Indirect Detection of Carbenes by Electron Spin Resonance: Triplet Trapping

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Transient triplet carbenes have been converted into relatively long-lived iminoxyls by reaction with nitric oxide and hence been detected indirectly by e.s.r. spectroscopy. The process is formally analogous to spin trapping of monoradicals by nitrones and nitroso-compounds. Triplet nitrenes could not be trapped in this way.

EVIDENCE for the transient formation of carbenes and nitrenes in chemical reactions is usually drawn from product studies,[1] reference being made to a known reaction(s) of these intermediates and the effect which additives (sensitisers, quenchers) have on the product distribution. Direct observation of triplet carbenes and nitrenes in solution by e.s.r. is not possible and hence we have attempted to develop an indirect method for their detection by a simple modification of the now well established ' spin trapping ' method.[2a]

' Spin trapping ' involves the conversion of a transient radical into a long-lived one (usually nitroxide) by reaction with a diamagnetic scavenger (usually nitrone or nitroso-compound) [equation (i)]. For the analogous ' triplet trapping ' it is necessary to replace the diamagnetic scavenger by a long-lived paramagnetic scavenger,

$$R \cdot X + R'NO \longrightarrow RN(\dot{O})R' \qquad (i)$$

the one most closely studied in this work being nitric oxide [equation (ii)].[2b] This should give iminoxyls[3] from

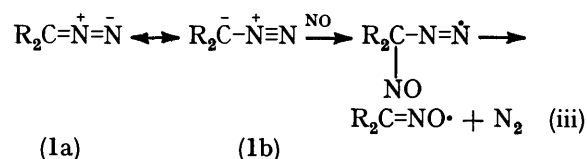$$\dot{T} + NO \longrightarrow T = N - \dot{O} \qquad (ii)$$
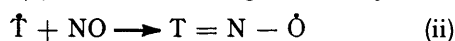
carbenes and diazinoxyls[4] from nitrenes from whose spectra it should be possible to derive structural information about the first-formed triplet.

Carbene Trapping.—From diazo-compounds. These were the most convenient sources of carbenes and 31 were examined (Table 1). In each case a thoroughly degassed solution (freeze–pump–thaw) of the diazo-compound in petroleum or petroleum–benzene was saturated with nitric oxide and then irradiated with a 1 kW or 100 W mercury vapour lamp in the cavity of the e.s.r. spectrometer. Some diazo-compounds reacted with nitric oxide to give iminoxyls before irradiation. In these cases the temperature of the cavity was lowered until the thermal reaction was suppressed and iminoxyls were generated only on commencement of irradiation. 22 Of the 31 diazo-compounds studied gave iminoxyls in this way. Six of the remaining diazo-compounds did not give iminoxyls over the temperature range —60 to +60 °C with or without irradiation. Prolonged irradiation of two of these with nitric oxide at —100 °C in frozen petroleum followed by slow warming to room temperature also failed to give iminoxyls. The other three gave iminoxyls only at >20 °C, the concentrations of which were not increased by irradiation.

We have shown by visible spectroscopy that the thermal reaction of nitric oxide with certain diazo-compounds proceeds more rapidly than the thermal decomposition of the diazo-compounds. The former reaction has been previously formulated[5] as indicated [equation (iii)]. The relative importance of contributions (1a and b) to the structure of the diazo-compound can be gauged from the stretching vibration of the N–N bond.[6] Since it seemed

$$R_2C=\overset{+}{N}=\overset{-}{N} \longleftrightarrow R_2\overset{-}{C}-\overset{+}{N}\equiv N \overset{NO}{\longrightarrow} R_2C-N=\overset{\cdot}{N} \longrightarrow$$
$$\underset{NO}{|}$$
$$R_2C=NO \cdot + N_2 \qquad (iii)$$

(1a)   (1b)

reasonable to expect that diazo-compounds whose structures resembled (1a) more closely than (1b) [equation (iii)] should react more readily with nitric oxide we attempted to correlate ν_{N-N} with the temperature below which the thermal reaction was suppressed (T_{min}). For the series of diazo-compounds, alkyl aryl (four examples)–diaryl (six examples)–diacyl (five examples), T_{min} (*ca.* —50; 0—40; 20—40 °C, respectively) appears to increase as ν_{N-N} (2 037—2 043; 2 040—2 065; 2 130—2 190 cm⁻¹, respectively) increases. However, the correlation is not linear and we cannot yet explain the apparently anomalous unreactivity of several of the diazo-compounds listed in Table 1. An alternative explanation of iminoxyl formation from triplet carbene entails hydrogen abstraction by triplet carbene from solvent followed by coupling of the resulting alkyl radicals with nitric oxide. This procedure has been used previously in gas phase[7] and matrix[8] studies of hydrogen abstraction by triplet methylene. Although it is conceivable that the nitroso-compound so formed in our system could then rapidly tautomerise to oxime which would in turn yield iminoxyl on oxidation we do not favour this route. In other work[9] we have shown that when primary alkylnitroso-compounds (*e.g.* PhCH₂NO) are generated under photolytic conditions, iminoxyls (*e.g.* PhCH=NO·) are not detected by e.s.r., nor for that matter are the corresponding dialkyl nitroxides.

Sensitisers.—The effect of sensitisers was most closely studied with ethyl diazomalonate since complementary product analyses have been reported.[10] Irradiation of this diazo-ester with nitric oxide in a Pyrex tube at room temperature gave no iminoxyl. However, with the triplet sensitiser benzophenone present, the rate of iminoxyl production was greater (by about an order of

TABLE 1
Radicals produced from diazo-compounds and nitric oxide

| Diazo-compounds	Solvent	Thermal[a] (°C)	Photo-chemical[b] (°C)	Iminoxyl hyperfine splitting (G)	Nitroxide hyperfine splitting (G)	Ref.[c]
(1; R = H)	Petroleum	>0	<0	a_N 31.5, a_H 1.4 (2 H)		3, 19
(1; R = Et)	Petroleum	>0	<0	a_N 31.8, a_H 1.45 (2 H), 0.5 (1 H)		3
				a_N 30.0[d]		3
(1; R = OMe)	Petroleum	>22	<22	a_N 32.2, a_H 1.43 (2 H), 0.5 (1 H)	a_N 14.4 (w)	3, 20
				a_N 30.0[d]		
(2)[e]	Petroleum		0—20	a_N 30.5, a_H 2.63 (1 H)	a_N 12.3, a_H 5.3 (4 H)	3, 20
(3)	Petroleum–dioxan		20—40	a_N 31.6, a_H 2.9 (1 H)	a_N 14.25 (w)	3
(3)	Petroleum–benzene		20—40	a_N 31.6, a_H 2.9 (1 H)	a_N 14.5, a_H 4.3 (2 H); a_N 7.5	3
(4)	Petroleum–benzene		20	a_N 31.2, a_H 3.0 (1 H)	a_N 12.3, a_H 5.3 (4 H)	3
(4)	Petroleum–dioxan					
(4)	Petroleum–Pr$^i_2$O				a_N 14.0	
(5; R¹ = R² = H)	Petroleum	>20	<20[f]	a_N 31.4, a_H 5.8 (1 H), 1.4 (2 H)		3, 21
				a_N 29.2, a_H 25.9 (1 H)		22
(5; R¹ = MeO, R² = H)	Petroleum	<60		a_N 31.4, a_H 5.6 (1 H), 1.3 (2 H)		3
(5; R¹ = NO₂, R² = H)	Petroleum	>20			a_N 14.5	3
(5; R¹ = H, R³ = Cl)	Petroleum			a_N 32.2, a_H 6.5 (1 H), 2.5 (2 H)		3
				a_N 29.4, a_H 25.9 (1 H)		
(6; R = Me)	Petroleum	>−50	<−50	a_N 31.0[g]	a_N 13.15 (w)	21, 23
(6; R = Et)	Petroleum	>−50	<−50	a_N 31.5[g]	a_N 13.50 (w)	19
(6; R = Pr^i)	Petroleum	>−50	<−40	a_N 29.9[g]		19
(6; R = Bu^t)	Petroleum	>−60	<−60	a_N 31.0[g]		23, 24
				a_N 30.9, a_H 0.87 (9 H)		
				a_N ca. 31.0, a_H 0.15 (many H)		
(7; R = H)[h]	Petroleum	>20	<20	a_N 31.0, a_H 0.5 (2 H)	a_N 13.8	19, 22
(7; R = Ph)	Petroleum–benzene					
(8)[h]	Petroleum–benzene					
(9)	Petroleum–benzene					
Me₂C=N₂	Petroleum	>−40	<−40	a_N 30.6, a_H 1.6 (6 H)	a_N 12.6	19, 22
(9a; R¹ = PhCO, R² = H)	Petroleum	>10	<10	a_N 28.6, a_H 5.5 (1 H),[i]	a_N 6.7	3
(9a; R¹ = CO₂Et, R² = H)	Petroleum		20	a_N 31.3, a_H 3.25 (1 H)	a_N 6.6, a_H 1.0 (1 H)	23
(9a; R¹ = Ph, R² = PhCO)	Petroleum[j]			a_N 31.5, a_H 1.0 (2 H)	a_N 7.0, a_H 14.0	
(10)					a_N 14.0, a_H 7.0	
(11)	Petroleum	>−30	<−30	a_N 26.4, a_H 1.50 (2 H)	a_N 14.0	25
				a_N 32.8, a_H 2.57 (2 H), 1.55 (2 H)		
(12)	Petroleum	>−30	<−30	a_N 27.0[g]	a_N 14.0	25
				a_N 33.5, a_H 2.10 (1 H), 1.54 (1 H), 0.58 (2 H)		
(13)	Petroleum–dioxan		<20	a_N 29.25	a_N 12.3, a_H 5.3 (4 H)[k]	26
(13)	DMF					
(14)	Petroleum[l]		22—40	[k]	a_N 11.0, a_H 1.6 (1 H) (w)	26
(9a; R¹ = CO₂Et, R² = CO₂Et)				a_N 31.8		26
(9a; R¹ = CH₂CO, R² = CO₂Et)	Petroleum		22—40	a_N 29.4	a_N 6.1	26
(EtO₂S)₂C=N₂	Petroleum–dioxan		22	a_N 33.0, a_H 1.5 (3 H)	a_N 12.5	
				a_N 30.3		
(CN)₂C=N₂	Petroleum–benzene		−70[m]	a_N 31.0		

[a] Temperature at which thermal reaction of nitric oxide and diazo-compound occurs exclusively. [b] Temperature at which photochemical reaction of nitric oxide and diazo-compound is detectable. [c] Reference to previous generation of this iminoxyl. [d] Poorly resolved proton subsplittings. [e] Irradiation in a Pyrex tube with and without the sensitiser Michler's ketone had little effect on the rate at which iminoxyl is produced. [f] Signal increased three-fold on irradiation. [g] Complex proton hyperfine splitting, not fully interpreted. [h] Prolonged irradiation at −100 °C with nitric oxide in a petroleum matrix followed by slow warming to room temperature also failed to generate an iminoxyl. [i] This spectrum was not intensified when Michler's ketone was added; much weaker spectra were observed using a Pyrex tube. [j] No iminoxyl when acetonitrile, ethanol, or benzene-petroleum was used as solvent. [k] Radical with a_N 7.2 (2 N) and g 2.004 detected; tentatively assigned to (14a). [l] Similar results were obtained using petroleum-dioxan but no iminoxyl was detected when carbon tetrachloride, benzene, or methylene dichloride was used. [m] Very weak spectrum also produced in petroleum–methylene dichloride. In ethanol $(CN)_2\dot{C}\dot{C}(CN)_2$ was detected, a_N 1.6 G and g 2.0030.
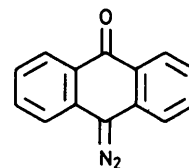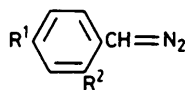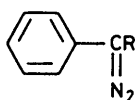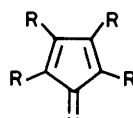
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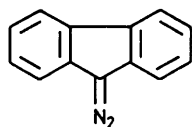
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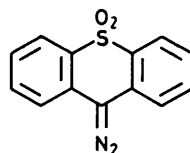
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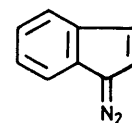
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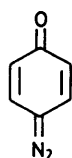
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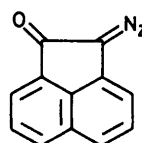
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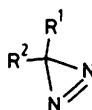(13)

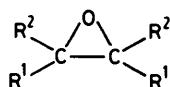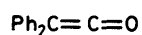(14)

(14a)

(15)

(16)

$Ph_2C=C=O$

(17)

(18)

$PhHgCCl_3$
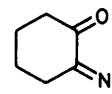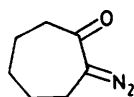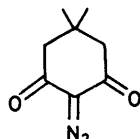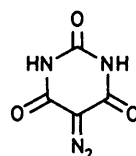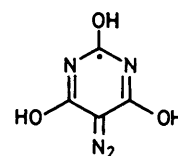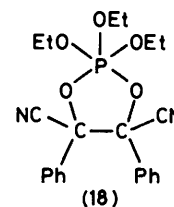
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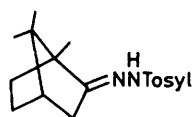
(20)

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magnitude) than that using a silica tube and no sensitiser (Figure 1). In the same series of experiments we showed that the rate of iminoxyl production was also dependent on diazo-ester concentration. Indeed, at high concentration (100 mg ml⁻¹) iminoxyl formation was totally suppressed (Figure 1). This result implies that reaction can occur between the triplet carbene and its diazo-precursor, presumably to give the corresponding azine, and that iminoxyls are not readily genera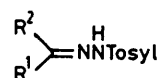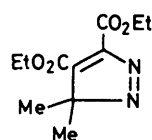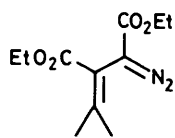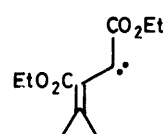ted from azines.[5] We cannot exclude the possibility that nitric oxide itself enhances intersystem crossing but we have no experimental evidence to support this view.
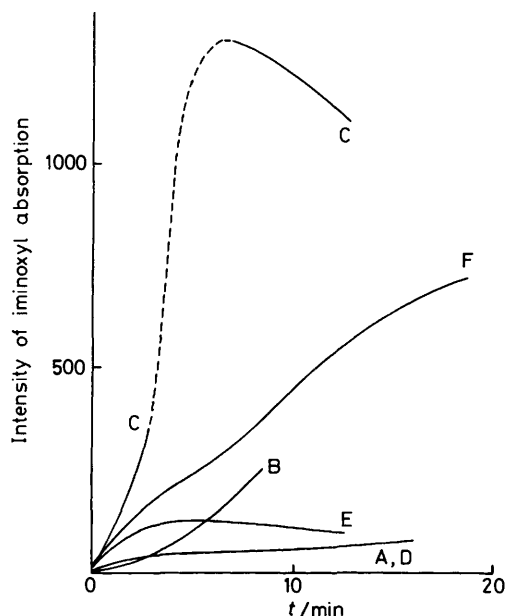

FIGURE 1 Photolyses of diazomalonate with nitric oxide. [diethyl diazomalonate]/mg ml⁻¹, triplet sensitiser, tube, lamp: A, 10, —, Pyrex, 100 W; B, 10, —, silica, 100 W; C, 10, +, Pyrex, 100 W; D, 100, —, silica, 1 kW; E, 10, —, silica, 1 kW; F, 5, —, silica, 1 kW

The detection of iminoxyls formed from carbenes such as propylidene and cyclohexylidene, which normally react in solution as singlets, is indicative of an equilibrium between singlet and triplet states under the conditions of the experiment.

Solvents.—A more frequently encountered problem was the low solubility of several diazo-compounds in petroleum or petroleum–benzene. Although these solvents were the most useful for this work the relatively low solubility [11] of nitric oxide in them is a disadvantage (solubility coefficient for nitric oxide in hexane is 4.5 × 10⁻⁵ mol l⁻¹ mm⁻¹). Ethereal solvents such as dioxan, diethyl ether, and glyme are better solvents for both diazo-compounds and nitric oxide but iminoxyl production in these solvents is usually suppressed in favour of nitroxides, complex spectra of several species often being detected. We did not pursue the origin of these nitroxides but note that (a) acyl diazo-compounds often gave acyl nitroxides (a_N 6—7 G), (b) diaryl and alkyl aryl diazo-compounds gave dialkyl nitroxides with relatively

low a_N values (13—14 G) indicative [12] of the presence of electron-withdrawing substituents on the α-carbon atoms, and (c) when dioxan was used as cosolvent a nitroxide with a_N 12.4 G and a_H 5.3 (4 H) G, g 2.0067 usually predominated. We ascribe this spectrum to a nitroxide of structure $\dot{O}N(CH_2COX)_2$. Significantly, this radical can also be produced simply by shaking nitric oxide (trace of NO_2?) with dioxan. Use of carbon tetrachloride, methylene dichloride, acetonitrile, or ethanol as solvent or cosolvent in this work usually resulted in only nitroxides being detected.

Other Carbene Sources.—Iminoxyls were also generated on irradiation of the diazirines [13-16] [15; R^1=R^2=CO_2Et and R^1R^2=$(CH_2)_5$] and the oxiran [16] (16; R^1=H, R^2=Ph) with nitric oxide but diphenylketen (17),[16] phenyl(trichloromethyl)mercury [14,16] (19), and the phospholan [15,16] (18) gave only nitroxides (Table 2). Presumably, these failures are due to competing reactions of the substrate with nitric oxide and/or production of mainly singlet carbene (*e.g.* CCl_2). Irradiation of the lithio-salts of tosylhydrazones [16] (20) and (21) with nitric oxide was also unsuccessful but the low solubility of these substrates in hydrocarbon solvents necessitated the use of ethereal solvents and these we knew to be less satisfactory.

Vinyl diazo-compounds and vinyl carbenes are thought [17] to mediate in the photochemical conversion of 3H-pyrazoles into cyclopropenes. Hence, we photolysed the 3H-pyrazole (22) with nitric oxide in petroleum above and below room temperature. The only radical detected was a nitroxide (a_N 14.5 G) at 60 °C. Addition of benzophenone as sensitiser produced a myriad of nitroxides. This result is consistent with previous proposals that the carbenes produced in such photolysis are in the singlet state.[17]

Reactions with Alkenes.—Addition of carbenes to alkenes usually occurs easily [1] and hence it was of interest to examine the effect of alkenes on iminoxyl production from photolysis of ethyl diazomalonate and nitric oxide. Cyclohexene, tetramethylethylene, 2- and 4-methylpent-2-enes, tetrachloroethylene, and hex-1-ene were examined and iminoxyl formation was suppressed with all but the last two, which are the least nucleophilic of the six. Nitroxides were formed in all cases but since many of these were also produced simply from nitric oxide (trace of NO_2?) and the alkene there is no evidence for reaction as indicated in (iv). Because of this and the complexity of nitric oxide–nitrogen dioxide–alkene reactions [18a] in general we did not pursue this aspect of the work. However, a similar technique for trapping biradicals (formed from excited cyclic ketones) with nitric oxide to give cyclic nitroxides has subsequently been reported.[18b]

Spectra of Iminoxyls.—Many of the iminoxyls generated in this work have been reported previously.[13-18] Our a_N and a_H values, measured at room temperature or above, in general agreed with the literature values. However, the spectra of iminoxyls generated from nitric oxide and diazo-compounds have much narrower linewidths, are more lasting, and, in the early stages of the

TABLE 2

Photolysis of other carbene sources with nitric oxide

Carbene source	Solvent	Photolysis (°C)	Iminoxyl hyperfine splitting (G)	Nitroxide hyperfine splitting (G)	Ref.
(15; R¹ = R² = CO₂Et)	Petroleum	22	a_N 31.8		26
[15; R¹R² = (CH₂)₅]	Petroleum	22	a_N 30.6		27
(15; R¹ = Ph, R² = Cl)	Petroleum			a_N 12.8 (w) a_N 7.0	
(16; R¹ = H, R² = Ph)	Petroleum	50	a_N 29.7, a_H 27.0 ᵇ (vw)	a_N 7.5, a_H 1.1; a_N 14.2	
(16; R¹ = R² = Ph)	Petroleum–benzene			a_N 15.8	
(17)	Petroleum–benzene			a_N 13.1; a_N 6.7, a_H 2.2	
(18)	Petroleum–benzene			a_N 14.0, a_H 7.5	
(19)	Petroleum–benzene			a_N 6.5	
(20)	Acetonitrile				
(21; R¹ = R² = Ph)	2-MeTHF				
(21; R¹R² = 2,2'-C₆H₄C₆H₄)	2-MeTHF				
(22)	Petroleum			a_N 14.25, a_H 3.8 (2 H)	

ª Reference to previous measurements of this iminoxyl. ᵇ Very weak transient iminoxyl signal.

reaction at least, are less contaminated with nitroxide spectra than those obtained from oximes and lead tetra-acetate. Also, it soon became clear, and especially after the variable-temperature measurements, that the spectra of aryl iminoxyls measured at room temperature or above are often deceptively simple.

$$\ce{>C=C< + R2\overset{\bullet}{C}\cdot -> >C-\overset{\overset{\bullet}{\;}}{C}< ->[NO] >C-C<} \quad \text{(iv)}$$
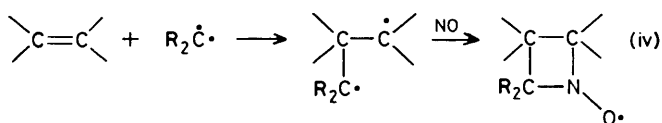
Iminoxyls exist in two geometrically isomeric forms exchange between which occurs at a rate dependent, inter alia, on structure and temperature.[19] This rate can be fast enough for 'averaged spectra' to be observed. Many of the aryliminoxyls previously reported appear to
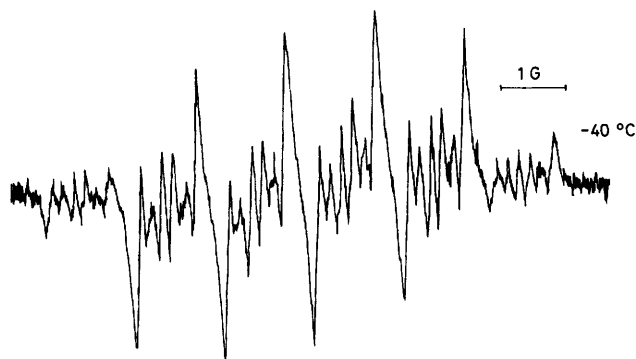
FIGURE 2 Spectrum of MeC(=NȮ)Ph; one component of nitrogen triplet

fall into this category. However, it has been recognised[22] that if the spectra of individual isomers could be measured and interpreted iminoxyls would provide useful models for the study of unpaired electron delocalisation through σ–π interaction. Evidence for extensive unpaired electron delocalisation into the π-system of iminoxyls is provided by the spectrum of diphenyl-iminoxyl measured at low temperature.[28] However, the complex hyperfine splitting has not yet been interpreted and hence the extent of interaction with the meta-

and para-protons of the syn-ring and with the protons of the anti-ring is not known. It is not appropriate to discuss all of our spectra here but suffice it to say that for most of the aryl iminoxyls which we have measured there is abundant evidence of coupling with meta- and para- as well as ortho-protons. Figures 2 and 3 are illustrative.
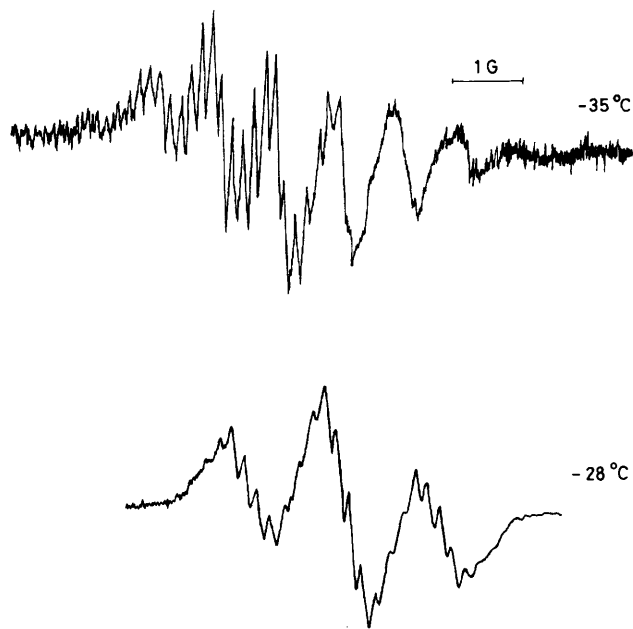
FIGURE 3 Spectra of BuᵗC(=NȮ)Ph (upper) and Ph₂C=NȮ (lower); each = one component of nitrogen triplet

Nitrene Trapping.—Photolysis of phenyl, 2-biphenylyl, benzoyl-, p-tolylsulphonyl, and ethoxycarbonyl azides with nitric oxide in hexane in the cavity of the spectro-meter failed to produce the corresponding diazinoxyl. The azides were photolysed over a wide temperature range and in only one case, ethoxycarbonyl azide, was even a nitroxide detected (a_N 8.7 G). Sensitisation of the phenyl and 2-biphenylyl azide photolyses was similarly unsuccessful although several nitroxides were formed in each case. Since we consider that the aryl-

diazinoxyls at least would have survived under the above conditions we conclude that nitrenes cannot be trapped by reaction with nitric oxide.

EXPERIMENTAL

Sample Preparation and E.s.r. Measurements.—A solution of the diazo-compound in hexane (or other solvent) contained in an e.s.r. tube was thoroughly degassed on a high-vacuum line using several freeze–pump–thaw cycles. Nitric oxide, from a bulb reservoir on line, was then introduced into the space (*ca.* 5 ml) above the frozen solution and the gas was condensed into the tube. The tube was sealed, disconnected and placed in the cavity of an E3 spectrometer at −70 °C. Several scans were made as the temperature was raised stepwise to room temperature. Once it had been established at which temperature (if any) reaction occurred between diazo-compound and nitric oxide, the experiment was repeated with continuous irradiation (100 W or 1 kW Hg vapour lamp) of the sample at a temperature at which the thermal reaction was suppressed.

Compounds.—The diazo-compounds and other carbene precursors were all known compounds and were prepared by the literature methods. Nitric oxide was purified by slow passage through soda asbestos (B.D.H.) which removed both higher oxides of nitrogen and water.

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