Tetrahedron Letters,Vol.24,No.49,pp 5547-5550,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain ©1983 Pergamon Press Ltd.

NITROSOCARBONYLBENZENE AS A SPIN TRAP

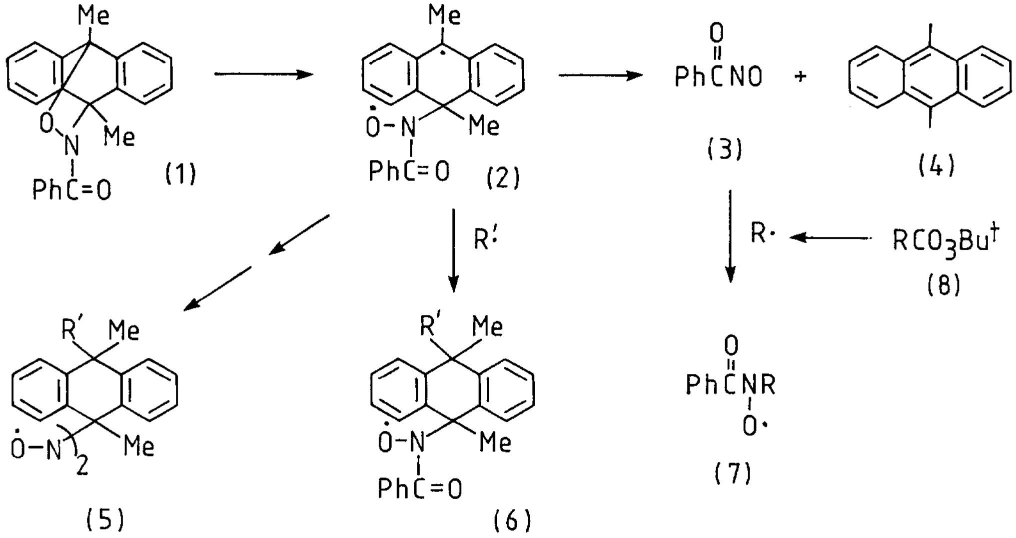
Alexander R. Forrester, John Henderson and Karen Reid

Chemistry Department, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland

Nitrosocarbonylbenzene spin traps only nucleophilic carbon radicals. With nitrosoarenes it yields diaryl nitroxides and readily gives rise to acyl nitroxides on reaction with alkenes.

Investigation of the chemistry of acyl nitroso compounds has been largely confined to their participation in inter- and intra- molecular 4+2 cycloadditions[1] and to ene reactions with alkenes.[1,2] However, nitroso compounds usually also react readily with short-lived radicals to give nitroxides, hence their use as spin traps.[3] Acyl nitroso compounds have not been investigated for this purpose although we previously postulated[4] such behaviour to account for radicals detected during oxidation of N-acyloxyamides with di-t-butyl peroxalate. We now report on reactions of nitrosocarbonylbenzene (3) with several free radical precursors as measured by e.s.r. spectroscopy.

Nitrosocarbonylbenzene was generated from its adduct (1) with dimethylanthracene (DMA) (4) as described by Kirby.[1] Interestingly, when solutions of this adduct (1) in chlorobenzene were warmed to 40-80°C in the cavity of an e.s.r. spectrometer spectra arising from several nitroxides were detected. The main radical, whose spectrum grew steadily at room temperature, was a t-alkyl acyl nitroxide (a_N = 8.1G). At 70°C much weaker signals developed due *inter alia* to a second t-alkyl acyl nitroxide (a_N = 7.5G) and a di-t-alkyl nitroxide (a_N = 14.7G). The most likely structure for the main radical is (6; R'=PhCO, Ph, NO?) and for the di-t-alkyl nitroxide (5). However, whatever the exact structures of these nitroxides their ease of formation implies that dissociation of the adduct into DMA and nitrosocarbonylbenzene occurs to some extent at least by a non-concerted route.



Reaction with several free radical precursors was investigated by addition of the precursor (10 mg) to a degassed solution of the adduct (10 mg) in chlorobenzene and monitoring the changes by e.s.r. spectroscopy as the solution was slowly warmed from room temperature to 90°C.

Aryl radical precursors. Addition of benzoyl peroxide, N-nitroso-p-chloroacetanilide, t-butyl perbenzoate, or phenylazotriphenylmethane did not lead to the detection of benzoyl phenyl nitroxide. The rate of formation of the acyl nitroxide (6) (a_N = 8.1G) and of the previously mentioned minor radicals was affected in all cases but only with phenylazotriphenylmethane was a new radical detected. This had a_N = 8.7G and is probably due to benzoyl triphenylmethyl nitroxide (7; $R=Ph_3C$).

t-Butoxyl radical precursors. Addition of di-t-butyl peroxalate to a solution of the adduct in chlorobenzene or irradiation (u.v.) of a solution of the adduct in di-t-butyl peroxide again merely altered the relative rates of production of the radicals previously detected. No t-butoxy benzoyl nitroxide[5] was detected.

Alkyl radical precursors. (a) t-Alkyl radicals. Addition of azobisisobutyronitrile lead only to a rapid increase in the rate of formation of the nitroxides with a_N = 8.1G and a_N = 14.7G. When the perester (8; $R=PhOCMe_2$) was added and the solution was heated to 80°C an intense triplet (a_N = 8.2G) was detected which we attribute to the acyl t-alkyl nitroxide (7; $R=PhOCMe_2$).

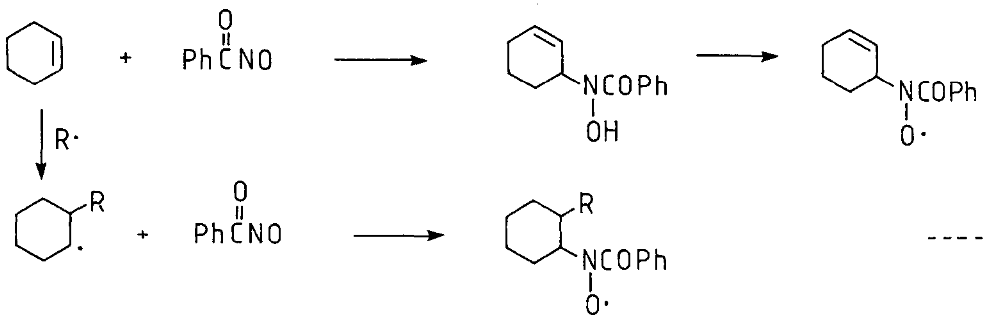
(b) Secondary alkyl radicals. Reaction of the peresters (8; R=Ph_2CH and cyclo-C_6H_{11}) with the adduct (1) gave nitroxides with a_N = 7.4 and a_H = 2.15(1H) G and a_N = 7.4 and a_H = 2.0(1H)(broad) G, respectively. Further, when a mixture of fluorene and benzoyl peroxide was added and the solution was heated to 80°C a triplet of doublets a_N = 7.35 and a_H 0 2.1 G was again detected. These spectra are consistent with the production of secondary alkyl acyl nitroxides.[6]

(c) Primary alkyl radicals. Addition of the peresters (8; R=$PhOCH_2$; o-$PhC_6H_4OCH_2$; p-$MeC_6H_4SCH_2$) and lauryl peroxide to a solution of the adduct followed by heating to 80°C gave in each case a spectrum corresponding to a primary alkyl acyl nitroxide (a_N = 7.05, a_H = 3.72(2H); a_N = 7.25, a_H = 4.25(2H); a_N = 7.25, a_H = 4.3(2H); a_N = 7.6, a_H = 6.0(2H) G, respectively).

These results indicate that the use of a nitrosocarbonyl benzene as a spin trap is limited. Relatively efficient trapping was only achieved with nucleophilic radicals. Electrophilic (RO·) and neutral (Ph·) radicals if trapped did not give lasting nitroxides. A further complication in many cases is the presence of the acyl nitroxide (6) (a_N = 8.1 G) which can obscure other spectra.

Reaction with Nitrosoarenes. In experiments where no radical was trapped by (3) a second trap (nitroso-benzene, -durene or p-chloronitrosobenzene) was added to establish that trappable radicals were present in the solution. It soon became clear that there was a reaction between nitrosoarene and (3) (or a product derived therefrom) to give a diaryl nitroxide. In the absence of the adduct (1) the nitrosoarenes gave rise to only very weak spectra of diarylnitroxides.[7] A similar result was obtained on oxidation of benzohydroxamic acid with periodate in the presence of nitrosoarene and simply by treating a solution of nitrosoarene with nitric oxide. We consider these results as evidence for the fragmentation (minor?) of (3) to benzoyl and nitric oxide the latter reacting with nitrosoarene by the known[9] sequence. ($ArNO + NO \rightarrow ArN(NO)ONO \rightarrow ArN_2ONO_2 \rightarrow Ar\cdot + N_2 + \cdot NO_3$). Further support for this fragmentation was obtained by warming a solution of the adduct of 2-nitrosocarbonylbiphenyl and DMA when fluorenone (27%) was formed.[8]

Ene Reaction. Because of the difficulty in preventing partial oxidation of hydroxamic acids to the corresponding acyl nitroxides it was of interest to repeat in the e.s.r. cavity previously described[2] ene reactions of nitrosocarbonylbenzene with certain alkenes (eq. i)



---- (i)

-------- (ii)

Reaction with both cyclohexene and cycloheptene resulted in strong signals of secondary alkyl acyl nitroxides (a_N = 7.3, a_H = 3.4; a_N = 6.5, a_H = 2.3 G). These could be products of the ene reaction (eq. i) or of radical addition (eq. ii). The latter process certainly occurs with the terminal alkene oct-1-ene since it gave a complicated spectrum due to three radicals, one of which arises from a secondary alkyl acyl nitroxide (a_N = 7.5, a_H = 2.5 G). There was no indication of formation of a primary alkyl acyl nitroxide. Hence, the e.s.r. experiment is presumably monitoring the radical addition reaction (eq. ii). However, with 1-methylhexene a triplet of doublets (a_N = 7.3, a_H = 2.5 G) was observed indicating that in this case the ene reaction is being observed.

References

[1] G. Kirby, *Chem. Soc. Rev.*, 1977, *6*, 1 and ref. cited therein.

[2] G.E. Keck, R.R. Webb, and J.B. Yates, *Tetrahedron*, 1981, *37*, 4007.

[3] M.J. Perkins, *Adv. Phys. Org. Chem.*, 1980, *17*, 1.

[4] A.R. Forrester, J. Henderson, E.M. Johansson and R.H. Thomson, *Tetrahedron Letters*, 1978, 5139.

[5] A.R. Forrester, E.M. Johansson and R.H. Thomson, *J.C.S. Perkin 1*, 1979, 1112.

[6] A.R. Forrester, "Magnetic Properties of Free Radicals", New Series Landolt-Bornstein, Springer Verlag, Heidelberg, 1978, Vol. 8, part C, Chapter 6.

[7] C. Chatgilaloglu and K.U. Ingold, *J. Am. Chem. Soc.*, 1981, *103*, 4833.

[8] A.R. Forrester and J. Henderson, unpublished work.

[9] P.A.S. Smith, "Open Chain Nitrogen Compounds", Pt. 2, Benjamin, New York, 1962, p.373.

(Received in UK 19 September 1983)