# **Brief Communications**

### Photolysis of a methanolic solution of benzyl acetate in low acoustic fields

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The influence of low acoustic fields on the photolysis of benzyl acetate in solution was investigated. A change in the contributions of alternative photolysis mechanisms is caused by destruction of solvate shells.

Key words: benzyl acetate, photolysis, acoustic fields.

It has been demonstrated by us previously 1-5 that the temperature, the concentration of the starting components, the solvent, the level of IR irradiation, the diameter of the ampule (reaction vessel), the grade of deuteration of the solvent and the reagents, the rotation of the ampule (the field of centrifugal forces) and the homogeneity or heterogeneity of the reaction media strongly affect the photolysis of organic substances in solution. The mechanism of the photolysis and its manifestations (the temperature, concentration, and other dependences of the yields of the reaction products; the magnetic and spin effects) are determined mainly by the association of the starting reagents with each other, with the solvent, and with the surface of the reaction vessel, and by the conformation of the resulting triplet biradicals. It has been showed by us<sup>3</sup> that the photolysis depends on the excitation of the oscillational degrees of freedom of the radicals (biradicals). The life-time of the radicals (the rate of the cross relaxation transfers in biradicals) is a function of the energy obtained when they form, and therefore depends on many factors (for example, on the solvent even if it is completely chemically inert). One can significantly affect the life-time of radicals by choosing the source of the radicals, the method of their generation, and the external conditions.

Due to technical difficulties we were not able for a long time to investigate the photolysis of organic substances simultaneously undergoing sonication (photolysis in an acoustic field). Now a unit has been created and preliminary investigations of the photolysis of benzylacetate in methanol have been carried out. Benzylacetate was chosen as the object of the investigation after taking into account the previous study of its photolysis, the convenience of monitoring the products of the photolysis by NMR, and the existence of two photolysis pathways: cage recombination of the methyl

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 1, pp. 180–181, January, 1995. 1066-5285/95/4401-0176 \$12.50 © 1995 Plenum Publishing Corporation and benzyl radicals (ethylbenzene is the product) and solvolysis (the products are acetic acid and benzylmethyl-d<sub>3</sub> ether)

It was found that during photolysis in a low acoustic field the ratio of the yield of ethylbenzene to the yields of acetic acid and benzylmethyl-d<sub>3</sub> ether increases. The alteration of this ratio by electric power equal  $3 \cdot 10^{-3}$  W was  $10\pm3$  %.

In our opinion, the alterations observed result from the fact that even small disturbances (excitation of the oscillational degrees of freedom) can influence the relationship of the contributions of the alternative processes, especially when the substance is in a metastable state. These disturbances in this case are acoustic fields, which destroy the solvate shells and thus decrease the contribution of photosolvolysis to the total process. For further investigations and to understand the effects of the acoustic field it will be necessary to study in more detail the processes of the association (complexation) of the starting reagents and the role of small active additives (impurities).

#### Experimental

Solutions (0.05 mol  $L^{-1}$ ) of benzylacetate in CD<sub>3</sub>OD (degree of deuteration was 98 %) were investigated. The irradia-

tion was carried out in quartz cuvette by the light of a DRSh-500 lamp (working current ~7 A). The low acoustic fields  $(W \approx 3 \cdot 10^{-3} \text{ W}; \text{ discrete working frequencies } f_1 = 200 \text{ kHz}, f_2 = 5 \text{ MHz}, f_3 = 10 \text{ MHz})$  were created by a quartz generator. The reaction products were analyzed on BS-567A (100 MHz), MSL-300 (300 MHz), and WM-360 (360 MHz) NMR spectrometers. The results of the measurements were treated by the method of least squares.

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## Rearrangement of enol acetates of $\alpha$ -(3,5-dimethyl-1,2,4-triazol-1-yl)-2,4-dichloroacetophenone and $\alpha$ -(1,2,4-triazol-1-yl)-2,4-dichloropropiophenone

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At 140 °C in acetic anhydride enol acetates of  $\alpha$ -(3,5-dimethyl-1,2,4-triazol-1-yl)-2,4-dichloroacetophenone and  $\alpha$ -(1,2,4-triazol-1-yl)-2,4-dichloropropiophenone undergo 1,3- and 1,5-rearrangement, respectively.

**Key words:** enol acetates, diketones, ketones, aryl-(1,2,4-triazol-1-yl)methylketones; migration of the acyl group, rearrangement.

1,3-Rearrangements to yield  $\beta$ -diketones are typical of enol acylates of carbonyl compounds.<sup>1,2</sup> We have found previously<sup>3</sup> that under the conditions of thermo-

lysis, enol acylates of aryl-(1,2,4-triazol-1-yl)methylketones undergo 1,5-rearrangement with the migration of the acyl group to the C(5) atom of the triazole ring.

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