Photolysis of 2,6-Bis(alkylthio)-3,5-diphenyl-4*H*-thiopyran-4-one: Formation of Cyclopentadienones

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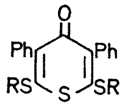
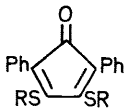
Summary Irradiation of 2,6-bis(alkylthio)-3,5-diphenyl-4*H*-thiopyran-4-ones with a medium-pressure mercury lamp with a Pyrex filter produced 3,4-bis(alkylthio)-2,5-diphenylcyclopentadienones.

RECENT reports dealing with the photochemistry of cyclic keto-sulphides[1] and a sulphoxide[2] have shown ring-contracted and ring-expanded products. The cyclic keto-sulphides and the sulphoxide studied have an sp^3 carbon at the α-position to the sulphur atom. During irradiation the α-carbon–sulphur bond is cleaved. We report here on the photochemistry of 2,6-bis(alkylthio)-3,5-diphenyl-4*H*-thiopyran-4-ones (**1**), a process involving the sp^2 carbon adjacent to the sulphur atom in the ring.

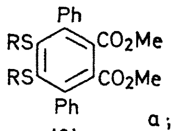


(1)

R
a; Me
b; Et
c; CH_2Ph

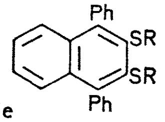


(2)



(3)

R
a; Me
b; Et

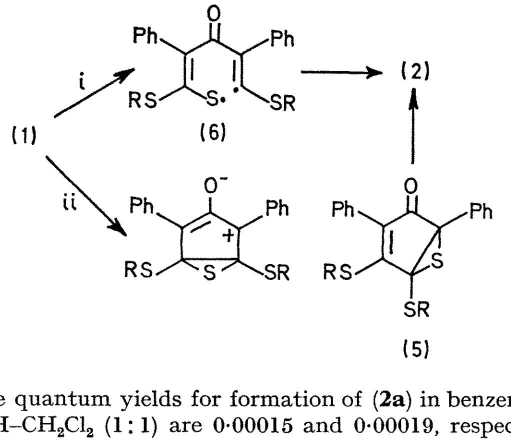


(4)

Irradiation of 2,6-bis(methylthio)-3,5-diphenyl-4*H*-thiopyran-4-one[3] (**1a**) [λ_{max} ($CHCl_3$) 280 (log ϵ 4·39), 308 nm (4·19)] in MeOH–CH_2Cl_2 (1 : 1), using a Taika 100 W medium-pressure mercury lamp with a Pyrex filter, produced 3,4-bis(methylthio)-2,5-diphenylcyclopentadienone† (**2a**) [m.p. 123—124°; λ_{max} ($CHCl_3$) 269 (log ϵ 4·27), 336 (4·04), 519 nm (3·69)] and sulphur in nearly quantitative yield [26% conversion based on (**1a**)]. Irradiation of 2,6-bis(ethylthio)-3,5-diphenyl-4*H*-thiopyran-4-one[3] (**1b**) [λ_{max} ($CHCl_3$) 281 (log ϵ 4·17), 314 nm (4·30)] and 2,6-bis(benzylthio)-3,5-diphenyl-4*H*-thiopyran-4-one[3] (**1c**) [λ_{max} ($CHCl_3$) 281 (log ϵ 4·35), 317 nm (4·23)] under the same condition gave (**2b**) [m.p. 94—95°; λ_{max} ($CHCl_3$) 270 (log ϵ 4·27), 340 (4·04), 510 nm (2·67)] in 77% yield [20% conversion based on (**1b**)] and (**2c**) [m.p. 178—181°; λ_{max} ($CHCl_3$) 268 (log ϵ 5·22), 340 (4·91), 438 (2·99), 575nm (2·45)] in 30% yield,‡ respectively and also sulphur. Assignment of structure was based on spectral and chemical evidence.

The electronic spectra of (**2**) showed absorption maxima at 510—575 nm, which is characteristic of 2,5-diarylcyclopentadienones.[4] The i.r. spectra of (**2**) (KBr) lacked the 6·2 μm band [ν(C=O) due to the carbonyl moiety of 4*H*-thiopyran-4-ones[5]] and exhibited a strong band at 5·9 μm, (**2a**) 5·94; (**2b**) 5·95; (**2c**) 5·96 μm, in agreement with their being cyclopentadienones.[6] The n.m.r. spectra of the photoproducts ($CDCl_3$) showed a peak at δ 7·4, typical of the 2,5-diphenyl ring protons of cyclopentadienones;[7] (**2a**) δ 2·23 (s, 6H), 7·27—7·55 (m, 10H); (**2b**) δ 1·10 (t, *J* 6·0 Hz, 6H), 2·67 (q, *J* 5·5 Hz, 4H), 7·30—7·50 (m, 10H); (**2c**) δ 3·88 (s, 4H), 7·00—7·50 (m, 20H). The mass spectra of (**2**) (70 eV) showed their parent peaks at *m/e* 326 for (**2a**), 352 for (**2b**), and 475 for (**2c**).

When (**2**) is heated with dimethyl acetylenedicarboxylate in bromobenzene, (**3**) was formed; (**3a**) [70%; m.p. 194—195°; i.r. (KBr) 5·75, 5·83 μm; n.m.r. ($CDCl_3$), δ 2·12 (s, 6H), 3·45 (s, 6H), 7·30—7·50 (m, 10H); (**3b**) [84%; m.p. 106—109°; i.r. (KBr) 5·84 μm; n.m.r. ($CDCl_3$) δ 0·98 (t, *J* 7·0 Hz, 6H), 2·57 (q, *J* 6·5 Hz, 4H), 3·43 (s, 6H), 7·25—7·47 (m, 10H)]. The structure of (**3a**) was confirmed by desulphurization with Raney nickel catalyst. The product was identical with an authentic sample of dimethyl *p*-terphenyl-2,3-dicarboxylate, synthesized by the method of Alder.[8] Treatment of (**2**) with benzyne generated from diphenyliodonium-2-carboxylate[9] gave (**4**); (**4a**) [38%; m.p. 168—169°; λ_{max} ($CHCl_3$) 247 (log ϵ 4·59), 292 nm (4·13); n.m.r. ($CDCl_3$) δ 2·25 (s, 6H), 7·30—7·50 (m, 14H); (**4b**) [46%; m.p. 123—124°; λ_{max} ($CHCl_3$) 247 (log ϵ 4·64), 294 nm (4·15); n.m.r. ($CDCl_3$) δ 1·03 (t, *J* 7·0 Hz, 6H), 2·75 (q, *J* 6·5 Hz, 4H), 7·30—7·55 (m, 14H)]. These Diels–Alder reactions in which 1,4-adducts are decarbonylated to yield benzene and naphthalene derivatives, are characteristic of cyclopentadienones.[10]



The quantum yields for formation of (**2a**) in benzene and MeOH–CH_2Cl_2 (1 : 1) are 0·00015 and 0·00019, respectively at 313 nm.§ The formation of (**2a**) was quenched effectively by *cis*-piperylene, a good triplet quencher at the

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† Satisfactory elemental analyses were obtained for all new compounds described.

‡ T.l.c. of the reaction mixture showed at least one other weak spot besides (**2c**), which was not identified.

§ Light of 312—313 nm was isolated with a filter solution of $NiSO_4$–$CoSO_4$–potassium bisphthalate.[11] Quantum yield measurements were carried out on a rotating photochemical assembly in sealed degassed Pyrex tubes, using a benzophenone–benzhydrol actinometer.[13]

concentrations used[12] These results suggest that the photochemical reaction of (**1**) to (**2**) proceeds *via* the excited triplet state of (**1**)

A possible mechanistic rationalization of the photolysis of (**1**) involves homolysis of the C–S bond followed by diradical reorganization (route i) Alternatively, the reaction may initially proceed by rearrangement to (**5**), which is analogous to what happens with 2,6-dimethyl-4*H*-pyran-4-one[14] and 4,4-diphenylcyclohexa-2,5-dienone[15] The intermediate (**5**) then desulphurizes resulting in conversion into (**2**) (route ii) ¶

These results are in contrast to previous results on the photochemistry of 2,6-disubstituted-4*H*-thiopyran-4-ones, which yield a "head-to-tail" cage dimer or a dimer involving the cyclobutane ring[17]

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¶ While the photochemical and thermal extrusion of sulphur from an episulphide is known,[16] trapping of intermediate (**5**) or (**6**) is under investigation

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