Photochemical Formation of Dialkyl Nitroxides from Nitrosoalkanes Evidence for Fluorine *p*–π Conjugation

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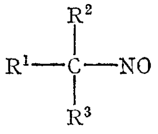
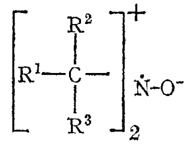
RECENTLY Theilacker *et al.*[1] found that a 0·1M-benzene solution of nitroso-compound (Ia) gave an e.s.r. signal. The spectrum arose from a nitrogen triplet with $A^N = 14{\cdot}5$ gauss. They also found that benzene solutions of nitrosobenzene and substituted nitrosobenzenes gave complex e.s.r. spectra with separation into three groups of bands. For nitrosobenzene the triplet separation was about 11 gauss. No e.s.r. signal, however, was found in solutions of nitroso-compounds which did not exist to some extent in dimeric form. Theilacker and co-workers attributed the e.s.r. signals to dimeric nitroso-biradicals with each electron capable of interacting with only one nitrogen atom.

In our studies of the photochemistry of nitroso-compounds, we found it necessary to investigate this phenomenon. A 0·1M-solution of (Ib) in benzene exhibited an e.s.r. signal from a nitrogen triplet, $A^N = 13{\cdot}9$ gauss. We found, however, that irradiation of the solution with u.v. light caused this same radical to *increase* in concentration. Maruyama *et al.*[2] have previously found that u.v. irradiation of nitrosobenzene, nitrosotoluenes, and chloronitrosobenzenes resulted in formation of diaryl nitroxides in a position-specific manner, *e.g.*, irradiation of *p*-nitrosotoluene gave di-*p*-tolyl nitroxide. By analogy we feel that the radicals observed by Theilacker *et al.* and by ourselves from nitrosoalkanes are the dialkyl nitroxides, (IIa and b). This explanation accounts for the observed interaction with only one nitrogen.



$$R^1\!-\!\overset{R^2}{\underset{R^3}{C}}\!-\!NO$$

(I)



$$\left[R^1\!-\!\overset{R^2}{\underset{R^3}{C}}\!-\right]_2^{+}\dot{N}\text{-}O^-$$

(II)

(a); $R^1{=}R^2{=}Me, R^3{=}OCOMe$

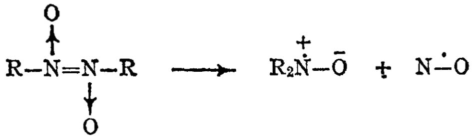
(b); $R^1{=}R^2{=}Me, R^3{=}COMe$

(c); $R^1{=}R^2{=}F, R^3{=}CF_2CO_2Me$

The observation that radicals are found only in nitroso-compounds capable of existing as dimers as well as the position specificity found by Maruyama and co-workers can be explained by the radicals arising from reaction (III), taking place spontaneously in solution or promoted by u.v. light. We have found that nitroso-compounds

NN-dimethyl-*p*-nitrosoaniline, trifluoronitrosomethane (carefully purified), and *N*-nitrosodiphenylamine, which exist only as monomers, do not give the disubstituted nitroxides on irradiation.

To show the formation of dialkyl nitroxides from nitrosoalkanes, it would be better to form a nitroxide with more distinctive hyperfine structure than a nitrogen triplet. A 0·1M-solution of (Ic), therefore, was irradiated with u.v. light. A spectrum was obtained with 15 main lines, each of which was split into quintets. The spectrum obviously comes from (IIc) with $A^{\mathrm{N}} = 9{\cdot}41 \pm 0{\cdot}08$, $A^{\mathrm{F}}_{\alpha} = 13{\cdot}79 \pm 0{\cdot}08$ and $A^{\mathrm{F}}_{\beta} = 0{\cdot}53 \pm 0{\cdot}02$ gauss. For $(CF_3)_2N{-}O$ in CF_3Cl, $A^{\mathrm{N}} = 9{\cdot}3$ and $A^{\mathrm{F}} = 8{\cdot}2$ gauss.[3] A 0·1M-benzene solution of nitrosocyclohexane dimer contained no radicals prior to irradiation, but exposure of the solution to u.v. light resulted in the formation of dicyclohexyl nitroxide with $A^{\mathrm{N}} = 14{\cdot}44 \pm 0{\cdot}12$, $A^{\mathrm{H}}_{\alpha} = 4{\cdot}17 \pm 0{\cdot}05$, and $A^{\mathrm{H}}_{\beta} = 0{\cdot}71 \pm 0{\cdot}02$ gauss.

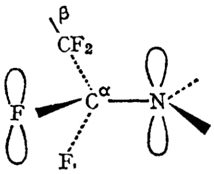


$$\mathrm{R{-}\overset{\overset{O}{\uparrow}}{N}{=}\underset{\underset{O}{\downarrow}}{N}{-}R \longrightarrow R_2\overset{+}{N}{-}\overset{-}{O} + N\overset{\cdot}{-}O}$$

(III)

We also found that a 0·1M-benzene solution of stock nitrosobenzene gave an e.s.r. spectrum rich in hyperfine structure. Radical concentration was markedly less, however, in a 0·1M-solution made up from recrystallized nitrosobenzene. The spectrum could be readily analyzed in terms of the following splittings: 11·85 (1H), 8·99 (1N), 2·84 (3H), and 0·97 gauss (2H). The spectrum apparently arises from phenyl nitroxide.[4]

The increase in α-fluorine splitting in (IIc) compared to bistrifluoromethyl nitroxide is remarkable and deserves further comment. Splitting from α-hydrogens is angular-dependent[5] and is maximum when the $HC_{\alpha}C{-}C_{\alpha}C$ π-orbital dihedral angle is 0°. For methyl hydrogens the average value of this angle is 45°. Because of steric hindrance substitution causes the average dihedral angle to be greater than 45° for α-methylene and methine hydrogens. As a result the α-splitting *decreases.*[6] The results here indicate that α-fluorine splitting will be maximum for a dihedral angle of 90°. This suggests that the interaction of the fluorine with the unpaired electron arises *via* 1,3-*p*–π-conjugation,[7] as shown in (IV), rather than from hyperconjugation.



(IV)

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[4] Splittings for phenyl nitroxide in benzene, generated by mixing phenylhydroxylamine and nitrosobenzene (G. A. Russell and E. J. Geels, *J. Amer. Chem. Soc.*, 1965, **87**, 122) are $A^{\mathrm{H}}_{\mathrm{N}} = 11{\cdot}87$, $A^{\mathrm{N}} = 9{\cdot}02$, $A^{\mathrm{H}}_{o,p} = 2{\cdot}88$, $A^{\mathrm{H}}_{m} = 1{\cdot}00$ gauss. G. A. Russell and E. J. Geels, private communication.

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[7] For a discussion of such effects see: W. A. Sheppard, *J. Amer. Chem. Soc.*, 1965, **87**, 2410.