Novel Radical 1, 3-Addition to Nitrones

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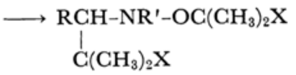
We wish to report novel radical 1, 3-addition to the nitrones. When α, α'-azobisisobutyronitrile (AIBN) was decomposed in xylene containing an equimolar α, *N*-diphenylnitrone (I) at 90—110°C, an addition compound, trisubstituted hydroxylamine (IV), was obtained in a 63% yield. Similar addition compounds (V, VIII, VI, and VII) were produced in the reaction of II or III with AIBN, and in the reaction of I or II with dimethyl α, α'-azobisisobutyrate (MAIB) under similar condition.

$\mathrm{RCH{=}N({\rightarrow}O)R' + 2(CH_3)_2\dot{C}X}$

I $\mathrm{R{=}R'{=}C_6H_5}$
II $\mathrm{R{=}C_6H_5,\ R'{=}C_6H_5CH_2}$
III $\mathrm{R{=}C_6H_5N({\rightarrow}O){=}CH{-},\ R'{=}C_6H_5}$


$$\longrightarrow \mathrm{RCH{-}NR'{-}OC(CH_3)_2X} \text{ with } \mathrm{C(CH_3)_2X} \text{ below CH}$$

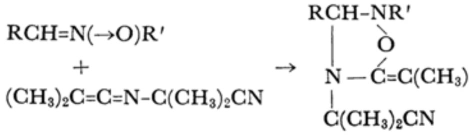
IV $\mathrm{R{=}R'{=}C_6H_5,\ X{=}CN}$
V $\mathrm{R{=}C_6H_5,\ R'{=}C_6H_5CH_2,\ X{=}CN}$
VI $\mathrm{R{=}R'{=}C_6H_5,\ X{=}CO_2CH_3}$
VII $\mathrm{R{=}C_6H_5,\ R'{=}C_6H_5CH_2,\ X{=}CO_2CH_3}$
VIII $\mathrm{R{=}C_6H_5N({\rightarrow}O){=}CH{-},\ R'{=}C_6H_5,\ X{=}CN}$

These results are summarized in Table 1.

TABLE 1. 1, 3-ADDITION PRODUCTS

Addition product	(%)	Mp, °C		Elemental analysis, % C	H	N
IV	(63)	142.5—143.5	Found	75.52	6.86	12.65
			Calcd	75.64	6.95	12.65
V	(46)	114—115	Found	75.94	7.54	12.09
			Calcd	76.05	7.25	12.10
VI	(50)	55—56	Found	69.47	7.56	3.69
			Calcd	69.15	7.32	3.51
VII	(40)	51—52	Found	69.56	7.53	3.40
			Calcd	69.71	7.56	3.39
VIII	(15)	134—134.5	Found	70.24	6.55	15.17
			Calcd	70.18	6.43	14.88

NMR and IR spectra of these addition compounds (IV-VIII) support the proposed structures. For example, in IV, NMR (in $CDCl_3$): τ 8.86 (3H), 8.65 (3H) 8.25 (3H), 8.05 (3H), 6.50 (1H, broad), 3.12, 2.95, 2.92 (5H in total), and 2.81 (5H). IR (KBr disk): 2220 (CN), 1592, 1277, 1220, 1198, 1160, 1083, 1030, 1015, 970, 950, 925, 915, 902, 890, 764, 740, 713, 700 cm^{-1} (phenyl and trisubstituted hydroxylamine[1]). However, some uncertainty remains in the cases of IV, V and VIII, because the decomposition of AIBN gives ketenimine (IX) as intermediate,[2] which is able to yield 1, 3-dipolar cyclic addition compounds (X) with nitrones, and the distinction between the two structures is difficult from these spectral data.



IX X

Heating of the compound IV with hydrochloric acid in ethanol gave hydrogen cyanide and acetone. Treatment of the compound V with an alkaline hydrogen peroxide gave a nitrile-amide, mp 182.5—183°C, IR (in Nujol): 3500, 3180, 2230, and 1690 cm^{-1}. Found: C, 72.56; H, 7.47; N, 11.62%. Calcd for $C_{22}H_{27}O_2N_3$: C, 72.30; H, 7.45; N, 11.50%. Its correct structure is uncertain yet. Similar additions took place also by using MAIB, which could not give a ketenimine intermediate on decomposition. These facts support the structures IV and V rather than the structure X. In the case of III, even if an excess of AIBN was used, the product was also VIII.

Therefore, it is reasonable that the addition compounds (IV—VIII) were produced by 1, 3-addition of two radicals to C atom and O atom in the nitrones system. It is probable that a radical adds first to the C atom.[3] This report is the first examples of radical 1, 3-addition. Further investigations are in progress.

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

[2] M. Talât-Erben and S. Bywater, *J. Am. Chem. Soc.*, **77**, 3710, 3712 (1955).

[3] M. Iwamura and N. Inamoto, This Bulletin, **40**, 703 (1967).