1604 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 57, 1604—1607 (1984)* [Vol. 57, No. 6

Photochemical Reaction of Phenyl-substituted 1,3-Diketones

Michikazu Yoshioka,* Tsuneji Suzuki, and Masashi Oka
Department of Chemistry, Faculty of Science, Saitama University, Shimo-okubo, Urawa, Saitama 338

(Received October 4, 1983)

Irradiation of 2,2-dimethyl-1-phenyl-1,3-diketones with 3-ethyl or 3-isopropyl substituents gave type II cyclization product, 3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone or 3-hydroxy-2,2,4,4-tetramethyl-3-phenylcyclobutanone, along with type I cleavage products. The type II cyclization/type I cleavage ratio is greater with a 3-isopropyl group than with a 3-ethyl group. A similar irradiation of 2,2-dimethyl-1-phenyl-1,3-butanedione gave type I cleavage products and no type II cyclization product. Irradiation of 2,4-dimethyl-1-phenyl-1,3-pentanedione gave 3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone and propiophenone. The geometry of 3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone which arose from 2,2-dimethyl-1-phenyl-1,3-pentanedione was cis with respect to phenyl and 4-methyl groups and that which arose from 2,4-dimethyl-1-phenyl-1,3-pentanedione was trans.

Two major photochemical processes, Norrish type I and Norrish type II, have been widely studied.$^{1)}$ The type II process is the most common photoreaction of monoketones with γ-hydrogens in the alkyl chain. However, in the case of 1,3-diketones, no example of type II photoreaction where an α-hydrogen to one carbonyl group undergoes 1,5-shift to another carbonyl oxygen has been found. Non- or difficultly-enolizable aliphatic 1,3-diketones have been found to undergo type I cleavage.$^{2)}$ The photochemistry of aromatic 1,3-diketones has been studied for 3-aroylchromones$^{3)}$ and 2-diaza-1-aryl-1,3-diketone compounds.$^{4)}$ Little attention has been given to aromatic 1,3-diketones with an sp^3 carbon α to both carbonyl groups.$^{5)}$ Since, for the same electronic and spin configuration, aryl alkyl ketones undergo type I cleavage more slowly than the analogous dialkyl ketones,$^{6)}$ 1-aryl-3-alkyl-1,3-diketone compounds may undergo type II photoreaction where the aromatic carbonyl oxygen abstracts a hydrogen from the α-carbon on the 3-alkyl substituent, in competition with type I cleavage. In this paper, we report the photochemistry of 1-phenyl-3-alkyl-1,3-diketone compounds.

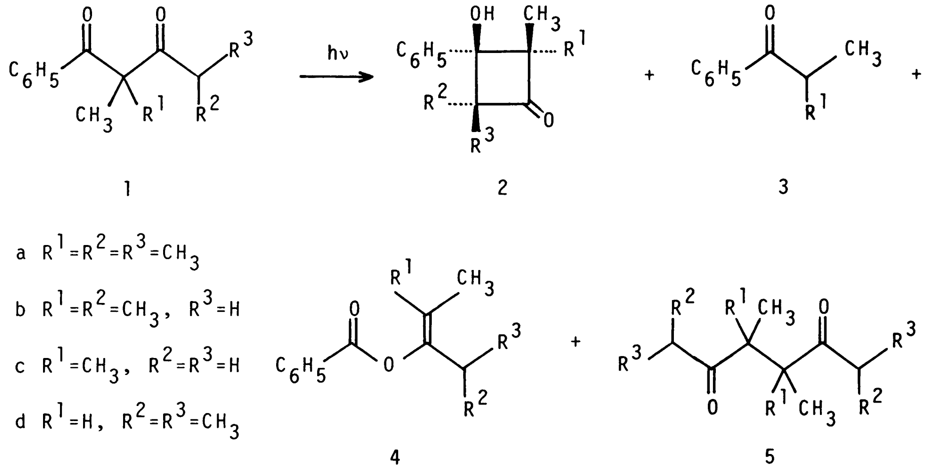
Results and Discussion

An acetonitrile solution of 2,2,4-trimethyl-1-phenyl-1,3-pentanedione (**1a**) was irradiated under nitrogen with a Pyrex filter. After removal of the solvent, 3-hydroxy-2,2,4,4-tetramethyl-3-phenylcyclobutanone (**2a**), isobutyrophenone (**3**), enol ester (**4a**), and 1,4-diketone (**5a**) were isolated by silica gel chromatography. A similar reaction was found to occur with 2,2-dimethyl-1-phenyl-1,3-pentanedione (**1b**). As shown in Table 1, the yield of **2** was higher with **1a** than with **1b**, and the yields of **4** and **5** were lower with **1a** than with **1b**. Irradiation of 2,2-dimethyl-1-phenyl-1,3-butanedione (**1c**) gave isobutyrophenone (**3**), enol ester (**4c**), and 1,4-diketone (**5c**), along with benzaldehyde and benzoic acid. In this case, no hydroxycyclobutanone was detected. Similar irradiation of 2,4-dimethyl-1-phenyl-1,3-pentanedione (**1d**) gave propiophenone (**3d**) and 3-hydroxy-2,2,4-trimethyl-3-phenylcyclobutanone (**2d**) which was a geometrical isomer of **2b**, along with several

Table 1. Photoreaction of **1** in acetonitrile$^{a)}$

1	Irradiation time / h	Conversion / %	Yield/% $2^{b)}$	$3^{c)}$	$4^{c)}$	$5^{c)}$
1a	3.5	78	47	2	6	8
1b	4	68	11	3	9	14
1c	11	45	—	11	7	27
1d	26	88	16	12	—	—

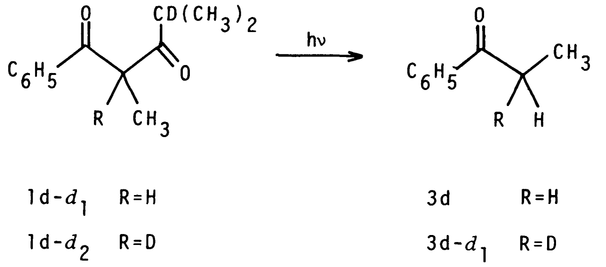
a) Irradiation of 20 mmol of **1** in 400 cm^3 of acetonitrile with a 450 W high-pressure mercury lamp through a Pyrex filter. b) Isolated yield. c) Determined by GLC.



Scheme 1.

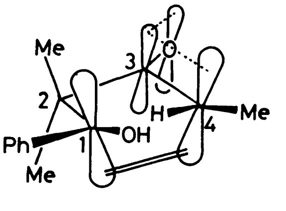
unidentified products. The structures of **2a**, **2b**, and **2d** were based on their spectroscopic and analytical properties and further supported by chemical evidence. The IR spectra showed a four-membered carbonyl band at 1770—1775 cm^{-1} and a hydroxyl band at 3600 cm^{-1}. The ^{1}H NMR spectrum of **2a** showed singlets at δ 1.38 and 1.40 due to four methyl groups, a singlet at δ 1.91 due to a hydroxyl group, and a singlet at δ 7.32 due to aromatic protons. This simple pattern is caused by the symmetry of the molecule. Compound **2a** underwent cycloreversion reaction to **1a** on heating at 150 °C or by treatment with aqueous sodium hydroxide. This chemical behavior strongly supports the proposed structure for **2a**. The ^{1}H NMR spectra of **2b** and **2d** resemble each other in their splitting patterns except for the aromatic protons, suggesting that they are geometrical isomers with respect to the phenyl and 4-methyl groups. In the spectrum of **2b**, the signal due to the aromatic protons appeared as a multiplet between δ 7.1—7.4, being consistent with the proposed structure in which the phenyl group was restricted to rotate by virtue of its cis-relationship to two methyl groups on C_2 and C_4. Whereas, in the spectrum of **2d**, the aromatic protons appeared as a singlet at δ 7.36. Compound **2b** underwent cycloreversion reaction to **1b** and **1d** in a ratio of 1:2 by heating at 150 °C, but **2d** converted mostly to **1d** under the same reaction conditions. The IR spectra of **4a**—**c** showed a strong band at 1730—1735 cm^{-1} due to ester carbonyl. The ^{1}H NMR spectra of **4a** and **4b** showed two singlets at the region between δ 1.5—1.8 due to two methyl groups attached to olefinic carbon atoms. The ^{1}H NMR spectrum of **4c** showed three singlets at δ 1.55, 1.75, and 1.95 due to three methyl groups attached to olefinic carbon atoms. These spectroscopic properties are consistent with the proposed structures for **4a**—**c**. The structures of **5a**—**c** were unambiguously assigned by their IR and NMR spectra.

The formation of **2** can best be explained by type II cyclization which involves 1,5-hydrogen shift from C_4 to the carbonyl oxygen on C_1. The product **3** may be formed by a type II elimination process or by a type I cleavage of the C_2–C_3 bond. It is known that α-diketones[7] and β,γ-unsaturated ketones[8] with γC–H bonds undergo type II cyclization and no type II elimination. The lack of elimination has been attributed to the perpendicular orientation of the p orbital on one radical site relative to the C_2–C_3 σ bond in the 1,4-biradical intermediate. In the 1,4-biradical formed from 1,3-diketone **1**, the C_4 radical site is allylic such that its π-system is completely perpendicular to the C_2–C_3 bond. This suggests that the 1,4-biradical will result in the formation of the cyclization product. Thus, **3** probably arises from a type I cleavage. In order to provide experimental information for the formation of **3**, photolysis of 2,4-dimethyl-1-phenyl-1,3-pentanedione-4-d_1 (**1d**-d_1) and 2,4-dimethyl-1-phenyl-1,3-pentanedione-2,4-d_2 (**1d**-d_2) was investigated. Photolysis of **1d**-d_1 in benzene gave propiophenone (**3d**) and not its deuterio derivative. Similar irradiation of **1d**-d_2 gave propiophenone-α-d_1 (**3d**-d_1) and no α,α-dideuterio derivative. These results suggest that **3** may arise from a type I cleavage.



Scheme 2.

It is noteworthy that **2b** and **2d** are geometrical isomers with respect to the phenyl and the 4-methyl groups. The ^{1}H NMR spectra of the irradiation mixtures showed no evidence for the formation of **2d** from **1b** and **2b** from **1d**. Lewis and Hilliard studied[9] the photochemistry of methyl-substituted 1-phenyl-1-butanones. They reported that both 2-methyl-1-phenyl-1-butanone and 1-phenyl-1-pentanone form 2-methyl-1-phenylcyclobutanol; however, only the trans isomer with respect to the phenyl and methyl groups is observed for 2-methyl-1-phenyl-1-butanone, whereas a 3.1:1 trans: cis ratio is observed for 1-phenyl-1-pentanone. They explained the specificity of 2-methyl-1-phenyl-1-butanone by a repulsive interaction of the phenyl and α-methyl groups in the 1,4-biradical. The interaction between the phenyl and γ-methyl groups in the 1,4-biradical was regarded as being small until the 1,4-bond is almost completely formed. The formation of *r*-3-hydroxy-2,2,*c*-4-trimethyl-3-phenylcyclobutanone **2d** from **1d** is consistent with their results. However, the preferential formation of *r*-3-hydroxy-2,2,*t*-4-trimethyl-3-phenylcyclobutanone **2b** rather than the corresponding 2,2,*c*-4-trimethyl isomer **2d** from **1b** is not expected. In the 1,4-biradical from **1b**, the methyl group on the C_4 radical site is probably trans to the C_2-C_3 bond owing to the steric effect, and the rotation of the C_1–C_2 bond is probably hindered by the interactions between the phenyl and α,α-dimethyl groups. Therefore, the transition state for cyclization of the 1,4-biradical from **1b** is pertinently depicted as **6** and results in the formation of **2b**.



6

Scheme 3.

The formation of **4** and **5** is explained by combination of radicals resulting from type I cleavage. Diketones **1a**, **1b**, and **1c** vary only at C_4. The photochemical results of **1a**—**c** indicate that as the C_4–H bond strength increases the type II cyclization decreases with increasing type I cleavage. Thus, as expected, appropriate 1-phenyl-1,3-diketones with 3-alkyl substituent undergo type II cyclization *via* 1,5-hydrogen shift from carbon atom α to aliphatic carbonyl group to the aromatic carbonyl oxygen, in competition with type I cleavage. Finally, both cyclization and α-

cleavage were completely quenched by 1,3-pentadiene suggesting a triplet state reaction.

Experimental

All melting points were uncorrected. ^{1}H NMR spectra were recorded on a Varian A-60D or a JEOL FX-90Q spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. IR spectra were recorded on a JASCO IRA-2 spectrometer. GLC analyses and preparative purification were performed on a Hitachi K-53 instrument using Silicone SE-30 as the stationary phase. Irradiations were carried out with an Ushio UM-452 high-pressure mercury lamp (450 W) or a Rikoh Kagaku UVL-100 high-pressure mercury lamp (100 W) with a water-cooled Pyrex jacket. For column chromatography, Wakogel C-300 or Merck Silica Gel 60 Art. 7734 was used.

Materials. Phenyl 1,3-diketones **1a**—**c** were prepared by condensation of isobutyrophenone with the corresponding aliphatic aldehydes using methylanilinomagnesium bromide as the condensing agent,[10] followed by chromium(VI) oxide oxidation. Similarly, **1d** was prepared from propiophenone and isobutyraldehyde. Compound **1a** was also prepared by a similar procedures from 2,4-dimethyl-3-pentanone and benzaldehyde. The deuterio derivatives (**1d**-d_1 and **1d**-d_2) of **1d** were prepared as follows. A mixture of 400 mg of **1d**, 100 mg of TsOH, 4 cm^3 of D_2O, and 4 cm^3 of dioxane was heated under reflux for 70 h. The solvent was evaporated, and the residue was extracted with ether. A usual work-up and purification by GLC gave 2,4-dimethyl-1-phenyl-1,3-pentanedione-2,4-d_2 (**1d**-d_2). A mixture of 100 mg of **1d**-d_2, a trace amount of TsOH, 2 cm^3 of H_2O, and 2 cm^3 of dioxane was heated at 80 °C for 40 h. The same procedures as described above gave 2,4-dimethyl-1-phenyl-1,3-pentanedione-4-d_1 (**1d**-d_1).

Photolysis of 1. A typical procedure is described. A solution of 20 mmol of **1** in 400 cm^3 of acetonitrile was irradiated. The progress of the reaction was monitored by TLC and GLC. After removal of the solvent, the residue was chromatographed on silica gel eluted with a hexane-ethyl acetate mixture as eluent to give **2**—**5**. Compounds **2a**, **2b**, and **2d** were recrystallized from a mixture of hexane and a small amount of benzene. Compounds **3**—**5** were purified by preparative GLC. Yields are given in Table 1 on the basis of **1** consumed. Physical properties of the isolated products are shown bellow.

3-Hydroxy-2,2,4,4-tetramethyl-3-phenylcyclobutanone (2a). Mp 135 °C. IR ($CHCl_3$) 1775 (C=O), 3600 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.38 (s, 6H, Me), 1.40 (s, 6H, Me), 1 91 (s, 1H, OH), and 7.32 (s, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ=18.643 (2q), 24.452 (2q), 63.538 (2s), 79.808 (s), 127.591 (d), 128.045 (2d), 128.374 (2d), 141.362 (s), and 221.386 (s). MS m/z (rel intensity) 218 (M^+, 3), 148 ($M^+-Me_2C=C=O$, 55), 105 (PhCO, 100), 77 (Ph, 96). Found: C, 77.07; H, 8.34%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

r-*3-Hydroxy-2,2,*t-*4-trimethyl-3-phenylcyclobutanone (2b).* Mp 126—127 °C. IR ($CHCl_3$) 1770 (C=O), 3600 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.80 (s, 3H, Me), 1.04 (d, J=7.2 Hz, 3H, Me), 1.48 (s, 3H, Me), 2.46 (s, 1H, OH), 3.96 (q, J=7.2 Hz, 1H, CH), and 7.1—7.4 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ=8.200 (q), 18.667 (q), 22.243 (q), 63.018 (d), 64.839 (s), 76.739 (s), 126.553 (2d), 126.943 (d), 127.854 (2d), 140.275 (s), and 215.191 (s). MS m/z (rel intensity) 204 (M^+, 10), 148 ($M^+-MeCH=C=O$, 32), 134 ($M^+-Me_2C=C=O$, 99), 105 (PhCO, 100), 77 (Ph, 39). Found: C, 76.42; H, 7.85%. Calcd for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89%.

r-*3-Hydroxy-2,2,*c-*4-trimethyl-3-phenylcyclobutanone (2d).* Mp 106—107 °C. IR ($CHCl_3$) 1775 (C=O), 3600 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.92 (s, 3H, Me), 1.22 (d, J=7.2 Hz, 3H, Me), 1.26 (s, 3H, Me), 1.94 (s, 1H, OH), 4.10 (q, J=7.2 Hz, 1H, CH), and 7.36 (s, 5H, Ph). MS m/z (rel intensity) 204 (M^+, 16), 148 ($M^+-MeCH=C=O$, 46), 134 ($M^+-Me_2C=C=O$, 67), 105 (PhCO, 100), 77 (Ph, 100). Found: C, 76.32; H, 7.89%. Calcd for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89%.

1-Isopropyl-2-methyl-1-propenyl Benzoate (4a). IR (CCl_4) 1735 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.08 (d, J=7.0 Hz, 6H, Me), 1.56 (s, 3H, Me), 1.81 (s, 3H, Me), 3.03 (hep, J=7.0 Hz, 1H, CH), 7.3—7.7 (m, 3H, aromatic), and 8.1—8.3 (m, 2H, aromatic). Found: C, 77.12; H, 8.33%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

1-Ethyl-2-methyl-1-propenyl Benzoate (4b). IR (CCl_4) 1730 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.02 (t, J=7.0 Hz, 3H, Me), 1.56 (s, 3H, Me), 1.74 (s, 3H, Me), 2.36 (q, J=7.0 Hz, 2H, CH_2), 7.3—7.7 (m, 3H, aromatic), and 8.0—8.2 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$) δ=11.581 (q), 17.626 (q), 18.406 (q), 23.350 (t), 117.969 (s), 128.374 (2d), 129.870 (2d), 130.455 (s), 132.926 (d), 144.372 (s), and 164.791 (s). Found: C, 76.34; H, 8.01%. Calcd for $C_{13}H_{16}O_2$: C, 76.43; H, 7.89%.

1,2-Dimethyl-1-propenyl benzoate (4c).[11] IR (CCl_4) 1730 (C=O) cm^{-1}. ^{1}H NMR (CCl_4) δ=1.55 (s, 3H, Me), 1.75 (s, 3H, Me), 1.95 (s, 3H, Me), 7.2—7.6 (m, 3H, aromatic), and 8.0—8.2 (m, 2H, aromatic). Found: C, 75.55; H, 7.40%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

2,4,4,5,5,7-Hexamethyl-3,6-octanedione (5a).[12] IR (CCl_4) 1700 (C=O) cm^{-1}. ^{1}H NMR (CCl_4) δ=1.01 (d, J=7.0 Hz, 12H, Me), 1.21 (s, 12H, Me), and 3.03 (hep, J=7.0 Hz, 2H, CH). Found: C, 73.98; H. 11.59%. Calcd for $C_{14}H_{26}O_2$: C, 74.28, H, 11.57%.

4,4,5,5-Tetramethyl-3,6-octanedione (5b). IR (CCl_4) 1700 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.00 (t, J=7.0 Hz, 6H, Me), 1.16 (s, 12H, Me), and 2.50 (q, J=7.0 Hz, 4H, CH_2). ^{13}C NMR ($CDCl_3$) δ=8.135 (2q), 22.438 (4q), 32.165 (2t), 52.679 (2s), and 215.841 (2s).

3,3,4,4-Tetramethyl-2,5-hexanedione (5c).[12] IR (CCl_4) 1700 (C=O) cm^{-1}. ^{1}H NMR (CCl_4) δ=1.14 (s, 12H, Me) and 2.05 (s, 6H, Me).

Pyrolysis of 2. Pyrolysis was done at 150 °C in a sealed Pyrex tube for 3 h. The ^{1}H NMR analysis revealed that **2a** was quantitatively converted to **1a**, **2b** was converted to a 1:2 mixture of **1b** and **1d**, while **2d** was converted to **1d** along with a trace of **1b**.

Treatment of 2a with Aqueous Sodium Hydroxide. To a solution of 50 mg of **2a** in 6 cm^3 of acetone was added one drop of 2 M (1 M=1 mol dm^{-3}) sodium hydroxide. The mixture was stirred at room temperature for 4 h, acidified with 3 M hydrochloric acid, and extracted with ether. A usual work-up gave **1a** in quantitative yield.

Irradiation of 1d-d_1 *and 1d-*d_2. A solution of 40 mg of **1d**-d_1 in 4 cm^3 of benzene was placed in a Pyrex tube, and irradiated with a 100 W high-pressure mercury lamp for 5 h. From the irradiation mixture, unlabelled propiophenone was isolated by preparative GLC. A similar irradiation of **1d**-d_2 gave propiophenone-α-d_1.

Irradiation of 1a,d in the Presence of 1,3-Pentadiene. a): A solution of 10 mg of **1a**,**d** in 1 cm^3 of acetonitrile was placed in a Pyrex tube. b): A solution of 10 mg of **1a**,**d** in 1 cm^3 of a 1:1 mixture of acetonitrile and 1,3-pentadiene was placed in a Pyrex tube. Both solutions were irradiated under the same conditions with a 100 W high-pressure mercury lamp for 5 h. The ^{1}H NMR analysis showed that no reaction occurred in the case of *b*), while complete disappearance of **1a**,**d** was observed in the case of *a*).

References

1) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, N. Schore, *Acc. Chem.*

Res., **5**, 92 (1972); P. J. Wagner, *Top. Curr. Chem.*, **66**, 1 (1976).

2) H. Nozaki, Z. Yamaguti, T. Okada, R. Noyori, and M. Kawanisi, *Tetrahedron*, **23**, 3993 (1967); H. Kato, N. Miyamoto, M. Kawanisi, and H. Nozaki, *ibid.*, **26**, 2975 (1970).

3) P. G. Sammes and T. W. Wallace, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1845.

4) H. Tomioka, N. Hayashi, T. Asano, and Y. Izawa, *Bull. Chem. Soc. Jpn.*, **56**, 758 (1983).

5) M. Feldkimel-Gorodetsky and Y. Mazur, *Tetrahedron Lett.*, **1963**, 369.

6) N. J. Turro, "Modern Molecular Photochemistry" The Benjamin/Cummings Publishing Co., (1978).

7) W. H. Urry and D. J. Trecker, *J. Am. Cem. Soc.*, **84**, 118 (1962).

8) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, **1966**, 3671.

9) F. D. Lewis and T. A. Hilliard, *J. Am. Chem. Soc.*, **92**, 6672 (1970).

10) A. T. Nielsen, C. Gibbons, and C. A. Zimmerman, *J. Am. Chem. Soc.*, **73**, 4696 (1951).

11) W. M. Muir, P. D. Pitchie, and D. J. Lyman, *J. Org. Chem.*, **31**, 3790 (1966).

12) M. F. Ansell, W. J. Hickinbottom, and P. G. Holton, *J. Chem. Soc.*, **1955**, 349.