EFFECT OF STRUCTURE OF ACYL GROUP ON PHOTOCHEMICAL CONVERSIONS OF 1-ACYLOXY-9,10-ANTHRAQUINONE DERIVATIVES

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Photochemical conversions of 0-acyl derivatives of 1-hydroxy-2-methoxy-9,10anthraquinone have been studied by low temperature and pulsed photolysis. Acyl group structure has a substantial effect on the rate of thermal migration. Replacement of methyl by ethoxy decreases the rate constant by two orders of magnitude; replacement by diethylamino reduces it nearly five orders of magnitude. The log rate constant of the aroyl rearrangement is linearly dependent on the electrophilic constant of the substituents in the phenyl nucleus of the migrant.

We have previously discovered and studied a new photochemical conversion, viz., the photoinduced thermally reversible intramolecular transfer of an acyl group, as exemplified by derivatives of peri-acetoxy-9,10- and 1,4-anthraquinone [1, 2].

In continuing the search for practically important 1-acyloxy-9,10-anthraquinones, it was advisable to study the photochemical properties of derivatives in which the electron donor subsitutent is bonded directly to the reaction center. In this particular case a substantial decrease in the rate of dark migration of the acyl group at room temperature is to be expected [3, 4]. Therefore in the present work we have synthesized and studied a number of previously unknown O-acyl derivatives of 1-hydroxy-2-methoxy-9,10-anthraquinone containing acyl substituted hydroxy and amino groups in the migrating group (Table 1).

EXPERIMENTAL

Photolysis was carried out at liquid nitrogen temperature by the procedure of [5]. The vitrifying solvents were ethanol and 1:1 (by volume) THF-toluene. The concentration of the initial 1-acyloxy-9,10-anthraquinone was $(0.5-2)\cdot10^{-3}$ mole/liter. Irradiation was carried out with a DRSh-500 lamp through a UFS-1 light filter.

Products that were unstable at ~20°C were recorded with an automated pulse-photolysis lamp unit [6]. Reagents were dissolved in benzene or toluene at $(0.2-1)\cdot10^{-1}$ mole/liter. Temperature was 285 ± 1 K. Kinetic parameters were determined by a nonlinear rms regression [7]. Precision of rate constant determination was 5%.

RESULTS AND DISCUSSION

Low-temperature Photolysis. The spectra of the O-acyl derivatives of 1-hydroxy-2methoxy-9,10-anthraquinones (I)-(VII) contain two intense bands in the near UV, with maximum at 333-337 and 365-377 nm (Table 1). During the irradiation of glassy solutions of (I)-(VII) at 77 K, compounds are formed that absorb in the visible region of the spectrum with two maxima at 519-527 and 560-566 nm. These spectral changes are completely analogous to those of the 1-acetoxy-9,10-anthraquinone derivatives studied in [1, 2]. This provides confirmation that the newly obtained derivatives also undergo photochemical migration of the acyl group, which isomerizes the structure of the 9,10-anthraquinone to 1,10-anthraquinoid. The nature of the substitutent on the carbonyl carbon of the migrating group has little effect on the

Institute of Chemical Kinetics and Combustion, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2721-2725, December, 1990. Original article submitted October 24, 1989. TABLE 1. Maxima of Long Wave Bands in Electron Absorption Spectra of 1-Acyloxy-2-methoxy-9,10-anthraquinones (I)-(VII) Before and After Irradiation at 77 K, and Rate Constants of Thermal Migration of Acyl Groups in 9-Acyloxy-2-methoxy-1,10anthraquinones (Ia)-(Va) at 285 K in Benzene



Com- pound	Migrating CO-R ^{**} group	λ_{max} , nm		Jr 000 ⁻¹
		before irra- diation	after irra- diation	ĸ, sec
(I)	CO-O-C ₂ H ₅	337, 368	526, 566 (sh)	3.1.103
·(II)	CO-O-Ph	335, 365	520, 560 (sh)	5,0.104
·(111)	co	333, 366	519, 560 (sh)	4,3.10*
(IV)	CON(CH ₃) ₂	327, 370 (sh)	-	4,3·10 ³
-(V)	$CO-N(C_2H_5)_2$	337, 377	526, 562	2,9
(VI)	$CO_N < CH_3 Ph$	337, 377	527, 560	•
(VII)	CO-N < Ph Ph Ph	337, 362	52 6, 560	*

*Conversion is second order reaction **When $R = CH_3$, $k = 2.5 \cdot 10^5 \text{ sec}^{-1}$.

location of the long-wave maxima in the spectra of the products (Table 1). At the same time, complication of the structure of the migrating acyl reduces the quantum yield of photolysis of (I)-(VII) by at least two orders of magnitude at 77 K, as compared with 1-acetoxy-2-me-thoxy-9,10-anthraquinone ($\varphi = 0.45 \pm 0.05$).

The reverse transfer back to the initial compounds takes place only thermally when the samples are thawed. Phototransfer and thermal transfer can be repeated many times; since they are accompanied by a substantial change in color, compounds (I)-(VII) are photochromic. But during the photochromic conversions the carbamoyl derivatives (V)-(VII) undergo substantial destruction.

<u>Pulsed Photolysis</u>. During the pulsed excitation of (I)-(V) at 285 K in benzene or toluene, short-lived products were recorded, with spectra analogous to those obtained during steady-state irradiation at 77 K. Consequently at about 20°C the respective 2-methoxy-9acyloxy-1,10-anthraquinones (Ia)-(Va) also are formed. The kinetic curves for the decrease in absorption of (Ia)-(Va) show an exponential dependence on time, due to the reverse thermal migration of the acyl group. The experimental rate constants for acyl migration are shown in Table 1. Here the nature of the substituent at the carbonyl carbon of the migrating group has a substantial influence on the rate constant. When methyl is replaced by ethoxy the rate constant falls about two orders of magnitude. However the introduction of phenoxy (IIa) reduces the effect of the oxygen-containing substituent at the reaction center by about an order of magnitude; this is related to the participation of the phenyl ring in the redistribution of electron density. Introduction of a pyromucyl group (IIIa) as an acyl group gives the same value of rate constant. Thus the introduction of substituted hydroxy groups into the migrating group permits the rate constant of rearrangement at room temperature to be decreased by up to two orders of magnitude. Replacement of methyl by diethylamino drops the rate constant for the dark migration of acyl by nearly five orders of magnitude; this approaches the possibility of recording the photoproduct by steady-state methods.

We also studied the effect of substituents in the phenyl nucleus of the migrating group on the rate of thermal migration of aroyl. Figure 1 shows the dependence of log rate constant for aroyl rearrangement on σ^+ , the electrophilic constant of the substituent in the aryl ring of the migrating group. There is a good linear dependence, the slope of which, ρ , is 0.60 ± 0.01, and the correlation coefficient, r, is 0.99. The positive sign of ρ indicates that the acyl migration rate is greater, the larger is the positive charge on the carbon of the migrating acyl.

<u>Photolysis of 1-Carbamoyloxy-2-methoxy-9,10-anthraquinones Containing Phenyl (VI),</u> (VII). In the steady-state irradiation at ~20°C of toluene and benzene solutions of 1-(N,Ndiphenyl)carbamoyloxy-2-methoxy-9,10-anthraquinone (VII), the electron absorption spectrum of photolysis product (VIII) shows two long-wave bands with maxima at 516 and 660 nm (Fig. 2). Under dark conditions the intensity of the long-wave bands gradually decreases, and a new band appears at 430 nm. This spectrum (line 5, Fig. 2) coincides with that of 1-hydroxy-2methoxy-9,10-anthraquinone (IX). Chromatographic and mass spectrometric analyses showed that the compound was indeed (IX). It is apparently formed by the reaction of photoproduct (VIII) with traces of water in the solvent. Dehydration of the solvent substantially (about 5 times for toluene) reduced the rate of the dark conversions of photoproduct (VIII).

When 1-(N,N-methylphenyl)carbamoyloxy-2-methoxy-9,10-anthraquinone (VI) is irradiated under steady-state conditions, (IX) is formed immediately. But under pulsed photolysis a compound is recorded whose spectrum is identical with that of (VIII) (Fig. 2, spectrum 2). The 6-sec lifetime of this intermediate is apparently also determined by reaction with traces of water in the solvent.

The spectral changes during the low temperature (77 K) photolysis of (VI) and (VII) are completely analogous to those of (I)-(V), but differ pronouncedly from the changes that occur at ~20°C. Consequently (VIII) is not the 1,10-anthraquinone derivtive with the structure of (VIIa).

Under pulsed excitation of (VII), (VIII) is formed by a second-order reaction. Possibly (VIIa) is the precursor of (VIII). The value of k_2/ϵ_{516} was determined experimentally as $(8.0^{\circ} \pm 0.5) \cdot 10^{4}$ cm/sec. Using $\epsilon_{516} = 6.2 \cdot 10^{3}$ liter/mole cm, we get $k_2 = (5.0 \pm 0.5) \cdot 10^{8}$ liter/mole sec for the second order rate constant.



Fig. 1. Correlation of rate constant of dark migration at 285 K in benzene with electrophilic constants of substituents in phenyl nucleus of migrating acyl group.

Fig. 2. Absorption spectrum of 1-(N,N-diphenyl)carbamoyloxy-2-methoxy-9,10anthraquinone in toluene (1) and changes therein after 15-sec irradiation (2), and after 5 min (3), 15 min (4), and 1 h (5) of dark conversions of photoproduct. Compound (VIII) could not be separated because of its rapid conversion to (IX). Therefore the PMR spectrum of the photoproduct was recorded during the irradiation of (VII) directly in the NMR spectrometer in CS_2 solution. In the PMR spectrum of (VIII) the H³ proton signal is shifted toward the strong field by 1.03 ppm, as compared with the spectrum of (VII). The signal of the methoxy at position 2 also shifts toward the strong field by 0.3 ppm. The signal of H⁸ of the unsubstituted quinone ring changes its location; it shifts toward the strong field by 0.6 ppm relative to H⁵, whereas in the initial compound H⁵ and H⁸ are equivalent at 8.16 ppm. According to [8, 9] the features of the spectrum that we have noted are evidence for rearrangement of the 9,10-anthraquinone to a 1,10-anthraquinoid.

Thus the PMR spectrum and the chemical behavior are evidence that photoproduct (VIII) has the structure of a 1,10-anthraquinone. However the difference between the electron spectrum of (VIII) and the spectra of the 9-acetoxy-1,10-anthraquinone derivatives of [2], and the presence of the precursor from which (VIII) is formed by a second-order reaction both complicate the interpretation of its structure.

LITERATURE CITED

- S. A. Russkikh, L. S. Klimenko, N. P. Gritsan, and E. P. Fokin, Zh. Org. Khim., <u>13</u>, No. 10, 2224 (1982).
- N. P. Gritsan, S. A. Russkikh, L. S. Klimenko, and V. F. Plyusnin, Teor. Eksp. Khim., <u>18</u>, No. 4, 455 (1983).
- 3. V. I. Minkin, L. P. Olekhnovich, and Yu. A. Zhdanov, Molecular Design of Tautomeric Systems [in Russian], Rostov State Univ. Press (1978), p. 67.
- 4. V. I. Minkin, L. P. Olekhnovich, Yu. A. Zhdanov, et al., Zh. Org. Khim., <u>13</u>, No. 4, 777 (1977).
- 5. N. P. Gritsan, V. A. Rogov, N. M. Bazhin, et al., Teor. Éksp. Khim., <u>15</u>, No. 3, 290 (1979).
- 6. E. A. Pritchina and N. P. Gritsan, J. Photochem. Photobiol. A: Chemistry, <u>43</u>, No. 2, 165 (1988).
- 7. K. J. Johnson, Numerical Methods in Chemistry, Dekker, New York (1980).
- 8. E. P. Fokin, S. A. Russkikh, L. S. Klimenko, and V. V. Russkikh, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, <u>3</u>, No. 7, 110 (1978).
- 9. F. Setiabudi and P. Boldt, Tetrahedron Lett., 22, No. 30, 2863 (1981).

COMPLEXATION IN THE CuCl2-C2H5OH-H2O SYSTEM

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Depending on the ethanol-water ratio, five individual compounds of copper(II) of the following compositions are formed in the $CuCl_2-C_2H_5OH-H_2O$ system: $[CuCl_2(C_2H_5OH)_4]$ (I), cis- $[CuCl_2(C_2H_5OH)_2 \cdot (H_2O)_2]$ (II), trans- $[CuCl_2(C_2H_5OH)_2 \cdot (H_2O)_2]$ (II), $[Cu(H_2O)_6]^{2+}$ (IV), and $[Cu(OH)_2(H_2O)_4]$ (V).

Papers [1-5] are devoted to investigations of complexation of $CuCl_2$ in water-alcohol solutions. Interest in this topic is due, firstly, to the need to determine the composition of complexes coexisting in solution and the constants of equilibrium between them and, secondly, to study, by various physical methods, the electronic structure of the complexes and the nature of the metal-ligand bond. The most informative method for solution of these problems is EPR. The parameters of EPR spectra depend significantly on the composition and structure of the coordination sphere, which often makes it possible to establish the composition of the complexes unambiguously. When the solutions contain several types of

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