PHOTOREARRANGEMENT OF YLIDENE TAUTOMERS OF AZINYL(o-NITROPHENYL)-CARBOMETHOXYMETHANES

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The photochemical properties of ylidene tautomers of azinyl(o-nitrophenyl)carbomethoxymethanes have been examined. Photolysis at the absorption wavelength of the ylidene tautomer results in selective rearrangement of a type hitherto unknown in o-nitrostyrenes, involving transfer of an oxygen atom to exocyclic carbon, and reduction of the nitro group to nitroso.

The photochemical reaction of o-nitrobenzyl derivatives of nitrogen heterocycles A \ddagger B has been reported [1]. It has been found that the photoinduced form in neutral media has the ylidene tautomeric structure B [2].⁺ In addition to the reversible reaction A \ddagger B, both tautomeric forms of the nitrobenzyl derivatives decomposed on photolysis [4].



Despite numerous investigations of the photochemical reactions of o-nitrobenzyl derivatives of heterocycles, information on the photoinduced reactions of the ylidene tautomeric form B is lacking.

We have now examined the photochemical behavior of the tautomeric form B of azinyl(onitrophenyl)carbomethoxymethanes, which contain in equilibrium considerable amounts of the ylidene tautomer.

The most convenient subject was 2-quinolyl-(2,4-dinitrophenyl)carbomethoxymethane (I) which, unlike the photochromic nitrobenzyl derivatives, is present in solution almost wholly in the ylidene tautomeric form, since according to PMR in CDCl₃ the proportion of the ylidene tautomeric form was \sim 95%. The UV spectrum of (I) showed strong absorption at 440 and 305 nm characteristic of the ylidene tautomer.

Irradiation of a solution of (I) in organic solvents (chloroform, benzene, ether, and alcohol) with filtered light in the region of absorption of form B resulted in decolorization of the solution. HPLC examination showed that in all cases the sole photoreaction product was (II), with λ_{max} 235 nm. The reaction was independent of the wavelength of the exciting irradiation over the range 300-500 nm. Photolysis with the full spectrum of a mercury lamp resulted in the formation of a complex mixture of products.

Compound (II) was isolated, and was shown by high-resolution mass spectroscopy to have the same empirical formula as (I).

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[†]The terminology used in this article (azinyl-ylidene tautomerism, and ylidene tautomer B) has been proposed in a review [3] for the A \neq B tautomeric equilibrium in azines.

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The IR spectrum of (II) showed strong absorption for the unconjugated ester group at 1750 cm⁻¹, and absorption corresponding to symmetrical and antisymmetrical vibrations of the nitro group (1550 and 1350 cm⁻¹). The presence of the nitroso group was shown by the low-intensity absorption in the UV spectrum (λ_{max} 740 nm, ε 35). The PMR spectrum of (II) contained signals for the aromatic protons of the quinoline and phenyl rings. The shift for the H³' proton of the phenyl group to higher field, with a small shift to lower field of the H⁵' and H⁶' protons, showed that the nitro group had been reduced to nitroso [5]. The broadened singlet at 7.68 ppm was attributed to the signal for the hydroxy group. The magnitude of the shift of the signal to lower field is due to the presence of three acceptor substituents at the exocyclic carbon atom, and to the involvement of the hydroxyl group in hydrogen bonding with the quinoline nitrogen. From its spectral data, (II) was assigned the structure 2-quinolyl-(2-nitroso-4-nitrophenyl)carbomethoxymethyl carbinol. The formation of the carbinol (II) on photolysis of the ylidene tautomer was unexpected. By analogy with literature reports [6], (II) would be expected to be formed by photolysis of the tautomer (A), while the photo-induced reactions of ortho-nitrostyrenes (it is this fragment which is the key in the photoisomerization of (I)) usually take a different course [7, 8]. Further, since form A does not absorb

at 300 nm, the possibility of reaction (IA) $\xrightarrow{h\nu}$ (II) may be ignored.

By analogy with a literature report [8], the reaction (IB) $\stackrel{h\nu}{\rightarrow}$ (II) may be postulated, which requires the intermediate formation of the compound (III). However, the further reactions of (III) are different from those described in [7, 8], apparently as a result of the presence in the molecule of a labile proton in the NH group.

The quantum yield of the observed rearrangement is ~ 0.02 (Table 1). With such a low quantum yield in the reaction (I) $\xrightarrow{h\nu}$ (II), competing reactions would be expected to occur, especially photoreduction of the nitro group [9]. Reduction of the nitro group would be most likely to occur in 2-propanol. According to HPLC, however, photolysis of (I) in 2-propanol with filtered light in the region of absorption of the tautomeric form B resulted in the formation of no by-products whatsoever.

The observed photoisomerization apparently occurs in the triplet $n\pi^*$ excited state. This is shown by the occurrence of the reaction with triplet sensitization. With sensitizers such as naphthalene and 1-nitronaphthalene, (II) is the sole reaction product (Table 1). The presence in the quinolylmethane (I) solutions of sensitizers such as benzil, anthracene, benzophenone, and naphthoquinone leads to the formation of (II) together with by-products.

Like the quinolylmethane (I), photoisomerization occurs in other azinyl(o-nitrophenyl)carbomethoxymethanes in which form B is present in the equilibrium mixture. For example, photolysis of 5-nitro-2-pyridyl-(2,4-dinitrophenyl)carbomethoxymethane (IV) and 5-nitro-2-pyridyl-(2-nitrophenyl)carboxymethane (V) in the region of absorption of form B (\sim 400 nm) proceeds in a similar way. 5-Nitro-2-pyridyl-(2-nitroso-4-nitrophenyl)carbomethoxycarbinol (VI), formed on photorearrangement of the nitropyridylmethane (IV), was isolated and characterized. According to HPLC, photolysis of the nitropyridylmethane (V) gave a single product, although this could not be isolated in view of its low thermal stability. The presence in the UV spectrum of the photolysis product of absorption for the nitroso group (at 760 nm) suggests that the rearrangement proceeds similarly in this case also.

Compound	Solvent	λ_{exc}	Φ×10 ²
(I)	Benzene	436	1,9
(1)	CHCI3	430	1,5
(1)	Benzene	303-313	1,2
(I)	Benzene (+ naphthalene, C = 1.5·10 ⁻² mole/liter)	303-313	2,3
(I)	Benzene (+1-nitronaphthalene, C = $3 \cdot 10^{-3}$ mole/liter)	365	1,3
(IV)	Benzene	436	1,2
(IV)	CHCl ₃	436	1,1
(V)	Benzene	436	1.9

TABLE 1. Quantum Yields in the Photoisomerization of the Ylidene Tautomer



In contrast to the quinolylmethane (I), the nitropyridylmethanes (IV) and (V) form equilibrium mixtures containing comparable amounts of both tautomers. According to PMR spectroscopy, the proportions of the ylidene form B in CDCl₃ are 70 and 17% for (IV) and (V) respectively. Since the rate of tautomeric interconversion $A \neq B$ is small [3], when the intensity of the exciting irradiation is sufficiently great, selective "burnout" of the ylidene tautomer may occur, with the formation of nonequilibrium concentrations of the tautomers. For instance, irradiation of solutions of (IV) and (V) in benzene (DRSh-500 lamp, SZS-22 filter) results in rapid decolorization of the solutions with photoisomerization of the ylidene tautomer. Under dark conditions, following establishment of equilibrium, the color of the solutions returns, but with lower extinctions. This observation confirms that the formation of azinyl carbinols on photolysis occurs by photorearrangement of the ylidene tautomer only.

EXPERIMENTAL

The PMR spectra of 0.5-1% solutions in CDCl₃ were obtained on a Bruker WP 200 SY instrument, mass spectra on a Finigan MAT MS-8200, IR spectra in KBr on a UR-20, and UV spectra on Specord UV-VIS and SF-16 spectrophotometers.

HPLC was carried out on a Milikhrom chromatograph, 64×2 mm column, sorbent Lichrosorb RP18, eluent methanol-water (gradient, content of methanol from 50 to 100%). The column efficiency was 2500 theoretical plates.

Photolysis of (I), (IV), and (V) was carried out with light from DRSh-500 and DRK-120 lamps fitted with a condenser and water filter. In order to select strong bands of the mercury spectrum, standard filters were used. When measuring quantum yields, the concentrations of (I), (IV), and (V) were $(2-3) \cdot 10^{-3}$ mole/liter, resulting in the absorption of 98-99% of the exciting light. The rate of photoisomerization was found from the absorption of the starting compound at 500-520 nm. Light intensities were measured with a ferrous oxalate actinometer [10].

Measurement of the quantum yield in the photolysis of (I) was carried out using a DRSh-500 lamp, and in the photolysis of (IV) and (V), with a DRK-120 lamp, use of which did not give rise to a nonequilibrium mixture of tautomers.

The solutions were not degassed, since preliminary experiments showed that dissolved oxygen had no effect on the mode and rate of isomerization.

The synthesis of (V) has been reported [11].

2-Quinolyl-(2,4-dinitrophenyl)carbomethoxymethane (I) was obtained from 2,4-dinitrophenylacetic ester and quinoline N-oxide in acetic anhydride in the usual way [12]. Yield 40%, mp 158-160°C (from methanol). Found: C 58.3; H 3.5; N 11.3%, m/z 367.0868 (M⁺). $C_{18}H_{13}N_{3}O_{6}$. Calculated: C 58.8; H 3.5; N 11.3%. M 367.0804. PMR spectrum (δ , ppm, J, Hz), form B: 13.4 s (1H, NH), 8.78 d (1H, H^{3'}, J = 2.5), 8.38 d.d (1H, H^{5'}, J = 8; 2.5), 7.61 d (1H, H^{6'}, J = 8), 7.15-7.55 m (5H, H³-H⁷), 6.54 d.d (1H, H⁸, J = 9.1), 3.6 s (3H, Me). UV spectrum (CHCl₃, λ_{max} (log ϵ)): 305 (4.33), 440 (4.15).

<u>2-Quinolyl-(2-nitroso-4-nitrophenyl)carbomethoxymethyl Carbinol (II)</u>. This was obtained by photolysis of 100 mg of (I) in 100 ml of chloroform with a high-pressure mercury lamp and an SZS-22 filter. When the red color of the solution had disappeared, the solution was evaporated under reduced pressure to give a quantitative yield of (II) containing trace amounts of the starting material, mp 148-150°C (from hexane). Found: m⁺/z 367.0821 (M⁺). $C_{18}H_{13}O_6N_3$. Calculated: M 367.0804. IR spectrum (ν , cm⁻¹): 1750 (C=O), 1350, 1550 (NO₂). UV spectrum (ethanol): $\lambda_{max} 235$ nm (log ϵ 4.36), 740 (ϵ 35). PMR spectrum (δ , ppm, J, Hz): 8.4 d.d (1H, H⁵', J = 2.5; 8) 8.23 d (1H, H⁴, J = 8.5), 8.18 d (1H, H⁸, J = 8), 7.22 d (1H, H³, J = 8.5), 7.75-7.9 m (2H, H⁵,⁷), 7.58-7.72 m (3H, OH, H⁶, H⁶'), 6.98 d (1H, H³', J = 2.5), 3.64 s (3H, Me).

<u>5-Nitro-2-pyridyl-(2,4-dinitrophenyl)carbomethoxymethane (IV).</u> A mixture of 0.4 g of 5nitro-2-chloropyridine and the Na salt of 2,4-dinitrophenylacetic ester (obtained from 1 g of the ester and 0.15 g of 80% NaH) in 10 ml of dry DMF was heated for 2 h at 100°C, then poured into 50 ml of water, neutralized with conc. HCl, and extracted with benzene. The benzene extract was dried over MgSO₄, evaporated, and separated by preparative TLC (silica gel/CHCl₃). Yield 0.5 g (70%), mp 127-129°C (from methanol). Found: C 46.4; H 2.7; N 15.5%. C_{14H10}N₄O₈. Calculated: C 46.4; H 2.8; N 15.5%. UV spectrum (ethanol, λ_{max} , (log ε)): 245 (4.34), 405 (3.76). PMR spectrum, form B (δ , ppm, J, Hz): 13.9 s (1H, NH), 8.85 d (1H, H³', J = 2), 8.4-8.55 m (2H, H⁴, H⁵'), 7.55-7.7 m (2H, H⁶, H⁶'), 6.33 d (1H, H³, J = 10), 3.6 s (3H, Me).

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