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NEW METHOD FOR THE DETERMINATION OF THE QUANTUM YIELDS IN THE PHOTOISOMERIZATION OF PHOTOCHROMIC EPOXYDIARYLINDANONES

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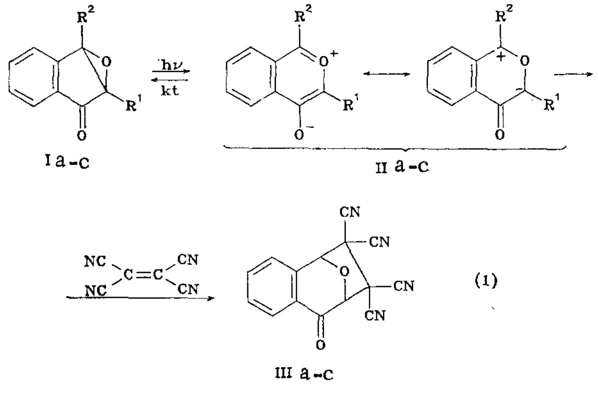
A method for the determination of the quantum yield in the formation of the unstable photoinduced form of 2,3-epoxy-2,3-diphenylindanone based on the reaction with tetracyanoethylene is proposed. The products of 1,3-dipolar addition of tetracyanoethylene to the photoinduced forms of the investigated compounds were isolated and characterized.

Unstable 2-benzopyrylia-4-oxides II are formed as a result of the photochemical valence isomerization of 2,3-epoxyindanones I [1]. We have developed a new simple method for the determination of the quantum yields in the photoisomerization of epoxydiarylindanones.

The measurement of the quantum yields in the photoisomerization of photochromic compounds always presents certain difficulties and requires special procedures for each type of compound [2]. In the case of 2,3-epoxydiarylindanones the complications are due to the fact that decomposition of the photoinduced form, viz., benzopyryliaoxide II, by air oxygen occurs in addition to photochromic transformations (photoelectric coloring and photoelectric and thermal decolorization) during UV irradiation.

The known [1] method for the measurement of the quantum yield in the formation of the photoinduced form of 2,3-epoxy-2,3-diphenylindanone requires prior measurement of the extinction coefficient of the colored form, which is a special problem all by itself [1, 3], as well as thorough removal of the oxygen from the solution of the epoxyindanone to avoid oxidation of the benzopyryliaoxide [1].

The method that we propose is based on the ability of benzopyryliaoxides II to undergo 1,3-dipolar cycloaddition with unsaturated compounds to give adducts III [4].



A necessary condition for the correct use of this method is the absence of absorption of the adduct in the visible part of the spectrum, as well as a high rate of tying up of the colored form in the adduct that significantly exceeds the rates of the dark reaction and

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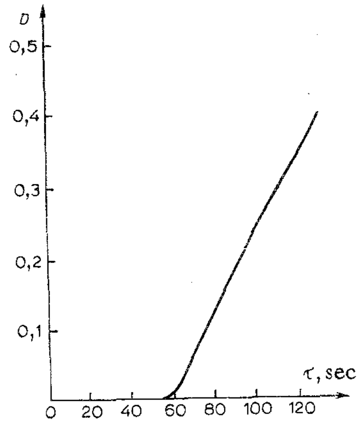

Fig. 1

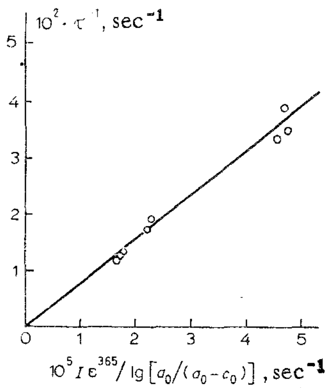

Fig. 2

Fig. 1. Kinetic curve of the change in the optical density D (λ 552 nm) in the irradiation (λ_{Hg} 365 nm) of a benzene solution of 2,3-epoxy-2-(p-methoxyphenyl)-3-phenylindanone ($3.57 \cdot 10^{-4}$ mole) and TCE ($7.14 \cdot 10^{-5}$ mole) at 20°C ($I = 12.5 \cdot 10^{-9}$ erg·cm^{-2}·sec^{-1}).

Fig. 2. Dependence of τ^{-1} for complete tying up of TCE by the photoinduced form of 2,3-epoxy-2-(p-methoxyphenyl)-3-phenylindanone in benzene at 20°C ($\varepsilon^{365} = 172$ liters·mole^{-1}·cm^{-1}; $I = 12.5 \cdot 10^{-9}$ erg·cm^{-2}·sec^{-1}) on $I\varepsilon^{365}/\log\,[a_9/(a_0 - c_0)]$.

oxidation of the benzopyryliaoxide. Tetracyanoethylene (TCE), which we previously used for the determination of the extinction coefficients of benzopyryliaoxides in solution [3], proved to be an unsaturated reagent that satisfies this condition.

The essential features of the method are as follows. A solution of the epoxyindanone and TCE ([I]/[TCE] > 1) was subjected to UV irradiation. After a certain time interval, the solution remained colorless, since the resulting photoinduced form is very rapidly tied up by TCE to give adduct III. After all of the TCE had vanished, the concentration of the photoinduced form increased markedly; we were able to record this spectrophotometrically at the wavelength of the maximum of the long-wave absorption band of benzoypyryliaoxide (Fig. 1). The amount of benzopyryliaoxide formed and tied up in an adduct from the start of irradiation of the solution to time τ, which corresponds to the development of the colored form, is equal to the molar amount of TCE.

The processes that occur during UV irradiation of the solution of the epoxyindanone and TCE can be represented by the scheme

$$\mathrm{I} + \mathrm{TCE} \rightarrow \mathrm{II} + \mathrm{TCE} \rightarrow \mathrm{III} \tag{2}$$

The differential equation of the change in the concentration of the I form during photoisomerization under the conditions of a thin optical layer has the form

$$da/d\tau = -2.3\varphi I\varepsilon^{365}a,$$

where a is the instantaneous concentration, ε^{365} is the coefficient of molar absorption of the starting form at the wavelength of the activating light (λ 365 nm), I is the intensity of the incident initiating light, and φ is the quantum yield of the photochemical formation of colored form II. After integration we obtain

$$\varphi = \frac{\lg\,[a_0/(a_0 - c_0)]}{I\varepsilon^{365}\tau},$$

where a_0 and c_0 are the starting concentrations of the epoxyindanone and TCE, respectively. Thus in the system of $I\varepsilon^{365}/\log[a_0/(a_0 - c_0)]$ and τ^{-1} coordinates, the slope of the line to the axis of abscissas will be numerically equal to the quantum yield of the photoinduced form (Fig. 2). Deviations of the dependence of the time required for complete tying up of TCE on its concentration, which should occur when processes that have a substantial effect

TABLE 1. Extinction Coefficients (ε^{365}) of Epoxyindanones Ia-c at the Initiating Light Wavelength (λ 365 nm) and Quantum Yields of the Corresponding Benzopyryliaoxides IIa-c in Benzene at 20°C

Compound	R^1	R^2	ε^{365}, liters·mole^{-1}·cm^{-1}	φ
a	C_6H_5	C_6H_5	115	0,85
b	$C_6H_4OCH_3$-*n*	C_6H_5	172	0,80
c	C_6H_5	$C_6H_4OCH_3$-p	170	1,00

on photocoloration and cycloaddition are present, were not observed when the molar ratio of the reagents was changed.

It was shown by special experiments that substantial photodecomposition of TCE does not occur during irradiation of the solution and that TCE does not react with the epoxyindanone in the absence of UV light. We obtained adducts IIIa-c in the UV irradiation of benzene solutions of epoxyindanones Ia-c in the presence of TCE; this was confirmed by the results of elementary analysis and the molecular masses of adducts IIIa, b found by mass spectrometry (the mass spectrum of adduct IIIc does not contain a molecular-ion peak because of retrodiene fragmentation).

We have previously verified the completeness of the reaction of TCE with benzopyryliaoxide under the conditions of the method for the determination of the quantum yields [3].

The results of measurement of the quantum yields in the isomerization of the synthesized epoxyindanones [3] are presented in Table 1.

The mean square error in the measurements was 0.06. It was shown by special experiments that the error in the determination because of incomplete tying up to TCE does not exceed the indicated mean square error.

The photochromic compounds presented in Table 1 are characterized by high φ values.

It should be noted that the value that we found for photoinduced form IIa is substantially higher than the value presented in [1] (0.56 ± 0.04), in which the previously measured extinction coefficient of benzopyryliaoxide IIa (26,750) was used. When we used the value that we found in [3] (18,400) in the calculation of φ by the method in [1], we obtained a φ value of 0.81 ± 0.05, which is close to the value found by an independent method in the present research.

Thus we have developed a simple method that makes it possible to measure under normal conditions — at room temperature and in the presence of air oxygen — the quantum yields in the photoisomerization of compounds of the 2,3-epoxyindanone series without the use of the extinction coefficients of the photoinduced forms.

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EXPERIMENTAL

2,3-Epoxy-2,3-diphenylindanone (Ia), with mp 140-141°C (from ethanol), was obtained by the method in [5], 2,3-epoxy-2-(p-methoxyphenyl)-3-phenylindanone (Ib), with mp 123-124°C (from ethanol), was obtained by the method in [3], and 2,3-epoxy-2-phenyl-3-(p-methoxyphenyl)indanone (Ic), with mp 112-113°C (from a mixture of CCl_4 with isopropyl alcohol and ethanol), was obtained by the method in [3]. The tetracyanoethylene was purified by the method in [6] and had mp 197-199°C (in a sealed capillary; mp 198-200°C [6]). Ultrapure-grade benzene was dried with activity II Al_2O_3 and distilled.

Irradiation of the solutions with UV light was carried out in a thermostatable (20°C) rectangular quartz cuvette under conditions of a thin optical layer. The optical density at the wavelength of the initiating light did not exceed 0.05. The extinction coefficients (ε^{365}) of the epoxyindanones in benzene at the activating light wavelength (365 nm) were measured with a VSU2P spectrophotometer. A PRK-4 lamp with a 365 Hg light filter was used as the source of activating light; the intensity of the light was measured by means of a ferrioxalate actinometer [7].

The mass spectra were recorded with a Varian MAT CH-6 spectrometer at 70 eV and 45°C.

Adducts of TCE with 2-Benzopyrylia-4-oxides IIa-c. Small portions of a solution of $4.7 \cdot 10^{-4}$ mole of TCE in 3 ml of benzene were added with stirring at the instant of the development of the red color of benzopyryliaoxides IIa-c to a solution of $4.7 \cdot 10^{-4}$ mole of 2,3-epoxy-2,3-diarylindanones Ia-c in 6 ml of benzene irradiated with the complete light of an SVD-120A lamp (i = 1.6 A) at a distance of 20 cm. At the end of the reaction the solution was evaporated, the residue was crystallized by trituration with a small amount of hexane, and the adduct was removed by filtration.

4,7-Epoxy-5,5,6,6-tetracyano-4,7-diphenyl-3-benzo[1,2]cycloheptenone (IIIa). The procedure described above gave 0.017 g (85%) of a product with mp 168-169°C (benzene—hexane). Found: C 76.2; H 3.3; N 13.0%; M^+ 426. $C_{27}H_{14}N_4O_2$. Calculated: C 76.1; H 3.3; N 13.1; M 426.

4,7-Epoxy-5,5,6,6-tetracyano-4-(p-methoxyphenyl)-7-phenyl-3-benzo[1,2]cycloheptenone (IIIb). The same procedure gave 0.16 g (77%) of a product with mp 170-171°C (benzene—hexane). Found: C 73.7; H 3.6; N 11.8%; M^+ 456. $C_{28}H_{16}N_4O_3$. Calculated: C 73.7; H 3.5; N 12.2%; M 456.

4,7-Epoxy-5,5,6,6-tetracyano-7-(p-methoxyphenyl)-4-phenyl-3-benzo[1,2]cycloheptenone (IIIc). The same procedure gave 0.15 g (70%) of a product with mp 163-164°C (after reprecipitation from solution in benzene by means of heptane). Found: C 74.0; H 3.80%. $C_{28}H_{16}N_4O_3$. Calculated: C 73.7; H 3.5%.

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