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CHEMICALLY INDUCED NUCLEAR POLARIZATION OBSERVED IN ADDITION OF 1-CYANO-1-METHYLETHYL RADICALS TO NITRONES

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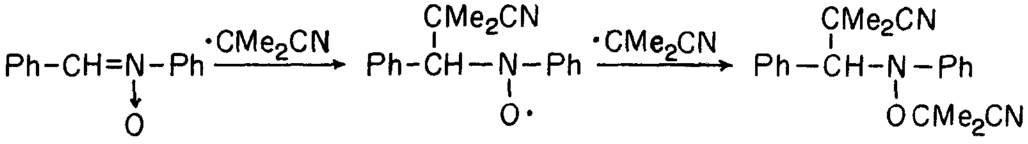
It has been shown by one of the present authors that thermal decomposition of α,α'-azobisisobutyronitrile (AIBN) in the presence of α,N-diphenylnitrone (I) proceed through the initial attack of a 1-cyano-1-methylethyl radical to the carbon atom of the nitrone group to form the intermediate nitroxide (II), followed by addition of a second free radical to give the trisubstituted hydroxylamine (III).[1] We would like to report the observation of chemically induced nuclear polarization during this reaction.



$$\mathrm{Ph{-}CH{=}\underset{\underset{O}{\downarrow}}{N}{-}Ph} \xrightarrow{\cdot\mathrm{CMe_2CN}} \mathrm{Ph{-}\overset{\overset{CMe_2CN}{|}}{C}H{-}\underset{\underset{O\cdot}{|}}{N}{-}Ph} \xrightarrow{\cdot\mathrm{CMe_2CN}} \mathrm{Ph{-}\overset{\overset{CMe_2CN}{|}}{C}H{-}\underset{\underset{OCMe_2CN}{|}}{N}{-}Ph}$$

I II III

When a solution of 50 mg of I and 14 mg of AIBN in 0.4 ml of 1,1,2,2-tetrachloroethane was placed in an nmr probe which had been heated at 130°, AIBN decomposed with an approximate half-life of 20 sec as indicated by exponential decay of its nmr absorption at δ 1.66 ppm.[2] At the same time, intense emission lines appeared at 1.41 and 1.70 ppm along with a pair of emission at 1.30 and enhanced absorption at 1.23 ppm (see Figure 1a). The latter pair was found to be originated from the methyl protons of isobutyronitrile formed by disproportionation of the 1-cyano-1-methylethyl radicals.[3] The amplitude of the former emission signals reached a maximum in negative sign at ca. 40 sec after insertion of the sample tube, and decayed as shown in Figure 2. In addition to these peaks there came out after 30 sec three singlet lines at 1.19, 1.46 and 1.88 ppm the intensity of which increased smoothly as expected for a normal growth of the chemical species as the reaction proceeds. In 150 sec the four peaks at 1.19, 1.41, 1.70 and 1.88 ppm ended up with equal intensity, and were superimposable with the methyl proton spectra of the authentic III(Figure 1b).[4] The intense peak at 1.46 ppm was identified as 2,3-dicyano-2,3-dimethylbutane produced by dimerization of the 1-cyano-1-methylethyl radicals.

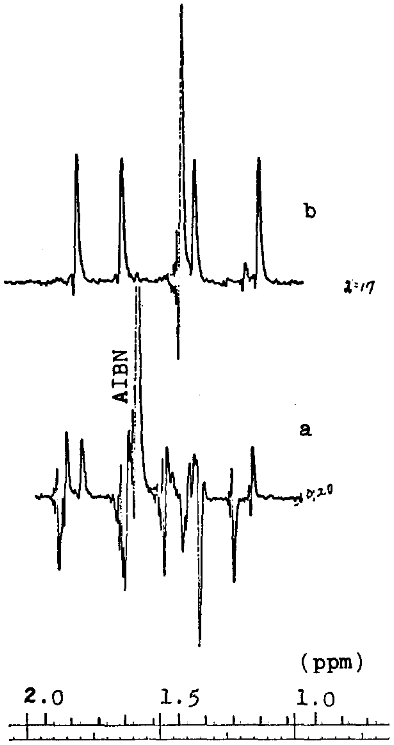


Figure 1. 100-MHz nmr spectra of a solution of I and AIBN in tetrachloroethane at 130°.

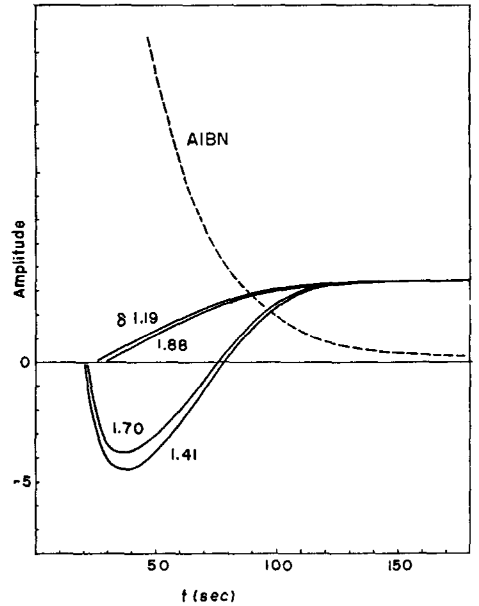
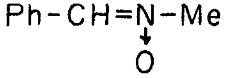


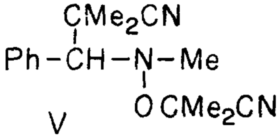
Figure 2. Time dependence of the amplitude of the four C-methyl signals of III.

AIBN was similarly decomposed in a solution of N-methyl-α-phenylnitrone (IV). Out of four C-methyl signals at 1.18, 1.53, 1.61 and 1.70 ppm of the adduct V, only a pair at 1.53 and 1.61 ppm appeared as the emission spectra. The methine and N-methyl proton regions of the spectra were investigated in another run at 120°. Both singlets at 3.90 and 2.72 ppm increased smoothly until their intensities reached a maximum at ca. 60 sec after the sample was introduced in the heated nmr cavity. Thereafter the amplitude decayed to that corresponding to the final concentration of the product V. Since V was confirmed to be stable under the experimental conditions, the phenomenon can be regarded as manifestation of the positive nuclear polarization.



$\mathrm{Ph{-}CH{=}\underset{\overset{\downarrow}{O}}{N}{-}Me}$

IV



$\mathrm{Ph{-}\overset{CMe_2CN}{\overset{|}{C}H}{-}\underset{OCMe_2CN}{\underset{|}{N}}{-}Me}$

V

The present findings that only two of the four C-methyl signals in III and V showed negatively polarized nmr may be considered to indicate that this pair correspond to the methyl protons on the same 1-cyano-1-methylethyl group attached to the oxygen rather than the carbon atom, becuase it is more likely that the radical moiety added at the later stage of the reaction path is more strongly polarized.[5] Actually the intermediate nitroxide radicals have been shown under favorable conditions to have a reasonably long life-time to be studied by esr spectroscopy. Thus it is probable that the dipolar polarization in the methyl protons of the nitroxide such as II has relaxed before entering into the diamagnetic final products. It is interesting to note, in this respect, that the methine and N-methyl proton signals of V were positively polarized. This polarization appears to be derived from the scalar coupling in the intermediate nitroxide radical.[6]

This research is the first example in which the chemically induced nuclear polarization has been applied to the assignment of the nmr spectra. The method may find inverse application to discussing the chronology of the free radical addition when the assignment of the spectra is unambiguously available.

REFERENCES

(1) M. Iwamura and N. Inamoto, Bull. Chem. Soc. Japan, **40**, 702, 703 (1967); **43**, 856, 860 (1970).

(2) All the measurements were carried on a Varian HA-100 D nmr spectrometer. The proton signal of the solvent tetrachloroethane was used as the lock signal, and the chemical shifts are expressed relative to the internal tetramethylsilane.

(3) H. Fischer and J. Bargon, Accounts Chem. Res., **2**, 110 (1969). There were always observed additional emissions due to by-products of the AIBN decomposition.

(4) Due to the presence of the asymmetric carbon atom, a pair of the methyl groups on a 1-cyano-1-methylethyl group in III are mutually diastereomeric and show separate chemical shifts. The phenomenon characteristic of the nitrogen inversion and the restricted rotation of a hydroxylamine derivative takes place only at lower temperatures and will be described separately.

(5) It might be argued that the phenomenon could be due to a different spin-lattice relaxation time of the methyl groups in III and V. This possibility was ruled out by direct measurement of the T_1 in the reaction products by the method of adiabatic rapid passage through resonance (J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 83). The T_1's thus obtained were 2.5 sec for all the four methyl signals of III.

(6) By comparison with the structurally analogous nitroxides, the hyperfine coupling constants of the methine and N-methyl protons are expected to be 3 and 12 gauss, respectively.[7]

(7) G. Chapelet-Letourneux, H. Lemaire and A. Rassat, Bull. Soc. Chim. France, **1965**, 3283; M. Iwamura and N. Inamoto, unpublished work.