Investigation of Photolysis of *o*-Nitrophenols by Electron Spin Resonance Spectroscopy. Characterisation of 1,2-Benzoquinone Monohydroxyimine Free Radicals

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The photolysis of tetrahydrofuran (THF) solutions containing *o*-nitrophenols and di-t-butyl peroxide (DTBP) has been examined by e.s.r. spectroscopy. In carefully degassed solutions a series of 1,2-benzoquinone monohydroxyimine free radicals are formed, the structures of which have been confirmed using an unambiguous synthesis by oxidation of appropriate nitrosophenols in a flow system. The origin of hyperfine splittings is such radicals has been evaluated. Structures are tentatively proposed for free radicals observed during the photolysis of inefficiently degassed THF solutions of *o*-nitrophenols and DTBP; the same radicals are obtained when analogous nitrosophenols are photolysed under identical conditions.

THE mechanism of u.v. photolysis of nitrobenzene derivatives [1,2] and of nitroheteroarenes [3] in ether solvents has been established by e.s.r. studies. The radicals observed *during* photolysis are alkoxy aryl nitroxides [*cf.* (2)], the origin of which, for tetrahydrofuran (THF) solutions, is illustrated in Scheme 1.

In certain cases, *e.g.* for nitroarenes bearing $+M$ directing substituents, it is necessary [3] to add di-t-butyl peroxide (DTBP) to the substrate solution. The reason for the absence of nitroxides in these cases is unclear, but one possibility is that perturbation of the π^* level by the substituent has an adverse effect on the efficiency of the

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[1] D. J. Cowley and L. H. Sutcliffe, *J. Chem. Soc.* (*B*), 1970, 569.

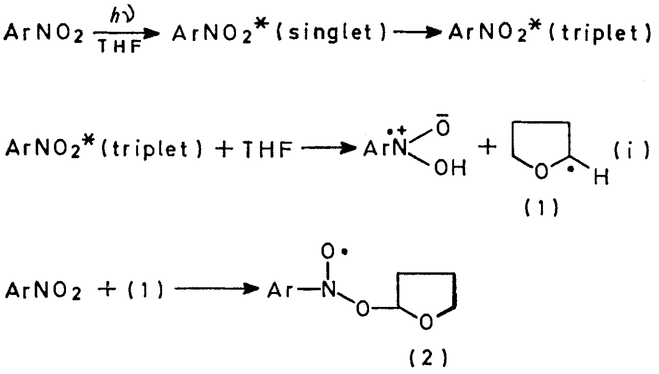
[2] S. K. Wong and J. K. S. Wan, *Canad. J. Chem.*, 1973, **51**, 753.

[3] R. B. Sleight and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1971, **67**, 2195.

n–π^* excited state in relation to the hydrogen abstraction reaction [reaction (i) in Scheme 1]. DTBP may operate by raising the stationary state concentration of THF-derived radicals (1) as follows:

$$\mathrm{DTBP} \xrightarrow{h\nu} 2\ \mathrm{Bu^tO}$$

$$\mathrm{Bu^tO\cdot} + \mathrm{THF} \longrightarrow (1) + \mathrm{Bu^tOH}$$



SCHEME 1

As part of an earlier investigation[4] of organosilicon alkoxy aryl nitroxides and their organic analogues, we noted evidence of an intramolecular interaction in o-nitro-t-butylbenzene and on this basis we have initiated a wider research programme[5,6] involving e.s.r. examination of the photolysis of a variety of *ortho*-substituted nitrobenzene derivatives. We now report the results of our studies on the photolysis of o-nitrophenols.

TABLE 1

E.s.r. hyperfine splitting constants (mT) for radicals (5) obtained by photolysis of nitrophenols in tetrahydrofuran

Position of substituents in (5)				Hyperfine splitting constants (mT)[a]				
3	4	5	6	a_N	a_3	a_4	a_5	a_6
H	H	H	H	2.686	0.215	0.044	0.044	0.044
H	H	Me	H	2.612	0.205	0.051	0.051(3)	0.051
H	Me	H	H	2.601	0.200		0.040	0.040
Me	H	H	H	2.612		0.042	0.042	0.042
H	Me	H	Me	2.572	0.211		0.040	0.040(3)
H	Me	Me	H	2.580	0.200		0.047(3)	0.047
Me	H	Me	H	2.622		0.051	0.051(3)	0.051
Me	Me	H	Me	2.601			0.041	0.041(3)
H	H	F	H	2.708	0.211	0.211[b]	0.036	0.036
F	H	H	H	2.708	0.221[b]	*c*	*c*	*c*
H	H	Cl	H	2.654	0.200	*c*		*c*
Cl	H	Cl	H	2.825		*c*		*c*

[a] Numbers in parentheses refer to the number of hydrogens (attached to Me) giving rise to hfs. [b] Refers to fluorine hfs. [c] Lines not resolved.

For comparative purposes the photolysis of a THF solution containing p-nitrophenol and DTBP was carried out. The e.s.r. spectrum of the radical observed during photolysis was in accord with an alkoxy aryl nitroxide structure (2; Ar=p-$\mathrm{HOC_6H_4}$); normal[1,3] values of hyperfine splitting (hfs) constants were obtained, *viz.* a_N 1.55; $a_{o\text{-H}}$ 0.275; $a_{m\text{-H}}$ 0.099 mT.

An entirely different type of spectrum was obtained when o-nitrophenol was photolysed in carefully degassed solutions of THF containing DTBP (see Table 1). The spectrum of this radical (g 2.00574) can be rationalised in terms of a large nitrogen splitting (a_N 2.686 mT) with additional doublet (a_H 0.215 mT) and quartet (a_H 0.044 mT) splittings. Identical behaviour was observed when other ether solvents were used (*e.g.* $\mathrm{Et_2O}$ or $\mathrm{PhCH_2OMe}$) but the radical was not generated during photolysis in benzene, cyclohexane, or alcoholic solutions (*e.g.* MeOH or EtOH). No effect on the spectrum was observed by the use of o-nitrophen[^{2}H]ol or by the photolysis of o-nitrophenol in perdeuteriotetrahydrofuran containing DTBP; no significant changes were noted when the photolyses were carried out in the range −30° to room temperature. No radicals were observed below −35°. The generality of the reaction was demonstrated by photolysing a variety of o-nitrophenol derivatives (Table 1).

The values of nitrogen hfs constants for these radicals are too high for sterically unhindered nitroxides[1] but they are in accord with iminoxyl radicals.[7] Since nitrosoarenes are likely[1,2] intermediates in the photoreduction of nitroarenes in THF, it was thought[8] that they may have given rise to the iminoxyl radicals. Accordingly, three nitrosophenol derivatives (3a—c) were oxidised with ceric sulphate in aqueous methanolic sulphuric acid using a conventional[9] flow system. The esr spectra of the radicals (4) obtained (see Table 2) were identical with those from the photolysis of analogous o-nitrophenol derivatives and established unambiguously the 1,2-benzoquinone monohydroxyimine structure.

Important features of the iminoxyl radicals [*e.g.* (5)] are discussed below in relation to available information

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[4] J. M. Lynch, P. N. Preston, R. B. Sleight, and L. H. Sutcliffe, *J. Organometallic Chem.*, 1969, **20**, 43.

[5] D. Döpp, R. G. Green, and L. H. Sutcliffe, unpublished results.

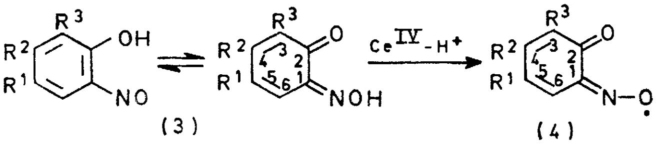
[6] R. G. Green, P. N. Preston, and L. H. Sutcliffe, *Spectrochimica Acta*, in the press.

[7] J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86** 1446.

[8] The photolysis of solutions of oximes containing DTBP is a convenient method for the generation of iminoxyl radicals; *cf.* J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 7040.

[9] *Cf.* W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 1965, 4628.

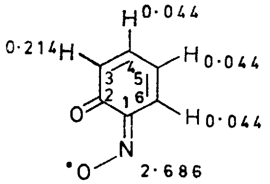
on the related compounds (6),[7] (7),[9] (8),[9] (9),[10,11] (10),[12] and (11);[12] the numbers within (6)—(11) refer to values of hfs constants.



(3) (4)

	R^1	R^2	R^3
a;	Cl	H	H
b;	H	MeO	H
c;	Me	H	Me

Ring Hydrogen Splittings.—The iminoxyl radical obtained from the oxidation of nitrosoresorcinol was speculatively assigned[7] structure (6) but this was later



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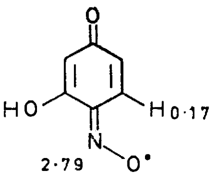

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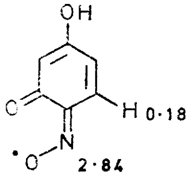

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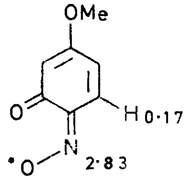

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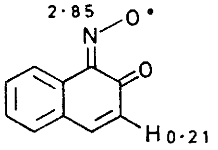

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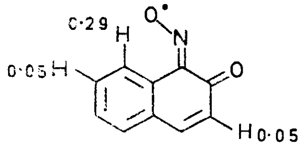

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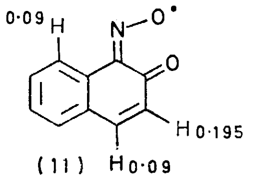

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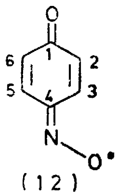

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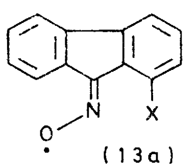
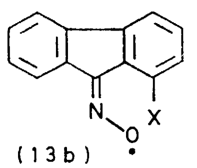


(13a)



(13b)

reformulated[9] as the tautomer (7) on the basis of its relatively low a_N value and also because of the similarity of its e.s.r spectrum to that of the methyl ether derivative (8). From studies[9] of related 1,4-benzoquinone monohydroxyimines it was concluded[9] that the small doublet splittings originated from ring hydrogens *trans* to the hydroxyimino-function. Subsequent studies of the closely related radicals (9),[11] (10),[12] and (11)[12] indicates that a hfs of *ca.* 0.2 mT can be definitely assigned[11] to a ring hydrogen which is separated from the hydroxyimino-function by a carbonyl group and which is *cis* to the hydroxyimino N–O bond. On this basis the iminoxyl radicals observed in the present work are assigned structure (5) in which the carbonyl group and the N–O bond are in a *cis*-configuration. Accordingly, the assignments of Fox and Waters[9] for the doublet splittings in (7) and (8) must be treated with caution since such splittings may arise from the hydrogen in the 3-position.

TABLE 2

E.s.r. hyperfine splitting constants (mT) for radicals (4) obtained by oxidation[a] of nitrosophenols (3)

Nitrosoarene	Hfs constants (mT)				
	a_N	a_3	a_4	a_5	a_6
(3a)	2.729	0.212	*b*	*b*	*b*
(3b)	2.84[c]	0.194[c]	*b*	*b*	*b*
(3c)	2.772		0.04	0.04(3)[d]	0.04

[a] The nitrosoarene derivative (10^{-2}—10^{-3}M) in methanol was oxidised by excees of ceric sulphate in N-H_2SO_4 using a conventional[9] flow technique. [b] Hfs not observed. [c] *cf.* literature[9] values of a_N 2.83 and a_H 0.17 mT. [d] Hfs originating from the hydrogens of the methyl group.

Splittings for Hydrogens of Methyl Groups.—For radicals of type (5) splittings originating from methyl groups are only observed in the 5- and 6- but not in the 3- and 4-positions, in marked contrast to the pattern for ring hydrogen splittings where the maximum value is at the 3-position; hfs constants of methyl hydrogens are either identical or almost identical with those for hydrogens at that position. These results are in marked contrast with those of Fox and Waters[9] on 1,4-benzoquinone monohydroxyimine. They noted the following trends. (i) No splittings were observed from hydrogens at positions 2 and 6. (ii) In the 3,5-dimethyl derivative, methyl hydrogen splittings of 0.3 and 0.1 mT are observed, the larger value being assigned[9] to the configuration with the N–O bond and the methyl group in a *cis*-configuration. (iii) In the 3-methyl derivative two radicals are observed corresponding to the two possible stereoisomers but the hfs constant for methyl hydrogens is the same in both cases (0.2 mT). (iv) Splittings from methyl hydrogens in the 2- and 6-positions are not observed.

An unusual feature of methyl splittings observed in the present work is that the stereochemistry is such that the methyl groups [at positions 5 and 6 in (5)] are directed away from the N–O bond.

Fluorine Splittings.—Previous observations of halogen hfs in derivatives of (12)[9] and of hydroxyimino-derivatives derived from fluorenone oximes (13; X = hal)[13] indicate the following. (i) For (12),[9] the trend in hfs is

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[10] M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1964, 1985.

[11] W. M. Fox and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 1503.

[12] B. C. Gilbert and R. O. C. Norman, *J. Phys. Chem.*, 1967, **71**, 14.

[13] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1967, 981.

$a_H \approx a_{Cl} < a_F$ (for a *cis*-configuration) and $a_H < a_F$ (Cl not observed) for a *trans*-configuration. (ii) For both (13a)[13] and (13b)[13] the relative magnitudes are $a_H \approx a_{Cl} < a_F$.

In both cases [(12) and (13)] larger splittings are noted for configurations in which the hydroxyimino-function is *cis* to the appropriate hydrogen or halogen atom.

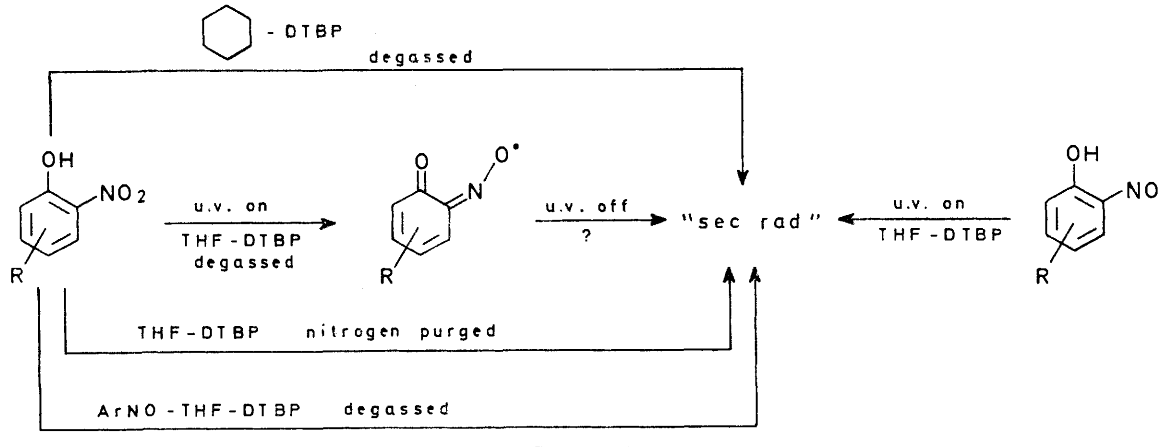
For radicals (5) prepared in the present work a similar trend ($a_F > a_H$) is evident for a 5-substituent, but for substitution at the 3-position, $a_H \approx a_F$. It is interesting that the magnitudes of fluorine splittings in both 3- and 5-positions are almost identical despite the fact that they are in different configurations with respect to the hydroxyimino-function.

TABLE 3

E.s.r. hyperfine splitting constants (mT) for secondary radicals obtained by photolysis of nitrophenols in the presence of di-t-butyl peroxide

Position of substituents as in (5)									
3	4	5	6	Solvent	a_N	a_{ortho}	a_{meta}	a_{para}	a_{other}[b]
H	H	H	H	THF	0.94	0.36	0.09	0.36	0.04(2)
H	H	H	H	[$^2H_8$]-THF	0.91	0.35	0.09	0.35	
H	H	Me	H	THF	0.93	0.36	0.08	0.36	0.04(2)
Me	H	Me	H	THF	0.94	0.36		0.36	*a*
Me	Me	H	Me	THF	1.27		*a*		*a*
H	H	F	H	THF	0.90	0.32	*a*	0.32	*a*
F	H	H	H	THF	0.91	0.33	*a*	0.33	*a*
H	H	Cl	H	THF	0.90	0.35	*a*	0.35	*a*
Cl	H	Cl	H	THF	0.92	0.35		0.35	0.07(1)

[a] Splittings not resolved. [b] Numbers in parentheses refer to the number of splittings from hydrogen nuclei.



SCHEME 2

Origin of the Iminoxyl Radicals.—At the outset of the work it became clear that iminoxyl radicals could only be prepared using carefully vacuum-degassed solutions; using a less thorough ' nitrogen purging ' procedure they were observed only in low concentration and decomposed rapidly, and other radicals were obtained (see Table 3). Interestingly, during an attempt to determine whether the iminoxyl radicals originated from a photochemical reaction of *o*-nitrosophenols with DTBP in THF, an identical type of reaction was noted (see Table 3); the inter-relationship in this context is illustrated in Scheme 2 from which we draw the following conclusions. (i) The formation of iminoxyl radicals necessarily requires the use of ether solvents. (ii) Although an increase in concentration of ' secondary radicals ' (' sec rad ', *cf.* Scheme 2) occurs in the dark period after photolysis in degassed THF, it cannot be concluded that the ' secondary radicals ' originate from the iminoxyl radicals, hence the question mark in Scheme 2. (iii) In a competitive photochemical reaction involving nitroarene and nitrosoarene, the ' secondary ' rather than the iminoxyl radicals are formed.

The detailed mechanism of formation of iminoxyl radicals is unclear. The absence of observable (e.s.r.) alkoxy aryl nitroxides [*e.g.* (2; Ar=*o*-HOC_6H_4)] during photolysis of *o*-nitrophenols in the temperature range —35—20° is surprising and one possibility is that they are converted into the iminoxyl radicals by an intramolecular mechanism. Such a mechanism would be aided by the intramolecular hydrogen bonding observed by i.r.[14] and microwave[15] spectroscopy for 2-nitrophenol. An alternative route is outlined in Scheme 3, although it should be noted that a reaction of this type has no

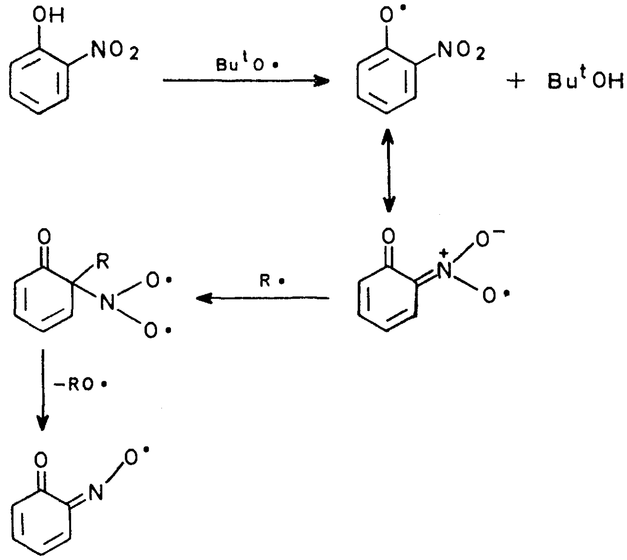
[14] Yung Sung Su and Hwei-Kwan Hong, *Spectrochimica Acta*, 1968, **24A**, 1461.

[15] S. Leavell and R. F. Curl, *J. Mol. Spectroscopy*, 1973, **45**, 428.

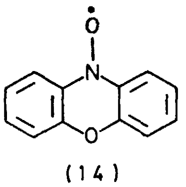
precedent in the chemistry of nitro-compounds; furthermore an analogous type of reaction would be expected from *p*-nitrophenol derivatives and this is not observed.

As yet we have not evaluated the structure of the 'secondary radicals' (*cf.* Table 3); the type of reaction involved in the photolysis of *o*-nitrosophenols is different from the photolysis of nitrosobenzene in THF (which gives [16] diphenyl nitroxide) and of *p*-nitrosophenol which provides a complicated asymmetrical spectrum.

Recently Konaka *et al.*[17] reported that phenoxazine *N*-oxyl (14) is formed when phenol is oxidised in the presence of nitrosobenzene as a spin trap; intermediate spin adducts of type (15a) are suggested.[17] Analogous behaviour in the present work implies the intermediacy of nitroxides [*e.g.* (15b)] which would be expected to decompose rapidly to nitrones (16) (*cf.* the behaviour [18] of analogous α-nitro nitroxides). We believe the 'secondary radicals' may originate from such nitrones by a 'spin-trapping' reaction with solvent radicals. In support of the conclusion the spectrum of the typical 'secondary radical', that derived from 2-nitrophenol is found to be greatly simplified using [$^2H_8$]THF as solvent; the deuterium hyperfine splittings being too small to be observed. We are presently examining the preparative scale photolysis of *o*-nitrophenols with a view to isolating products of this type for spin-trapping experiments.



SCHEME 3 R may be a solvent-derived radical, or a radical (*e.g.* ·CH_3) derived from decomposition of DTBP



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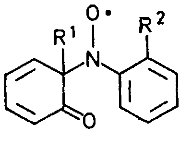

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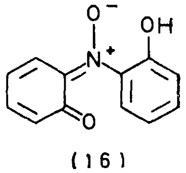

(16)

a; $R^1 = R^2 = H$
b; $R^1 = NO, R^2 = OH$

EXPERIMENTAL

2-Nitrophenol, 3-hydroxy-4-nitrotoluene, and 4-hydroxy-3-nitrotoluene were obtained from Koch-Light Laboratories; 4-chloro-2-nitrophenol, 2,4-dichloro-6-nitrophenol, and 5-methoxy-2-nitrosophenol were obtained from Kodak Limited; 2-fluoro-6-nitrophenol and 4-fluoro-2-nitrophenol were obtained from Fluka Limited. All other 2-nitrophenols used were prepared from the corresponding methyl-substituted phenol obtained from Fluka Limited: they were nitrated by standard methods and steam distilled in order to separate the products. 4-Chloro-2-nitrosophenol and 4,6-dimethyl-2-nitrosophenol were prepared by Cronheim's method.[19]

All compounds were recrystallised twice from ethanol and structures confirmed by ^1H n.m.r. spectroscopy. Deuteriophenol was prepared by shaking 2-nitrophenol with D_2O and dried on a vacuum line. The structure was confirmed by ^1H n.m.r. spectroscopy.

Photolysis was carried out in the cavity of a Varian E4 e.s.r. spectrometer equipped with a Varian temperature control unit. A Hanovia UV 100 u.v. lamp was used in conjunction with a Chance OX1 filter to remove wavelengths <300 nm. Flow experiments were performed using a Varian flow cell, the nitrogen purged liquids being gravity fed through the cell. Typical flow rates were 3 $cm^3 s^{-1}$.

All samples were either nitrogen purged for 15 min or vacuum degassed by the freeze–thaw method.

[5/193 *Received, 29th January,* 1975]

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[16] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.* (*B*), 1966, 904.

[17] S. Terabe, K. Kuruma, and R. Konaka, *Chem. Letters*, 1972, 115.

[18] T. A. B. M. Bolsman and Th. J. De Boer, *Tetrahedron*, 1973, **29**, 3579.

[19] G. Cronheim, *J. Org. Chem.*, 1947, **12**, 7.