

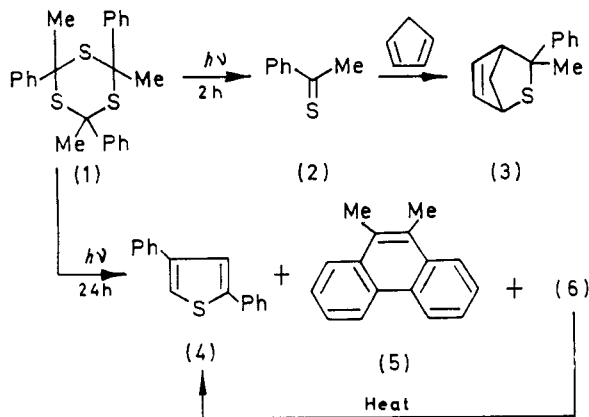
## Photochemical Reaction of Thioacetophenone Trimer (2,4,6-Trimethyl-2,4,6-triphenyl-1,3,5-trithiolan)

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**Summary** Irradiation of thioacetophenone trimer (1) in cyclohexane affords 2,4-diphenylthiophen (4) and 9,10-dimethylphenanthrene (5) via thioacetophenone (2).

RECENTLY, we reported the photochemical reaction of thiobenzophenone with conjugated dienes to give the



alkyl-aryl thioketones are unstable and readily trimerize at room temperature. When compound (1) in cyclohexane was irradiated with a low pressure mercury lamp through a quartz filter under nitrogen for 2 h, the solution turned blue ( $\lambda_{\max}$  575 nm)<sup>3</sup> showing the formation of thioacetophenone (2). After irradiation, the addition of cyclopentadiene to (2) gave a 1:1 adduct (3) (a mixture of *endo*- and *exo*-isomers),  $\tau$  ( $\text{CHCl}_3$ ) 8.49 (s, 3H, *endo*-Me), 8.39 (s, 3H, *exo*-Me), 8.11 (m, 2H,  $\text{CH}_2$ ), 6.63 and 6.03 (m, 2H, CH), 3.90 and 3.68 (m, 2H, vinyl), and 3.05—2.20 (m, 5H, Ph).

Prolonged irradiation (24 h) of (1) gave 2,4-diphenylthiophen (4), m.p. 118.5—120.5° (lit.,<sup>4</sup> 121.0—121.5°); 9,10-dimethylphenanthrene (5), m.p. 138.0—139.0° (lit.,<sup>5</sup> 139.0°); and an unidentified product (6), which was converted into (4) by distillation (175—178° at 2 mmHg). Compounds (3) and (5) were identified on the basis of their i.r., u.v., n.m.r., and mass spectra and their elemental analyses. Compound (4) was identified by direct comparison with an authentic sample.<sup>6</sup> The formation of (5) seems to proceed via dimethylstilbene, while thiobenzophenone gave tetraphenylethylene on irradiation.<sup>1</sup> Possible mechanisms for the formation of (4) and the photoreactions of other thioketone trimers are under investigation.

1,4- or 1,2-adduct.<sup>1,2</sup> Generally, monomeric dialkyl or

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<sup>5</sup> S. I. Heilbron, "Dictionary of Organic Compounds", Eyre and Spottiswoode, London, 1953, Vol. I, p. 330.

<sup>6</sup> B.P. 696,439/1953.