seem to be sterically possible. Compound **7** is normally produced during acid- or base-catalyzed dehydration of 2,3,4-trimethylcyclopent-2-en-1-ol, along with the major product, compound **6**.[12] Because of this fact, we believe that **7** may be formed through a heterogeneous mechanism, perhaps catalyzed by the walls of the flow reactor. At this time we have no information on this point.



6 **7** **8** (7)

We conclude that the gross nature of the rearrangement of **5** is well explained as an intramolecular 1,5 shift of a methyl group in general agreement with previous workers.

Registry No.—**4**, 464-17-5; **5**, 4249-09-6.

Acknowledgment.—The support of the National Science Foundation (Grant No. GP-247) is gratefully acknowledged.

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[20] L. Pauling, "Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948, p 189.

[21] K. Alder and R. Muders, *Ber.*, **91**, 1083 (1958).

[22] J. W. De Haan and H. Kloosterziel, *Rec. Trav. Chim. Pays Bas*, **84**, 1594 (1965).

[23] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[24] J. A. Berson, *ibid.*, **1**, 152 (1968).

[25] D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 277 (1963); S. McLean and P. Haynes, *Tetrahedron Lett.*, 2385 (1964); S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965); W. R. Roth, *Tetrahedron Lett.*, (1964).