

PHOTOLYSIS OF 2,4,6-TRI-*t*-BUTYLNITROSOBENZENE

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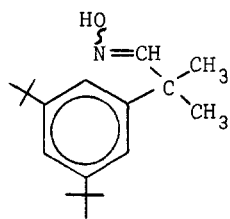
Aromatic C-nitroso compounds are known to undergo photolysis to yield phenylnitroxides (1,2) and products derived from these radicals (3). Recently nitrosobenzene was found to undergo photoreduction in 2-propanol analogous to nitrobenzene (4).

Aromatic nitro compounds bearing *ortho* *t*-butyl groups undergo photocyclizations into a methyl group on the side chain (5,6). We are extending our study of photolysis of hindered aromatic compounds to hindered nitroso compounds such as 2,4,6-tri-*t*-butylnitrosobenzene (I), which has the advantage for this study of existing in the monomer state (7). A recent report by Terabe and Konaka (8) emphasizing the *stability* of I towards photolysis prompted us to report on our exploratory photochemistry of I.

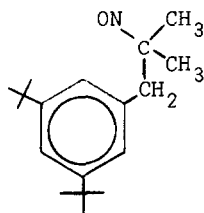
A benzene solution of I (8.0 m mole in 600 ml. benzene) in a pyrex vessel was photolyzed (N_2 atmosphere) with a Hanovia 450W high pressure mercury vapor lamp. Conversion of I to products was approximately 90% in 20 hrs as measured by the diminution in the typical long wavelength (770 nm) absorption band for I. Chromatography of the photolysis mixture on basic alumina resulted in the separation of unreacted I, some minor components, and two new crystalline compounds II (31%), m.p. 95-96° and III (13%), m.p. 146°. Compound II has the formula $C_{18}H_{29}NO$ (accurate mass measurement). It gave i.r. bands (KBr) at 3300 (broad) and 1590 cm^{-1} . N.m.r. resonances (CCl_4 containing tetramethylsilane) appeared at 8.68 (singlet, 18H, $2 \times (CH_3)_3C-$), 8.50 (singlet, 6H,

$(\text{CH}_3)_2\text{C}$), 2.89 (doublet, $J=1.7$ cps, 2H, aryl-2,6), 2.77 (triplet, $J=1.7$ cps, 1H, aryl-4), 2.53 (singlet, 1H, $-\text{CH}=\text{N}-$), and 0.84τ (singlet, 1H, exchanges with D_2O , $-\text{OH}$). Treatment of II with acetic anhydride in the presence of triethylamine yielded an acetoxyl derivative, m.p. 60° , i.r. 1780 cm^{-1} (strong), with n.m.r. resonances at 8.67 (singlet, 18H, $2\times(\text{CH}_3)_3\text{C}-$), 8.45 (singlet, 6H, $(\text{CH}_3)_2\text{C}$), 7.93 (singlet, 3H, CH_3CO), 2.91 (doublet, $J=1.7$ cps, 2H, aryl-2,6), 2.78 (triplet, $J=1.7$ cps, 1H, aryl-4), and 2.43τ (singlet, 1H, $-\text{CH}=\text{N}-$). The spectral results on II and its acetoxyl derivative indicate that its structure is 2-methyl-2-(3,5-di-*t*-butyl)phenylpropanal oxime (II).

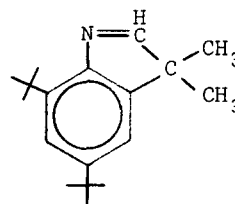
Compound III also has the formula $\text{C}_{18}\text{H}_{29}\text{NO}$ according to an accurate mass measurement of the parent ion at $m/e = 275$. There was also a weak peak in the mass spectrum in the region for a dimer at $m/e = 550$. N.m.r. resonances appeared at 8.67, 8.62 (singlets, ratio 3:1 partly resolved, 24H, $2\times(\text{CH}_3)_3\text{C}-$ and $(\text{CH}_3)_2\text{C}-$), 5.58 (singlet, 2H, benzylic- CH_2-) and 2.79τ (singlet, 3H, aromatic H^{S}). At its melting point, III changed from colorless to green. The structure proposed for III is 2-methyl-2-nitroso-3-(3,5-di-*t*-butyl) phenylpropane. The compound apparently exists as the dimer at ordinary temperatures.



II



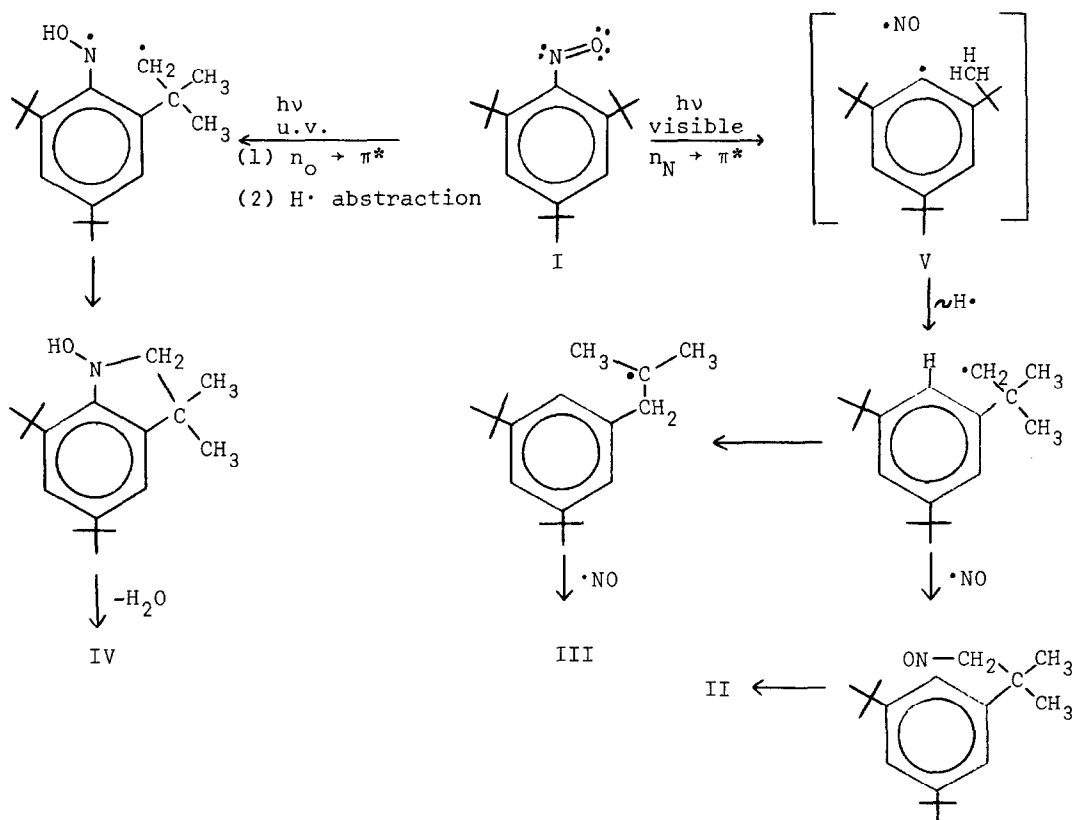
III



IV

Photolysis of 2,4,6-tri-*t*-butylbromobenzene by ultraviolet irradiation of a benzene or a cyclohexane solution in a Rayonet Reactor yielded 1,3,5-tri-*t*-butylbenzene as the main product. This hydrocarbon may form via an aryl radical (9). In an attempt to trap the expected 2,4,6-tri-*t*-butylphenyl

radical, a benzene solution of the bromo compound (1 m mole) was photolyzed in the presence of the nitroso compound (I) (2 m mole) as a free radical trap (8). Under these conditions, the bromo compound was partially converted into the hydrocarbon but there was no evidence for a nitroxide radical. The nitroso compound was partially (50%) recovered. Alumina chromatography also separated a compound m.p. 127° (50% yield corrected for recovered I). This compound showed n.m.r. resonances at 8.70 (singlet, 6H, $(\text{CH}_3)_2\text{C}-$), 8.65 (singlet, 9H, $(\text{CH}_3)_3\text{C}-$), 8.47 (singlet, 9H, $(\text{CH}_3)_3\text{C}-$), 2.77 (AB quartet, $J=2$ cps, 2H, aryl H^{S}), 2.23 τ (singlet, 1H, $-\text{CH}=\text{N}-$). This spectrum is consistent with the structure 3,3-dimethyl-5,7-di-*t*-butyl-3H-indole (IV) reported earlier (6) as a minor component from photolysis of crystalline 2,4,6-tri-*t*-butylnitrobenzene. Our sample also proved to be identical to IV (6) by mixed melting point and i.r. spectra.



Scheme 1

A brief account for the formation of our photoproducts from I is offered in Scheme 1. Visible irradiation involving an $n_N \rightarrow \pi^*$ transition (10) could lead to radicals or a radical pair (V)(11). Hydrogen atom migration from a nearby H-C bond followed by radical recombination accounts for II and neophyl rearrangement preceding recombination accounts for III. Alternately III may be a photoproduct of II. An $n_O \rightarrow \pi^*$ type excited state resulting from irradiation in the near u.v. (10) would result in hydrogen abstraction by the oxygen (in this case from an *o-t*-butyl) analogous to that familiar to a $n \rightarrow \pi^*$ state of a carbonyl group. Cyclization and dehydration accounts for IV.

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