PHENYL-SUBSTITUTED 1,4-BENZOQUINONE DIAZIDES

I. SYNTHESIS AND THERMAL AND PHYSICOCHEMICAL STABILITY

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Phenyl-substituted 1,4-benzoquinone diazines have not previously been known. The development of a method for their production and an evaluation of their thermal and photochemical stability form the aim of the present work.

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To synthesize phenyl-substituted quinone diazides we used the method of Ried and Dietrich [1], which we modified and transformed into a one-stage process



The condensation of p-toluenesulfonhydrazide and p-benzoquinone was effected in a mixture of ether and ethanol in the presence of one equivalent of HCl with heating. Then, without the isolation of the intermediate hydrazones, the reaction mixture was subjected to treatment with aqueous caustic soda solution.

Good results were also obtained when boron trifluoride etherate was used as catalyst. In this case, condensation takes place at room temperature in dry THF. Where necessary, the corresponding hydrazone can be isolated in high yield. We performed this reaction for the case of 3,5-diphenyl-1,4-benzoquinone diazide. According to IR spectroscopy (presence of the band of an OH group at 3510 cm^{-1} and the absence of the C=O band) in KBr, the intermediate tosylhydrazone exists as the azo form, while in CDCl₃ solution (under the conditions of recording the PMR spectrum) it exists in the hydrazone form (absence of a signal from an OH proton in the 4-6 ppm region). Alkaline cleavage of the hydrazone in CH₂Cl₂ gave the corresponding benzoquinone diazide. The modified method that we have developed was also used for the synthesis of 2,6-di-tert-butyl-1,4-benzoquinone diazide. The yields, constants, and spectral characteristics of the quinone diazides obtained are given in Table 1.

Reactions of two types are characteristic for the quinone diazides: azo-coupling reactions with the retention of the N atoms, and reactions with the evolution of N₂ (thermolysis and photolysis), leading to the formation of cyclohexadienone carbenes. For reactions of the first type one must take into account the existence of the quinone diazide \neq diazonium salt equilibrium in the presence of acids. Where the carbonyl group is sterically screened or when electronegative substituents are present in the ring of the quinone diazide, this equilibrium must shift in the direction of more acidic pH values



This is in harmony with the results of measurements of the acid-base equilibrium constants (pK_a) of the quinone diazides obtained (see Table 1). The pK_a value of the 2,6-diphenyl-1,4-benzoquinone diazide is shifted in the direction of low pH values, which is apparently connected with the electronic effects of the phenyl groups. The introduction of

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TABLE 1. 1,4-Benzoquinone Diazide

R	Ri	R²	mp, °C	Yield, %	λ _{max} , nm	log e	"CN₂, cm ⁻¹	рКа	k ₈₀ ° ·10-4, sec-1	Ф ³⁶⁵ р
H C (CH ₃) 3 C (CH ₃) 3 C ₆ H ₅ C ₆ H ₅ C ₆ H ₅ Br	H C (CH ₃) ₃ C ₆ H ₅ C ₆ H ₅ C ₆ H ₅ Br	H H H OCH ₃ Cl H	$\begin{array}{r} 90-91\\ 110-111\\ 96-97\\ 136-137\\ 120-121\\ 104-105\\ 135-136\end{array}$	- 89 80 85 30 27 -	257,354 264,358 288,370 304,376 287,370 295,369 278,369	3,66; 4,74 3,76; 4,47 4,00; 4,51 4,08; 4,47 3,84; 4,38 4,13; 4,47 3,91; 4,64	2133 † 2110, 2080 2318 2272 2273 2273 2272 2123 †	3,19 ‡ 1,65 ‡ 2,37 1,70 1,56 0,37 0,00 **	$\begin{array}{c} 0.28 \\ 2.22 \\ 2.42 \\ 2.88 \\ 2.38 \\ 2.62 \\ 1.27 \end{array}$	$\begin{array}{c} 0,27\\ 0,40\\ 0,39\\ 0,36\\ 0,29\\ 0,37\\ 0,60 \end{array}$

*All the 1,4-benzoquinone diazides apart from these shown have a maximum in the 500 nm region (log $\epsilon \simeq 2$), the position of which is highly dependent on the polarity of the solvent (n- π * band).

[†]Figures taken from the literature [2], measurements in CH₃OH and CH₃COCH₃. [‡]Figures taken from [3].

**Figures taken from [4].

additional substituents (OCH₃ and Cl) into the quinone ring regularly displaces the equilibrium in the direction of low pH values, and this the more strong the higher the electronegativity of the substituents. The pK_{α} value of 2-tert-butyl-6-phenyl-1,4-benzoquinone diazide, conversely, is shifted in the direction of high pH values and approximates to the pK_{α} values for poorly screened benzoquinone diazides [3]. The main factor affecting pK_{α} is formed by the electronic effects of the tert-butyl group which, together with a decrease in the steric hindrance for protonation, leads to a displacement of the pK_{α} in the direction of high pH values.

There is no quantitative information in the literature on the thermochemical and photochemical stability of 1,4-benzoquinone diazides; in the present work these properties have been studied not only for phenyl-substituted quinone diazides but also for some others that were known previously. Table 1 gives the rate constant for the thermolysis of 1,4-benzoquinone diazides in dioxane at 80°C. The rate of thermolysis of the quinone diazides depends linearly only on their initial concentration. The rate constant rises by approximately an order of magnitude when any substituents whatever are introduced into the quinone ring; no clear dependence on the electronic effects of the substituents can be observed. We investigated the influence of the polarity of the solvent on the rate of thermolysis for the case of 2,6-di-tert-butyl-1,4-benzoquinone diazide (Table 2). The rate constants of thermolysis at 80°C change only twofold when the polarity of the solvent (dielectric constant) changes by an order of magnitude. The activation energies of these processes also differ insignificantly. It is obvious that the polarity of the medium has no fundamental influence on the rate of thermolysis of quinone diazides. This indirectly shows the homolytic nature of the thermolysis reaction of quinone diazides (formation of cyclohexadienone carbenes).

1,4-Benzoquinone diazides are extremely sensitive to light. The rate of their photolysis depends linearly on the intensity of the light but it does not depend on the gaseous medium (air or argon) and depends only slightly on the nature of the solvent (methanol, hexane). Table 1 gives the quantum yields of the photolysis of quinone diazides under the action of light (λ 365 nm); the quantum yields are high. The most light-sensitive is 2,6-dibromo-1,4-benzoquinone diazide, and the most stable to the action of light is 1,4-benzoquinone diazide.* The quantum yield of the photolysis of quinone diazides, while it does depend on the wave-length of the irradiating light, nevertheless remains fairly high (Table 3) (as far as 450 nm). This will permit the use of 1,4-benzoquinone diazides as chemical actinometers.

In conclusion, it must be mentioned that the IR spectra of the phenyl-substituted 1,4benzoquinone diazides show an anomalously high displacement of the band of the CN₂ group in

^{*}In the literature [5], a quantum yield of 0.53 is given for the photolysis of 1,4-benzoquinone diazide in methanol. The twofold difference from our results may be connected with the fact that, judging from the log ε value of 4.54, 1,4-benzoquinone diazide tetrahydrate was used in the previous investigation.

TABLE 2. Kinetic Parameters of the Thermolysis of 2,6-Di-tert-butyl-1,4-benzoquinone Diazide in Various Media

Solvent	k ₈₀ • ·10−4, sec-1	E, kca1/ mole	ε
Cyclohexane Cyclohexane Dioxane n-Butanol sec-Butanol tert-Butanol Di-n-propyl ketone Acetonitrile Dimethylformamide	3,72 3,39 2,22 2,52 2,39 3,35 2,11 2,06 1,82	28,9 27,4 28,9 27,1 27,9 29,1 28,3 26,1 25,9	2,02 2,21 17,10 15,80 10,90 36,20 36,70

TABLE 3. Dependence of the Quantum Yield (Φ_p) of the Photodecomposition of 2,6-Ditert-butyl-1,4-benzoquinone Diazide on the Wavelength of the Irradiating Light

λ, n m	Φp	λ, nm	Φp	۸, n m	Φp
313	0,48 *	365	0,40	436	0,31
333	0,37	405	0,38	546	0,062

*The quantum yield is high because we used a combination of glass filters (ZhS-3 and UVS-2) to isolate the mercury line.

the short-wave direction, which cannot be explained only by the electronic effect of the phenyl groups.

EXPERIMENTAL

<u>Phenyl-Substituted 1,4-Benzoquinone Diazides.</u> A solution of 0.01 mole of benzoquinone in 100-200 ml of ether was added to a solution of 0.01 mole of p-toluenesulfonhydrazide in a mixture of 10 ml of methanol and 50 ml of ether containing 1 ml of concentrated HCl, the mixture was stirred with the ether boiling for 2 h, and it was then cooled and was diluted twofold with water. The ethereal layer was separated off, shaken with 20 ml of 1 N aqueous KOH solution, and washed with water; the solvent was driven off in vacuum, and the residue was chromatographed in a thin layer of silica gel L40/100 μ m in the benzene—ether (20:1, by volume) system. The yields, constants, and spectral characteristics of the quinone diazides are given in Table 1. Elementary analysis of the quinone diazides obtained for their C, H, and N contents gave results deviating from the calculated figures by not more than 0.5%.

<u>2,6-Diphenyl-1,4-benzoquinone Tosylhydrazone</u>. A solution of 41.6 g (0.16 mole) of 2,6diphenyl-p-benzoquinone and 29.8 g (0.16 mole) of p-toluenesulfonhydrazide in 400 ml of dry THF containing 0.5 ml of boron trifluoride etherate was kept at $\sim 20^{\circ}$ C for 3 min and was then poured into 1 liter of water containing ice. The hydrazone was extracted with CH₂Cl₂ and, after drying and evaporation in vacuum, the residue was crystallized from methanol. This gave 57 g (83%) of the hydrazone, with mp 134-135°C. Found: C 69.90, H 4.51%. C₂₅H₂₀O₃N₂S. Calculated: C 70.15; H 4.73%. UV spectrum: λ_{max} 246 and 297 nm. The hydrazone obtained was subjected to alkaline cleavage. The yield of 2,6-diphenyl-1,4-benzoquinone diazide was 91%; mp 136-137°C.

Physicochemical Investigation. The 1,4-benzoquinone diazide and its 2,6-dibrome derivative required for the comparative investigations were obtained by the diazotization of the corresponding p-aminophenols. The constants of the compounds obtained corresponded to those given in the literature [4, 6]. The solvents were purified and dried by a handbook method [7].

The IR and UV spectra of the benzoquinone diazides were recorded on spectrometers of the "Specord" type in KBr tablets (IR) and in methanol solution (UV). The equilibrium constants (pK_{α}) were determined spectrophotometrically in standard cells 1 cm thick at 22 ± 0.1°C on a "Specord UV-VIS" instrument. Aqueous methanol containing 1% of methanol was used as the solvent. The equilibrium constants were found graphically on the basis of measurements of the absorption of the quinone diazides in the 250-370 nm region as a function of the pH.

The kinetic parameters of the thermolysis of the quinone diazides were obtained spectrophotometrically by measuring the change in the optical density of their absorption in the 350-370 nm regions with the time on a "Specord UV-VIS instrument. The samples were thermostated with an accuracy of $\pm 0.1^{\circ}$ C.

The quantum yields (Φ_p) of photodecomposition of the quinone diazides in absolute methanol were calculated from the change in their density in the 350-370 nm region during irradiation, using the following equations:

 $\log(e^{-2,3D_0} - 1)/(e^{-2,3D} - 1)] = \Phi_p I_0 et$ 313 and 356 nm $\log[(D_0 - D_\infty)/(D - D_\infty)] = \Phi_p I_0 et$ 405, 436 and 546 nm

Irradiation was carried out with a DRSh-1000 mercury lamp, the lines of the mercury spectrum being isolated by means of interference filters, and where necessary the luminous flux was attenuated by neutral glasses. The standard ferrioxalate method was used for actinometry [8].

SUMMARY

1. A method of synthesizing phenyl-substituted 1,4-benzoquinone diazides has been developed.

2. The equilibrium constants in the quinone diazide \ddagger diazonium salt reaction for the phenyl-substituted 1,4-benzoquinone diazides have been determined.

3. The parameters of the thermal and photochemical stability of a number of 1,4-benzoquinone diazides have been obtained.

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CATALYTIC SYNTHESIS OF METHYLTHIOPHENES AND THIOPHENE FROM

C₅ HYDROCARBONS AND HYDROGEN SULFIDE

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Methylthiophenes are formed from some C_5 hydrocarbons and H_2S in the presence of Crcontaining catalysts [1-4]. In the case of the reaction of n-butane with H_2S , heterocyclizing properties have been detected for Re-containing catalysts [5]. In the present work we have studied the heterocyclization of C_5 hydrocarbons of various structures with H_2S on a Crcontaining catalyst and have made a comparison of the properties of Re oxide, Re sulfide, and mixed Re-Cr-containing catalysts in the reaction of n-pentane with H_2S in the presence of CO_2 or N_2 , which permit the selectivity of the catalysts to be raised considerably [6].

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EXPERIMENTAL

The work was carried out with chromatographically pure n-pentene, isopentene, and 2methylbut-2-ene, with 89.4% pure pent-1-yne, and with an isoamylene fraction with the following composition: 9.5% of but-1-ene, 4.5% of but-2-ene, 5.2% of 3-methylbut-1-ene, 26.7% of 2-methylbut-1-ene, and 54.1% of 2-methylbut-2-ene.

The H₂S was obtained by burning the gas isolated from the spent monoethanolamine used for purifying hydrocarbon gases obtained in the treatment of sulfur-containing petroleum oils.

The catalysts were prepared by the impregnation with aqueous salt of γ -Al₂O₃ of type A-1 (S = 249 m²/g) previously calcined in the air at 500° for 3.5 h and having a grain size of 2-3 mm. A chromium-containing catalyst with the composition 5% of Cr₂O₃ and 5% of Polirit (CeO₂, 2.7; La₂O₃, 1.3; Nd₂O₃, 0.75; Pr₂O₃, 0.25), 1% of K₂O, and 89% of Al₂O₃ [7] was prepared by impregnating γ -Al₂O₃ first with a solution of Polirit (REEs) in 13% HNO₃ with the

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