Chemically Induced Nuclear Polarization in the Hydroxylamine Derivatives Obtained by Addition of 1-Cyano-1-methylethyl Radicals

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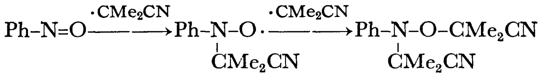
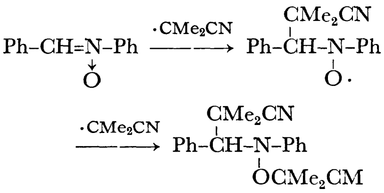
We would like to report the observation of polarized NMR in the adducts I and II of 1-cyano-1-methylethyl radicals. When a solution of α,α'-azobisisobutyronitrile (AIBN) and excess nitrosobenzene in 1,1,2,2-tetrachloroethane/*o*-dichlorobenzene (1 : 1 v/v) was placed in an NMR probe which had been heated at 110°, AIBN decomposed with an approximate half-life of 89 sec as judged by exponential decay of its NMR absorption at 1.61 ppm.[1] At the same time an intense emission line was observed at 1.44 ppm. The amplitude reached its maximum in a negative sense at 40 sec after insertion of the sample tube, and decayed to the apparent zero in 80 sec.[2] By comparison with the authentic sample[3] it was found that the emission originated from one of the methyl signals of adduct I. Intensity of the remaining methyl signal at 1.51 ppm, on the other hand, increased exponentially as expected for a normal growth of the chemical species as the reaction proceeds.



$$\mathrm{Ph{-}N{=}O} \xrightarrow{\cdot\mathrm{CMe_2CN}} \underset{\underset{\mathrm{III}}{\mathrm{CMe_2CN}}}{\mathrm{Ph{-}N{-}O\cdot}} \xrightarrow{\cdot\mathrm{CMe_2CN}} \underset{\underset{\mathrm{I}}{\mathrm{CMe_2CN}}}{\mathrm{Ph{-}N{-}O{-}CMe_2CN}}$$

AIBN was similarly decomposed thermally in the presence of α,N-diphenylnitrone.[4] Adduct II shows four separate peaks (δ 1.19, 1.41, 1.70 and 1.88 ppm) of the methyl protons due to the presence of the asymmetric carbon atom in the molecule. Out of these four only a pair at 1.41 and 1.70 gave emission signals.[2]



$$\underset{\mathrm{O}}{\underset{\downarrow}{\mathrm{Ph{-}CH{=}N{-}Ph}}} \xrightarrow{\cdot\mathrm{CMe_2CN}} \overset{\mathrm{CMe_2CN}}{\underset{\mathrm{O\cdot}}{\mathrm{Ph{-}CH{-}N{-}Ph}}} \quad \mathrm{(IV)}$$

$$\xrightarrow{\cdot\mathrm{CMe_2CN}} \overset{\mathrm{CMe_2CN}}{\underset{\mathrm{OCMe_2CM}}{\mathrm{Ph{-}CH{-}N{-}Ph}}}$$

(II)

It is reasonably assumed that the first addition of a 1-cyano-1-methylethyl radical would lead to more or less stable nitroxide radicals III and IV.[4,5] Thus the present findings that only half of the methyl groups in I and II showed emission can be considered to indicate that nuclear polarization which is developed by dipolar cross relaxation during the second step of the free radical addition is observable as emission signals.[6] It then follows that the methyl signals which appeared as emission should be assigned to the *O*-$\mathrm{CMe_2CN}$ of the hydroxylamine derivatives I and II.

This is the first example in which the polarized NMR signals have been applied to the assignment of the spectra. Conversely the method will find application for discussing the chronology of free radical addition when the assignment of the spectra is unambiguously available.

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[1] NMR measurements were carried out on a Japan Electron Optics 4H-100 spectrometer. The proton signal of the solvent tetrachloroethane was used as the lock signal and the chemical shifts are expressed relative to the internal TMS.

[2] In addition to this emission two pairs of polarized NMR were always observed in the *C*-methyl region of the spectra due to isobutyronitrile and methacrylonitrile formed by disproportionation of the 1-cyano-1-methylethyl radicals. See H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969), and H. Iwamura and M. Iwamura, *Tetrahedron Lett.*, **1970**, 3723.

[3] B. A. Gingras and W. A. Waters, *J. Chem. Soc.*, **1954**, 1920.

[4] M. Iwamura and N. Inamoto, This Bulletin, **40**, 702, 703 (1967); **43**, 856, 860 (1970).

[5] A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer and J. D. W. van Voorst, *Tetrahedron Lett.*, **1966**, 2115.

[6] The spin-lattice relaxation time was found to be 2.5 sec for all the four methyl signals of II.