

Kinetics of the Decomposition of Diazirines

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Thermal decomposition of a series of *meta*-substituted 3-chloro-3-aryldiazirines in cyclohexene has been investigated over the temperature range 60–95 °C. In contrast to the kinetics of the *para*-substituted compounds in cyclohexene, the rates of decomposition of this series of compounds are linearly related to their respective σ values. The kinetics of decomposition of both series of compounds have been examined in acetic acid at 75 °C, and are similar to those observed in cyclohexene. Plausible mechanisms are proposed to account for the observed products. In addition, the thermal decompositions of 3-chloro-3-cyclopropyl- and 3-chloro-3-cycloheptyl-diazirine have been studied. The results are consistent with a polarized radical-like transition state for the decomposition of diazirines.

IN considering the mechanism of decomposition of diazirine, the initial problem is a choice between a concerted and a two-step mechanism. For the thermal unimolecular isomerization of 3-methyl-3-vinyldiazirine,¹ the results suggest that the decomposition occurs in a

stepwise manner. While there is sufficient evidence that a stepwise mechanism occurs in diazirine decomposition, it is not certain whether the intermediate is

¹ M. T. H. Liu and K. Toriyama, *Canad. J. Chem.*, 1973, **51**, 2393.

diradical or ionic in character. In the pyrolysis of *para*-substituted 3-chloro-3-aryldiazirines, the possibility of both homolytic and heterolytic dissociation has been suggested:² it was observed that the plot of $\log k$ vs. σ for the *para*-series was not linear and did not fit any of the usual non-linear Hammett relationships. We now wish to report the kinetic data on the pyrolysis of a series of *meta*-substituted 3-chloro-3-aryldiazirines in cyclohexene and in acetic acid. This work has been undertaken to determine whether or not the pyrolysis of diazirines in a protic medium is substantially different from that in an aprotic medium.

The effects of the cyclopropyl group on ionic and radical transition states have been reported recently.³⁻⁵ Accordingly, the decompositions of 3-chloro-3-cyclopropyl- and 3-chloro-3-cycloheptyl-diazirine have been carried out to compare the effects of the cyclopropyl and cycloheptyl groups on the transition states in diazirine decompositions.

EXPERIMENTAL

I.r. and n.m.r. spectra were obtained with Perkin-Elmer model 137 and Varian Associates T 60 instruments. U.v. spectra were measured with a Unicam SP 800 spectrophotometer and mass spectra with a Hitachi-Perkin-Elmer model RMS-4 spectrometer.

Materials.—Cyclohexene was passed through a silica gel column and then fractionally distilled. Diethylene glycol monoethyl ether (DEGME) and dimethyl sulphoxide (DMSO) were stirred with calcium hydride for 1 day and fractionally distilled under anhydrous conditions. Glacial acetic acid was used without further purification. All the diazirines were prepared from the corresponding amidine hydrochlorides in the presence of lithium chloride in DMSO solution;⁶ purification was accomplished by column chromatography and each compound exhibited a single spot on t.l.c. The physical properties of the various compounds are listed in Table 1. The n.m.r. spectra were

TABLE 1
Physical properties of diazirines

Diazirine	$\nu(\text{N}=\text{N})/\text{cm}^{-1}$	$\lambda_{\text{max.}}/\text{nm}$ (log ϵ)
3-Cl-3- <i>m</i> -ClC ₆ H ₄ -	1569	370 (2.37) *
3-Cl-3- <i>m</i> -NO ₂ -C ₆ H ₄ -	1580	362 (2.43) *
3-Cl-3- <i>m</i> -MeC ₆ H ₄ -	1575	371 (2.37) *
3-Cl-3-cyclo-C ₃ H ₅ -	1565	345 (2.53) *
3-Cl-3-cyclo-C ₇ H ₁₃ -	1560	344 (2.18) †

* Recorded in cyclohexane. † Recorded in dodec-1-ene.

consistent with the proposed structures in all cases. Elemental analyses for the diazirine compounds were not possible owing to their explosive nature. The physical properties of the *para*-substituted compounds have been reported.²

Kinetic Procedure.—The rates of reaction were measured by following the disappearance of diazirine. A solution of diazirine (10^{-3}M) in cyclohexene was sealed in a Pyrex tube and suspended in a constant temperature oil-bath regulated to $\pm 0.1^\circ$. After a specific time the tube was removed from the oil-bath and the reaction was quenched in a dry ice-

² M. T. H. Liu and K. Toriyama, *Canad. J. Chem.*, 1972, **50**, 3009.

³ E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, 1973, **95**, 2397.

acetone bath. The optical density of the solution was observed and the first-order rate coefficient was determined graphically from the plot of $\log(A_t - A_\infty)$ against time (t), where A_t is the optical density at the wavelength of observation and A_∞ corresponds to that of the complete reaction.

Reaction Products.—The expected 7-chloro-7-arylnorcaranes were the main products from the thermal decomposition of 3-chloro-3-aryldiazirines in cyclohexene. The procedure for the isolation and the characterization of these norcaranes was the same as that used for the *para*-substituted compounds.² The n.m.r. spectra of products showed major peaks at δ 1.0–2.0 (m, cyclohexane ring-H) and 7.5–8.1 (m, aromatic-H). The mass spectra of 7-chloro-7-*m*-nitrophenyl- and 7-chloro-7-*m*-methylphenyl-norcarane show parent peaks at m/e 251 and 220 respectively which are consistent with the molecular weight of these compounds. In acetic acid, the decomposition products for 3-chloro-3-*p*-tolylidiazirine were nitrogen and *p*-methylbenzaldehyde. For 3-chloro-3-cyclopropyldiazirine and 3-chloro-3-cycloheptyldiazirine, the products were chiefly nitrogen, chloromethylenecyclopropane (yield 90%) [δ 2.80 (2H, t), 2.40 (2H, sext), and 5.80 (1H, s)], and chloromethylenecycloheptane (yield 95%) [δ 1.60 (8H, m), 2.35 (4H, m), and 5.80 (1H, m)] respectively.

RESULTS AND DISCUSSION

Decomposition of meta-Substituted Diazirines in Cyclohexene.—The thermal decomposition of 3-chloro-3-*m*-chlorophenyl-, 3-chloro-3-*m*-nitrophenyl-, and 3-chloro-3-*m*-methylphenyl-diazirine gave nitrogen, the corresponding norcaranes, and small amounts of the insertion products. The organic products obtained were similar to those reported in the thermal decomposition of the corresponding *para*-substituted diazirines.² The decompositions were first order under the conditions employed. Rate constants were determined at six temperatures (Table 2). The data gave excellent

TABLE 2
Rate constants for decomposition of 3-chloro-3-aryl-diazirines in cyclohexene

3-chloro-3- <i>m</i> -chlorophenyldiazirine *						
Temp. ($^\circ\text{C}$)	60.0	70.0	75.0	80.0	90.0	95.0
$10^4 k/\text{s}^{-1}$	0.30	0.97	1.79	3.09	8.92	15.90
3-chloro-3- <i>m</i> -nitrophenyldiazirine						
Temp. ($^\circ\text{C}$)	70.0	75.0	80.1	84.8	89.8	95.0
$10^4 k/\text{s}^{-1}$	0.76	1.58	2.57	4.93	7.68	12.72
3-chloro-3- <i>m</i> -methylphenyldiazirine						
Temp. ($^\circ\text{C}$)	71.0	75.0	80.0	85.2	90.0	94.9
$10^4 k/\text{s}^{-1}$	1.19	1.96	3.43	5.67	10.02	16.66

* $k_1 = 1.96 \times 10^{-4} \text{ s}^{-1}$ at 75° in diethylene glycol monoethyl ether. $k_1 = 2.34 \times 10^{-4} \text{ s}^{-1}$ at 75° in dimethyl sulphoxide.

Arrhenius plots from which the following equations were obtained by least-squares analysis: k (*m*-chlorophenyl) = $10^{13.56 \pm 0.12} \exp[(-115,400 \pm 840)/RT]$; k (*m*-nitrophenyl) = $10^{13.80 \pm 0.50} \exp[(-117,600 \pm 3,300)/RT]$.

⁴ H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, 1973, **95**, 2400.

⁵ J. C. Martin and J. W. Timberlake, *J. Amer. Chem. Soc.*, 1970, **92**, 978.

⁶ W. H. Graham, *J. Amer. Chem. Soc.*, 1965, **87**, 4396

RT]; k (*m*-methylphenyl) = $10^{13.62 \pm 0.23} \exp[(-115,600 \pm 1500)/RT]$ s⁻¹, where R is taken as 8.314 J mol⁻¹ K⁻¹ throughout the text.

The results indicate that the thermal decompositions of *meta*-substituted phenyldiazirines are typically unimolecular reactions with A factors equal to $10^{13.7 \pm 0.5}$. The minor solvent effects on the thermal decomposition of these compounds also agree with the data reported in earlier studies.² The trend towards a lower activation energy in going from *meta*-substituted 3-chloro-3-aryldiazirines to 3-chloro-3-methyldiazirines can be rationalized in terms of the resonance stabilization effects of the aryl group.

Our present data also provide evidence that electro-negative substituents such as NO₂ and Cl retard the rate of decomposition of the corresponding *meta*-substituted diazirines. The faster rates observed for

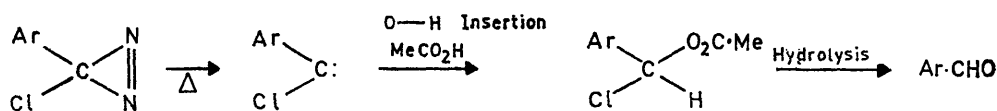
acid was studied at 75 °C. The rate constants are given in Table 4. The decompositions were first order and

TABLE 4

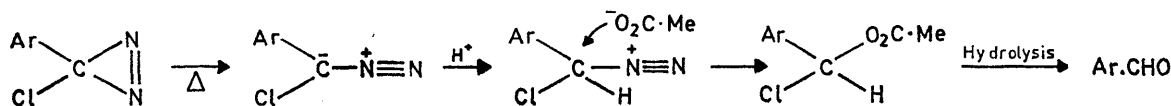
Rate constants for decomposition of 3-chloro-3-aryldiazirine in acetic acid at 75 °C

Aryl	10 ⁴ k /s ⁻¹	Aryl	10 ⁴ k /s ⁻¹
<i>p</i> -MeOC ₆ H ₄	5.80	C ₆ H ₅	1.91
<i>p</i> -ClC ₆ H ₄	2.10	<i>m</i> -ClC ₆ H ₄	1.77
<i>p</i> -MeC ₆ H ₄	2.97	<i>m</i> -MeC ₆ H ₄	1.96
<i>p</i> -NO ₂ C ₆ H ₄	1.95	<i>m</i> -NO ₂ C ₆ H ₄	1.53

only one compound, 3-chloro-3-*p*-tolylidiazirine, was studied in detail over the 70–100 °C temperature range. The Arrhenius equation yielded $k = 10^{13.81 \pm 0.22} \exp[(-115,500 \pm 1500)/RT]$ s⁻¹. The products of the decomposition were nitrogen and *p*-methylbenzaldehyde. The formation of the product can be rationalized through either Scheme 1 or 2. In Scheme 1, the product



SCHEME 1



SCHEME 2

the *p*-chloro- and *p*-nitro-derivatives may be due to resonance stabilization effects in their transition states. The activation parameters for the *meta*- and *para*-substituted compounds are shown in Table 3. There is

TABLE 3

Activation parameters for various 3-chloro-3-aryldiazirines at 100 °C

X	ΔS^\ddagger /J mol ⁻¹ K ⁻¹	ΔH^\ddagger /kJ mol ⁻¹	ΔG^\ddagger /kJ mol ⁻¹
H	10.5	114.2	110.0
<i>p</i> -MeO	1.7	107.9	107.1
<i>p</i> -Me	12.1	113.4	109.2
<i>p</i> -Cl	9.6	113.0	109.2
<i>p</i> -NO ₂	9.6	113.4	110.0
<i>m</i> -Cl	4.6	112.1	110.5
<i>m</i> -NO ₂	9.6	114.6	110.9
<i>m</i> -Me	5.9	112.5	110.5

a good correlation between ΔH^\ddagger and ΔS^\ddagger for the *meta*-series but only a fair correlation is obtained with the *para*-compounds. It is noted that the variation in the ΔH^\ddagger and ΔS^\ddagger values is small and this suggests that the effect of solvation on the ground state and the transition state is similar throughout the series.

Decomposition of *para*- and *meta*-Substituted Diazirines in Acetic Acid.—The thermal decomposition of the *para*- and *meta*-substituted 3-chloro-3-aryldiazirine in acetic

⁷ Y. Yamamoto and I. Moritani, *Tetrahedron Letters*, 1969, 3087.

is formed *via* the insertion of the carbene into the O–H bond of acetic acid; and in Scheme 2, the product is formed from the protonation of a diazomethane intermediate. As discussed below, we favour a mechanism in which there is a build-up of positive character in the carbon atom of the diazirine ring and we reject Scheme 2 since it would involve a build-up of negative charge in the carbon atom.

A third possible scheme would involve protonation on the diazirine ring before decomposition takes place. However, this mechanism is unlikely, especially in view of the foregoing kinetic results, since it would require the rate constants in protic and aprotic solvents to be different. Since the rate constants and the Arrhenius parameters were similar in cyclohexene and in acetic acid, the decomposition is likely to occur *via* Scheme 1.

In the thermal decomposition of diethyl diazosuccinate in acetic acid,⁷ the major process for olefin formation (66%) is the carbenic process, and the diazonium ion-carbonium ion process occurs to a minor extent (34%). However, in the presence of mineral acid, the decomposition proceeds solely by the diazonium ion-carbonium ion process. Bradley has studied the alicyclic series ranging from cyclopentanespiro-3'-diazirine to cyclooctanespiro-3'-diazirine.⁸ Photolysis of cyclopentanespiro-3'-diazirine in acetic acid led to the formation of

⁸ G. F. Bradley, Ph.D. Thesis, University of Southampton, 1967.

cyclopentyl acetate (39.9%) and hydrocarbon products (60.1%). The yield of acetate gradually decreased to 31% over the series. This was explained by a corresponding increase in stability of the linear diazo-compounds. Similar results have been obtained in the pyrolysis of the same diazirines in acetic acid. Bradley has also examined the photolysis of 3-phenyldiazirine in a mixture of cyclohexene and acetic acid, which gives benzyl acetate (77.6%) and hydrocarbons (22.4%). Bradley proposed that this is a direct method for measuring the participation of an ionic mechanism, because the carbonium ion can only react with the acetate ion and cannot undergo an intramolecular loss of a proton. He concluded that *ca.* 75% of the primary process, in the photolysis of a diazirine in acetic acid, is the isomerization to its linear isomer. Although mechanisms in photolysis and pyrolysis are not necessarily the same, we have reason to believe that Bradley's suggestion is not totally valid in view of the possible mechanism proposed in Scheme 1. The pathway for decomposition in acetic acid is much more complex. Furthermore, no evidence which clearly establishes the percentage of primary process going to a linear isomer or directly to the carbene has been found.

Hammett Plot.—In our earlier work on the decomposition of a series of *para*-substituted 3-chloro-3-aryldiazirines in cyclohexene,² it was shown that the plot of $\log k$ vs. σ was not linear. However, a smooth curve could be drawn through all the points except for that of the unsubstituted compound. This curvature was ascribed to the varying resonance interactions of the substituents in the transition state of the *para*-substituted compounds. If this explanation is correct, lower rate constants should be observed with the *meta*-substituted diazirines since the substituents cannot interact effectively by a direct conjugate effect in the transition state. This is what is observed in the Figure, which shows a straight line obtained by plotting $\log k$ vs. σ . There is a separation of the data into two categories; one for the *meta*-substituents (including the unsubstituted compound) and one for the *para*-substituents. Similar Hammett relationships of this type have also been observed for the reactions of substituted benzyl chlorides with trimethylamine in benzene,⁹ and in the studies on the decomposition of tetra-alkylammonium salts.¹⁰

Generally, a concave upward curve in the Hammett plot indicates a change in the mechanism of the reaction. In our present work, the concave curve is interpreted as being the result of the conjugative effects between the substituent and the reaction site. The plot of $\log k$ vs. $\sigma^+ - \sigma$ as shown in Figure 3 of reference 2 supports the idea of a substantial conjugative demand on the substituent. The negative Hammett ρ value found in

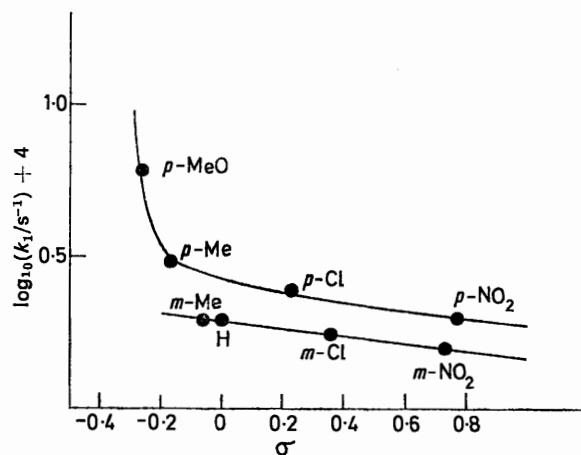
⁹ C. G. Swain and W. P. Langsdorf, *J. Amer. Chem. Soc.*, 1951, **73**, 2813.

¹⁰ E. C. F. Ko and K. T. Leffek, *Canad. J. Chem.*, 1970, **48**, 1865.

¹¹ P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, 1966, **88**, 4735.

the present work can also be explained by the contribution of a structure such as $\text{>C}^+-\text{N}=\text{N}^-$. The Hammett plot in acetic acid is similar to those shown in the Figure.

Decomposition of 3-Chloro-3-cyclopropyl- and 3-Chloro-3-cycloheptyl-diazirine in Cyclohexene.—The decompositions were carried out in cyclohexene over the 70–110 °C temperature range. The products were nitrogen, chloromethylenecyclopropane, and chloromethylenecycloheptane. It is interesting to note that the gas-phase photolysis of cyclopropyl(diazo)methane produced acetylene (30.1%), ethylene (30.1), butadiene (25.3), and very little cyclobutene.¹¹ Methylenecyclopropane was not among the products. However, the reaction of carbon atoms with cyclopropane on a cold surface gave methylenecyclopropane (65%) as the major product.¹² It is apparent that the cyclopropylcarbinyl carbenes produced from various reactions are of different



Hammett plot for *meta*- and *para*-substituted 3-chloro-3-aryldiazirines in cyclohexene at 75 °C. Data obtained from Table 3 of ref. 2 and from Table 2 of the present text

energy content. It is also clear from the following data that the presence of a chlorine atom on the carbene considerably modifies the product distribution. In the pyrolysis of isopropyldiazirine,¹³ the relative yields of 2-methylpropene and methylcyclopropane were 53.6 and 45.5%, respectively. However, in the thermal decomposition of 3-chloro-3-isopropyldiazirine,¹⁴ 1-chloro-2-methylpropene was the only olefinic product.

The rate constants for the decomposition of 3-chloro-3-cyclopropyl- and 3-chloro-3-cycloheptyldiazirine in cyclohexene are given in Table 5. The Arrhenius equations with errors quoted in standard deviation are: k (3-chloro-3-cyclopropyldiazirine) = $10^{13.64 \pm 0.11} \exp[(-115,000 \pm 460)/RT]$ and k (3-chloro-3-cycloheptyldiazirine in cyclohexene) = $10^{13.53 \pm 0.11} \exp[(-121,800 \pm 750)/RT]$ s⁻¹. For the purpose of comparison the rate constants for the thermal decomposition of diazirines in

¹² R. R. Engel and P. S. Skell, *J. Amer. Chem. Soc.*, 1965, **87**, 4663.

¹³ A. M. Mansoor and I. D. R. Stevens, *Tetrahedron Letters*, 1966, 1733.

¹⁴ H. M. Frey and M. T. H. Liu, *J. Chem. Soc. (A)*, 1970, 1916.

cyclohexene at 90 °C are: 3-chloro-3-ethyl,¹⁵ $k = 0.94 \times 10^{-4}$; 3-chloro-3-cycloheptyl-, $k = 1.0 \times 10^{-4}$;

TABLE 5

Rate constants for the decomposition of 3-chloro-3-cycloalkyldiazirine in cyclohexene

3-chloro-3-cyclopropyldiazirine

Temp. (°C)	71.0	74.9	80.0	85.2	90.1	95.0
$10^4 k/s^{-1}$	1.54	2.38	4.22	7.43	12.51	21.06

3-chloro-3-cycloheptyldiazirine

Temp. (°C)	85.1	89.9	95.2	100.1	105.0	110.2
$10^4 k/s^{-1}$	0.58	1.00	1.84	3.03	5.08	8.41

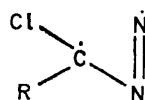
3-chloro-3-phenyl,² $k = 10.0 \times 10^{-4}$; 3-chloro-3-cyclopropyl-, $k = 12.5 \times 10^{-4} s^{-1}$.

From the above results, it is seen that the cyclopropyl and the cycloheptyl substituents do not have similar effects on rates of decomposition; the rate constant for

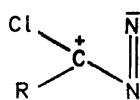
position. Hence, the heterolytic decomposition cannot be rejected on the grounds of solvent effects.

The effects of a cyclopropyl group on ionic and on radical transition states have been reported. For the solvolysis of a series of substituted *p*-nitrobenzoates, it is evident that cyclopropyl is better than phenyl in stabilizing a positive charge.^{3,4} On the other hand, in the free radical decomposition of azoalkanes,^{5,16} this order is reversed. In the decomposition of diazirines, the effects of phenyl and cyclopropyl groups on decomposition rates are similar. These results are consistent with a polarized radical-like transition state as might be given by a hybrid of (1) and (2).

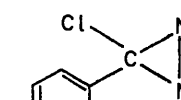
In the pyrolysis of *para*-substituted 3-chloro-3-aryldiazirine² (3), the following rates were observed: MeO > Me > Cl > H \approx NO₂. If the transition state is purely radical, one might expect the same substituent



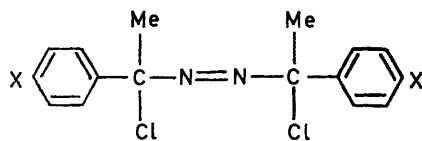
(1)



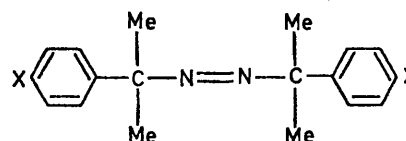
(2)



(3)



(4)



(5)

cyclopropyl is one order of magnitude greater than that for the cycloheptyl compound. The cycloheptyl substituent has an effect similar to that of an alkyl substituent.

Mechanism for the Decomposition of Diazirines.—Our recent work on the isomerization of 3-methyl-3-vinyldiazirine to yield 3-methylpyrazole suggests that the decomposition of diazirine may occur by a two-step mechanism.¹ For a stepwise mechanism, there remains the question of whether the one-bond (C-N) breaking process is homolytic or heterolytic or both. A homolytic decomposition gives rise to a diradical and a heterolytic decomposition to a diazomethane intermediate. In general, the solvent effects are always small in diazirine decomposition,^{1,2} and this is probably due to the small difference between the dipole moments of diazirines and diazoalkanes, such that only a small change in solvation is to be expected in the decom-

position for phenyl substituted chlorodiazirines as in model azo-compounds (4) (Cl > Me > H)¹⁷ and (5) (Cl > Me > MeO > H).^{18,19} The fact that they do not agree seems to rule against pure (1) and seems to indicate a hybrid of (1) and (2). The extent of the polarization would depend on the substituent present in the diazirine ring. One of the most striking examples in this series for a polarized transition state is the 3-chloro-3-*p*-methoxyphenyldiazirine in which (2) is stabilized through conjugation by the *p*-methoxyphenyl substituent.

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¹⁵ M. T. H. Liu and D. H. T. Chien, *Canad. J. Chem.*, 1974, **52**, 246.

¹⁶ S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1966, **88**, 137.

¹⁷ S. Goldschmidt and B. Acksteiner, *Annalen*, 1958, **618**, 173.

¹⁸ J. W. Timberlake and M. L. Hodges, *Tetrahedron Letters*, 1970, 4147.

¹⁹ P. Kovacic, R. R. Flynn, J. F. Gormish, A. H. Kappelman, and J. R. Shelton, *J. Org. Chem.*, 1969, **34**, 3312.