Photolysis of 2,6-Diphenyl-4*H*-pyran-4-thione

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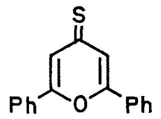
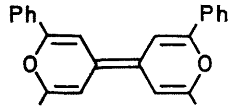
Summary Photolysis of 2,6-diphenyl-4*H*-pyran-4-thione in dioxan results in desulphurization to give 2,2′,6,6′-tetraphenyl-4,4′-bi(pyranylidene).

PHOTOLYSIS of both 4*H*-pyran-4-one[1] and 4*H*-thiopyran-4-one derivatives[2,3] produces the photodimeric cage compounds. We report on another photochemical dimerization of 2,6-diphenyl-4*H*-pyran-4-thione which is accompanied by elimination of sulphur.‡

Irradiation (100 w medium pressure mercury lamp, Pyrex filter, $1{\cdot}3 \times 10^{-2}$ mole/l) of 2,6-diphenyl-4*H*-pyran-4-thione (I) in dioxan for 50 hr. gave 2,2′,6,6′-tetraphenyl-4,4′-bi(pyranylidene)§ (II), m.p. 318—319° (lit.[4] m.p. 313°), in 80% yield. The structure of the photoproduct was established by comparison of its i.r. and u.v. spectra [λ_{max} 270 nm (ϵ $3{\cdot}3 \times 10^4$, shoulder), 276 ($3{\cdot}4 \times 10^4$), 437 ($3{\cdot}7 \times 10^4$, shoulder), 458 ($5{\cdot}0 \times 10^4$) in dioxan)¶ with those of an authentic sample.[4] The mass spectrum of (II) displays important fragments at *m/e* (relative intensity, %): (50 ev), 466(7·2), 465(37·4), 464(100), 435(3·6), 359(11·4), 341(3·6), 257(6·8), 254(6·2), 253(6·2), 232(26·0), 105(44·2), 104(17·7), 91(22·4), and 77(28·2).

This photodimerization with cleavage of a C–S bond does not occur to any great extent (0—3%) in the case of either 4*H*-pyran-4-thione (III) or 2,6-dimethyl-4*H*-pyran-4-thione (IV). Irradiation of (III) in dioxan at the same concentration gives only a polymeric compound, while irradiation of (IV) results in recovery of starting material. This dimerization with desulphurization was observed on heating (I). However, heating (III) or (IV) did not give any dimer.[4,5]


(I)


(II)

Irradiation of (I) at 5461 Å[6] under the same conditions gave the starting material.** Anthraquinone (E_T 62·4 kcal/mole) was found to sensitize the photodimerization of (I) to (II) more effectively than pyrene (E_T 48·7 kcal/mole), biacetyl (E_T 54·9 kcal/mole), benzophenone (E_T 68·5 kcal/mole), and acetophenone (E_T 73·6 kcal/mole). The formation of (II) was quenched by piperylene. These results suggest that the photodimerization of (I) to (II) proceeds *via* the π–π^* triplet state of (I).

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‡ Elimination of sulphur gave hydrogen sulphide gas.

§ Satisfactory elemental analysis was obtained for the photoproduct.

¶ (II) is insoluble in the common solvents for n.m.r.

** After irradiation for 35hr. only a trace of the photoproduct (II) was detected by u.v. and t.l.c. (silica gel).

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