

The Photochemistry of the System Dimethyl Maleate–Dimethyl Fumarate–Acetone. A New Mechanism for Oxetane Formation¹

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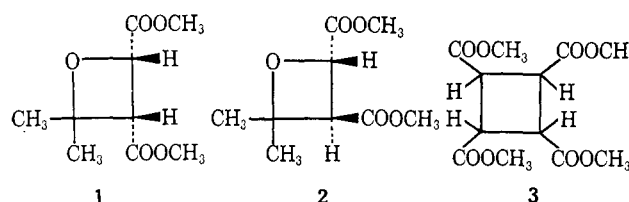
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Abstract: The influence of ultraviolet radiation on acetone solutions of dimethyl maleate and dimethyl fumarate has been studied. Rates of reaction at irradiation time zero have been obtained, thereby separating the oxetane-forming reaction data from the influence of the simultaneous, rapid *cis*–*trans* photoisomerization reaction of the unsaturated diesters. Maleate yielded both *cis*- and *trans*-2,2-dimethyl-3,4-dimethoxycarbonyloxetanes (1 and 2), ratio 1:6.35, whereas fumarate produced only the latter compound. No cyclobutane was observed. A detailed correlation of reaction rates with spectral data is consistent with a mechanism involving attack of excited unsaturated diester on ground-state ketone while at variance with one involving attack of excited ketone on ground-state diester. Some evidence further suggests that the oxetane-forming state of the unsaturated diester may differ from that involved in *cis*–*trans* photoisomerization.

The mechanistic work of Arnold³ and of Yang⁴ on the photocyclization reaction of ketones with olefins to form oxetanes, in accord with the earlier proposal of Büchi,⁵ suggests that the electron-deficient oxygen atom of excited ketone (usually the ³(*n*,*π**) state) reacts with ground-state olefin giving an intermediate diradical which on ring closure produces oxetane. The generality of this mechanism has recently been questioned by Saltiel⁶ and by Turro.⁷ The work presented here further suggests that this mechanism is not adequate to account for the formation of oxetane in the photosystem dimethyl maleate–dimethyl fumarate–acetone, but rather that a mechanism involving attack of excited unsaturated diester on ground-state ketone is more appropriate.

Methods and Results

Acetone solutions of dimethyl maleate and dimethyl fumarate were irradiated using a medium-pressure mercury arc in conjunction with either quartz or borosilicate glass filters. The former transmitted light down to 200 mμ whereas the latter was opaque below 280 mμ. Both *cis*- and *trans*-2,2-dimethyl-3,4-dimethoxycarbonyloxetanes (1 and 2) were produced although no cyclobutane (3) could be detected even by glpc. The oxetanes were identified from spectral data,⁸ and stereochemistry was assigned by identifying the *cis* isomer with the product derived *via* hydrolysis and esterification from the oxetane adduct⁹ of maleic anhydride with acetone, and on the basis of equilibration experiments with sodium methoxide in dry methanol.¹⁰



A mechanistic investigation of oxetane formation was greatly complicated by the simultaneous occurrence of rapid *cis*–*trans* photoisomerization of the unsaturated diesters. Attention was focused, therefore, on the photochemistry of the system under the standard conditions prevailing at irradiation time zero.¹¹ Kinetic experiments were devised to follow oxetane formation. A series of irradiations was undertaken using both maleate and fumarate solution and each filter. The geometry of the apparatus was maintained constant throughout the series so that meaningful comparisons could be made between data obtained from different irradiations. The uv lamp output was monitored continuously (230–420 mμ) as separate experiments had revealed a $\pm 18\%$ output fluctuation associated with a voltage variation of $\pm 2.4\%$. Such compensation could not be made between the quartz and borosilicate glass series of irradiations but only within them, since the substitution of one filter by another in itself caused a variation in photomonitor deflection. At this point the possibility of error up to $\pm 20\%$ was introduced.

Concentration–irradiation time plots of reaction products were obtained by glpc and initial rates of reaction with corresponding standard deviations determined by a least-squares curve fitting procedure. These data, recorded in Table I, were correlated with spectral data given in Table II. Although these spectral data are necessarily approximate, they are of sufficient accuracy for the deductions to be made.

Discussion

General. With the exception of the irradiation of maleate in acetone using quartz, where the *cis*-oxetane

(11) The method of extrapolation to irradiation time zero circumvented other problems inherent in any quantitative photochemical study such as are associated with film formation in the reactor, slight warming of the solution, and the occurrence of secondary reactions. Both oxetane diesters were slowly decomposed on prolonged irradiation in acetone.

(1) Abstracted from the author's D.Phil. Thesis, Oxford, 1966.

(2) Address inquiries to the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, N. Y. 11790.

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(5) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, 76, 4327 (1954).

(6) J. Saltiel, R. M. Coates, and W. G. Dauben, *ibid.*, 88, 2745 (1966).

(7) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, 89, 3950 (1967).

(8) It is interesting that these oxetanes do not give a peak in the mass spectrum at *m/e* 144 corresponding to $C_6H_8O_4^+$ as expected. Peaks at *m/e* 143 and 145 are, however, quite strong.

(9) Kindly supplied by P. W. Grubb.

(10) Either isomer yielded the same mixture of 90% *trans*- and 10% *cis*-oxetane diester.

Table I. Initial Rates (with Standard Deviations) of Photoproduct Formation

Irradiation		Product, $M \text{ hr}^{-1}$			
Compound, M	Filter ^a	Maleate	Fumarate	<i>cis</i> -Oxetane diester	<i>trans</i> -Oxetane diester
Fumarate, 0.23	q	0.194 (0.006)	...	0 (<0.0003)	0.0447 (0.0020)
Fumarate, 0.23	b	0.00704 (0.0001)	...	0	0.00166 (0.00007)
Maleate, 0.23	q	...	0.105 (0.011)	0.00095 (0.00006)	0.00604 (0.00021)
Maleate, 0.23	b	...	0.0107 (0.0004)	0 (<0.0001)	0 (<0.0001)
Fumarate, ^b 0.025	q	0.30 ^c	-0.29 (0.01)	0	0.00844 (0.00097)
Fumarate, ^b 0.47	q	0.16 (0.02)	...	0 ($<5.4 \times 10^{-5}$)	0.0479 (0.00097)

^aq, quartz; b, borosilicate glass. ^bCorrected to light flux (uv) in 0.23 M fumarate irradiation. ^cError uncertain, but rate certainly >0.23 .

Table II. Photon Fractions Absorbed at Irradiation Time Zero^a

Irradiation	Absorbing species	Filter	
		Quartz	Boro-silicate glass
0.23 M fumarate-acetone	Fumarate	0.14	0.015
	Acetone	0.86	0.985
0.23 M maleate-acetone	Maleate	0.11	0.0026
	Acetone	0.89	0.997

^a Within the photoactive wavelength range, the ratio of the photon flux transmitted by quartz to that transmitted by borosilicate glass is 1,000:0.273. Data were calculated on the basis of data supplied by the manufacturers of the filters and the lamp used and on the basis of spectra of reagents recorded in ethanol. Ethanol was used since acetone exhibits uv (ethanol) 272 and (acetone) 272.5 $m\mu$. The possibility of spectral shifts due to complex formation at the actual diester-acetone concentrations used in irradiations cannot be eliminated although a cursory uv examination (0.1-mm path length) did not reveal evidence of this above 240 $m\mu$.

diester was a minor product (*cis*-oxetane:*trans*-oxetane diester, 1:6.35), *trans*-oxetane diester was the only oxetane formed at irradiation time zero in any irradiation. In such cases a lag in formation of the *cis*-oxetane revealed that it was formed by a secondary reaction (e.g., fumarate \rightarrow maleate \rightarrow *cis*-oxetane diester). This lag varied from 15 min for 0.23 M fumarate-acetone in quartz to 10 hr for the same mixture in borosilicate. In the 0.47 M fumarate-acetone quartz case the lag was 1 hr. When 0.23 M maleate-acetone was irradiated using borosilicate the extraordinary observation was made that whereas photoisomerization to fumarate occurred at an appreciable rate, no oxetane at all could be detected for 1.5 hr.¹²

Mechanistic. The tabulated data are in good accord with certain postulates of reaction mechanism. An analysis is employed which predicts a rate in borosilicate¹³ from that observed in quartz or *vice versa*, using

(12) These data will be shown to be consistent with the mechanism $M^* + A \rightarrow$ oxetane. When eventually oxetane became detectable the *cis*-oxetane:*trans*-oxetane ratio was found to be much higher than in the maleate-quartz case ($\sim 1:1$). This possibly represents a very slow reaction proceeding by a different mechanism (e.g., $M + A^* \rightarrow$ oxetane) which becomes evident when the much faster $M^* + A \rightarrow$ oxetane reaction is suppressed, in this case by the borosilicate glass filter.

(13) The borosilicate glass used was opaque below 280 $m\mu$ (transmittance: 280 $m\mu$, $<1\%$; 290 $m\mu$, 10%) whereas the quartz was transparent to $\sim 200 m\mu$. In quartz, both acetone and the unsaturated diester absorbed considerable proportions of light (Table II), whereas in borosilicate glass, most of the light energy was absorbed by acetone. Here fumarate with tail absorption had to compete with the great ex-

cess of acetone. Maleate absorbed at shorter wavelengths than fumarate.

the spectral data and simple mechanistic hypotheses. Such simple predictions depend on irradiations being conducted on solutions of identical initial composition, thus eliminating complications arising from concentration effects. It was assumed that, for a given uv absorption band, quantum yields were independent of wavelength. As well as being expected on general grounds in view of the rapid dissipation of excess vibrational energy in liquids, this was found to provide a consistent rationalization of the data.

Two mechanistic hypotheses will be considered for the formation of oxetane from fumarate: (i) $F + A^* \rightarrow$ oxetane, and (ii) $F^* + A \rightarrow$ oxetane, where F represents fumarate, A acetone, and * an unspecified degree of electronic excitation. Maleate photochemistry will then be considered from a similar standpoint. It will emerge that the data favor the second mechanism for both fumarate and maleate, suggesting that oxetanes are formed by attack of excited unsaturated diester on ground-state acetone with no participation of an energy-transfer process from acetone.

0.23 M Fumarate Irradiations. a. The rate of formation of oxetane in quartz is calculated from that observed in borosilicate glass on the basis of the postulated mechanism



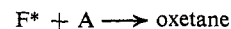
to be (borosilicate rate) $\times 0.86/(0.273 \times 0.985) = 0.0053 M \text{ hr}^{-1}$. The numerical factors are taken from Table II and correct for the change in total flux absorbed by the solution on going from quartz to borosilicate as well as for the variation in the fraction of that flux which is absorbed by acetone.

The actual rate in quartz could exceed this value if the energy-transfer process



occurred. The maximum rate possible would occur if this process were 100% efficient, and is (borosilicate rate)/0.273 = 0.0061 $M \text{ hr}^{-1}$. This is only one-seventh the observed quartz rate. The postulates are at variance with the observations.

b. On the alternative assumption that oxetane is only formed by the reaction



cess of acetone. Maleate absorbed at shorter wavelengths than fumarate.

with no energy-transfer contribution, the rate in borosilicate is calculated, (quartz rate) $\times 0.273$ (0.015/0.14) = 0.00131 $M \text{ hr}^{-1}$, which is within the $\pm 20\%$ error of comparison of the observed borosilicate rate, 0.00166 $M \text{ hr}^{-1}$. This is evidence in favor of the "excited fumarate mechanism."

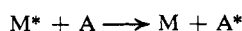
c. Fumarate absorbed 14% of the active flux entering the solution in quartz but only 1.5% in borosilicate glass. Additionally the total rate of reaction, rate of formation of oxetane plus rate of formation of maleate, was 27.4 times greater in quartz than in borosilicate. Yet under these widely differing conditions, the ratio (initial rate of oxetane formation):(initial total rate of reaction) was constant, being 0.191 in borosilicate and 0.187 in quartz. This strongly suggests that excited states of the same molecule, presumably fumarate, are responsible for both reactions.

0.23 M Maleate Irradiations. Consider now the formation of oxetane (*cis* plus *trans*) from 0.23 M maleate in acetone. Again, simple comparisons between the quartz and borosilicate data were valid since the solutions irradiated were of identical initial composition.

a. The minimum possible rate of oxetane formation in borosilicate is calculated from that observed in quartz on the basis of the mechanism



if the energy-transfer reaction



occurs with 100% efficiency, and is

$$0.00699 \times 0.273 = 0.00191 M \text{ hr}^{-1}$$

However, the observed rate was certainly less than 0.0002 $M \text{ hr}^{-1}$. Clearly the postulated mechanism does not fit the data.

b. If oxetane is formed by the reaction



and if no energy transfer from excited acetone occurs, the initial rate of formation of oxetane in borosilicate glass, calculated from the quartz data, is 0.000045 $M \text{ hr}^{-1}$. This is consistent with the observation that the initial rate of oxetane formation is less than 0.0002 $M \text{ hr}^{-1}$. Thus, evidence favors the "excited maleate mechanism" over the "excited acetone mechanism."

Maleate-Fumarate Photoisomerization. A similar analysis was applied to the photoisomerization reactions of maleate to fumarate and fumarate to maleate. As expected, the data were rationalized on the basis of the mechanisms $F^* \rightarrow M$ and $M^* \rightarrow F$. Maleate differed from fumarate in that $M^* \rightarrow F$ was photosensitized to some extent by acetone, whereas $F^* \rightarrow M$ was not. Acetone photosensitization of the maleate \rightarrow fumarate photoisomerization reaction led to different values for the ratio (initial rate of oxetane formation):(initial total rate of reaction), namely, 0.0624 in quartz and a maximum possible value of 0.0183 in borosilicate glass. If the deduction that excited maleate is responsible for both reactions is valid, it is likely that different excited states of maleate are involved in these reactions, one sensitized by acetone and one not.¹⁴ Such states might be singlet and triplet states.⁷

(14) An interesting example of a related photochemical reaction in which two excited states of the same molecule are invoked is provided by

With this in mind, the very different concentration dependences of the photoisomerization and oxetane-forming reactions of fumarate (Table I) indicate that different excited states are probably involved here also. That quenching processes are important is shown by the fact that the total rate of reaction decreases as fumarate concentration increases. In view of such complications one can do little more here than point to the decrease in photoisomerization rate accompanying the increase in oxetane formation rate with increase in fumarate concentration and note also the strange absence of cyclobutane formation in this system as suggesting lines for further research.

The energies of triplet maleate and fumarate are not known with precision¹⁵ and so oxygen perturbation experiments were undertaken in an attempt to observe directly the singlet-triplet absorption spectra. Ultraviolet spectra were recorded in chloroform saturated with oxygen at 1800–2000 psi; maleate, λ_{max} 333 μ (ϵ 0.023), fumarate, λ_{max} 343 μ (ϵ 0.024). Absence of significant fine structure made it impossible to deduce the energies of the chemically important (0,0) bands.

Experimental Section

The irradiation apparatus consisted of a cylindrical vessel into which identical water-cooled probes of quartz or of borosilicate glass could be inserted. A 500-W Hanovia medium-pressure mercury arc was suspended inside the probe to irradiate the solution (250 ml) confined to the annular space between the probe and the outer vessel. Solutions to be irradiated were previously deoxygenated by refluxing and cooling in a stream of nitrogen, and were transferred to the reactor under nitrogen.

***cis*- and *trans*-2,2-Dimethyl-3,4-dimethoxycarbonyloxetanes (1 and 2).** The combined crude product from a series of quartz irradiations (>18 hr) of 0.23 M acetone solutions of maleate or fumarate was distilled, bp 108–160° (2 cm), and subjected to preparative glpc (16 ft \times 0.75 in. 15% Carbowax 6000, 60–100 mesh Embracel, 150° rising to 170° at 0.5°/min, 770 F & M gas chromatograph). The two oxetane peaks were collected and distilled, bp ~80° (air-bath temperature, 0.1 mm).

***cis*-Oxetane diester 1** showed the following physical properties: ir (CCl_4) 1745 and 1740 (ester C=O), 1450, 1432, 1370, 1360, 1285, 1197, 1163, 1080, 1035, and 970 (oxetane ring) cm^{-1} ; nmr (CCl_4) τ 5.11 (d, 1, $J = 9.0$ cps; ring proton), 6.26 (d, 1, $J = 9.0$ cps; ring proton), 6.26 (s, 3, ester methyl), 6.33 (s, 3, ester methyl), 8.45 (s, 3, *gem*-methyl), and 8.60 (s, 3, *gem*-methyl); mass spectrum m/e (relative intensity) 202 (0.5), 145 (18), 143 (20), 115 (94), 114 (36), 113 (75), and 83 (100).

Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}_5$: C, 53.46; H, 6.98. Found: C, 53.57; H, 6.67.

***trans*-Oxetane diester 2** showed the following physical properties: ir (liquid film) 1760 and 1740 (ester C=O), 1460, 1437, 1380, 1369, 1330, 1255, 1215, 1170, 1077, 1043, 1022, and 975 (oxetane ring) cm^{-1} ; nmr (CCl_4) τ 4.94 (d, 1, $J = 6.9$ cps; ring proton), 6.49 (d, 1, $J = 6.9$ cps; ring proton), 6.23 (s, 3, ester methyl), 6.25 (s, 3, ester methyl), 8.47 (s, 3, *gem*-methyl), and 8.67 (s, 3, *gem*-methyl); mass spectrum m/e (relative intensity) 202 (0.8), 145 (31), 143 (16), 115 (100), 114 (22), 113 (68), and 83 (87); M (osmometer) 209 \pm 4%.

Anal. Calcd for $\text{C}_9\text{H}_{14}\text{O}_5$: C, 53.46; H, 6.98. Found: C, 52.67; H, 7.01.

Kinetic Experiments. Acetone (Analar grade) solutions of dimethyl fumarate (recrystallized benzene, pure to glpc) (0.025, 0.23, and 0.47 M) and of dimethyl maleate (bp 100–102° (2 cm), pure to glpc) (0.23 M) were irradiated using the quartz probe. Acetone solutions of fumarate (0.23 M) and of maleate (0.23 M) were irradiated using the borosilicate glass probe also. So that the series of irradiations formed a unity, the entire irradiation apparatus was reassembled with identical geometry for each experi-

the recent work of N. C. Yang, R. Loeschen, and D. Mitchell, *J. Am. Chem. Soc.*, **89**, 5465 (1967).

(15) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, H. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

ment. A continuously recording photomonitor incorporating a Rank Cintel QVA39S (antimony-cesium) photocell in conjunction with a 1.9-mm thickness filter of Chance OX7 glass was constructed to detect and compensate for fluctuations in uv output (230–420 m μ) of the lamp with time.

At frequent intervals (5 min, initially) during an irradiation, samples (1 ml) were taken from the reactor solution (maintained constantly agitated by a stream of nitrogen) and a known volume (50 μ l) of marker solution (2 ml of methyl salicylate in 10 ml of acetone solution) was added to each sample. These were analyzed quantitatively by glpc (2 m \times 0.25 in. 15% polypropylene glycol LB-550 x, 60–80 mesh 85% Chromosorb W; nitrogen carrier, 10 psi; 125° rapidly rising to 160° after 18 min; Perkin-Elmer F11 gas chromatograph). Approximate retention times were as follows: dimethyl fumarate, 12 min; dimethyl maleate, 16 min; methyl salicylate, 29 min; *trans*-oxetane diester, 37 min; *cis*-oxetane diester, 45 min. Peak areas were estimated by cutting and weighing (precision $\pm 1.2\%$ for peak area 1 in.³). Absolute concentrations (precision $\sim \pm 3.4\%$) were estimated following a calibration experiment.

Unweighted experimental data (18–26 points/curve) were submitted to a computerized polynomial least-squares curve fitting procedure in order to estimate gradients (with standard deviations) at irradiation time zero. The order fit chosen (never above 4) was the lowest order function consistent with estimated random error in the points.

Exceptions to this procedure were cases (production of fumarate from maleate and of maleate from fumarate (0.23 M) in quartz) where fewer points were submitted for analysis owing to a significant change in curve form after a limited period of irradiation. The 0.025 M fumarate irradiation was an extreme case. The very rapid photoisomerization of fumarate led to a photoequilibrium of maleate and fumarate with the former predominating (8.5:1) within

10-min irradiation so that after 4 points had been taken, all the curve forms had changed radically. In this case, all estimated initial gradients were based on only 4 points. However, the possible errors were greatly overestimated in order to eliminate the possibility of misleading deductions.

No 1,2,3,4-tetramethoxycarbonylcyclobutane (3) was detected by glpc (*cis,trans,cis* isomer, retention time 57 min at 200° on polypropylene glycol column).

Initial rates of decay of starting materials were not estimated owing to error caused by gas chromatograph overloading. However, material balance checks were conducted at longer irradiation times. The occurrence of significant side reactions was only noted in the 0.025 M fumarate irradiation.

Further experiments demonstrated that the photochemistry of this system was not sensitive to trace amounts of oxygen such as might have remained after degassing.

Oxygen perturbation experiments were conducted on 1 M chloroform (May and Baker, "Reagent" grade) solutions of dimethyl maleate and dimethyl fumarate saturated with oxygen for 15 min at 1800–2000 psi in a 5-cm, high-pressure cell, supplied by D. F. Evans. The cell was balanced against a regular 5-cm cell of the same solution and spectra were recorded on a Unicam SP800 spectrophotometer fitted with a scale expander. A base line was obtained after the oxygenation experiment, thus correcting for spectral changes arising from the possible formation of oxidation products.

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Stable Carbonium Ions. LXV.¹ Protonation of Hydrogen Cyanide and Alkyl nitriles in FSO₃H–SbF₅–SO₂ Solution. Comparative Study of Meerwein's N-Alkyl nitrilium Ions

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received February 8, 1968

Abstract: Protonation of hydrogen cyanide, alkyl- and alkenyl nitriles, dinitriles, and bifunctional nitriles was studied by H¹, C¹³, and N¹⁵ nuclear magnetic resonance spectroscopy in the strong acid system FSO₃H–SbF₅–SO₂. Nuclear magnetic resonance and infrared spectroscopic studies of Meerwein's N-alkyl nitrilium ions were also undertaken and the results compared with those of protonated nitriles.

The possible formation of protonated nitriles when anhydrous HCl is dissolved in nitriles was discussed by Janz and Danyluk,³ but they could draw no firm conclusion. Klages, *et al.*,⁴ showed that no such species is formed under the conditions. The latter authors, however, succeeded in isolating acetonitrilium hexachloroantimonate, CH₃CNH⁺SbCl₆[–]. Peach and Waddington^{5a} studied nitriles in anhydrous HCl and claimed the presence of RC \equiv NH⁺ ions on the basis of conductivity measurements. Deno^{5b} studied the pro-

tonation of acetonitrile, propionitrile, and benzonitrile in sulfuric acid and oleum by pmr spectroscopy under conditions where obvious rapid exchange made it impossible to obtain analyzable spectra.

As a continuation of our study of protonation of organic compounds in strong acids, we have now undertaken a study of the protonation of nitriles in FSO₃H–SbF₅–SO₂ solution. In addition, protonation of alkenyl nitriles, dinitriles and bifunctional nitriles was also investigated. For comparison, we have also investigated Meerwein's related N-alkyl nitrilium salts (RC \equiv NR)⁺X[–], for which no nmr data have been reported.⁶

Results and Discussion

N-Protonated nitriles were obtained by protonation of nitriles in FSO₃H–SbF₅–SO₂ solution generally at

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(2) Postdoctoral Research Investigator, 1967–1968.

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(5) (a) M. E. Peach and J. C. Waddington, *J. Chem. Soc.*, 600 (1962);

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