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PHOTOREACTIONS VIA π-π^* AND n-π^* TRIPLET STATES OF FLAVANONES1)

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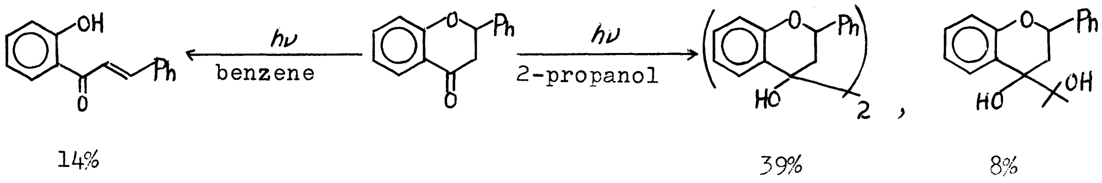
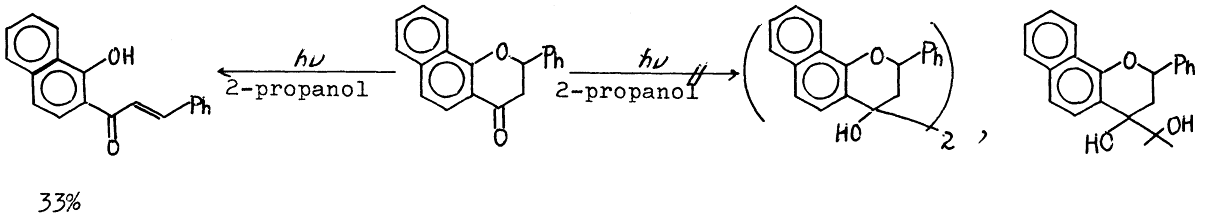
Photolyses of flavanone and substituted flavanones in benzene led to the cleavage of the pyrone ring to give corresponding 2'-hydroxychalcones, while similar irradiation of flavanone or 4-chromanone in 2-propanol gave coupling products (pinacols and solvent adducts). However, photolysis of 7,8-benzoflavanone in 2-propanol led to the cleavage of the pyrone ring instead of the formation of coupling products. It is implied that the cleavage of the pyrone ring takes place via π-π^* triplet states, while formation of coupling products via n-π^* triplet states.

Upon irradiation under nitrogen atomosphere at room temperature with a 100 W high pressure mercury lamp, a benzene solution of flavanone (10^{-2} M) gave a ring cleavage product (2'-hydroxychalcone), while in 2-propanol coupling products were obtained. The products were assigned from their elemental analyses and NMR and IR spectra. Similar irradiation of 4-chromanone in benzene for 15 hours gave no photoproducts, while irradiation in 2-propanol for 5 hours gave isomeric mixtures of 4-chromanone pinacols (89%). Photolyses of benzene solutions of substituted flavanones (e.g., 6-methoxy-, 7-methoxy-, 4'-methoxy-, 4'-carbomethoxy-, and 2-methyl-7-methoxy-, derivatives) gave corresponding 2'-hydroxychalcones, which were identified by comparing their NMR and IR spectra with those of authentic samples.



The yields of 2'-hydroxy-4-methoxychalcone, in the photolyses of 4'-methoxyflavanone with a 400 W high pressure mercury lamp for 3 hours, were 69% in benzene, 66% in pyridine, 48% in acetonitrile, and 31% in carbon tetrachloride.

Irradiation of 7,8-benzoflavanone in 2-propanol gave no coupling products at all, but a ring cleavage product was obtained. The lack of the photoreduction may imply that the lowest triplet state of 7,8-benzoflavanone is $^{3}\pi$-π^*.



Similarly, photoformation of 2'-hydroxychalcones from flavanone and substituted flavanones in benzene may be assumed to involve π-π^* triplet states. Methoxylated flavanones are assumed to have considerable π-π^* character in their lowest triplet states, since analogous acetophenone derivatives, such as 4-methoxyacetophenone, show π-π^* character in their lowest triplet states.2) To the contrary, 4-chromanone, which gave no cleavage of the pyrone ring by irradiation in benzene, seems to have essentially n-π^* character in its triplet states.3)

References and Notes

1) Partially presented at the meeting of the Chubu-Kagakukankeigakukyokai-Shiburengo, October 22, 1975 (Nagoya).

2) K. Tokumaru, "Yuukikokagaku-Hannouron", Tokyo Kagaku Dozin, Tokyo (1973), pp. 100-102.

3) J. B. Gallivan and J. S. Brinen, Chem. Phys. Lett., 10, 455 (1971); J. B. Gallivan, Can. J. Chem., 50, 3601 (1972).

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