THERMAL DECOMPOSITION OF 2,6-DI-tert-BUTYL-p-BENZOQUINONE DIAZIDE IN AMINES

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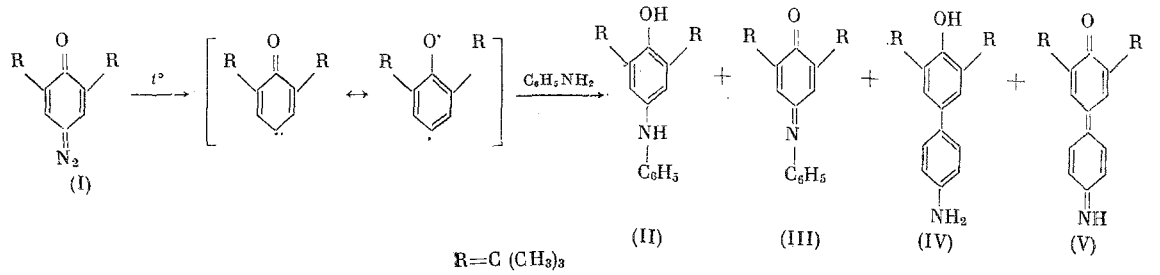
Previously we had shown that the thermal decomposition of 2,6-di-tert-butyl-p-benzoquinone diazide in alcohols and acids [1], aromatic hydrocarbons [2], olefins [3], and acetylenes [4] proceeds via the step of forming carbene, which then reacts with the medium. The decomposition rate of the starting quinone diazide is quite dependent on the reaction temperature. The process goes with sufficient speed at temperatures above 70° [1].

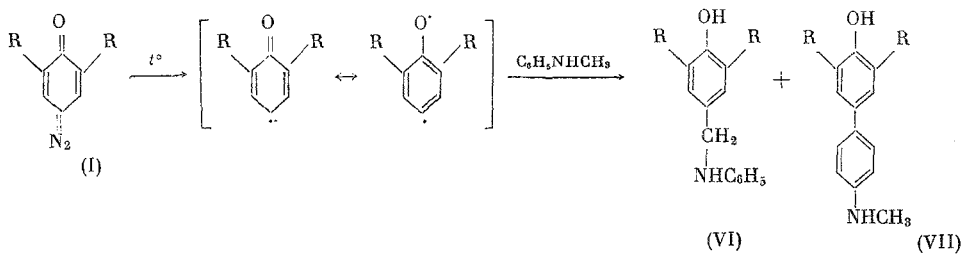
In the present paper was studied the decomposition of 2,6-di-tert-butyl-p-benzoquinone diazide (I) in solutions of aromatic and aliphatic amines. The thermal decomposition of quinone diazide (I) in aniline solution gives two principal compounds: 4-N-phenylamino-2,6-di-tert-butylphenol (II) and N-phenyl-2,6-di-tert-butyl-p-benzoiminoquinone (III). Besides this, from the reaction mixture were isolated, in small yield, 4-(4'-aminophenyl)-2,6-di-tert-butylphenol (IV) and its oxidation product, nemely, 2,6-di-tert-butyldiphenoiminoquinone (V)



R=C (CH$_3$)$_3$

The formation in the reaction mixture of quinoid compounds (III) and (V) is obviously associated with the dehydrogenation of phenols (II) and (IV) by the carbene, which is supported by the presence of 2,6-di-tert-butylphenol in the reaction mixture.

Somewhat different results were obtained when the reaction was run in N-methylaniline solution. In this case the product of addition to the nitrogen atom of the amine could not be obtained. From the reaction mixture were isolated N-phenyl-4-hydroxy-3,5-di-tert-butylbenzylamine (VI) (57% yield) and 4-(4'-N-methylaminophenyl)-2,6-di-tert-butylphenol (VII) (34% yield)



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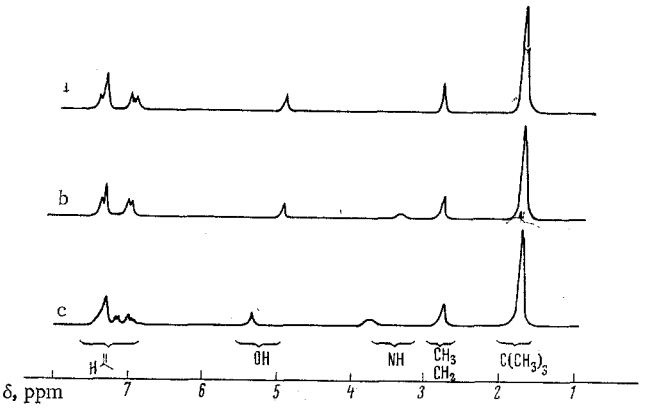


Fig. 1. NMR spectra: a) 4-(4'-N,N-dimethylaminophenyl)-2,6-di-tert-butylphenol; 2) 4-(4'-N-methylaminophenyl)-2,6-di-tert-butylphenol; c) N-phenyl-4-hydroxy-3,5-di-tert-butylbenzylamine. Solvent = CCl_4, standard = hexamethyldisiloxane.

The structure of the obtained compounds was confirmed by chemical and spectral methods. Thus, the reduction of benzoiminoquinone (III) and diphenoiminoquinone (V) with zinc in glacial acetic acid gave the corresponding phenol derivatives (II) and (IV). Acylation of benzylamine (VI) with acetic anhydride in glacial acetic acid gave the corresponding N-acetyl derivative. In this connection the spectral characteristics of the compound also change. If in the IR spectrum of benzylamine (VI) are present the absorption bands of the OH (3610 cm^{-1}) and NH (3400 cm^{-1}) groups, then for the acetyl derivative the band of the OH group does not change, but the band of the NH group disappears, and a band, corresponding to the absorption of the carbonyl group, appears. The NMR spectrum of benzylamine (VI) contains signals from the protons of the tert-butyl groups (δ = 1.56 ppm), the methylene group (δ = 2.88 ppm), a broad signal from the NH group (δ = 3.9 ppm), the OH group (δ = 5.16 ppm), and signals from the phenyl protons (δ = 6.58, 6.65, 6.70, 6.77, 6.98, and 7.59 ppm).

The spectral characteristics of phenol (VII) fully correspond to its structure. In the UV spectrum is observed an absorption maximum at 280 nm, which is characteristic for diphenyl derivatives [2]; the IR spectrum contains absorption bands of the OH (3510 cm^{-1}) and NH (3375 cm^{-1}) groups, while the NMR spectrum contains the signals of the protons of the tert-butyl groups (δ = 1.56 ppm), methyl group (δ = 2.89 ppm), NH group (δ = 3.48 ppm), OH group (δ = 5.01 ppm), and the signals from the phenyl protons (δ = 6.52, 6.60, 7.26, and 7.35 ppm). In Fig. 1 are given the NMR spectra of benzylamine (VI) and phenol (VII), and, also for comparison, of 4-(4'-N,N-dimethylaminophenyl)-2,6-di-tert-butylphenol, obtained previously by the decomposition of quinone diazide (I) in dimethylaniline [2].

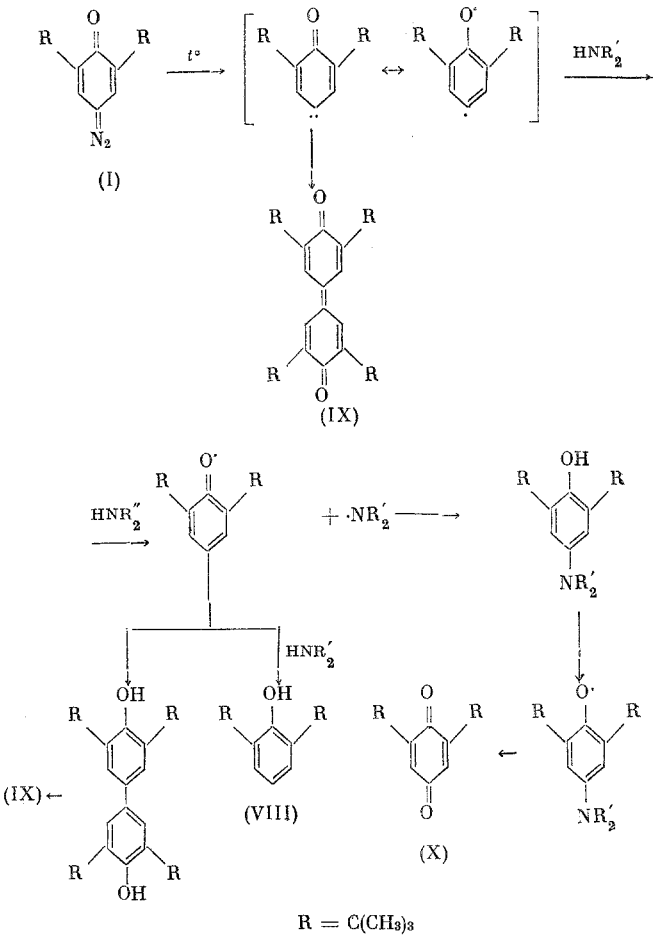
In the IR spectra of (II) and (IV) are present the absorption bands of the OH (3640 cm^{-1}) and NH (3400 cm^{-1}) groups. The absorption maximum in the UV spectrum of phenol (VI) has a shape and position that are characteristic for diphenyl derivatives [2], whereas the UV spectrum of (II) coincides with the spectrum of 4-hydroxy-3,5-di-tert-butylbenzylamine. The IR spectra of the oxidation products of these phenols, namely, (III) and (V), contain the doublet bands of a conjugated carbonyl group in the 1650 cm^{-1} region, which coincides with their quinoid structure.

When studying the decomposition of benzoquinone diazide (I) in solutions of aliphatic amines we used diisopropylamine, di-n-propylamine, and di-n-butylamine as solvents. The selection of the amines was determined by their boiling point, since benzoquinone diazide (I) decomposes with sufficient speed, with the formation of carbene and molecular nitrogen, at temperatures above 70°. In all three cases we were unable to isolate the expected 4-N,N-dialkylamino-2,6-di-tert-butylphenols. The end reaction products were: 2,6-di-tert-butylphenol (VIII), 3,3',5,5'-tetra-tert-butyldiphenoquinone (IX), and 2,6-di-tert-butyl-p-benzoquinone (X). The formation of the indicated products during the thermal decomposition of (I) can be depicted by Scheme 1.

As can be seen from Scheme 1, diphenoquinone (IX) is formed as the result of the dimerization of both the intermediate carbene and the 2,6-di-tert-butylphenoxyl, with subsequent dehydrogenation of the diphenyl derivative. As is known [5], phenoxyl radicals in the series of sterically hindered phenols possess dehydrogenating properties. Evidently, under the reaction conditions the 2,6-di-tert-butylphenoxyl can dehydrogenate the amine, used as solvent, and the substituted phenols with the formation of phenol (VIII). On the other hand, this phenoxyl radical can react with the radical $R_2N^{\cdot}$, giving the 4-N,N-dialkyl-2,6-di-tert-butylphenol. The latter, on dehydrogenation by carbene or the phenoxyl radical in the presence of oxygen, is converted to p-benzoquinone (X).

EXPERIMENTAL METHOD

Thermal Decomposition of 2,6-Di-tert-butyl-p-benzoquinone Diazide (I) in Aniline Solution. A solution of 0.5 g of the quinone diazide (I) in 15 ml of freshly distilled aniline was heated on the boiling water bath for 1 h. Then



Scheme 1

the excess aniline was removed in vacuo, the residue was dissolved in ether, and the ether solution was washed with 2% HCl solution and then with water. After drying, the ether was removed in vacuo, and the residue was dissolved in the minimum amount of hexane and chromatographed on a thin layer of aluminum oxide in the system: hexane – ether (97 : 3 by volume). After removal of the solvent in vacuo we obtained: 1) phenol (II), yield 46%, mp 134-135° (from hexane). Found: C 80.86; H 9.39%. $C_{20}H_{27}ON$. Calculated: C 80.76; H 9.49%; 2) quinonimine (III), yield 18%, mp 76-77° (from [6]: mp 77-78°); 3) phenol (IV), yield 10%, mp 66-67°. Found: C 80.65; H 9.40%. $C_{20}H_{27}ON$. Calculated: C 80.76; H 9.49%; 4) iminoquinone (V), yield 8%, mp 120-121°. Found: C 81.23; H 8.61%. $C_{20}H_{25}ON$. Calculated: C 81.31; H 8.53%.

Thermal Decomposition of 2,6-Di-tert-butyl-p-benzoquinone Diazide (I) in N-Methylaniline Solution. A solution of 0.5 g of the quinone diazide (I) in 15 ml of N-methylaniline was heated on the boiling water bath for 1 h. After the same treatment of the reaction mixture as before we obtained: 1) benzylamine (VI), yield 57%, mp 148-149° (from hexane). Found: C 80.94; H 9.38%. $C_{21}H_{29}ON$. Calculated: C 80.98; H 9.38%; 2) compound (VII), yield 34%, mp 101-102° (from hexane). Found: C 81.00; H 9.20%. $C_{21}H_{29}ON$. Calculated: C 80.98; H 9.38%.

N-Acetyl-N-phenyl-4-hydroxy-3,5-di-tert-butylbenzylamine. To a solution of 0.33 g of benzylamine (VI) in 10 ml of glacial acetic acid was added 0.5 ml of acetic anhydride. The mixture was heated at 70° for 30 min, after which 30 ml of water was added, and the mixture was refluxed until the acetic anhydride had decomposed completely. The reaction mixture was cooled and extracted with ether. The ether extracts were washed with water and dried. After removal of the solvent in vacuo we obtained 0.3 g (86% of theory) of the acetyl derivative, mp 143-144° (from hexane). Found: C 78.10; H 8.90%. $C_{23}H_{31}O_2N$. Calculated: C 78.15; H 8.84%.

Thermal Decomposition of 2,6-di-tert-butyl-p-benzoquinone Diazide (I) in Diisopropylamine Solution. A solution of 0.5 g of the quinone diazide (I) in 20 ml of diisopropylamine was heated on the boiling water bath for 2 h. Then the excess amine was removed in vacuo, while the residue was dissolved in the minimum

amount of hexane and chromatographed on a thin layer of aluminum oxide in the system: hexane – benzene (9:1, by volume). After removal of the solvent we obtained: 1) 0.23 g (52% of theory) of phenol (VIII), mp 36-37° (sublimation). From [6]: mp 36.5°; 2) 0.07 g (16% of theory) of diphenoquinone (IX), mp 246°. From [7]: mp 246°; 3) 0.15 g (31% of theory) of compound (X), mp 67-68° (sublimation). From [8]: mp 67-68°.

Analogous products were obtained when solutions of benzoquinone diazide (I) in di-n-propylamine and di-n-butylamine were heated.

CONCLUSIONS

A study was made of the thermal decomposition of 2,6-di-tert-butyl-p-benzoquinone diazide in solutions of aromatic and aliphatic amines.

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