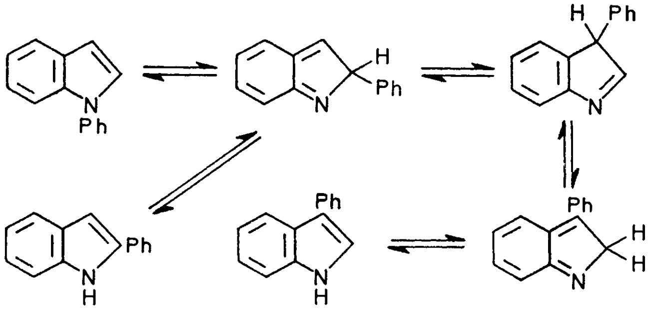
Reactive Intermediates. Part XXV.[1] Investigation of the Pyrolysis of 1,4- and 1,5-Diphenyl-1,2,3-triazoles by Use of ^{13}C-Labelled Compounds

By **Thomas L. Gilchrist,* Charles W. Rees,*** and **Colin Thomas,** The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

1,4-Diphenyl-[4-^{13}C]1,2,3-triazole (1) and 1,5-diphenyl-[5-^{13}C]1,2,3-triazole (2) have been prepared by the addition of azidobenzene to phenyl[1-^{13}C]acetylene. Pyrolysis of the triazoles in the vapour phase gave the same four compounds in each case: 1-, 2-, and 3-phenylindole, and *N*-(phenylvinylidene)aniline, which was isolated as its hydrolysis product, phenylacetanilide. It has also been established that 1-, 2-, and 3-phenylindoles can be interconverted by vapour phase pyrolysis. ^{13}C N.m.r. spectra of these indoles, and of phenylacetanilide, are reported. An analysis by fast Fourier transform ^{13}C n.m.r. of the positions of ^{13}C enrichment in the products derived from the triazoles has shown a substantial degree of scrambling of the ^{13}C label in the products derived from 1,5-diphenyl-[5-^{13}C]1,2,3-triazole, which provides strong evidence for the intermediacy of a 1*H*-azirine in the reactions. The products derived from 1,4-diphenyl-[4-^{13}C]1,2,3-triazole show little or no scrambling of the label.

In a preliminary investigation of the vapour phase pyrolysis of 1,4- and 1,5-diphenyl-1,2,3-triazoles, both 2- and 3-phenylindoles were isolated.[1] Although the formation of the mixtures of indoles could be ascribed to the intermediacy of 1*H*-azirines in the reactions,[1] this interpretation was not the only one possible, since, in particular, 2- and 3-phenylindole were shown to be thermally interconvertible. We have therefore undertaken a more definitive investigation of the mechanism of the triazole decompositions, using the specifically ^{13}C-labelled compounds 1,4-diphenyl-[4-^{13}C]1,2,3-triazole (1) and 1,5-diphenyl-[5-^{13}C]1,2,3-triazole (2). These were prepared by the cycloaddition of azidobenzene to phenyl[1-^{13}C]-acetylene, in a modification of the procedure described by Kirmse and Horner [2] for the unlabelled triazoles. The thermal interconversion of 2- and 3-phenylindoles has also been investigated further; under the conditions required to bring about the interconversion (a packed tube at 800° and 10^{-2} mmHg) small amounts of 1-phenylindole were also detected. The pyrolysis of 1-phenylindole under the same conditions also gave a mixture of the three isomers. In all cases, 2-phenylindole was the major component, and 1-phenylindole a minor component. No other products appeared to be formed in the pyrolyses. The equilibration of the phenylindoles probably involves successive [1,5] phenyl and hydrogen shifts (Scheme 1) analogous to those observed in thermal rearrangements of phenyl-substituted indenes.[3]

The optimum conditions for the pyrolysis of the triazoles (1) and (2) were found by using unlabelled analogues; the oven temperature (615—630°; empty silica tube) was the minimum required to decompose the triazoles completely. The presence of *N*-(phenylvinylidene) aniline in the product mixture was indicated by a strong absorption at 2010 cm^{-1} in the i.r. spectrum of a solution in chloroform. The vinylideneamine was hydrolysed by warming the product mixture in moist chloroform–ethyl acetate; the products were then separated by layer chromatography, isolated in the yields quoted, and identified by comparison with authentic specimens. 1,4-Diphenyltriazole gave, in duplicate experiments, 1-phenylindole (2 and 1%), 2-phenylindole (18 and 6%), 3-phenylindole (32 and 25%), and phenylacetanilide (28 and 33%). 1,5-Diphenyltriazole gave 1-phenylindole (1·5%), 2-phenylindole (25%), 3-phenylindole (13%), and phenylacetanilide (29%).



Scheme 1

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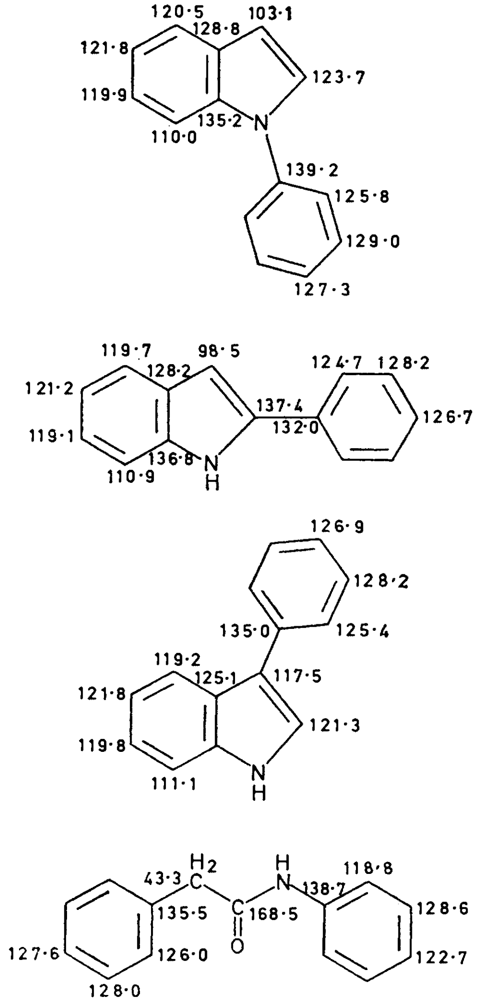
[1] Part XXIV, T. L. Gilchrist, G. E. Gymer, and C. W. Rees, preceding paper.

[2] W. Kirmse and L. Horner, *Annalen*, 1958, **614**, 1.

[3] C. F. Koelsch and P. R. Johnson, *J. Amer. Chem. Soc.*, 1943, **65**, 567; L. L. Miller, R. Greisinger, and R. F. Boyer, *ibid.*, 1969, **91**, 1578; L. L. Miller and R. F. Boyer, *ibid.*, 1971, **93**, 650; J. J. McCullough and M. R. McClory, *ibid.*, 1974, **96**, 1962.

Pyrolysis of the ^{13}C-labelled triazoles (1) and (2) gave sufficient 2- and 3-phenylindoles and phenylacetanilide



25·2 MHz ^{13}C N.m.r. spectra at 35° of 1-phenylindole (in [^{2}H]chloroform), 2-phenylindole (in [^{2}H]chloroform–[$^2H_6$]dimethyl sulphoxide, 10 : 3), 3-phenylindole (in [^{2}H]chloroform), and phenylacetanilide (in [$^2H_6$]dimethyl sulphoxide); chemical shifts are in p.p.m. downfield from tetramethylsilane

for their ^{13}C n.m.r. spectra to be recorded. These spectra were compared with the natural abundance spectra, and the positions of enrichment were determined. The ^{13}C spectra of the phenylindoles and of phenylacetanilide have not been reported previously; the assignments (deduced by comparison of the spectra with those in a published compilation,[4] and, in the case of the indoles, with those of related indoles [5]) are shown in the Figure. The important assignments from the point of view of this work are those for the C-2 and -3 of 2- and 3-phenylindoles, and for the CH_2 and C=O of phenylacetanilide; these assignments could be made unambiguously.

The degrees of enrichment at C-2 and -3 of the labelled indoles and at CH_2 and C=O of the labelled phenylacetanilide were calculated as follows. The peak heights in the enriched spectra were normalised by multiplying by a mean scaling factor $(\Sigma_i x_i/y_i)/N$ where x_i are the peak heights in the natural abundance spectrum; y_i are the corresponding peak heights in the spectrum of the labelled compound, of those signals which are not enriched; and N is the number of peaks used.

The standard deviation of the normalisation factor for each of the enriched spectra was then determined. The degrees of enrichment at each of the key positions were calculated as ratios of the normalised peak heights in the enriched spectra to those in the natural abundance spectra; these are shown, with standard deviations, in the Table. A value of 1·0 thus represents no enrichment. Since the peak heights are not a completely accurate reflection of the ^{13}C content (they depend, for example, on the number of computer plot data points used in compilation of the spectra), the absolute values of these ratios are probably not significant, but the qualitative picture which they convey is a reliable one. The indoles derived from 1,4-diphenyl-[4-^{13}C]1,2,3-triazole (1) contain the label exclusively at C-3, and the phenylacetanilide derived from this triazole is labelled predominantly, if not exclusively, at the CH_2. All the products derived from 1,5-diphenyl-[5-^{13}C]1,2,3-triazole (2), on the other hand, show scrambling of the label.

A summary of the ways in which these compounds can be formed is shown in Scheme 2. The detection of *N*-(phenylvinylidene)aniline as a primary product implies that the reactions involve singlet iminocarbenes (3) and (4) as intermediates. These can then rearrange in three ways: by Wolff rearrangement to the vinylideneamine, by cyclisation on to the *N*-phenyl group to give indoles, and by closure to give 1,2-diphenyl-1*H*-azirine (5). The indoles may then isomerise by thermal [1,5] shifts, as was established in the preliminary experiments. The possibility was considered that the Wolff rearrangement to the vinylideneamine might be reversible (there is evidence that the diphenylketen can rearrange photochemically to

Ratio of peak heights in enriched and natural abundance ^{13}C spectra

	2-Phenylindole		3-Phenylindole		Phenylacetanilide	
	C-2	C-3	C-2	C-3	CO	CH_2
From 1,4-diphenyl-[4-^{13}C]1,2,3-triazole (1)	†		0·8 ± 0·2	5·9 ± 1·3	1·6 ± 0·2	15·2 ± 1·9
From 1,5-diphenyl-[5-^{13}C]1,2,3-triazole (2)	16·1 ± 4·8	2·4 ± 0·8	2·1 ± 0·6	6·6 ± 1·8	18·2 ± 1·6	4·0 ± 0·3

† Natural abundance signals in this enriched spectrum were negligibly small in comparison with the enriched signal for C-3. No enrichment was detected at C-2.

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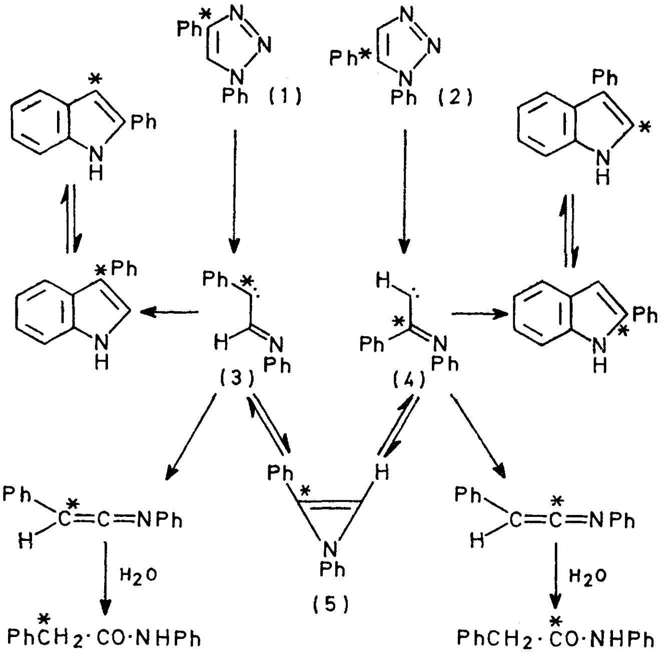
[4] L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Interscience, New York, 1972.

[5] R. G. Parker and J. D. Roberts, *J. Org. Chem.*, 1970, **35**, 996; E. Wenkert, J. S. Bindra, C.-J. Chang, D. W. Cochran, and F. M. Schell, *Accounts Chem. Res.*, 1974, **7**, 46.

diphenyloxiren[6]). Pyrolysis of an independently prepared specimen of *N*-(phenylvinylidene)aniline at 800° gave none of the 1-, 2-, or 3-phenylindoles that would be expected if the reaction were reversible, however.

When the results of the labelling experiments are compared with the rationale proposed in Scheme 2, it is found that all the products derived from 1,4-diphenyl-[4-^{13}C]1,2,3-triazole (1) can be accounted for without involving the 1*H*-azirine (5) as an intermediate. Thus, 3-phenylindole is exclusively labelled at C-3, so is probably formed by direct ring closure of the carbene (3). 2-Phenylindole, which is formed in lower yield than 3-phenylindole, is also labelled exclusively at C-3, and must be formed by rearrangement of 3-phenyl[3-^{13}C]indole. Phenylacetanilide is labelled at the methylene group, and is therefore also derived from the carbene (3).



SCHEME 2 * Indicates ^{13}C-enriched carbon atom

2-Phenylindole derived from 1,5-diphenyl[5-^{13}C]triazole (2) is labelled both at C-2 and at -3, with most of the label at C-2. 2-Phenyl[2-^{13}C]indole can be formed by direct ring closure of the carbene (4), but 2-phenyl[3-^{13}C]indole is formed from the isomeric carbene (3), the carbenes being interconverted through 1,2-diphenyl-1*H*-azirine (5). Similarly, 3-phenylindole is labelled both at C-2 and -3, the majority of the label being at C-3. Most of the 3-phenylindole is thus formed from the isomeric carbene (3) *via* the 1*H*-azirine intermediate. The phenylacetanilide also shows enhancement at both the methylene and the carbonyl group: the major pathway for its formation is from the carbene (4) but a significant amount is formed from the carbene (3).

The reactions of the carbene (4) derived from 1,5-diphenyl-1,2,3-triazole thus appear to involve the three possible types of rearrangement (vinylideneamine formation, cyclisation to 2-phenylindole, and collapse to 1,2-diphenyl-1*H*-azirine), whereas those of the carbene (3) derived from 1,4-diphenyl-1,2,3-triazole involve only the formation of *N*-(phenylyinylidene)aniline and the cyclisation to 3-phenylindole as primary reactions. 1,2-Diphenyl-1*H*-azirine may intervene as an intermediate from the carbene (4) because of the proximity of the phenyl substituents, the formation of the three-membered ring removing any steric interaction between them. The collapse to a three-membered ring may not be so favourable for the carbene (3); conversely, this carbene should undergo Wolff rearrangement more easily than its isomer (4) because the rearrangement involves a hydrogen shift rather than a phenyl shift. In a study of the photochemical decomposition of 1,4- and 1,5-diphenyl-1,2,3-triazoles,[7] Burgess and his co-workers found that the rearrangement to *N*-(phenylvinylidene)aniline was the major reaction in both cases (formation of indoles being the minor reaction). From 1,4-diphenyl-1,2,3-triazole, the vinylideneamine was virtually the only product, whereas from 1,5-diphenyltriazole, the vinylideneamine and 2-phenylindole were isolated in the ratio 3 : 1. Although the authors explained the results in terms of the relative ease of indole formation, the ratios could instead reflect the relative ease of Wolff rearrangement of the carbenes.

The results obtained from the pyrolysis of these triazoles indicate that 1*H*-azirine intermediates may be involved even when favourable alternative reaction pathways exist. In conjunction with the work reported in the preceding paper,[1] they show that 1*H*-azirines should be considered as possible intermediates in the thermal decomposition of all 1,2,3-triazoles.

EXPERIMENTAL

^{13}C N.m.r. spectra were recorded with a Varian XL100 15FT spectrometer with an 8K Varian 620L computer, by using the fast Fourier transform technique, at 25·197 MHz (5120 Hz sweep width and 2048 computer plot data points). Chemical shifts are accurate to $\pm 2{\cdot}5$ Hz ($\pm 0{\cdot}1$ p.p.m.). Samples were run in 12 mm tubes with a 5 mm concentric tube of ^2H_2O to provide the instrument lock signal except where deuteriochloroform was used as both solvent and to provide the lock signal. Tetramethylsilane was used as internal standard. G.l.c. was carried out using a Pye series 104 chromatograph with a flame ionisation detector (hydrogen at 45 lb in^{-1}, nitrogen at 45 lb in^{-2}, and air at 700 ml min^{-1}). Quantitative traces were obtained by using the chromatograph coupled to a Vidar 6300 digital computer. Mass spectra were obtained on an A.E.I. MS902 machine. The flash vacuum pyrolysis apparatus has been described earlier.[8] Preparative layer chromatography was carried out using glass plates coated with silica gel PF$_{254}$ (Merck). Petroleum refers to the fraction of b.p. 60—80°.

Materials.—Barium [^{13}C]carbonate (90 atom % ^{13}C) was supplied by Prochem. 2-Phenylindole (Emanuel) was re-

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[6] J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1973, **95**, 124.

[7] E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, 1968, **90**, 1923.

[8] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, C. W. Rees, and E. Stanton, *J.C.S. Perkin I*, 1972, 1317.

crystallised before use and had m.p. 191·5—192·5° (from cyclohexane). 1-Phenylindole[9] (oil; purified by layer chromatography immediately before use), 3-phenylindole,[10] m.p. 86—87° (from hexane), *N*-(phenylvinylidene)aniline,[11] and phenylacetanilide,[12] m.p. 116—116·5° (from propan-2-ol), were prepared by the literature procedures indicated.

1,4-*Diphenyl*-[4-^{13}C]1,2,3-*triazole* (1) *and* 1,5-*Diphenyl*-[5-^{13}C]1,2,3-*triazole* (2).—(a) *Phenyl*[1-^{13}C]*acetylene*. A modification of the procedure of Casanova, Geisel, and Morris[13] was used.

(i) *Benzoic* [^{13}C]*acid*.[14] This was obtained (2·38 g, 81%) by the reaction of phenylmagnesium bromide with carbon dioxide generated from barium [^{13}C]carbonate (4·8 g, 24·2 mmol).

(ii) [1-^{13}C]*Acetophenone*.[15] Benzoic [^{13}C]acid (2·38 g, 19·5 mmol) was dissolved in dry ether (50 ml) under nitrogen and a solution of methyl-lithium in ether (0·92M; 46 ml) was added. The solution was heated under reflux for 35 min, then cooled, and water (50 ml) was added. The aqueous layer was washed with ether (3 × 10 ml) and the combined ethereal solutions were dried and evaporated to leave [1-^{13}C]acetophenone (2·2 g, 94%) as a mobile liquid.

(iii) By using the procedure described in ref. 13, [1-^{13}C]-acetophenone (2·2 g) was treated with phosphorus pentachloride (5·1 g) to give a mixture (2·85 g) of 1-chloro-1-phenyl[1-^{13}C]ethylene and 1,1-dichloro-1-phenyl[1-^{13}C]-ethane. This was dehydrochlorinated by reaction with sodamide in liquid ammonia to give phenyl[1-^{13}C]acetylene (1·48 g, 79%) as an oil, which was diluted with unlabelled phenylacetylene (3·7 g) for use in the next stage.

(b) *Reaction with azidobenzene*.[2] Azidobenzene (5·95 g, 0·05 mol) and phenyl[1-^{13}C]acetylene (5·10 g, 0·05 mol) were heated in toluene (50 ml) under reflux for 26 h. The solution was cooled, and crystals separated. Recrystallisation gave 1,4-diphenyl-[4-^{13}C]1,2,3-triazole (2) (3·10 g, 28%), m.p. 183—185° (from ethanol–toluene) (lit.,[2] 184—185°); *m/e* 222 (1·0%) and 221 (3·0), equivalent to 13·5 mol % ^{13}C. The C-4 n.m.r. signal is 146·8 p.p.m. downfield from Me$_4$Si. After removal of the solid from the reaction mixture, the filtrate was evaporated and the residue (5·0 g) subjected to layer chromatography. Development with chloroform–ethyl acetate (47 : 3) gave crystalline material (3·7 g) which was substantially the 1,5-isomer but which contained a trace of the 1,4-isomer. Recrystallisation gave 1,5-diphenyl-[5-^{13}C]1,2,3-triazole (2·80 g, 25%), m.p. 109—111° [from petroleum (b.p. 80—100°)] (lit.,[2] 112°); *m/e* 222 (1·0%) and 221 (3·0), equivalent to 13·5 mol % ^{13}C. The C-5 n.m.r. is 137·1 p.p.m. downfield from Me$_4$Si.

Pyrolyses.—(a) 1,4-*Diphenyl*-[4-^{13}C]1,2,3-*triazole*. The triazole (100 mg) was pyrolysed at 620° and 0·01 mmHg in an empty silica tube. The product mixture was warmed in ethyl acetate–chloroform to facilitate hydrolysis of *N*-(phenylvinylidene)aniline, and was then separated by layer chromatography on silica. Petroleum–ether (7 : 3) eluted 1-phenylindole (1·8 mg, 2%), 2-phenylindole (15·4 mg, 18%), and 3-phenylindole (28·4 mg, 32%). The base-line material was extracted and again subjected to layer chromatography. Chloroform–ethyl acetate (19 : 1) eluted phenylacetanilide (26·3 mg, 28%). A second pyrolysis of the triazole (200 mg) gave 1-phenylindole (1%), 2-phenylindole (6%), 3-phenylindole (25%), and phenylacetanilide (33%). The distribution of ^{13}C in 2- and 3-phenylindole and in phenylacetanilide was determined by ^{13}C n.m.r.

(b) 1,5-*Diphenyl*-[5-^{13}C]1,2,3-*triazole*. The triazole (203 mg) was pyrolysed at 615° and 0·01 mmHg. Layer chromatography of the product mixture on silica gave [with petroleum–ether (7 : 3)] 1-phenylindole (2·7 mg, 1·5%), 2-phenylindole (43·6 mg, 25%), and 3-phenylindole (22·5 mg, 13%). The base-line material was again subjected to layer chromatography. Chloroform–ethyl acetate (19 : 1) eluted phenylacetanilide (56·0 mg, 29%). The distribution of ^{13}C in 2- and 3-phenylindole and in phenylacetanilide was determined from the ^{13}C n.m.r. spectra.

(c) 1-*Phenylindole*. 1-Phenylindole (30·6 mg) was pyrolysed at 800° and 0·01 mmHg in a tube packed with silicon carbide chips. The pale yellow solid product was examined by t.l.c., which showed it to consist of a mixture of 1-, 2-, and 3-phenylindole. Analysis by g.l.c. (2% OVI silicone on Celite; 250°) gave a ratio of 1-, 2-, and 3-phenylindole of 1·00 : 2·54 : 2·38.

(d) 2-*Phenylindole*. 2-Phenylindole was recovered unchanged at 600° (empty tube). At 800° and 0·001 mmHg (packed tube), 2-phenylindole (30 mg) gave, after layer chromatography of the product mixture [petroleum–ether (7 : 3)], 1-phenylindole (0·7 mg, 2%), 2-phenylindole (15·5 mg, 52%), and 3-phenylindole (9·3 mg, 31%).

(e) 3-*Phenylindole*. 3-Phenylindole was recovered unchanged at 600° (empty tube). At 800° and 0·005 mmHg (packed tube), 3-phenylindole (30 mg) gave, after layer chromatography of the product mixture, 1-phenylindole (1·4 mg, 5%), 2-phenylindole (18·7 mg, 62%), and 3-phenylindole (4·5 mg, 15%).

(f) N-(*Phenylvinylidene*)*aniline*. The vinylideneamine[11] (100 mg) was pyrolysed at 800° and 0·01 mmHg. It was necessary to warm the imine in order to vaporise it, and it partially resinified. The pyrolysate, a pale yellow gum, was examined by t.l.c., which showed that 1-, 2-, and 3-phenylindole were absent. The pyrolysis products were not investigated.

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[9] L. J. Dolby and P. D. Lord, *J. Org. Chem.*, 1969, **34**, 2988.

[10] F. Henle, *Ber.*, 1905, **38**, 1362.

[11] M. Masaki, K. Fukui, and M. Ohta, *J. Org. Chem.*, 1967, **32**, 3564.

[12] S. S. Jenkins, *J. Amer. Chem. Soc.*, 1933, **55**, 703.

[13] J. Casanova, M. Geisel, and R. N. Morris, *Org. Prep. Procedures*, 1969, **1**, 81.

[14] A. Murray and D. L. Williams, 'Organic Syntheses with Isotopes,' Interscience, New York, 1958, part 1, p. 86.

[15] *Cf.* C. Tegner, *Acta Chem. Scand.*, 1952, **6**, 782. (This procedure gives a higher yield of acetophenone than the method described in ref 13.)