Properties and Reactions of Free Alkyl Radicals in Solution. Part VII. Reactions with Quinone Imides, Nitric Oxide, and Nitroso-compounds.*

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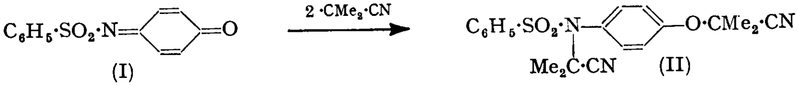
2-Cyano-2-propyl radicals add on to *p*-benzoquinone monobenzenesulphonimide in the same way as they do to quinones (Parts I and V), but corresponding products could not be isolated from acylated quinone di-imides. Nitric oxide and several tertiary nitroso-compounds combine with 2-cyano-2-propyl radicals to form trisubstituted hydroxylamines. On acid hydrolysis these lose one cyanopropyl group with formation of acetone. The aryl-*ON*-di-(2-cyano-2-propyl)hydroxylamines when reduced with zinc dust and acetic anhydride give aryl-*N*-(2-cyano-2-propyl)hydroxylamines, aromatic azo-compounds and arylacetamides, but all in rather poor yield.

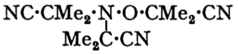
2-Cyano-2-propyl radicals do not react with *s*-trinitrobenzene, 2 : 4-dinitrochlorobenzene, or azoxybenzene.

2-Cyano-2-propyl radicals, produced by thermal decomposition of solutions of αα′-azo*iso*butyronitrile, have been shown to add on to the carbon atoms of easily polymerisable olefins, and to the oxygen atoms of quinones (Part I, *J.*, 1950, 1764; Part V, *J.*, 1952, 4666) but show little or no tendency to add on to isolated C=O groups (Part IV, *J.*, 1952, 3108), to C=N or N=N groups, or to the nitrogen atoms of radicals formed by homolytic halogen abstraction from *N*-halogenoanilides (Part VI, *loc. cit.*).

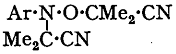
We have been successful, however, in effecting addition to *p*-benzoquinone monobenzenesulphonimide (I) (Adams and Looker, *J. Amer. Chem. Soc.*, 1951, **73**, 1145) and obtained the expected product (II), which had an infra-red spectrum of requisite character. We failed, however, to demonstrate the occurrence of similar addition to two acylated quinone di-imides, very few of which have sufficient thermal stability to withstand heating to the required temperature.


(I) (II)

Although many aromatic nitro-compounds are effective retarders or inhibitors of vinyl polymerisation, and presumably act by combining somehow with hydrocarbon radicals (Bartlett and Kwart, *ibid.*, 1950, **72**, 1051), we have found that 2-cyano-2-propyl radicals do not react detectably in boiling toluene solution with *s*-trinitrobenzene or 2 : 4-dinitrobenzene, and so must, in this respect, be much less active than triphenylmethyl radicals which at once attack the NO_2 group of nitrobenzene (Hammond and Ravve, *ibid.*, 1951, **73**, 1891). Azoxybenzene also did not react. The N=O bonds of nitro-compounds, however, do not have full double-bond character, and the N⟶O group of azoxybenzene clearly has no unsaturation. The unsaturated N=O group is, however, the characteristically reactive feature of nitroso-compounds, and, as we mentioned in a preliminary note (*Chem. and Ind.*, 1953, 615), we have found that 2-cyano-2-propyl radicals react not merely with the odd electron of nitric oxide, but with tertiary nitroso-compounds too, to give the fully substituted hydroxylamines of structures (III) and (IV). Several new compounds of type (IV) are listed in Table 1.

(III)


$$NC{\cdot}CMe_2{\cdot}\underset{Me_2C\cdot CN}{N}{\cdot}O{\cdot}CMe_2{\cdot}CN$$


(IV)

$$Ar{\cdot}\underset{Me_2C\cdot CN}{N}{\cdot}O{\cdot}CMe_2{\cdot}CN$$

Though it has been known for a long time that nitric oxide reacts with free radicals, Schlenk, Mair, and Bornhardt (*Ber.*, 1911, **44**, 1169) failed to isolate the product formed from triphenylmethyl, which they assumed to be the simple addition compound $Ph_3C{\cdot}N{:}O$.

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* Part VI, *J.*, 1953, 3529.

Weitz, Müller, and Dinges (*Chem. Ber.*, 1952, **85**, 878), however, in a study of the radicals obtained by reducing triphenylmethane dyes, found that the reaction with nitric oxide was much more complex, and succeeded in isolating *NN*-diarylhydroxylamines, $Ar_2N{\cdot}OH$ [$Ar = (Me_2N{\cdot}C_6H_4)_3C$, etc.], in addition to dyes re-formed by the oxidation of the radicals by the nitric oxide.

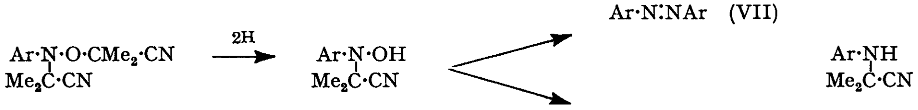
Hinshelwood and his colleagues (*Proc. Roy. Soc.*, 1937, *A*, **159**, 32) and many later workers have produced kinetic evidence of gas-phase combination of nitric oxide with free methyl and similar radicals but did not establish the initial formation of nitrosomethane. Raley, Rust, and Vaughan (*J. Amer. Chem. Soc.*, 1948, **70**, 88) found that the first stable product of the thermal reaction is formaldoxime, and Coe and Doumani (*ibid.*, p. 1516) succeeded in isolating nitrosomethane and its dimer from the products of vapour-phase photolysis of *tert.*-butyl nitrite at 25°. Chilton and Gowenlock recently (*J.*, 1953, 3232; *Nature*, 1953, **172**, 73) isolated acetoxime and an unidentified nitroso-compound, which they believe to be 2-nitrosopropane, from the gas-phase reaction of nitric oxide with free *iso*propyl radicals, and Haszeldine (*J.*, 1953, 2075) has prepared a series of monomeric nitrosoperfluoroalkanes. None of these workers had envisaged the possibility that nitric oxide itself might combine with more than one free radical.

The assignment of the structure tris-(2-cyano-2-propyl)hydroxylamine (III) to our radical adduct to nitric oxide is in full accord with the infra-red spectrum of our product. On hydrolysis with dilute sulphuric acid it yields acetone, but the *NN*-disubstituted hydroxylamine (V) could not be isolated. Since the same product (III) was also obtained

$$\underset{\text{(III)}}{(NC{\cdot}Me_2)_2N{\cdot}O{\cdot}CMe_2{\cdot}CN} + H_2O \longrightarrow \underset{\text{(V)}}{(NC{\cdot}CMe_2)_2N{\cdot}OH} + HCN + Me_2C{:}O$$

by the action of 2-cyano-2-propyl radicals on nitroso*iso*butyronitrile ($NC{\cdot}CMe_2{\cdot}N{:}O$) (Piloty, *Ber.*, 1898, **31**, 1878), as well as from *N*-nitrosodiphenylamine, which is known to dissociate slowly, $Ph_2N{\cdot}NO \rightleftharpoons Ph_2N{\cdot} + {\cdot}NO$, on heating, there can be little doubt of the disposition of the cyanopropyl groups in our reaction product.

The trisubstituted aromatic hydroxylamines (IV) give one equivalent of acetone on acid hydrolysis, but again the isolation of other pure reaction products was not successful. These hydroxylamines are resistant to reduction by sodium amalgam in aqueous alcohol, sodium dithionite, and hydrogen at up to 5 atm. pressure in the presence of Raney nickel. Reduction with zinc dust in hot acetic acid gave the corresponding unsubstituted *N*-aryl-acetamide (VIII), which proved that nuclear substitution of the aromatic ring had not occurred. Reduction with zinc dust and acetic anhydride in the presence of sodium acetate gives (VIII) and in most cases also the free secondary hydroxylamine (VI) and the



$$\underset{\text{(IV)}}{\begin{matrix}Ar{\cdot}N{\cdot}O{\cdot}CMe_2{\cdot}CN\\ Me_2C{\cdot}CN\end{matrix}} \xrightarrow{2H} \underset{\text{(VI)}}{\begin{matrix}Ar{\cdot}N{\cdot}OH\\ Me_2C{\cdot}CN\end{matrix}} \begin{matrix}\nearrow Ar{\cdot}N{:}NAr \text{ (VII)}\\ \searrow Ar{\cdot}NHAc \text{ (VIII)}\end{matrix} \qquad \underset{\text{(IX)}}{\begin{matrix}Ar{\cdot}NH\\ Me_2C{\cdot}CN\end{matrix}}$$

aromatic azo-compound (VII) though only in small yields. Secondary amines (IX) could not be isolated. The compound (IX; Ar = Ph), however, can be synthesised from aniline, acetone, and cyanide and is easily degraded to acetanilide by treatment with zinc dust and hot acetic acid. The reduction apparently cleaves the C–O rather than the N–O bond.

Few infra-red spectra of hydroxylamine derivatives have hitherto been reported. Table 3 lists the distinctive absorption bands of our products and gives some indication of the covalencies to which they may be due.

EXPERIMENTAL

Reaction between p-*Benzoquinone Monobenzenesulphonimide and αα′-Azo*iso*butyronitrile.*— The sulphonimide (Adams and Looker, *loc. cit.*) (4·94 g., 0·02 mole) and αα′-azo*iso*butyronitrile (3·28 g., 0·02 mole) were dissolved in toluene (50 c.c.) and heated under reflux for 2½ hr. The solvent and tetramethylsuccinonitrile (0·3 g., 11%) were removed by steam-distillation, the residue was extracted with ether, the extract dried ($MgSO_4$), and the solvent removed. When the residual oil (6·15 g.) was passed through a column of alumina there were obtained *p*-benzenesulphonamidophenol, m. p. 154°, and *4-(2-cyano-2-propoxy)-N-(2-cyano-2-propyl)-N-benzenesulphonanilide* (II) (0·4 g., 6·5%), which crystallized from ether–light petroleum (b. p. 20—40°); m. p. 92—93° (Found: C, 62·9; H, 5·6; N, 10·95; S, 8·3. $C_{20}H_{21}O_3N_3S$ requires C, 62·6; H, 5·4; N, 11·0; S, 8·35%). Its infra-red spectrum showed the typical CN band at 4·48 μ and a band at 12·04 μ, typical of *p*-substituted benzene derivatives, and was generally similar to that of *p*-benzenesulphonamidophenol in the 6·5—9·5 μ region, but had no absorption in the 3 μ region, thus showing absence of OH and NH groups.

No identifiable compounds were obtained from similar reactions with *p*-benzoquinone di-*p*-toluenesulphonimide (Adams and Nagarkatti, *J. Amer. Chem. Soc.*, 1950, **72**, 4601) or *p*-benzoquinone dibenzimide (Adams and Anderson, *ibid.*, p. 5154).

Reaction of Nitric Oxide with 2-Cyano-2-propyl Free Radicals.—A slow stream of nitric oxide, prepared as described by Gatterman ("Laboratory Methods of Organic Chemistry," Macmillan & Co., London, 1938), mixed with dry carbon dioxide, was passed through a gently refluxing solution of αα′-azo*iso*butyronitrile (3·28 g.) in benzene (100 c.c.). At first a deep green colour, indicative of a tertiary nitroso-compound, was formed but this gradually faded. Heating was continued for 2½ hr. to complete the decomposition of the azo-compound and the reaction mixture was then freed from nitric oxide by flushing with a rapid stream of carbon dioxide. The resulting solution was distilled in steam to remove benzene and tetramethylsuccinonitrile, and the residue was extracted with ether, dried ($MgSO_4$), and crystallised from ether–light petroleum (b. p. 20—40°) (yield, 1·54 g., 50%). The *tri-(2-cyano-2-propyl)hydroxylamine* (III) had m. p. 77—78° and was slightly soluble in water (Found: C, 61·4; H, 7·9; N, 23·4. $C_{12}H_{18}ON_4$ requires C, 61·5; H, 7·7; N, 23·9%). It was not affected by warming with dilute aqueous sodium hydroxide, but after refluxing for 8 hr. with 5% sulphuric acid, 50% of the material had decomposed, giving a solution which contained acetone (dinitrophenylhydrazone, m. p. and mixed m. p. 126°) but no products which could be extracted with ether under either acid or alkaline conditions.

*Reaction of Nitroso*iso*butyronitrile with 2-Cyano-2-propyl Radicals.*—A solution of nitroso*iso*butyronitrile (Piloty, *loc. cit.*) (1·95 g.) and αα′-azo*iso*butyronitrile (6·56 g.) in benzene (100 c.c.) was heated under reflux. The blue solution became green after 5 min. and then colourless in 30 min. The heating was continued for 2½ hr. and volatile products were then removed by steam-distillation. The residue (III), after ether extraction and crystallisation, had m. p. and mixed m. p. 78° (yield, 1·1 g., 25%).

TABLE 1. *Tertiary hydroxylamines*, $NC{\cdot}CMe_2{\cdot}NAr{\cdot}O{\cdot}CMe_2{\cdot}CN$.

			Found, %			Required, %		
Ar group	M. p.	Yield, %	C	H	N	C	H	N
C_6H_5	95°	75	69·4	7·0	17·2	69·1	7·0	17·2
o-$Me{\cdot}C_6H_4$	85	70	70·2	7·3	16·3	70·0	7·4	16·3
m-$Me{\cdot}C_6H_4$	74	60	70·2	7·8	16·3	,,	,,	,,
p-$Me{\cdot}C_6H_4$	89	35	70·2	7·7	16·1	,,	,,	,,
o-$Cl{\cdot}C_6H_4$	95	60	60·8	6·0	15·3	60·5	5·8	15·1 *
m-$Cl{\cdot}C_6H_4$	106	47	60·6	5·7	15·0	,,	,,	,, †
p-$Cl{\cdot}C_6H_4$	96	60	60·7	5·7	15·1	,,	,,	,, ‡
s-$Me_3C_6H_3$	122	20	71·8	8·2	14·5	71·6	8·0	14·7

* Found: Cl, 12·8. Required: Cl, 12·8%. † Found: Cl, 12·9%. ‡ Found: Cl, 12·2%.

Reaction between Diphenylnitrosamine and 2-Cyano-2-propyl Radicals.—Diphenylnitrosamine (5·94 g.) and αα′-azo*iso*butyronitrile (9·84 g.) were refluxed in toluene for 2½ hr. After steam-distillation and ether-extraction of the residue there were obtained 3·92 g. (56%) of (III), m. p. and mixed m. p. 78°, together with diphenylamine (m. p. and mixed m.p. 52°). Tetraphenylhydrazine, which yields diphenylnitrogen free radicals when heated, also gives diphenylamine, but no tertiary amine, when heated in solution with αα′-azo*iso*butyronitrile (personal communication from Dr. M. C. Ford).

Reactions of Aromatic Nitroso-compounds with 2-Cyano-2-propyl Radicals.—The nitroso-compounds were prepared by the general method of Lutz and Litton (*J. Org. Chem.*, 1937, **2**, 68). The following preparation is typical. αα′-Azo*iso*butyronitrile (16·4 g., 0·1 mole) and nitrosobenzene (5·35 g., 0·05 mole) were refluxed in toluene (200 c.c.) for 2½ hr. The green colour of the nitroso-compound disappeared in a few minutes and the solution became yellow. After steam-distillation, the residue, which was partly soluble in water, was extracted with ether, dried ($MgSO_4$), and crystallised by addition of light petroleum (b. p. 20—40°).

TABLE 2.

	Secondary hydroxylamines, Ar·N(OH)·CMe_2·CN							Azo-compounds, ArN:NAr	Arylacetamides, Ar·NHAc
		Found, %			Required, %				
Ar group	M. p.	C	H	N	C	H	N	M. p.	M. p.
C_6H_5	77°	68·3	6·8	15·8	68·2	6·8	15·9	66°	114°
o-Me·C_6H_4	66	(identified by its infra-red spectrum showing OH band at 3·07 μ)						55	110
m-Me·C_6H_4 ...	72	69·5	7·5	14·7	69·5	7·4	14·7	55	65
m-Cl·C_6H_4	98	57·8	5·5	13·3	57·0	5·2	13·3 *	99	72
p-Cl·C_6H_4	76	57·2	5·2	13·1	57·0	5·2	13·3 †	188	176

* Found: Cl, 17·1. Required: Cl, 16·9%. † Found: Cl, 16·7%.

TABLE 3. *Absorption bands taken from the infra-red spectra of* (III) *and compounds listed in Tables* 1 *and* 2 *in the* 7·5—12 μ *region.*

[All these compounds show bands at 4·5 μ (CN group) and at 7·22 and 7·33 μ (CMe_2 group). The secondary hydroxylamines (VI) also show bands at 3·0—3·1 μ (OH group).] *

Wave-lengths, μ:	7·5—8	8—8·5	8·5—9	9—9·5	9·5—10	10—10·5	10·5—11	11—12
$(CMe_2{\cdot}CN)_2N{\cdot}O(CMe_2{\cdot}CN)$	—	8·24 s	8·60 s	—	9·84 m	10·14 m	10·65 w	11·04 m
		8·42 m	8·77 s	—	—	10·50 s	10·75 s	11·98 s
Tertiary hydroxylamines (IV)								
Ar = Ph	7·80 m	8·19 m	8·59 s	9·30 s	9·78 w	10·00 w	10·65 w	11·15 m
		8·35 s	—	—	9·85 s	10·12 w	10·99 s	11·45 s
						10·41 s	—	11·83 m
Ar = *o*-Me·C_6H_4	7·76 m	8·15 m	8·51 s	9·00 s	9·51 m	10·30 s	10·52 w	11·07 m
		8·24 m	8·60 s	—	9·59 m	—	10·78 w	11·35 s
		8·40 s	—	—	9·83 m	—	—	11·60 w
Ar = *m*-Me·C_6H_4	7·64 w	8·04 m	8·51 s	9·15 m	9·61 w	10·03 w	10·57 m	11·25 s
		8·17 s	8·62 s	—	9·75 m	10·37 s	10·68 m	11·39 m
		8·31 s	—	—	—	—	10·95 s	11·88 s
		8·40 s						
Ar = *p*-Me·C_6H_4	7·82 w	8·15 m	8·60 s	—	9·62 w	10·30 m	10·58 w	11·05 w
		8·26 w	8·98 s	—	9·87 m	10·39 m	10·79 w	11·40 s
		8·35 s	—	—	—	—	—	11·95 m
		8·45 m	—	—	—	—	—	—
Ar = *o*-Cl·C_6H_4	7·94 m	8·20 s	8·64 s	9·48 s	9·65 s	10·35 s	10·76 m	11·08 m
		8·24 m	—	—	9·85 m	10·45 s	—	11·40 s
		8·36 s	—	—	—	—	—	11·60 m
Ar = *m*-Cl·C_6H_4	7·75 w	8·17 w	8·60 s	9·18 m	9·80 m	10·02 m	10·74 s	11·10 w
	7·88 w	8·35 s		9·30 s	—	10·38 s	—	11·35 s
Ar = *p*-Cl·C_6H_4	7·86 m	8·20 w	8·58 s	9·06 m	9·82 w	10·47 s	10·65 w	11·12 s
		8·26 w	8·65 s	9·20 s	9·90 s	—	10·82 w	11·45 s
		8·35 m	—	—	—	—	—	11·95 s
Ar = *s*-$Me_3C_6H_3$	—	8·13 m	8·52 s	—	9·64 m	10·20 s	10·61 w	11·10 m
		8·23 m	8·60 s	—	9·82 m	10·33 m	10·69 w	11·40 s
		8·37 w	—	—	—	10·45 m	10·76 w	11·58 s
Secondary hydroxylamines (VI)								
Ar = Ph	7·65 s	8·04 m	8·55 s	9·25 w	9·72 s	10·31 w	10·62 s	11·18 s
	7·75 w	8·20 s	8·67 w	—	9·82 s	—	—	11·57 s
		8·40 s	—	—	9·97 w	—	—	11·96 w
Ar = *o*-Me·C_6H_4	7·68 s	8·04 s	8·57 s	—	9·56 s	10·15 m	10·56 s	11·25 s
	—	8·19 s	8·97 s	—	9·76 s	—	10·68 w	11·31 w
		8·35 m	—	—	9·90 w	—	10·76 w	11·45 s
		8·43 m	—	—	—	—	—	11·70 w
Ar = *m*-Me·C_6H_4	7·75 s	8·20 s	8·53 s	9·13 m	9·70 s	10·03 w	10·63 s	11·40 s
	7·95 s	8·39 s	—	—	9·97 w	10·50 s	—	11·55 m
Ar = *m*-Cl·C_6H_4	7·68 s	8·03 s	8·57 s	9·15 s	9·74 s	10·06 s	10·59 s	11·45 m
	7·93 s	8·21 s	—	9·35 s	9·97 w	10·10 w	10·80 m	11·65 s
		8·38 s	—	—	—	10·27 w	—	—
Ar = *p*-Cl·C_6H_4	7·68 m	8·06 s	8·51 w	9·17 s	9·67 s	—	10·56 s	11·25 s
	7·77 m	8·18 s	8·55 s	—	9·95 s	—	—	11·44 m
		8·29 s	8·97 m	—	—	—	—	—

* s = Strong absorption; m = moderate absorption; w = weak absorption.

The tertiary hydroxylamines were insoluble in aqueous alkali but dissolved in warm dilute mineral acids. *ON*-Di-(2-cyano-2-propyl)-*N*-phenylhydroxylamine (8 g.) was refluxed for 8 hr. in 10% hydrochloric acid (300 c.c.). The solution had then darkened considerably. From a 10-c.c. sample of the aqueous solution, there was isolated 0·13 g. of acetone 2 : 4-dinitrophenylhydrazone. An eventual recovery of 1·86 g. of unchanged trisubstituted hydroxylamine being taken into account, the calculated recovery of acetone derivative is 0·17 g. for the hydrolysis of one *iso*propyl group and 0·35 g. for hydrolysis of both. No tractable products could be isolated from the neutralised hydrolysate.

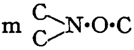
Reduction of ON-*Di*-(2-*cyano*-2-*propyl*)-N-*phenylhydroxylamine* (IV; Ar = Ph).—3 G. of zinc dust were added slowly to a cold solution of the hydroxylamine (3·0 g.) and powdered anhydrous sodium acetate (0·6 g.) in acetic anhydride (18 c.c.). The mixture was heated gently until it became clear and was then refluxed for not more than 10 min.; a red colour developed. Acetic acid (5 c.c.) was added, the mixture was filtered hot, and the residue washed with a little boiling acetic acid. The total filtrate was, while boiling, treated cautiously with sufficient water to destroy the free acetic anhydride, then cooled in ice-water, made alkaline (10% sodium hydroxide), and extracted with ether. The residue (1·5—2·5 g.) from the dried ether solution was chromatographed through alumina, and from the column there were isolated in the following order azobenzene (0·1 g., m. p. and mixed m. p. 66°), unchanged trisubstituted hydroxylamine, *N*-(2-cyano-2-propyl)-*N*-phenylhydroxylamine (0·3 g.) (VI; Ar = Ph), and acetanilide (0·8 g.).

Reductions of the other trisubstituted hydroxylamines were carried out similarly. From the *o*-chlorophenyl, mesityl, and *p*-tolyl compounds the secondary hydroxylamines could not be obtained even on prolonged heating, though correspondingly more aryl acetamides were then formed. The new reaction *products* are listed in Table 2.

Reduction of N-(2-*Cyano*-2-*propyl*)*aniline*.—This aniline (IX; Ar = Ph) (Bucherer and Grolee, *Ber.*, 1906, **39**, 986) (2 g.) was dissolved in acetic acid or anhydride (20 c.c.) and zinc dust (2 g.) was added. The mixture was heated for a few minutes under reflux, filtered, made alkaline after cooling, and extracted with ether. On addition of light petroleum (b. p. 20—40°) to the ether solution, acetanilide (0·5 g.) crystallised (m. p. and mixed m. p. 114°).

Reactions of s-*Trinitrobenzene and* 2 : 4-*Dinitrochlorobenzene with* 2-*Cyano*-2-*propyl Radicals*.—In each case, the nitro-compound (0·04 mole) was dissolved in toluene (100 c.c.) with αα′-azo*iso*butyronitrile (0·04 mole). After refluxing for 2½ hr., the solution was distilled in steam and from the distillate there was obtained tetramethylsuccinonitrile (75—80%). The nitro-compounds were recovered quantitatively from the residue of the steam-distillation by ether-extraction.

Few infra-red spectra of compounds containing N–O–C or N–O–H bands have been described hitherto, and it was hoped that the data collected in Table 3 would provide evidence for diagnostic characterisation of the N–O link. Aliphatic ethers are known to have rather wide absorption bands between 8 and 9 μ owing to flexing of the covalencies attached to the oxygen atom, whilst tertiary amines have similar bands in the 9—10 μ region.

Our tertiary hydroxylamines $R_1R_2N{\cdot}OR_1$ have at least 4 pronounced and sharply defined bands in the 8—9 μ region, most of which also appear in the secondary hydroxylamines $R_1R_2N{\cdot}OH$. Discrimination between the very similar covalencies of the system  $\genfrac{}{}{0pt}{}{C}{C}\!>\!N{\cdot}O{\cdot}C$ is difficult, for any movement of the nitrogen atom necessarily affects the bond angles and bond lengths of all the attached groups. Though no definite assignment to these covalencies can be made, we suggest that at least one of the bands regularly occurring in the 8—9 μ region is due to the N–O bond. Grouped bands are also found in the 9·5—11·5 μ region; this wave-length is shorter than those at which characteristic out-of-plane absorptions of aromatic substituents can be observed, and so these bands too can probably be ascribed to bending frequencies associated with the nitrogen or oxygen atoms of the hydroxylamines.

This work has been carried out during the tenure by one of us (B. A. G.) of a Post-doctorate Research Fellowship of the National Research Council of Canada, and subsequently of a Merck Post-doctorate Fellowship of the Merck & Co. Ltd., Montreal, Canada.

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