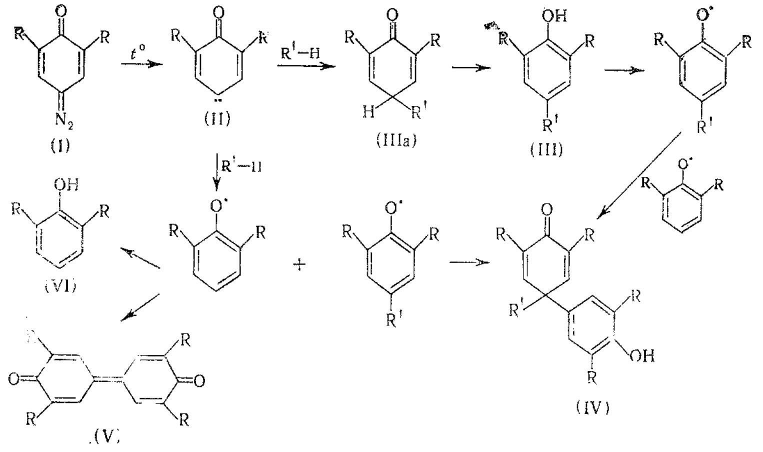
THERMAL DECOMPOSITION OF 2,6-DI-tert-BUTYL-p-BENZOQUINONE DIAZIDE IN HYDROCARBONS

L. G. Plekhanova, G. A. Nikiforov,
and V. V. Ershov

UDC 542.92+541.11+547.567

The initial step in the thermal decomposition of quinone diazide (I) is the formation of carbene (II), which then reacts with the medium to give various compounds [1-5]. The thermal decomposition products of quinone diazide (I) in the medium of saturated hydrocarbons (pentane, heptane, cyclopentane, and cyclohexane) are 4-alkyl-2,6-di-tert-butylphenols (III) (60-75%), 2,6-di-tert-butyl-4-alkyl-4-(4'-hydroxy-3',5'-di-tert-butylphenyl)-2,5-cyclohexadienones (IV) (20-25%), 3,3',5,5'-tetra-tert-butyldiphenoquinone (V) and 2,6-di-tert-butylphenol (VI). The formation of the indicated products can be explained by the following scheme:



$R = C(CH_3)_3$; $R' = C_5H_9$; C_6H_{11}; C_5H_{11}; C_7H_{15}.

The formation of (III) in the reaction medium is either the result of insertion of the intermediate carbene at the C – H bond of the hydrocarbon, or, to a lesser degree, the result of the dehydrogenating capacity (at elevated temperature) of the 4-alkyl-2,6-di-tert-butylphenoxyl radicals [6]. The latter also explains the appearance of (VI) in the reaction mixture. The direct insertion of carbene (II) across the C – H bond as an intermediate step predicates the formation of (IIIa), which subsequently spoontaneously rearranges to the 4-alkyl-2,6-di-tert-butylphenol [7]. The decomposition of (I) in pentane yields phenols that contain isomeric amyl moieties in the p-position, and specifically: the 4-amyl-, 4-(α-ethyl)propyl- and 4-(α-methyl)butyl-2,6-di-tert-butylphenols, and also (VI). All of these phenols were identified by GLC. A similar complex mixture of phenols was also obtained during the thermolysis of (I) in heptane medium.

The structure of (III) was confirmed by spectral and chemical methods. The UV spectra of these phenols have an aromatic character, while the absorption band of the hydroxyl group (3632 cm^{-1}) is observed in the IR spectra. In the case of 4-cyclopentyl-2,6-di-tert-butylphenol the EPR signal of the corresponding phenoxyl radical consists of a doublet of triplets with the splitting a_H = 1.9 Oe by the meta-protons of the aromatic ring and a_{CH} = 6.3 Oe by the protons of the methylene linkage. The corresponding methylenequinone

---

Institute of Chemical Physics, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.1, pp.189-191, January, 1971. Original article submitted April 27, 1970.

was isolated when this phenol was oxidized with potassium ferricyanide, which had a characteristic UV spectrum (λ_{max} = 320 nm), and in whose IR spectrum was present the doublet band of a conjugated carbonyl group (1616 and 1575 cm^{-1}).

The structure of the dienones (IV) (R = C_5H_9 and C_6H_{11}) was confirmed by UV, IR, NMR, and EPR spectroscopy and by chemical methods. In the UV region the given compounds have an absorption maximum at λ = 236 nm, while in the IR spectra are present the absorption bands of the hydroxyl group (3640 cm^{-1}) and the doublet absorption bands of a conjugated carbonyl group in the 1650 cm^{-1} region. The NMR spectrum of compound (IV, R = C_5H_9) contains signals from the protons of the tert-butyl groups (τ = 8.85; 8.69), OH groups (τ = 5.13), phenyl protons (τ = 3.13) and protons of the cyclohexadiene ring (τ = 3.65), a symmetrical quartet from the methine proton (τ = 7.02), and a group of signals from the protons of the methylene groups. The EPR spectrum of the corresponding phenoxyl radical from (IV, R = C_5H_9 and C_6H_{11}) consists of a triplet (a_H = 1.9 Oe), caused by the coupling of the unpaired electron with the meta-protons of the phenyl ring, which corroborates the presence of a quaternary carbon atom, found in the p-position of the phenoxyl. We also recorded the EPR signal of the anion-radical, formed during the electrochemical reduction of (IV, R = C_5H_9) in the presence of tetrabutylammonium fluoborate, in tetrahydrofuran, at −70°C, with splitting by the meta-protons, a_H = 7.65 ± 0.2 Oe [8]. The treatment of (IV, R = C_5H_9) with a mixture of acetic and sulfuric acids (9 : 1) at room temperature leads to a cleavage of the cyclopentyl moiety with the formation of 2,2',6,6'-tetra-tert-butylbisphenol. The thermolysis of (I) in n-pentane and in n-heptane failed to permit the isolation of the pure cyclohexadiene derivatives (IV). However, the IR- and UV-spectroscopy data for the fractions, isolated by means of TLC, testify that the latter are a mixture of isomers having a cyclohexadiene structure.

EXPERIMENTAL

Decomposition of Quinone Diazide (I) in Cyclopentane. A solution of 1 g of (I) in 20 ml of cyclopentane was heated at 100°C in an autoclave for 2 h. The solvent was removed in vacuo, and the residue was chromatographed on a thin layer of Al_2O_3 in the system: hexane – benzene (9 : 1, by volume). We obtained: a) 0.75 g (64%) of 2,6-di-tert-butyl-4-cyclopentylphenol, mp 58-59° (from hexane): found: C 82.82; H 11.05%. $C_{19}H_{30}O$. Calculated: C 83.15; H 11.02%; b) 0.25 g (20%) of 2,6-di-tert-butyl-4-cyclopentyl-4-(4'-hydroxy-3',5'-di-tert-butylphenyl)-2,5-cyclohexadienone (IVa), mp 175° (from hexane). Found: C 82.74; H 10.56%; mol. wt. 480 ± 1 (mass spectroscopy). $C_{33}H_{50}O_2$. Calculated: C 82.69; H 10.52%; mol. wt. 478.73. Ultraviolet spectrum (hexane): λ_{max} 236 nm, log ε = 4.28; c) 0.1 g (11.5%) of 3,3',5,5'-tetra-tert-butyldiphenoquinone, mp 246° [9].

A solution of 0.15 g of (IVa) in 20 ml of a mixture of acetic and sulfuric acids (9 : 1, by volume) was stirred for 4 h at 20°. The mixture was diluted with water, extracted with ether, washed in succession with water and $NaHCO_3$ solution, and the solvent was distilled off. The residue was recrystallized from hexane. We obtained 0.12 g of 2,2',6,6'-tetra-tert-butylbisphenol, mp 183-184° [10].

To a solution of 1 g of (III, R = C_5H_9) in 25 ml of benzene was added, in an argon stream, a solution of 2.5 g of KOH and 2 g of potassium ferricyanide in 25 ml of water. The mixture was stirred vigorously at 40-45° for 2 h, and then the benzene solution was separated, washed with water until neutral, and the solvent was distilled off. The residue was recrystallized from hexane. We obtained 0.95 g (96%) of α,α-tetramethylene-2,6-di-tert-butyl-p-methylenequinone, mp 115°. Found: C 83.98; H 10.29%. $C_{19}H_{28}O$. Calculated: C 83.79; H 10.32%.

Decomposition of (I) in Cyclohexane. A solution of 1 g of (I) in 20 ml of cyclohexane was heated at 100° in an autoclave for 2 h. The mixture was worked up in the same manner as in the first experiment. We obtained: a) 0.9 g (72.5%) of 2,6-di-tert-butyl-4-cyclohexylphenol, mp 91-92° [11]; b) 0.26 g (25%) of 2,6-di-tert-butyl-4-cyclohexyl-4-(4'-hydroxy-3',5'-di-tert-butylphenyl)-2,5-cyclohexadienone, mp 156° (from hexane). Found: C 83.80; H 10.63%. $C_{34}H_{52}O_2$. Calculated: C 83.87; H 10.64%. Ultraviolet spectrum (hexane): λ_{max} = 236 nm, log ε = 4.32.

Decomposition of (I) in Pentane. A solution of 1 g of (I) in 30 ml of pentane was heated in an autoclave at 100° for 2 h. After the same workup as in the first experiment we obtained: a) 0.8 g (60%) of a mixture of phenols (III), in which by GLC (15% polymethylphenylsiloxane fluid 4 deposited on Celite 545, column temperature 220°, vaporizer temperature 250°) were identified: 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-4-amylphenol, 2,6-di-tert-butyl-4-(α-ethyl)propylphenol + 2,6-di-tert-butyl-4-(α-methyl)butylphenol in a ratio of 1 : 3 : 10, b) 3,3',5,5'-tetra-tert-butyldiphenoquinone, mp 246° [9].

Decomposition of (I) in Heptane. A solution of 1 g of (I) in 30 ml of heptane was heated in an autoclave at 100° for 2 h. After the same workup as in the first experiment we obtained: a) 0.94 g (72%) of a mixture of phenols (2,6-di-tert-butylphenol and isomeric 4-heptyl-2,6-di-tert-butylphenols); b) 0.16 g (20%) of 2,3',5,5'-tetra-tert-butyldiphenoquinone, mp 246° [9].

CONCLUSIONS

A study was made of the thermal decomposition of 2,6-di-tert-butyl-p-benzoquinone diazide in the medium of cyclic and alicyclic aliphatic hydrocarbons.

LITERATURE CITED

1. G. A. Nikiforov and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 2341 (1967).
2. L. G. Plekhanova, G. A. Nikiforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 961 (1969).
3. G. A. Nikiforov, L. G. Plekhanova, V. V. Ershov, A. N. Rozenberg, G. N. Bogdanov, A. I. Prokof'ev, and S. P. Solodovnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 204 (1968).
4. G. A. Nikiforov, B. D. Sviridov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 558 (1968).
5. G. A. Nikiforov, B. D. Sviridov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1653 (1968).
6. M. B. Neiman, Yu. T. Mamedova, P. Blenke, and A. L. Buchachenko, Dokl. Akad. Nauk SSSR, 144, 392 (1962).
7. W. Pirkle and G. Koser, Tetrahedron Letters, No. 36, 3959 (1968).
8. A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1712 (1968).
9. M. Kharasch and B. Joshi, J. Org. Chem., 22, 1435 (1957).
10. M. Kharasch and B. Joshi, J. Org. Chem., 22, 1439 (1957).
11. G. Stillson, D. Sawyer, and C. Hunt, J. Am. Chem. Soc., 67, 303 (1945).