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POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES
18.* PHOTOCHEMICAL TRANSFORMATION OF 2-NITROARYLDIFURYLMETHANES

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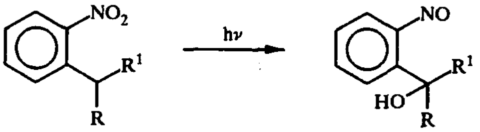
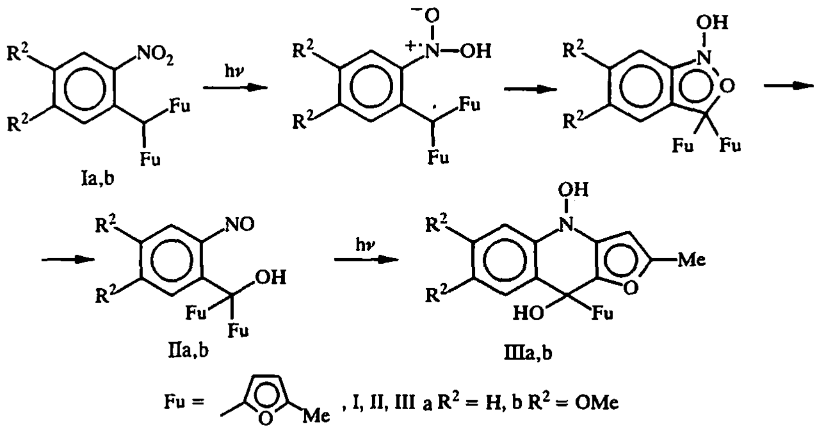
During UV irradiation or storage in light, solutions of 2-nitroaryldifurylmethanes in THF are converted into derivatives of 4,9-dihydrofuro[3,2-b]quinoline.

At the present time a large number of intramolecular rearrangements are known in the series of aromatic nitro compounds where the substituent at the *ortho* position contains a C−H bond [2]. Thus, the photolysis of 2-nitrotriphenylmethane leads to 2-nitrosotriphenylmethanol [3]. These rearrangements can be described by the following general scheme:



While continuing research into the chemical characteristics of 2-nitroaryldifurylmethanes [4, 5], in the present work we examined their photochemical transformations.

Scheme 1



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*For communication 17 see [1].

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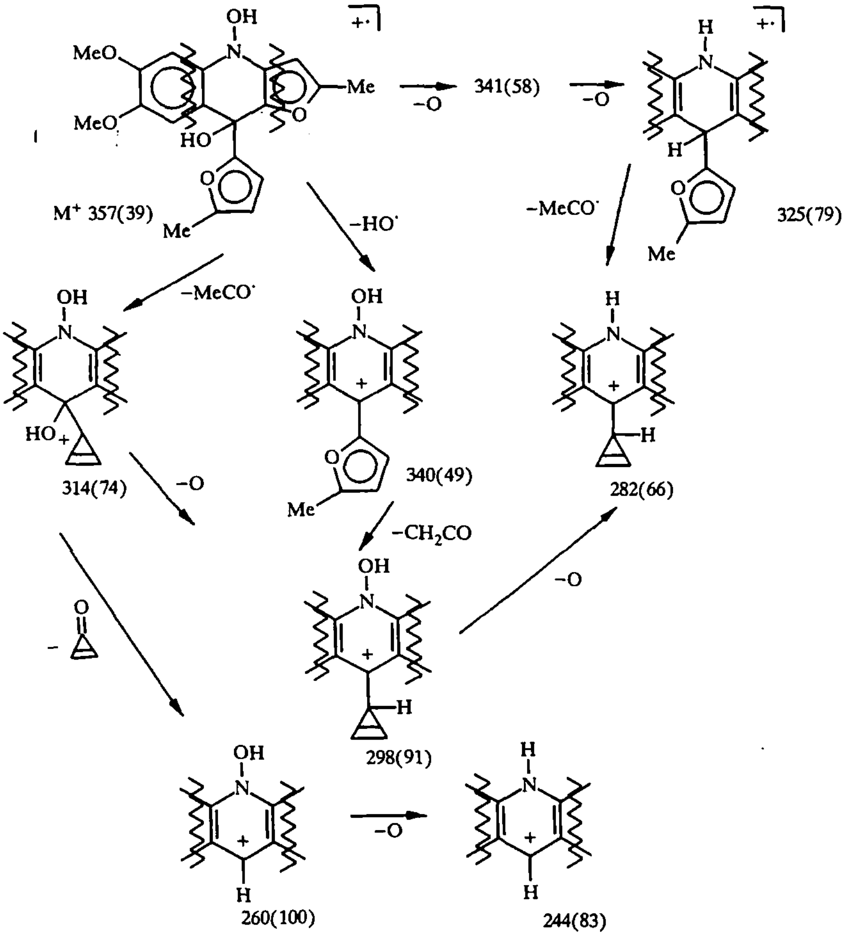
As a result of exposure to an ultraviolet lamp or storage in light at room temperature solutions of 2-nitroaryldifurylmethanes (Ia, b) in tetrahydrofuran acquire a bright-orange color. The initial methanes (Ia, b) and small amounts of the dihydrofuroquinoline derivatives (IIIa, b) were isolated from the reaction mixtures by column chromatography. The expected 2-nitrosoaryldifurylmethanols (IIa, b) were not detected due probably to their instability and their susceptibility to further transformations. This idea is supported by the considerable resin formation in the course of the reaction. The probable mechanism of the transformation (I) → (III) is shown in Scheme 1.

During irradiation the nitroaryldifurylmethanes (I) are probably converted first into compounds (II) according to the familiar scheme [6]. Photolysis of the products then leads to the removal of the β-proton of one of the furyl groups by the excited nitroso group. The intramolecular recombination of the radicals formed here results in the formation of compounds (III).

The structures of the dihydrofuroquinolines (IIIa, b) were proved on the basis of their IR and PMR spectra, mass spectrometry, and elemental analysis. Thus, the IR spectrum of compound (IIIb), in contrast to that of the initial compound (Ib), contains broad absorption bands at 3460 and 3280 cm^{-1}, characteristic of the stretching vibrations of the O−H bonds.

Our suggestion that β-substitution in one of the furan rings occurs in the course of the reaction is confirmed by the presence of doublets for the protons of one of the furan rings in the region of 5.70-6.10 ppm and a singlet for the proton of the other ring in the region of 7.00-7.15 ppm in the PMR spectra of compounds (IIIa, b).

Scheme 2



A characteristic feature of the dissociation of compound (IIIb) under electron impact is the formation of stable furoquinolinium cations. The principal initial fragmentation paths are shown in Scheme 2.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 instrument in tablets with potassium bromide. The PMR spectra were recorded on a Tesla BS-487 instrument at 80 MHz with HMDS as internal standard. The mass spectra were obtained on a

Varian MAT-112 spectrometer with direct injection of the sample into the source at 70 eV. The reactions and the individuality of the products were monitored by TLC on Silufol UV-254 plates.

4,9-Dihydroxy-2-methyl-9-(5-methyl-2-furyl)-6,7-dimethoxy-4,9-dihydrofuro[3,2-*b*]quinoline (IIIb). A solution of 1.0 g (28 mmole) of compound (Ib) in 15 ml of THF in a quartz flask was exposed to a UV lamp for 8 h. (Longer exposures did not lead to an increased yield.) The solvent was distilled at reduced pressure, and the residue was chromatographed on silica gel L 40/100 with a 1:1 mixture of ethyl acetate and petroleum ether as eluant, giving 0.4 g of the initial compound (Ib) and 0.13 g (22%) of yellow crystals of compound (IIIb); mp 200-202°C (from the eluant); R_f 0.25. IR spectrum, cm^{-1}: 3460, 3280 (OH). PMR spectrum (deuterochloroform, δ, ppm): 2.13 (3H, s, CH_3); 2.16 (3H, s, CH_3); 3.78 (3H, s, OCH_3); 3.89 (3H, s, OCH_3); 5.32 (1H, bs, OH); 5.82 (1H, d, J = 3.2 Hz, 4-H_{Fur}); 6.10 (1H, d, J = 3.2 Hz, 3-H_{Fur}); 6.82 (1H, s, H_{arom}); 7.04 (2H, s, H_{arom} + H_{Fur}). Mass spectrum, m/z (I_{rel}, %): 357 (39) M^+, 341 (53), 340 (49), 325 (79), 314 (74), 299 (48), 298 (91), 286 (60), 282 (66), 271 (31), 270 (96), 260 (100), 259 (66), 256 (46), 251 (51), 244 (83), 232 (42), 228 (33), 179 (38), 164 (45), 162 (34), 156 (53), 139 (58), 136 (35), 108 (43), 101 (31) (the signals with I_{rel} ≥ 30% are given). Found %: C 63.93; H 5.27; N 4.05. $C_{19}H_{19}O_6$. Calculated %: C 63.86; H 5.36; N 3.92.

Compound (IIIa) was obtained similarly with an 18% yield; mp 156-158°C (from the eluant); R_f 0.25. PMR spectrum (deuterochloroform, δ, ppm): 2.13 (3H, s, CH_3); 2.20 (3H, s, CH_3); 4.95 (1H, bs, OH); 5.81 (1H, d, J = 3.2 Hz, 4-H_{Fur}); 6.10 (1H, d, J = 3.2 Hz, 3-H_{Fur}); 7.14 (1H, s, H_{Fur}); 7.33-7.62 (4H, m, H_{arom}). Found %: C 68.61; H 4.93; N 4.83. $C_{17}H_{15}NO_4$. Calculated %: C 68.68; H 5.08; N 4.71.

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