Novel Formation of Nitroxide Radicals by Radical Addition to Nitrones

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In reactions of nitrones with aliphatic azo compounds, we have found novel radical 1, 3-addition to C atom and O atom in nitrone system.[1] Extended similar reaction to *N-t*-butylnitrones and a related compound, very stable nitroxide radicals were produced.

Reaction of α, α'-azobisisobutyronitrile (AIBN) with *N-t*-butyl-α-phenylnitrone (I) in xylene at 110°C gave *N-t*-butyl-*N*-[α-(2-cyanoisopropyl)-benzyl]nitroxide (III) as red needles in a 3.2% yield after column chromatography on silica gel. Mp 121—122°C, $\lambda_{max}^{\mathrm{EtOH}}$ 437 mμ (ε=48). Found: C, 73.25; H, 8.70; N, 11.47%. Calcd for $C_{15}H_{21}ON_2$: C, 73.43; H, 8.63; N, 11.42%. Analysis of the ESR spectrum in tetrahydrofuran (THF) is given in Table 1. The nitroxide (III) is quite stable for a diffused light, temperature below 100°C, and also chromatography on alumina, and no change was observed on standing over one year in air.

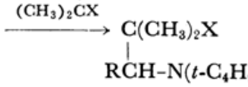
TABLE 1. NITROXIDE RADICALS

Reactant	Nitroxide	ESR g	ESR a_N*	ESR a_H*	Solvent
I+AIBN	III	2.0044	14.6	3.07	THF
I+MAIB	IV	—	13.4	3.7	Xylenes
II+AIBN	V	—	14.5	0.8	Xylenes
II+MAIB	VI	—	15.7	**	o-$Cl_2C_6H_4$

* In gauss.
** Not determined because of broadening of signals.

$RCH{=}N({\rightarrow}O)\text{-}t\text{-}C_4H_9$

I $R=C_6H_5$
II $R=t\text{-}C_4H_9N({\rightarrow}O){=}CH\text{-}$

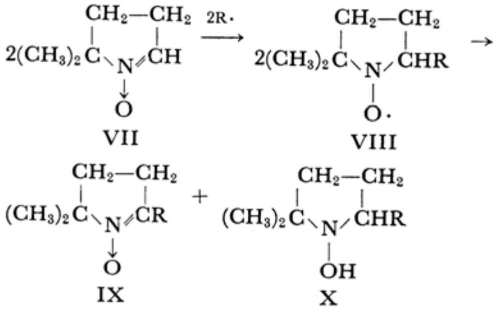


$$\xrightarrow{(CH_3)_2\dot{C}X} \overset{C(CH_3)_2X}{\overset{|}{R}}CH\text{-}N(t\text{-}C_4H_9)\text{-}O\cdot$$

III $R=C_6H_5$, $X=CN$
IV $R=C_6H_5$, $X=CO_2CH_3$
V $R=t\text{-}C_4H_9N({\rightarrow}O){=}CH\text{-}$, $X=CN$
VI $R=t\text{-}C_4H_9N({\rightarrow}O){=}CH\text{-}$, $X=CO_2CH_3$

Similar reactions were carried out with dimethyl α, α'-azobisisobutyrate (MAIB). The radicals IV—VI are not isolated in pure state yet, but the structures are confirmed by the ESR spectra. These results are given in Table 1.

Reaction mixture of cyclic nitrone (VII) with AIBN in xylene exhibited ESR signal of a nitroxide radical (VIII), a_N=14.6 and a_H=20.4 gauss,[2] and a new nitrone (IX), mp 93—94.5°C (Found: C, 66.83; H, 8.93; N, 15.43%. Calcd for $C_{10}H_{16}ON_2$: C, 66.63; H, 8.95; N, 15.55%), was isolated in a 6.5% yield after chromatography on silica gel. In this case, the nitroxide VIII seems to be disproportionated to IX and X which is not isolated yet.



R·: $(CH_3)_2\dot{C}CN$

The nitroxides possessing α-hydrogen atom tend to disproportionate readily. A cyclic nitroxide, which possesses α-hydrogen atom but is prohibited from disproportionation because of Bredt's rule, has been reported recently.[3] However, our stable nitroxides (III—VI) are regarded as the first examples of that prohibited from disproportionation due to a spatial congestion round the α-hydrogen atom. Further investigations are in progress.

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[1] M. Iwamura and N. Inamoto, This Bulletin, **40**, 702 (1967).

[2] In cyclic nitroxide radicals, a_H value is about 20 gauss. *Cf.*, G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, **1965**, 3283.

[3] R.-M. Dupeyre and A. Rassat, *J. Am. Chem. Soc.*, **88**, 3180 (1966).