

A NOVEL HYDRIDE REDUCTION OF 2,4,6-TRI-*t*-BUTYLNITROBENZENE

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We are investigating the hydride reduction of hindered aromatic nitro compounds such as 2,4,6-tri-*t*-butylnitrobenzene (I) to prepare the corresponding hindered amines and at the same time study intermediate reduction products. Reduction of I with excess lithium aluminum hydride in boiling tetrahydrofuran (Table 1, No.1) gave a high yield of 2,4,6-tri-*t*-butylaniline (II). This provides a convenient synthesis of II compared to the sodium amalgam reduction of I (1). With an equimolar amount of reducing agent and shorter time (Table 1, No.2), there was obtained some 2,4,6-tri-*t*-butylnitrosobenzene (III) (2) as well as II. In ethyl ether only a small amount of II was obtained (Table 1, No.3) together with a new compound IV. The latter was the major product from reduction of I with sodium bis(2-methoxyethoxy) aluminum hydride (Vitrider) in benzene (Table 1, No.4).

Compound IV (m.p.169-170°) has the formula $C_{18}H_{31}NO$ (accurate mass determination). The infrared spectrum (CCl_4) showed a strong band at 3599 cm^{-1} . The ultraviolet spectrum showed bands at $\lambda_{\text{max}} 216\text{ nm}$ ($\epsilon = 6000$) and $\lambda_{\text{max}} 306\text{ nm}$ ($\epsilon = 2900$). The n.m.r. spectrum of IV (CCl_4) showed three singlets at 9.10, 8.88 and 8.71 τ of relative intensities 9:9:9 and assigned to the three *t*-butyls. The remainder of the spectrum consisted of a singlet at 1.38 τ (1H) and three groups of spin-spin coupled bands each integrating for 1 H; a doublet at 7.02 τ , a quartet (two sets of doublets) at 4.20 τ and a doublet at 3.75 τ .

TABLE 1
Hydride Reduction of 2,4,6-Tri-*t*-butylnitrobenzene (I)

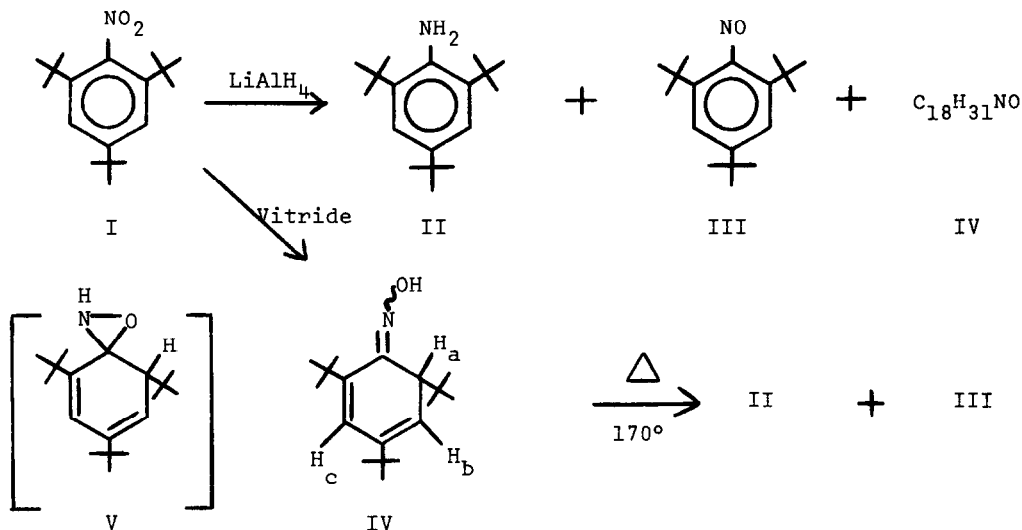
No.	Compound Reduced (m mole)	Reducing Agent (m mole)	Solvent	Conditions	Products (%) ^a
1	I (50)	LAH ^b (200)	THF	reflux, 14h	II (83), IV (2)
2	I (10)	LAH (10)	THF	reflux, 2½h	I, 2,4,6-tri- <i>t</i> -butylnitrosobenzene (III) (17), 2,4,6-tri- <i>t</i> -butylaniline (II) (23)
3	I (20)	LAH (20)	ethyl ether	reflux, 93h	I (69), II (6), IV (10)
4	I (18)	Vitride (47)	benzene	25°, 48h	I (43) ^c , IV (56)

a % refers to actual yields after chromatography on alumina, except in No.4 which is based on n.m.r. integrations.

b LAH = lithium aluminum hydride.

c A small amount of 2,4,6-tri-*t*-butylaniline was also detected. On longer reaction times, the conversion of I into IV was essentially complete.

The couplings were indicative of an ABC-type system, with $J_{AB} = 5.8$ cps and $J_{BC} = 2$ cps. Treatment of IV with acetic anhydride in benzene yielded the corresponding N-acetoxy derivative (m.p. 51-52°) which gave the expected n.m.r. spectrum and showed carbonyl absorption at 1780 cm^{-1} . From these results, the structure proposed for the reduction product, 2,4,6-tri-*t*-butyl-2,4-cyclohexadienone oxime (IV), is preferred over alternative formulas, such as V.



At its melting point, compound IV undergoes decomposition and the melt turns green. On heating a sample of IV for five minutes at 170° , a mixture of amine II and nitroso compound III resulted.

Vitride reduction of 2,4,6-triisopropylnitrobenzene under these conditions yielded 2,2',4,4',6,6'-hexaisopropylazoxybenzene (m.p. 105.5-106°). In this case, the reduction of the nitro arene followed the usual course as reported by Corbett (3).

Aryl nitro and nitroso compounds are known to readily form nitranion radicals during reduction by bases in alcohols or dimethylsulfoxide (4) (5) and these radicals couple in subsequent reactions to form azoxybenzenes. The benzene solution in the Vitride reduction of I to IV was deeply colored

(changing slowly from red to green or orange) and preliminary e.s.r. studies gave a strong persistent signal indicative of the presence of radicals and/or radical anions. Such intermediates derived from I or from III apparently cannot couple to give the usual product (an azoxybenzene) due to steric hindrance provided by ortho-*t*-butyl groups, so that a novel alternative reaction occurs leading to the non-benzenoid system (IV). The mechanism for formation of IV, its reactions, and applications of this novel reduction to other hindered nitro arenes are under investigation.

Satisfactory elemental, n.m.r. and mass spectral analyses were obtained for new compounds.

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