Nitroxide Radical Formation by the Addition of Aromatic *C*-Nitroso-compounds to Olefins

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E.s.r. measurements indicate that aromatic nitroso-compounds add to olefins by one-electron transfer from C=C to N=O bonds to give nitroxide radicals. The spectra of such radicals formed from 2,4,6-trichloronitrosobenzene and olefins having a wide range of substituent groups are tabulated. Possible reactions subsequent to the initial addition are proposed.

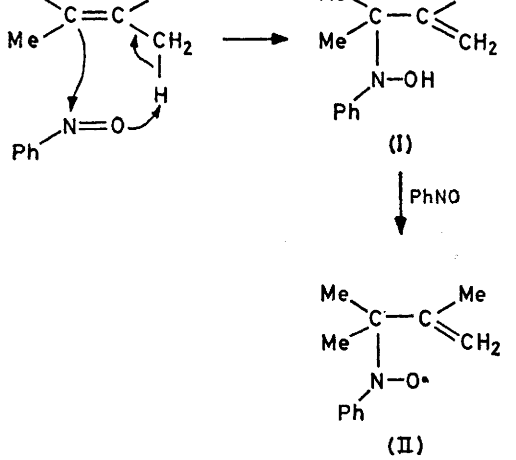
THE finding that the reaction between nitrosobenzene and phenylhydroxylamine to yield azoxybenzene is not a direct molecular condensation but a one-electron transfer followed by the dimerisation of phenylnitroxide radicals, PhNHO·,[1,2] has led us to search for other unsuspected radical-producing reactions of nitrosobenzenes. We now report experimental evidence to show that additions of *C*-nitroso-compounds to olefins are free radical reactions in which nitroxide radicals are at once formed by one-electron transfer from a C=C to a N=O bond.

The early chemistry of the addition of nitroso-compounds to olefins[3] is confused. Nitrosobenzene is a good dienophile but gives an anomalous cyclic product with cycloheptatriene;[4] with mono-olefins it may yield nitrones, adducts, $R_2C{:}CR_2,2PhNO$, and their breakdown products, or hydroxylamines.

Few e.s.r. studies of such reactions have been made though in 1963 Ginsburg *et al.*[5] reported that reactions between trifluoronitrosomethane and fluorinated olefins gave the e.s.r. spectra of radicals, $F_3C{-}N(O\cdot){-}CF_2{-}C\leqslant$ and that the reaction between trifluoronitrosomethane and styrene to give an adduct $2F_3CNO,PhCH{:}CH_2$ was accompanied by the production of paramagnetic particles. Nitroxide radicals were also formed from acrylates and from vinyl acetate. Later, Sullivan[6] obtained an immediate e.s.r. signal from the admixture under nitrogen of nitrosobenzene in benzene with 2,3-dimethylbut-2-ene. The signal which gradually increased in strength and resolvability eventually corresponded to that of the tertiary nitroxide (II). Following Banks *et al.*[7] he considered (II) to result from a cyclic ' ene ' addition (Scheme 1) and subsequent oxidation of the hydroxylamine (I) by nitrosobenzene, for previously Hamer and Macaluse[8] had found that azoxybenzene is a major reaction product of reactions between nitrosobenzene and many olefins.

Later Knight[9] isolated (I) from this reaction and oxidised it to the radical (II). A few other additions to which Scheme 1 may be cogent have been reported by later workers[10,11] but many olefins which cannot undergo ' ene ' addition also give nitroxides and clear e.s.r. spectra of radicals $RCH_2N(Ar)O\cdot$ and $R^1R^2CHN(Ar)O\cdot$ can be obtained immediately after admixture under nitrogen of nitrosobenzenes in benzene with olefins containing a wide range of substituents.

Observations.—In preliminary trials we obtained nitroxide spectra from oct-1-ene, cyclohexene, butadiene, and cycloheptatriene upon treatment under nitrogen with nitrosobenzene or *p*-chloronitrosobenzene. The hyperfine structures of these spectra gradually changed with time (*cf.* ref. 6) but took hours and sometimes days for complete disappearance. To simplify the e.s.r. line structures and so facilitate identification use was then made of easily accessible[12] 2,4,6-trichloronitrosobenzene which we commend as a stable spin-trapping reagent with which the structure of any adduct can clearly be deduced from the resulting e.s.r. spectrum. When a few (<10) mg of this compound, dissolved in 3—5 ml of warm benzene, were added to nitrogen-blown mixtures of 2—4 ml (or g) of an olefin in *ca.* 10 ml of benzene the



SCHEME 1

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resulting solutions gave within a few minutes the clearly defined spectra summarised in Tables 1—3. These reached their maximum intensity within 30 min though compounds containing ester or cyanide groups took longer for distinct structure development unless higher concentrations of the nitroso-compound were used whilst particularly strong signals were soon obtained from unsaturated alcohols. The reacting mixtures were pale blue initially but over hours gradually changed through green to pale yellow presumably on account of the slow development of hexachloroazoxybenzene.

TABLE 1

Splitting constants (G) of initial nitroxide radicals from olefinic compounds $CH_2{:}CHR$

Compound	a_N	a_{CH_2}	$a_{H\text{-}meta}$	Compound	a_N	a_{CH_2}	$a_{H\text{-}meta}$
Non-1-ene	12.8 ± 0.05	9.8 ± 0.05	0.6	1,3-Butadiene	12.8 ± 0.1	9.6 ± 0.1	0.6
Oct-1-ene	12.8 ± 0.1	9.7 ± 0.05	0.6	Vinyl cyanide	12.5 ± 0.05	9.3 ± 0.1	
Styrene	12.35 ± 0.05	9.05 ± 0.05	0.6	Methyl acylate	12.8 ± 0.05	9.45 ± 0.01	0.7
β-Pinene	12.7 ± 0.1	9.4 ± 0.1	0.7	Allyl alcohol	12.45 ± 0.05	10.6 ± 0.05	0.7
Saffrole *	12.7 ± 0.1	9.7 ± 0.1		Methyl vinyl ketone	12.5 ± 0.1	8.4 ± 0.1	0.7

* Initial very weak signal.

TABLE 2

Splitting constants (G) of nitroxide radicals from olefinic compounds $R^1CH{:}CHR^2$

Compound	a_N	a_{CH}	Compound	a_N	a_{CH}
Cyclohexene	12.8 ± 0.05	6.7 ± 0.05	Diethyl fumarate	12.6 ± 0.05	5.6 ± 0.1
Oct-2-ene	13.1 ± 0.1	8.1 ± 0.1	Diethyl maleate	12.65 ± 0.05	5.5 ± 0.1
1,2-Dichloroethene	13.1 ± 0.05	5.2 ± 0.05	1,2-Dibenzoylethylene	12.5 ± 0.05	5.45 ± 0.05
trans-Stilbene	12.6 ± 0.05	5.9 ± 0.1	Methyl cinnamate	12.5 ± 0.1	5.7 ± 0.1
Cycloheptatriene †	12.9 ± 0.1	*ca.* 5			

† See Experimental section.

All the olefins $CH_2{:}CHR$ which we tested (Table 1) at once give the e.s.r. spectra of nitroxides $ArN(O\cdot)\text{-}CH_2\text{–}$ the nine main lines [3 × (1,2,1)] of which show also the small (1,2,1) $a_{H\text{-}meta}$ splitting of the trichlorophenyl group. With most of these olefins secondary six-line spectra of a nitroxide $ArN(O\cdot)CH<$ gradually appear, increase to a steady intensity, and then persist for many hours and sometimes for days as the initial nine-line spectra slowly decay. The lines of these secondary spectra (Table 4) are too broad (>2 G) to show $a_{H\text{-}meta}$ splittings. In this respect they correspond to the six-line spectra obtained at once from olefins $R^1CH{:}CHR^2$ or $R^1CH{:}CR^2_2$ (Tables 2 and 3). The latter reach their maximum intensities in 10—30 min according to the compound tested and then persist for many hours though in some cases slight changes of splitting constant and line width slowly occur.

TABLE 3

Splitting constants (G) of initial nitroxide radicals from olefinic compounds $R^1CH{:}CR^2_2$

Compound	a_N	a_{CH}	Compound	a_N	a_{CH}
α-Pinene	12.5 ± 0.2	5.7 ± 0.2	α-Terpineol	12.7 ± 0.05	6.3 ± 0.1
Triphenylethene	12.7 ± 0.1	5.25 ± 0.1	Citronellol	12.7 ± 0.05	5.4 ± 0.05
Trichloroethene	12.7 ± 0.2	5.6 ± 0.2			

TABLE 4

Splitting constants (G) of secondary (stable) nitroxide radicals from olefinic compounds $CH_2{:}CHR$

Compound	a_N	a_{CH}	Compound	a_N	a_{CH}
Non-1-ene	13.0 ± 0.1	5.0 ± 0.1	Vinyl cyanide	12.7 ± 0.1	5.8 ± 0.1
Oct-1-ene	13.1 ± 0.1	8.0 ± 0.1	Methyl acylate	12.9 ± 0.1	7.4 ± 0.1
Butadiene	12.8 ± 0.05	5.7 ± 0.05	Saffrole	12.7 ± 0.1	5.2 ± 0.1
			Methyl vinyl ketone	12.3 ± 0.1	4.2 ± 0.1

As long as unchanged trichloronitrosobenzene is present in the reaction mixtures, as shown by the persistence of a blue or green colour, the initial e.s.r. spectra are not completely destroyed by the admission of a little air and soon regenerate in a closed vessel. The long-lived spectra, *e.g.* those of Table 4, seem to be stable in air. The nitroxide spectra of Tables 1—4 all have *g* values of 2.006 25 ± 5 × 10^{-5}; for this the trichlorophenyl group is evidently the controlling factor.

Suggested Reaction Mechanisms.—In this exploratory study we have observed the early stages of reaction sequences in which pseudo-equlibria between nitroxide formation and decay have been attained under conditions in which the olefin is present in very large excess (10^2—10^3 fold).

Tables 1 and 3 show clearly that the trichloronitrosobenzene has added to each olefin at the carbon atom indicative of a free radical and not a polar addition to the C=C bond. In particular the additions to non-1-ene, styrene, methyl acrylate, and vinyl cyanide all occur at the $\mathrm{CH_2}$ group. This accords with free radical addition but not that of a polar reagent such as hydrogen chloride.

Since static solutions have been examined in the spectrometer the persisting nitroxide spectra listed above cannot be those of biradicals, *e.g.* $\mathrm{ArN(O\cdot)CH_2{-}\dot{C}HR}$ containing trivalent carbon, since in the liquid phase at room temperature simple aliphatic carbon radicals have lifetimes of milliseconds; again no hyperfine line structure indicative of such radicals has been detected. Consequently following the slow addition of reaction (1) of Scheme 2 the tervalent carbon centre must rapidly be

$$\mathrm{ArN{:}O + CH_2{:}CHR \longrightarrow ArN(O\cdot)CH_2{-}\dot{C}HR}\ \text{slow} \tag{1}$$

$$\mathrm{2ArN(O\cdot)CH_2{-}\dot{C}HR \longrightarrow [ArN(O\cdot)CH_2{-}CHR{-}]_2} \tag{2}$$

$$\mathrm{ArNO + ArN(O\cdot)CH_2{-}\dot{C}H{-}CHR_2 \longrightarrow ArN(O\cdot)CH_2{-}CH{=}CR_2 + ArNHO\cdot} \tag{3}$$

$$\mathrm{ArNO + ArN(O\cdot)CH_2{-}\dot{C}HR \longrightarrow ArN(O\cdot)CH{=}CHR + ArNHO\cdot} \tag{4}$$

$$\mathrm{ArNO + ArN(O\cdot)CH_2{-}\dot{C}HR \longrightarrow ArN(O\cdot)CH_2{-}CHR{-}N(O\cdot)Ar} \tag{5}$$

SCHEME 2

destroyed by any of the reactions (2)—(5) which are well known in free radical chemistry. Slower decompositions of the nitroxide radicals themselves to give nitrones, hydroxylamines, *etc.*, may then follow.

Each of the reactions (2)—(5) can be exemplified from chemical literature.[3] Disproportionation and telomerisation are alternatives to (2); the latter can occur in reactions of trifluoronitrosomethane, with (5); as the chain-ending reaction. The ultimate products of additions (5) have been represented as oxadiazole oxides[13] and not biradicals. Reactions (3) and (4) lead to the formation of azoxybenzenes through the fairly fast dimerisation[1,2] of $\mathrm{ArNH\dot{O}\cdot}$ radicals; (3) is effectively the 'ene' reaction sequence as observed by Sullivan and others,[6,10,11] but (4) may well be a route of formation of the nitroxide radicals of Table 4. The formation of αβ-unsaturated hydroxylamines has been reported by Ginsburg *et al.*[5,14] Further oxidation by nitrosobenzenes could of course yield nitrones and reductions by arylnitroxides $\mathrm{ArNHO\cdot}$ would yield hydroxylamines.

Two of these additions merit special comment. (a) Radical formation by addition to butadiene clearly shows that cyclisation to a 2-aryl-3,6-dihydro-2*H*-1,2-oxazine is a stepwise process and not a concerted Diels–Alder addition; in fact 1,4-addition of two molecules of a nitrosobenzene to a butadiene has already been reported[15] and radical addition has been indicated by a product study.[16] (b) Our specimen of cycloheptatriene gives a confused e.s.r. signal probably that of a mixture of nitroxides with a_N 12.9 G. Addition could of course occur at any of the six unsaturated carbon atoms, and in this case stepwise cyclisation of free radical type would be expected[17,18] to give a five-membered ring adduct, as found,[4] rather than a six-membered ring product.

Confirmation of Scheme 2 will necessitate both quantitative spectral and product studies of individual reactions, but we consider that the present observations are of sufficient importance to merit publication now.

EXPERIMENTAL

Materials.—2,4,6-Trichloronitrosobenzene, prepared by the method of Holmes and Bayer,[12] was crystallised from ethanol as its dimer, m.p. 145°. The liquid olefins were obtained from freshly opened bottles of 'Reagent' quality materials or were freshly fractionated before use. A g.l.c. test showed that the α-pinene still contained 1% of β-isomer but the e.s.r. spectra gave the two signals initially at comparable intensities. Again oct-1-ene still contained some 2-isomers and cycloheptatriene, b.p. 112—113°, n_D^{23} 1.519, was evidently a mixture also. Slight amounts (*ca.* 0.01—0.1%) of phenolic inhibitors were not removed from the samples of styrene, methyl acrylate, or vinyl cyanide. Saffrole was examined for its historical interest.[19]

E.s.r. measurements were made with a Varian E4 instrument and the spectra were calibrated by comparison with Frémy's salt which was also used to obtain *g* values.

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