Photorearrangements of Isoflavones

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Summary Irradiation of 2-phenylisoflavones through a Pyrex filter gave 3,4-diphenylisocoumarins and phenanthro[9,10-*c*]isocoumarins; the former are precursors of the latter.

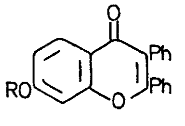
We report the photoisomerization of an isoflavone to an isocoumarin. The photorearrangements of flavones,[1] chromanones,[2] and isothiochromanones[3] have been reported recently.

Irradiation of 2-phenyl-7-methoxyisoflavone (**1a**) in methanol with a medium-pressure mercury arc using a Pyrex filter gave two major products. The first, m.p. 151·5—153·5°, (**2a**) (10%), appeared to be the initial product and was accompanied by another solid, m.p. 207—209°, (**3a**) (42%), which appeared to be derived from the first product and the amount of which increased with time.

Analytical data for the first photoproduct showed it to be isomeric with the reactant (**1a**) (M^+, m/e 328), and i.r. and u.v. data suggested that it was a coumarin or isocoumarin [$\nu_{C=O}$ 1760 cm^{-1}; λ_{max} (MeOH) 267 nm (log ϵ 4·67)]. Cold methanolic alkali on (**2a**) appeared first to form a yellow solution of a salt, treatment of which with acid regenerated (**2a**). Prolonged treatment of the product with methanolic alkali, followed by acidification with dil. HCl gave α-(2-carboxy-5-methoxy)phenyldeoxybenzoin. The photo-product with m.p. 207° was assigned structure (**3a**) on the basis of the following spectral data: M^+, m/e 326 [*cf.* m/e 328 for (**2a**)]; λ_{max} ($CHCl_3$) 257 (log ϵ 4·65), 278 (sh, 4·11), 288 (sh, 3·99), 300 (sh, 3·98), 330 (2·88), and 351 nm (2·32), indicating a phenanthrene unit; δ (CD_3OD), 3·75 (s, 3H), 6·7—8·0 (m, 8H), and 8·6—8·8 (m, 3H); i.r. (KBr) 1710 cm^{-1} ($\nu_{C=O}$).

Similar irradiation of 2-phenyl-7-hydroxyisoflavone (**1b**) in methanol afforded (**2b**), m.p. 299—301°, i.r. (KBr) 1700 cm^{-1} ($\nu_{C=O}$); λ_{max} (MeOH) 223 (sh, log ϵ 4·59), 248 (sh, 4·69), 254 (4·73), 289 (4·24), and 300 nm (4·19); m/e 312 ($M-2$) and (**3b**), m.p. 305—309° λ_{max} (MeOH) 254·5 (sh, log ϵ 4·41), 261 (4·43), 289·5 (sh, 4·16), 301·5 (4·08), 340·5 (3·75), 357·5 (3·87), 376·5 (3·89), and 394·5 nm (3·84); i.r. (KBr) 1670 cm^{-1} ($\nu_{C=O}$); δ (CD_3OD) 7·3—8·0 (m, 9H) and 8·7—8·9 (m, 2H); m/e 312 (M^+).

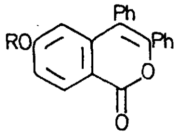
Irradiation of (**1b**) in the presence of iodine did not furnish (**2b**), but instead gave (**3b**) and another unidentified product. Photolysis of (**1b**) in methanol exposed to air gave only a polymeric compound. Irradiation of (**2b**) in methanol afforded (**3b**). These results clearly indicate that (**3**) is derived from oxidative photocyclization[4] of (**2**).



(1)

a; R = Me

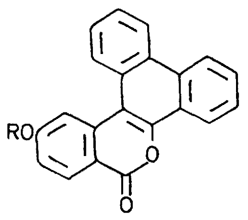
b; R = H



(2)

a; R = Me

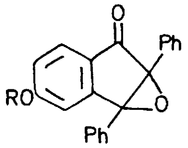
b; R = H



(3)

a; R = Me

b; R = H



(4)

This photoisomerization did not occur with 2-methylisoflavone, 2-methyl-7-hydroxyisoflavone, or flavone. Irradiation of these compounds in methanol through a Pyrex or Vycor filter resulted in recovery of the starting materials.

The formation of (**2**) from (**1**) suggests that the reaction proceeds by rearrangement of (**1**) to (**4**), followed by photochemical transformation to (**2**). Photochemical valence tautomerization of 2,3-epoxyindanones to benzopyrylium-3-oxides followed by isomerization to isocoumarins has been reported.[5]

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