REACTION OF NITROXYL RADICALS WITH DICHLOROCARBENE

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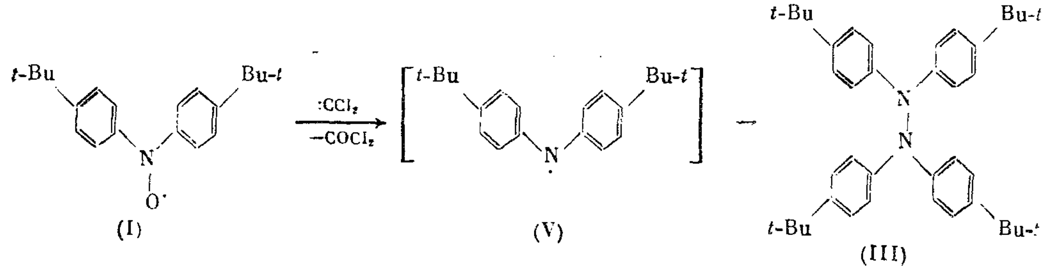
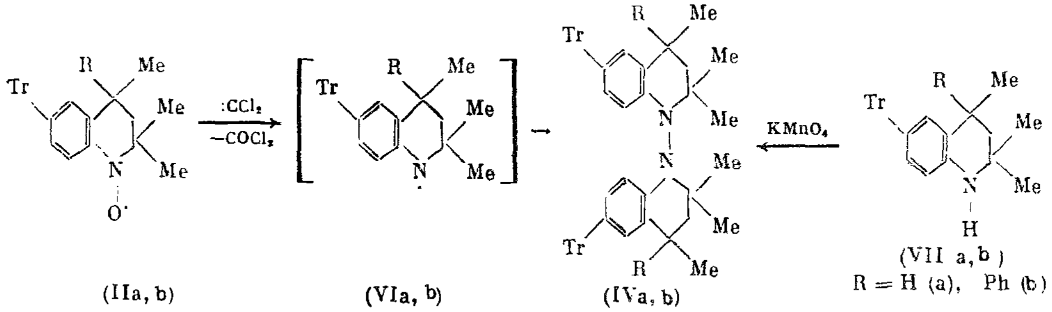
The reaction of diphenylcarbene with 4-R-2,2,6,6-tetramethylpiperidine 1-oxides leads to dexoxygenation of these oxides with the formation of benzophenone and the corresponding aminyl radicals, which are annihilated by the abstraction of a hydrogen atom from a solvent molecule [1].

In the present work, we studied the reaction of dichlorocarbene, generated under phase transfer conditions according to Makosza [2], with some stable aromatic nitroxyl radicals. The reaction of dichlorocarbene with 4,4'-di-tert-butyldiphenylnitrogen oxide (I) and 2,2,4-trimethyl-4-R-6-trityl-1,2,3,4-tetrahydroquinoline 1-oxides (IIa) and (IIb) gives the corresponding aromatic hydrazines (III) and (IVa, b) as the major products in 50-65% yield.





These results indicate that dichlorocarbene, which is a singlet in the ground state, deoxygenates nitroxyl radicals similarly to triplet diphenylcarbene [3]. This reaction also gives phosgene, which is hydrolyzed under the reaction conditions (50% aq. NaOH), and the corresponding aminyl radicals (V) and (VIa, b). Dimerization of these radicals leads to hydrazines (III) and (IVa, b).

We should note that the predominant formation of aminyl radicals such as (VIa) and (VIb), generated upon the photolysis of 2,2,4-trimethyl-6-R-1,2-dihydroquinolines, has been described by Kuz'min et al. [4].

Hydrazine (III) had spectral indices identical to those of a sample obtained by the oxidation of 4,4'-di-tert-butyldiphenylamine according to the Wieland method [5]. Hydrazines (IVa) and (IVb) were obtained by convergent synthesis by the same method from the corresponding tetrahydroquinolines (VIIa) and (VIIb). The PMR spectra of hydrazines (IVa) and (IVb) are virtually identical to those for (VIIa) and (VIIb) except that the NH singlets at 4.17-4.28 ppm [6] are lacking in the hydrazine spectra.

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EXPERIMENTAL

The reaction course and purity of the compounds obtained were monitored by thin-layer chromatography on Silufol UV-254 plates using 3:1 petroleum ether—benzene as the eluent and iodine vapor as the developer. The PMR spectra were taken on a Tesla BS-467 spectrometer in $CDCl_3$ at 60 MHz with TMS as the internal standard.

N,N,N',N'-Tetra(4-tert-butylphenyl)hydrazine (III). A sample of 1 g nitroxyl (I) was dissolved in 15 ml of $CHCl_3$ and, then, 10 ml 50% NaOH and 0.01 g triethylbenzylammonium chloride were added and stirred for 10 min in an argon atmosphere at about 20°C until the color of the starting nitroxyl disappeared. The organic layer was separated, washed with water and dried. Chloroform was distilled off at reduced pressure and the residue was subjected to chromatography on an alumina column using 1:1 CCl_4—hexane as the eluent, collecting the fraction with $R_f = 0.5$. The eluent was distilled off at reduced pressure and the residue was crystallized from the minimal amount of methanol to give 0.61 g (65%) (III) with indices corresponding to those given in our previous work [5].

2,2,4,2',2',4'-Hexamethyl-6,6'-ditrityl-1,2,3,4,1',2',3',4'-octahydroquinoline-1,1' (IVa) was obtained analogously from (IIa). Chromatogaphy gave a fraction with R_f 0.3 (3:1 petroleum ether—benzene). The yield of (IVa) was 57%, mp 226-227°C (dec.). Found: C 89.56; H, 7.44; N, 3.15%. Calculated for $C_{62}H_{60}N_2$: C, 89.42; H 7.21; N, 3.36%. PMR spectrum (δ, ppm): 1.16 s (3H, CMe_2), 1.24 s (3H, CMe_2), 1.54 d (3H, 4-Me), 1.74 d (2H, 3-CH_2), 2.82 m (1H, 4-CH), 6.7-6.9 m (3H, arom.), 7.19 s (15H, CPh_3). The authentic product was obtained by the oxidation of tetrahydroquinoline (VIIa) by $KMnO_4$.

2,2,4,2',2',4'-Hexamethyl-4,4'-diphenyl-6,6'ditrityl-1,2,3,4,1',2',3',4'-octahydroquinoline-1,1' (IVb) was obtained analogously from nitroxyl (IIb). Chromatography gave a fraction with R_f 0.4 (3:1 petroleum ether—benzene). The yield of (IVb) was 51%, mp 154-156°C (dec.). Found: C, 90.02; H, 7.10; N, 2.88%. Calculated for $C_{74}H_{68}N_2$: C, 90.24; H, 6.91; N, 2.85%. PMR spectrum (δ, ppm): 0.96 s (3H, CMe_2), 1.08 s (3H, CMe_2), 1.37 s (3H, 4-Me), 2.30 q (2H, 3-CH_2), 6.8-7.3 m (8H, arom.), 7.12 s (15H, CPh_3). The authentic product was isolated upon the oxidation of tetrahydroquinoline (VIIb).

CONCLUSIONS

The reaction of aromatic nitroxyl radicals with dichlorocarbene, generated under phase transfer catalysis conditions, leads to the corresponding hydrazine derivatives through the abstraction of the oxygen atom from the nitroxyl radicals and formation of aminyl radicals.

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