Photochemistry of 4-Diphenylmethylene-2,6-bis(methylthio)-3,5-diphenyl-4*H*-thiopyran. A Methylene Analogue of a 4*H*-Thiopyran-4-one

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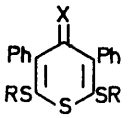
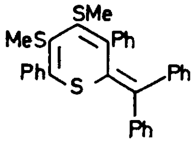
Summary U.v. irradiation of 4-diphenylmethylene-2,6-bis(methylthio)-3,5-diphenyl-4*H*-thiopyran affords 2-diphenylmethylene-4,5-bis(methylthio)-3,6-diphenyl-2*H*-thiopyran *via* the π,π* triplet state of the former.

THE photochemical rearrangement of the 2,6-bis(alkylthio)-4*H*-thiopyran-4-ones (I) to 3,4-bis(alkylthio)-2,5-diphenylcyclopentadienones has been reported, and evidence in favour of a mechanism involving the *n*,π* triplet state of (I) was given.[1] We have now examined the photochemistry of a system lacking *n*,π* excitation but having a similar π system. Accordingly, the diphenylmethylene analogue (II)† of (I) was studied.

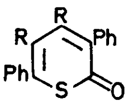
Irradiation of compound (II)[2] in benzene through Pyrex afforded the 2*H*-thiopyran (III) (90%). Elemental analyses‡ and mass spectral data (M^+ 506) for the photoproduct showed it to be an isomer of reactant (II), and the n.m.r. spectrum of (III) in $CDCl_3$ showed two SMe singlets at δ 2·30 (3H) and 2·32 (3H), while (II) exhibited an SMe singlet at δ 2·34. The presence of the diphenylmethylene group at C-2 was confirmed by the formation of compound (IV),‡ m.p. 153—154°, and benzophenone from the Methylene Blue-sensitized photo-oxygenation of (III).[3]



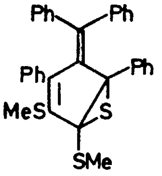
(I) X = O, R = alkyl
(II) X = CPh_2, R = Me



(III)



(IV) R = SMe
(V) R = H



(VI)

Firm structural assignment was obtained by degradation of compound (III) by desulphurization with Li-$EtNH_2$ to give 3,6-diphenyl-2*H*-thiopyran-2-one (V)[4] and benzophenone.§ Structure (V) was established by comparison (i.r. and n.m.r. spectra) with an authentic sample.[4]

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† Attempts to prepare 2,6-bis(methylthio)-3,5-diphenyl-4-methylene-4*H*-thiopyran from the Wittig reaction of methylenetriphenylphosphorane with (I; R=Me) or the 4-thiones derivative of (I) and from the reaction of diazomethane with the 4-thione derivative of (I) were unsuccessful.

‡ All new compounds reported here gave satisfactory analyses.

§ T.l.c. of the reaction mixture showed another spot besides the identified products. However, 2-diphenylmethylene-3,6-diphenyl-2*H*-thiopyran, m.p. 185—187°‡ was not obtained in this reaction.

Since (I) is known to rearrange *via* the n,π^* triplet state to give 3,4-bis(methylthio)-2,5-diphenylcyclopentadienone,[1] we sought to generate the triplet of (II) by thioxanthone sensitization ($E_T = 65{\cdot}5$ kcal/mol) under conditions where thioxanthone absorbed over 95% of the light. Under these conditions, (II) isomerized efficiently to (III). The photoisomerization of (II) to (III) was quenched partly by cyclo-octatetraene ($E_T < 40$ kcal/mol).[5] These results indicate that the photoisomerization of (II) to (III) occurs *via* the π,π^* triplet state of (II).

A tentative mechanism to account for this photoisomerization involves the rearrangement of (II) to (VI) which leads thermally or photochemically to (III). The photochemistry of related systems such as 1-methylene-4,4-diphenylcyclohexa-2,5-diene[6] and 2,3,4,4,5,6-hexamethyl-1-methylenecyclohexa-2,5-diene[7] was found to proceed *via* their π,π^* singlet states giving methylenebicyclo[3,1,0]hex-2-enes. In contrast to the photoisomerization of 1-methylenecyclohexa-2,5-dienes,[6,7] compound (VI), a possible intermediate, was not isolated in the photoisomerization of (II) and attempts to trap (VI) in the presence of triphenylphosphine have been unsuccessful so far. In assessing the reasons for the differing behaviour of the present diphenylmethylene analogue from that of 1-methylenecyclohexa-2,5-dienes, we recognize that heavy-atom substitution with sulphur results in an enhancement of spin–orbit coupling¶ and tends to favour reaction of the triplet. Additionally, this difference might derive from π-electron conjugation of the triene unit through the sulphur atom in our system.

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¶ The lifetime of phosphorescence of 4*H*-thiopyran-4-ones is less by an order of magnitude than that of corresponding 4*H*-pyran-4-ones (unpublished results.)

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