PHENYL-SUBSTITUTED 1,4-BENZOQUINONE DIAZIDES.

4. THERMAL DECOMPOSITION OF 2,6-DIPHENYL-1,4-BENZOQUINONE

DIAZIDE IN OXYGEN-CONTAINING ORGANIC SOLVENTS

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In studying the reaction of 3,5-diphenylcyclohexadienone carbene with CCl₄ [1] we found that its chemical behavior differed from the carbenes which we had studied previously [2]. In view of this, it would be of interest to study the behavior of this cyclohexadienonylidene in reactions with other organic compounds. In the present work we have carried out thermal decomposition of 2,6-diphenyl-1,4-benzoquinone diazide (I) in aliphatic alcohols (methyl, isopropyl, and t-butyl), acetic acid, and dioxane.

Thermolysis of the quinone diazide (I) in alcohols results in the formation of hydroquinone ethers (III) (45-70% yield) and 2,6-diphenylphenol (IV) (15-30%) (see Table 1)



Due to the low solubility of (I) in alcohols, the reaction proceeds slowly (10 h in isopropyl and 25 h in t-butyl alcohol). The product ratio depends on the alcohol (Table 1).

The formation of two phenolic compounds in the reaction is obviously due to the dual reactivity of the intermediate cyclohexadienone carbene (II). On one hand, it actively dehydrogenates the alcohol (evidently by a radical mechanism) to yield 2,6-diphenylphenol (III), and, on the other hand, it reacts with the alcohol to form an intermediate ylide, which, according to currently accepted ideas, rearranges to form the hydroquinone ether (IV). The increase in the yield of 2,6-diphenylphenol when thermolysis of (I) is effected in isopropanol in accord with the proposed mechanism, since this alcohol is the most readily dehydrogenated. Thermolysis of (I) in AcOH results in the formation of the hydroquinone acetate ester in a yield of 100%. Thermolysis of (I) in dioxane takes 2 h and yields a cyclic quinol ether (V) (33%), a cyclic hydroquinone ether (VI) (38%), and a polymeric product (VII) (25%)



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TABLE 1

Solvent	Reaction time, h	Yield,%		mp(°C) of 2, 6-
		(III)	(IV) *	quinone ethers
CH3OH CH (CH3) 2OH C (CH3) 3OH CH3COOH	56 10 25 2	70 45 50 95	20 35 23 -	62† Oi1 89–90 167
*mp 101°C; tcf. [4].	cf. [3].			

These compounds are evidently formed as a result of different reactions of a bipolar ion formed from an intermediate ylide. Intramolecular cyclization of this ion leads to the spiran (V) and ether (VI), and intermolecular reaction of the ion gives the polymer (VII) with alternating fragments from the quinone diazide and dioxane (the ratio of phenyl to ether protons in the PMR spectrum is 3:2). The structure of the ether products was confirmed by spectral and elementary analysis.

Comparison of the results obtained in the present work with those obtained for analogous reactions of 2,6-di-t-butyl-1,4-benzoquinone diazide [2] indicate that the direction of the reaction between the cyclohexadienone carbenes and a substrate depends on the nature of the ortho substituents. In the case of bulky alkyl groups, only para-substituted derivatives are formed. As the shielding of the carbonyl group decreases, reactions involving the oxygen atom also become possible.

EXPERIMENTAL

Thermolysis of 2,6-Diphenyl-1,4-benzoquinone Diazide (I) in Dioxane. A solution of 1 g (I) in 50 ml dioxane was heated on a water bath for 2 h. The solvent was removed in vacuo. The residue was chromatographed on a thin layer of silica gel (LSL₂₅₄ 5/40 μ) in benzene/ ether (10:1 by vol.) to give: a) 0.4 g (33%) of 4,6-diphenyl-1,16-dioxaspiro[2,5]dodeca-3, 6-dien-5-one, mp 149°C (from CHCl₃); UV spectrum (in hexane), $\lambda_{max} = 210$, 226, 282 nm; IR spectrum, vCO = 1645, 1670 cm⁻¹; PMR spectrum (δ , ppm) 2.9-4 m (CH₂O). Found: C 79.48; H 6.09%; mol. wt. 332 (mass spectrometric). C₂₂H₂₀O₃. Calculated: C 79.49; H 6.06%; mol. wt. 332. b) 0.47 g (38%) of the cyclic diethylene glycol ether of 2,6-diphenylhydroquinone, mp 178°C (from CHCl₃); UV spectrum (in hexane), $\lambda_{max} = 211$, 242, 310 nm; PMR spectrum (δ , ppm) 3.6-4 m (CH₂O), 2.3 m (CH₂). Found: C 79.72; H 6.10%; mol. wt. 332. C₂₂H₂₀O₃. Calculated: C 79.49; H 6.06%; mol. wt. 332.

Thermolysis of (I) in Alcohols and Acetic Acid. The decomposition of (I) in isopropyl and t-butyl alcohols and AcOH was effected similarly to the preceding experiment. The residue was chromatographed on Silufol UV-254 plates. The constants and yields of the resulting hydroquinone ethers are given in Table 1. Elementary analysis of the ethers for C and H gave results with a maximum deviation of 0.3% from the calculated values.

CONCLUSIONS

1. The thermolysis of 2,6-diphenyl-1,4-benzoquinone diazide in aliphatic alcohols proceeds by two routes, resulting in the formation of 4-alkoxy-2,6-diphenylphenols and 2,6-diphenylphenol.

2. The behavior of 3,5-diphenylcyclohexadienone carbene when reacted with dioxane is determined by the ability of both reaction centers of the carbene to participate in the reaction.

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