

STUDY OF PHOTOLYSIS OF 1,3-BIS(4-NITROPHENYL)-1-BUTENE IN ACETONITRILE AND 2-PROPANOL

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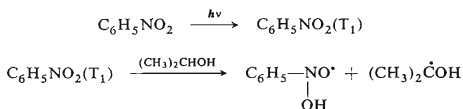
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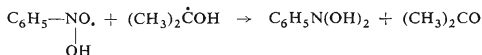
Photolysis of 1,3-bis(4-nitrophenyl)-1-butene (*I*) in acetonitrile and 2-propanol by polychromatic radiation of a mercury lamp was studied. The photolysis kinetics was followed by UV spectra and the reaction products were analysed by IR and mass spectroscopy and by gas-liquid chromatography. The reaction mechanism is markedly affected by the presence of oxygen. Photolysis of *I* in acetonitrile gives mainly 4-nitrobenzaldehyde, n-heptane and toluene, in 2-propanol the principal products are stereoisomeric 1,3-diphenyl-1-butenes.

Although photochemical reactions of aromatic nitro compounds have been widely studied, the present knowledge still cannot be regarded unequivocal. Unlike photolysis of other monotopic derivatives of aromatic hydrocarbons (such as aldehydes, hydroxy, methoxy or halogeno derivatives), the reaction of nitro compounds is mechanistically explained differently by different authors. Studies of photoreactivity of aromatic nitro compounds till 1968 are summarized by Morrison¹ whereas Horspool's contribution² includes papers published till 1975.

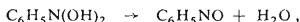
The first observed reaction of this type was the isomerization of 2-nitrobenzaldehyde to 2-nitrobenzoic acid, published by Ciamician and Silber³, however, a detailed mechanistic analysis of this process appeared only after 60 years^{4,5}. It is assumed that photoreduction of nitroaromatic compounds in 2-propanol is initiated by removal of hydrogen atom from the alcohol by excited triplet of the nitro group (or, less correctly, by addition of hydrogen to the excited triplet of the nitro group) according to the following scheme:



Further addition of hydrogen atom gives rise to acetone as the side-product:



The N-dihydroxy derivative is then dehydrated to the corresponding nitrosobenzene which can be further transformed to various products by a number of condensation, addition or substitution reactions.



The results of photolysis of compound *I* in acetonitrile and 2-propanol, reported in the present paper, do not completely confirm the published¹⁻⁵ results.

EXPERIMENTAL

1,3-Bis(4-nitrophenyl)-1-butene was prepared and chromatographically purified as described in ref.⁶. The UV spectra were taken in 1 cm stoppered quartz cells on a Specord UV-VIS spectrometer (Zeiss, GDR), IR spectra were recorded on a Specord IR-71 (Zeiss) instrument. The kinetic measurements were carried out in a CaF_2 cell. The compounds were irradiated in thermostated cells (20°C) by a medium-pressure mercury lamp RVK-125 (Tesla, Czechoslovakia); light flux intensity $1.88 \cdot 10^{-9} \text{ e cm}^2 \text{ s}^{-1}$. Photolysis experiments with direct introduction of oxygen and nitrogen were carried out in a cylindrical quartz reactor (RVK-125 lamp; light flux intensity $7.9 \cdot 10^{-7} \text{ e cm}^2 \text{ s}^{-1}$). ¹H NMR spectra were measured on a 100 MHz Jeol-FX instrument (tetramethylsilane as internal standard) with the aim to confirm that acetone was formed in the photolysis of *I* in 2-propanol. Gas-liquid chromatography, combined with mass spectrometric analyses of photolysis products, was carried out on a GC/MC 5985 A instrument (Hewlett Packard); column temperature 50–220°C heating rate 10°C min⁻¹, carrier gas nitrogen, FID-DUAL detector. 2 μl samples; column (1 200 mm diameter 4 mm): 5% SE 30 on Chromaton N AW – HMDS (particle size 0.16–0.20 μm). Mass spectra: emission 300 μA, electron energy 70 eV, ionization chamber temperature 200–222°C.

RESULTS AND DISCUSSION

The course of the photochemical reaction of *I* in acetonitrile and 2-propanol in the presence of air oxygen, expressed as dependence of the UV spectra on time, is given in Fig. 1 and 2. During the photolysis new absorption bands appear whose λ_{max} depends on the solvent employed. The rapid initial shifts toward shorter wavelengths are caused by the *trans* → *cis* isomerization ($\lambda_{\text{max}}^{\text{cis}} = 293 \text{ nm}$) (ref.⁶). In acetonitrile, a product of $\lambda_{\text{max}} = 267 \text{ nm}$ is formed (presumably *p*-nitrobenzaldehyde). In 2-propanol, the reaction takes a different course: the reaction mixture exhibits a UV-band at 248 nm which can be ascribed to 1,3-diphenyl-1-butene⁷. Prolonged reaction times result in intensity decrease of the absorption bands in both solvents. The photolysis of *I* was influenced by introduction of nitrogen into the solutions. The apparent quantum yields, given in Table I show that the photolysis was perceptibly accelerated only in acetonitrile whereas, on the contrary, in 2-propanol the introduction of nitrogen resulted in a slower reaction.

We tried to elucidate the photolysis mechanism and the effect of the oxygen on this reaction. The reaction course in acetonitrile in the presence of air oxygen, as fol-

lowed by IR spectroscopy, is given in Fig. 3. We see fast initial changes of the $\tilde{\nu}(\text{NO}_2)$ bands at 1 345 and 1 540 cm^{-1} and also marked changes in the region 1 640–1 730 cm^{-1} , apparent already after low exposures. No changes in the latter region were found when working in 2-propanol; significant changes were, however, observed in the region 1 200–1 600 cm^{-1} ; these were also characteristic for prolonged ir-

TABLE I

Apparent quantum yields of photolysis of *I*

t_{exp} min	$\Phi(\text{acetonitrile})$		$\Phi(2\text{-propanol})$	
	with O_2	without O_2	with O_2	without O_2
0.25	4.36	8.03	7.97	6.38
0.5	6.59	8.77	9.04	7.44
1.0	7.65	9.46	9.57	7.67
2.0	8.77	10.58	10.10	7.81
4.0	10.21	12.07	11.01	8.43
8.0	12.39	14.20	12.23	9.04
16.0	14.04	16.38	15.42	10.10

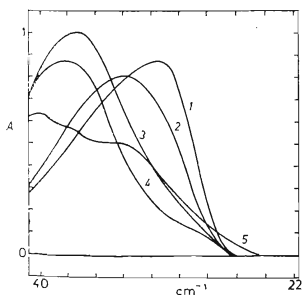


FIG. 1

Changes of UV spectra during photolysis of *I* in acetonitrile: 1 0; 2 3; 3 32; 4 200; 5 280 min

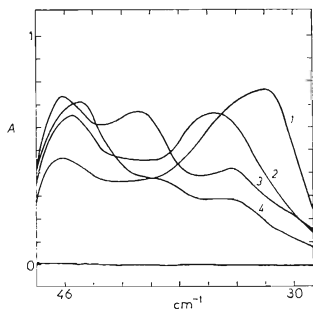


FIG. 2

Changes of UV spectra during photolysis of *I* in 2-propanol: 1 0; 2 16; 3 48; 4 110 min

radiation in acetonitrile. The photolysis course of the compound *I* which can react both at the aromatic nucleus and the aliphatic part of the molecule is thus strongly affected by the reaction medium.

On the basis of literature data¹ we assumed that, particularly in 2-propanol, the nitro groups in compound *I* are reduced, the nitrogen atoms being retained in the molecules of the fission products. However, mass spectral analysis of the products did not confirm this assumption. According to gas-liquid chromatography (Fig. 4), compound *I* was photolyzed in 2-propanol in the presence of oxygen to give five products of which the first two were present only in very small amounts. Mass spectra of the two principal products (peaks 3 and 4) were identical with those of authentic 1,3-diphenyl-1-butene, and the compounds were obviously its *cis* and *trans* stereoisomers. We ascribed the first chromatographic peak to phenylcyclopropane and the second one to allylbenzene: these compounds arise as primary photolysis products, capable of further reactions. Formation of cyclopropane derivatives was observed in photolysis of substituted styrene⁸ and can be ascribed to the 1,2-shift⁹. The fifth product remained unidentified; its high retention time suggested that it is a higher oligomer of styrene. This assumption was supported by the fact that photolysis of 1,3-diphenyl-1-butene gave a compound of the same retention time. As a side-product, we identified in the reaction mixture acetone, which was detected also by the ¹H NMR spectrum (singlet $\delta = 2.07$ ppm). Photolysis of compound *I* in 2-propanol under nitrogen (introduced continuously into the reaction mixture during irradiation) afforded during the same time seven products of which the principal two were benzene and toluene. Also in this case acetone was detected, however, its concentration was ten times lower than in the experiment in the oxygen atmo-

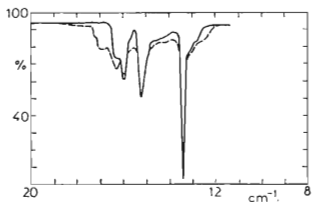


FIG. 3
Changes of IR spectra during photolysis of *I* in acetonitrile: — 0 min, - - - 32 min

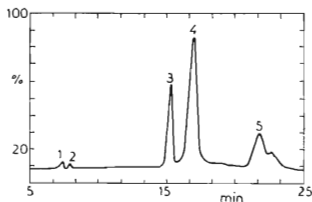


FIG. 4
Gas-liquid chromatogram of photolysis products from *I* in 2-propanol

sphere. The remaining products were not identified but we unequivocally excluded the presence of stereoisomeric 1,3-diphenyl-1-butenes or products with reduced nitro groups.

Our results are at variance with those reported in the literature¹⁻⁵. This discrepancy may be explained by the fact that in this case we are not dealing with a photo-reaction of an isolated aromatic nucleus or a condensed hydrocarbon but with photolysis of a styrene dimer with nitro groups in the *para*-positions. Since in such system obviously a lower energy state excitation operates, the fate of the nitro groups depends on that part of the molecule at which the excitation takes place ($\pi\pi^*$ of the hydrocarbon or $n\pi^*$ of the nitro group).

As known¹⁰, in nitro compounds in which the excitation energy is delocalized over the whole molecule (*e.g.* 1-nitronaphthalene) and in nitrobenzenes with electron-donating groups (*e.g.* methoxy groups) reduction of the nitro group is very difficult and takes place only with strong reducing agents. In such case the lowest excited state is the $\pi\pi^*$ state and the reaction at the aromatic nucleus operates preferring the substitution reaction course. Since also in our case we may assume a delocalization of the electron cloud over the whole molecule, the reaction of this type is probably preferred, the molecule being simultaneously cleaved at its aliphatic unsaturated part. The replacement of nitro as well as nitroso groups by hydrogen is already known^{11,12}.

The product composition is substantially influenced by the reaction medium. As already mentioned above, in acetonitrile the dissolved oxygen slowed down the photochemical reaction. Five reaction products were found: *n*-heptane, toluene, 4-nitrobenzaldehyde, 4-nitroacetophenone and 2-(4-nitrophenyl)propionaldehyde, the relative proportion of products depending on the dissolved oxygen concentra-

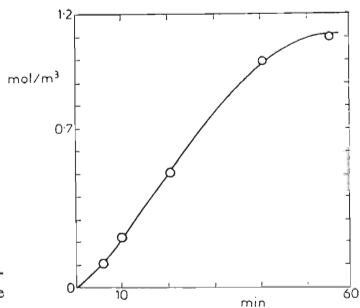
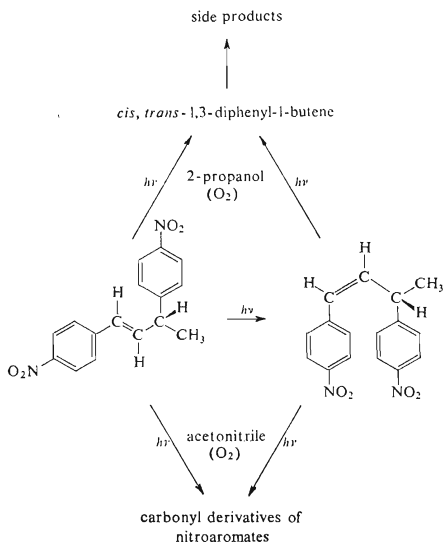


FIG. 5
Kinetic curve for 4-nitrobenzaldehyde formation during photolysis of I in acetonitrile

tion. Reaction in the presence of air oxygen gave toluene as the principal product but when the oxygen content was increased by its continuous introduction into the solution, the main product was 4-nitrobenzaldehyde (for kinetics see Fig. 5).

These results show that in our case photolysis of the nitro groups and of the aliphatic part of the molecule takes place together with the photooxidation process. This can also explain the observed IR and UV spectral changes. However, the oxidation of *I* does not appear to be a radical reaction because here a sensitized excitation of singlet oxygen ($^1\Delta_g$) can take place. The assumption that the photochemical reaction can proceed *via* singlet oxygen is supported also by studies on a substituted stilbene¹³. According to these studies photoisomerization of a *trans*-stilbene derivative containing one or two *para*-nitro groups is accompanied by formation of singlet oxygen whereas for other functional groups no similar effect was observed. Another support of this idea comes from the fact that addition of *N,N'*-diphenylpicryl hydrazide does not affect the course of photolysis of *I* in acetonitrile. No simple explanation of formation of cleavage products is available at present, we may, however, assume



SCHEME 1

that these products arise mainly *via* a hydroperoxide. The effect of oxygen on the photolysis of *I* in 2-propanol is more complex and the mechanistic differences can be to a certain extent ascribed to concurrent formation of acetone whose concentration depends on the amount of oxygen in the reaction mixture. The overall photolysis course can be depicted by Scheme 1.

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