SHORT COMMUNICATIONS

The Photochemical Fries Rearrangement of Phenyl Cinnamate*[1]

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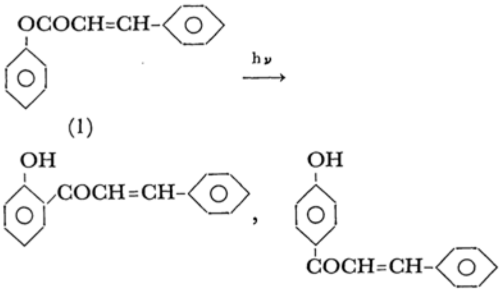
Recently, the migration of the acyl groups of such aromatic esters as phenyl acetate,(1) catechol monoacetate,(1) phenyl benzoate(2) and the *p-t*-butylphenyl esters of some aromatic carboxylic acids(3) by ultraviolet-light irradiation has been investigated. This investigation has supplied a convenient method for preparing some hydroxyaromatic ketones.

In such a photochemical Fries rearrangement, however, the migration of no unsaturated group like the cinnamoyl group has yet been observed. Our objective in this work was to examine the photochemical formation of hydroxychalcones from phenyl cinnamate (1), for if this photochemical rearrangement were successful, there may be the possibility of light-catalyzed syntheses of corresponding hydroxychalcones from various substituted phenyl cinnamates.



(1)

(2)

(3)

A solution of 1.0 g of phenyl cinnamate in benzene was irradiated for 20 hr under a nitrogen atmosphere at room temperature by a high-pressure 450 W mercury arc. During the irradiation, the absorption maximum at 283 mμ which is due to the phenyl cinnamate, decreased, while there was an increase in the absorbance at more than about 310 mμ which is caused by the formation of 2′-hydroxychalcone (2) (λ_{max}^{EtOH} 316 mμ) and 4′-hydroxychalcone (3) (λ_{max}^{EtOH} 322 mμ). After irradiation, the solvent was evaporated *in vacuo,* and the residual crude mixture was chromatographed on a 570×30 mm column of silica gel. Elution with benzene-ligroin (2 : 1) gave yellow crystals, which were then chromatographed once again by the same method. 2′-Hydroxychalcone (0.1 g) was obtained by recrystallization from methanol; it was identified by a comparison of its infrared spectrum with that of an authentic sample, and by a consideration of its melting point 87—88°C (lit. 89°C) and mixed melting point. Further elution of the chromatographic column with the same solvent gave 0.34 g of white crystals, which were identified as the unchanged starting materials by means of their infrared spectrum. Continuing elution with a mixture of benzene and ethanol (5 : 1) afforded brown viscous products, which were then recrystallized from benzene. This procedure gave 0.02 g of 4′-hydroxychalcone (mp 170—171°C (lit. mp 173°C)), which was identified by a comparison of its infrared spectrum with that of an authentic sample. The formation of the geometrical isomer or the dimeric cyclobutane derivative of (1) was expected in this experiment, but no pure compound could be isolated from the residual in the column. Similarly, *p*-tolyl cinnamate and phenyl *p*-methoxycinnamate were found to give 5′-methyl-2′-hydroxychalcone and 4-methoxy-2′-hydroxychalcone respectively.

Further investigations are now in progress.

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