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SYNTHESIS AND ABSORPTION SPECTRA OF EPOXYDIARYLINDANONES AND

THEIR PHOTOISOMERS

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Some previously undescribed 2,3-epoxy-2,3-diarylindanones were obtained, and the spectral characteristics of their photoinduced forms were measured. A simple method for the determination of the molar extinction of benzopyrylium oxides is proposed.

The photochromic transformations of 2, 3-epoxy-2, 3-diphenylindanone have been studied in detail by Ullman and Henderson [1]. The available information regarding the synthesis and properties of other representatives of this series is extremely limited.

In the present research we obtained some previously undescribed epoxyindanones (EI) with various substituents in the 2 and 3 positions and measured some spectral characteristics of their photoinduced forms (III).



The starting indones (Ia-f) were synthesized by a known method [3] — by reaction of benzalphthalides with Grignard reagents — with simplification of the method in the case of Ia,e. Nitrophenylindone If was obtained by nitration of diphenylindone Ia with cupric nitrate in acetic anhydride. It is known that under the conditions of nitration of indone Ia with nitric acid [4] or oxides of nitrogen [5] the reaction does not stop with the formation of nitrophenylindone If because of the extremely easy subsequent addition of the nitrating agent to the double bond. In the case of nitration with cupric nitrate we were able to lower the yield of the addition product and isolate the nitrophenylindone directly from the reaction mixture.

The epoxidation of indones Ia-f was carried out in alkaline alcohol solutions of hydrogen peroxide at 65-70°C [6]. In the oxidation of 2-(p-nitrophenyl)-3-phenylindone (If) the pH of the medium was maintained at 8-9 to avoid side processes. The UV spectra of the synthesized epoxyindanones IIa-f are presented in Figs. 1 and 2.

All Ia-f form colored 1,3-disubstituted 2-benzopyrylium 4-oxides (IIIa-f) when benzene solutions of them are irradiated with UV light (λ 365 nm) because of photochemical valence tautomerization [1]. The reverse reactions take place under the influence of heat or visible light. The maxima of the long-wave absorption bands in the spectra of III are presented in Table 1.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 605-608, May, 1978. Original article submitted March 21, 1977; revision submitted October 24, 1977.



Fig. 1. Electronic absorption spectra of 2,3-epoxyindanones (ethanol): 1) 2-(α -naphthy1)-3pheny1-; 2) 2-pheny1-3-(α -naphthy1)-; 3) 2,3-dipheny1-.



Fig. 2. Electronic absorption spectra of 2,3-epoxyindanones (ethanol): 1) 2-(p-methoxyphenyl)-3-phenyl-; 2) 2-phenyl-3-(p-methoxyphenyl)-; 3) 2-(p-nitrophenyl)-3-phenyl-.

TABLE 1. Spectral Characteristics of 2-Benzopyrylium 4-Oxides

Compound	R ¹	R²	λ _{max} , nm	ε·10 ⁻⁴ , liter/mole· cm	
IIIA IIIb IIIc IIId IIIe IIIf	C_6H_5 $p-C_6H_4OCH_3$ C_6H_5 $\alpha-C_{10}H_7$ C_6H_5 $p-C_6H_4NO_2$	$\begin{array}{c} C_{6}H_{5} \\ C_{6}H_{5} \\ p \cdot C_{6}H_{4}OCH_{3} \\ C_{6}H_{5} \\ \alpha \cdot C_{10}H_{7} \\ C_{6}H_{5} \end{array}$	545 552 553 540 542 566	1,84* 2,20 1,90 1,81 2,54	

*In [1] an ε value of 26,750 liters/mole cm at λ = 545 nm is given for a solution of IIIa in benzene.

It is apparent from the data presented in Table 1 that the introduction of a methoxy or nitro group in the phenyl substituent of the 2-benzopyrylium oxide molecule (in the 1 or 3 position) leads to a bathochromic shift of the maximum of the long-wave absorption band relative to IIIa: 7-8 nm for IIIb,c and 21 nm for IIIf. It is known that in series of arylsubstituted pyrylium [7] and benzopyrylium [8, 9] salt, similar substituents in the position adjacent to the heteroatom have a more substantial effect on the position of the absorption maximum — the bathochromic shift reaches 30-50 nm. Such a slight effect of substituents on the spectra of IIIb,c,f can evidently be ascribed to the presence of an oxide anion in the molecule.

Replacement of one of the phenyl substituents in IIIa by naphthyl substituents leads to a 3-5 nm hypsochromic shift of the maximum of the absorption band; this may be due to a certain amount of disruption of the coplanarity of the molecule.

The determination of the extinction coefficients of III reduces to finding the concentration of the latter in a solution that also contains the starting EI. The method previously used [1] for this purpose is based on complete tying up of the benzopyrylium oxide formed during UV irradiation in an adduct with norbornadiene via a 1,3-dipolar addition reaction (the norbornadiene concentration is two orders of magnitude higher than the EI concentration); the use of EI with a tritium label enabled Ullman and Henderson [1] to determine the amount of adduct formed by the method of isotropic dilution.

We used a simpler method for the determination of the extinction coefficient. The method consists essentially in rapid tying up of a portion of the benzopyrylium oxide formed during UV irradiation with a definite amount of an unsaturated compound. We used tetracyanoethylene (TCE), the reactivity of which in 1,3-dipolar addition to benzopyrylium oxide in benzene is, according to our estimates, several orders of magnitude higher than the reactivity of nor-



Fig. 3. Dependence of ΔD (λ 545 nm) for benzopyrylium oxide IIIa on the concentration (C₀) of tetracyanoethylene (1) and N-(p-nitrophenyl)maleimide (2) in benzene at 20°C (l is the thickness of the cuvette in centimeters).

bornadiene, as the unsaturated compound. Almost all of the TCE reacts with benzopyrylium oxide* in a period of time that is negligibly small for an appreciable change in the concentration of the latter as a consequence of the reverse dark reaction or oxidation.

We used the following procedure for the measurements. A solution of the epoxyindanone in benzene was irradiated with light with wavelength 365 nm from a PRK-4 lamp in a cuvette until an optical density (D₁) of about 0.5-1.0 was reached at λ_{max} . Irradiation was discontinued, and a solution of TCE in benzene with a known concentration (in the amount necessary for tying up a portion of the benzopyrylium oxide) was added immediately, as a result of which the optical density decreased to D₂. Under the condition of complete tying up of the TCE in an adduct, one should observe a linear dependence of ΔD ($\Delta D = D_0 - D_2$) on C₀ with passage of the line through the origin (D₀ is the initial optical density at λ_{max} , and C₀ is the starting concentration of the unsaturated reagent; both values were adopted with allowance for the dilution of the solution); this was actually confirmed experimentally (Fig. 3). The extinction coefficient was determined from the slope of the line constructed by the method of least squares; the confidence interval for a significance level of 0.1 was 0.02.

The extinction coefficients of the photoinduced forms of the synthesized epoxyindanones (II) at the maxima of the long-wave absorption bands were measured by the described method. The results of the measurements are presented in Table 1. We were unable to measure the extinction coefficient in the case of 2,3-epoxy-2-(α -naphthyl)-3-phenylindanone (IIId), which has a reverse dark reaction with a high rate and reacts relatively slowly with TCE.

Close ε values at 545 nm were obtained for benzopyryli-m oxide IIIa when both TCE and N-(p-nitrophenyl)maleimide were used as the unsaturated reagent (Fig. 3).

EXPERIMENTAL

The electronic spectra of the epoxyindanones in ethanol and of the benzopyrylium oxides in benzene were recorded with VSU2-P and SF-18 spectrophotometers. The extinction coefficients of the benzopyrylium oxides were measured in a 1-cm thick quartz cuvette at 20°C. The ultrapure-grade benzene was previously dried with activity II aluminum oxide and distilled. The tetracyanoethylene, which was purified by the method in [10], had mp 197-199°C (in a sealed capillary) (mp 198-200°C [10]). Chromatography was accomplished with Silufol UV-254 plates and elution with benzene.

<u>2,3-Diphenylindone (Ia)</u>. A solution of 11 g (0.05 mole) of 3-benzalphthalide in 105 ml of tetrahydrofuran (THF) was added to a Grignard reagent obtained from 4.8 g (0.2 g-atom) of magnesium and 32.2 g (0.2 mole) of bromobenzene in 65 ml of THF, and the mixture was refluxed for 4 h. A saturated solution of 38 g of NH₄Cl was added, and the organic layer that separated was treated with stirring with a mixture of concentrated hydrochloric (75 ml) and sulf-uric (10 ml) acids at a temperature no higher than 30°C. Workup after almost 16 h gave 11.6 g (83%) of a product with mp 150-151°C (mp 149-151°C [11]).

 $\frac{2-\text{Phenyl}-3-(\alpha-\text{naphthyl})\text{ indone (Ie).}}{(0.125 \text{ g-atom}) \text{ of magnesium, 17.4 g (0.084 mole) of α-bromonaphthalene, and 9 g (0.04 mole)}}$ of 3-benzalphthalide in 140 ml of THF. The oil that formed after the addition of the acids

^{*}The irreversibility of the reaction of benzopyrylium oxide with TCE was confirmed by the results of chromatographic analysis of a benzene solution of their adduct after the mixture had stood for many days.

TABLE 2. 2, 3-Epoxy-2, 3-Diarylindanones

Com- pound ^b	mp, deg C ^a	Found, %		Empirical	Calc., %		Yield.
		с	н	formula	с	Н	%
IIb IIc IId IIe IIf ^c	$123 - 124 \\110 - 111 \\155 - 156 \\160 - 161 \\131 - 132$	80,42 79,92 86,40 86,54 7 3,56	4,85 4,99 4,81 4,76 3,88	$\begin{array}{c} C_{22}H_{16}O_3\\ C_{22}H_{16}O_3\\ C_{25}H_{16}O_2\\ C_{25}H_{16}O_2\\ C_{25}H_{16}O_2\\ C_{21}H_{13}NO_4 \end{array}$	80,47 80,47 86,19 86,19 73,46	4,91 4,91 4,63 4,63 3,82	32,0 23,3 35,7 50,0 50,0

a) Recrystallization solvents: ethanol for IIb,d,f, and CCl₄ for IIc,e. b) 2,3-Epoxy-2,3-diphenylindanone with mp 140-141°C (ethanol) (mp 141°C [13]). Found: N 4.12%. Calculated: N 4.08%.

was washed with water and triturated with a small amount of ethanol to give 8 g (60%) of indanone Ie with mp 181-182°C (ethanol) (mp 180°C [12]).

 $\frac{2-(p-Nitropheny1)-3-phenylindone (If).}{2 \cdot 3H_20}$ was added in portions at 55°C to a solution of 8 g (0.028 mole) of 2,3-diphenylindole (Ia) in 150 ml of acetic anhydride, and the mixture was heated at 60°C for 3.5 h. It was then poured into water, and the aqueous mixture was worked up after about 16 h to give 2.6 g (28%) of a product with mp 162-163°C (ethanol) and Rf 0.49 (mp 164-165°C [4]).

Compound If can be isolated from the reaction product by reprecipitation from solution in acetone by the addition of water.

<u>Preparation of 2,3-Epoxy-2,3-diarylindanones.</u> A 1.7-ml sample of 15% hydrogen peroxide $(7.6 \cdot 10^{-3} \text{ mole})$ was added at $65-70^{\circ}$ C to a saturated solution of the correpsonding indone $(3.3 \cdot 10^{-3} \text{ mole})$ in ethanol, after which 1.7 ml of a 4 N solution of sodium hydroxide was added gradually. The reaction mixture was then allowed to stand at $65-70^{\circ}$ C until it became completely colorless. It was diluted with an equal volume of boiling water, and the mixture was allowed to stand in the dark for crystallization. The precipitate was washed with aqueous ethanol (1:1) and recrystallized.

The melting points, results of elementary analysis, and yields of the epoxyindanones (II) are presented in Table 2.

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