Photochemical Conversion of 2-Thioxo-1,3-dithioles into Tetrathiafulvalenes

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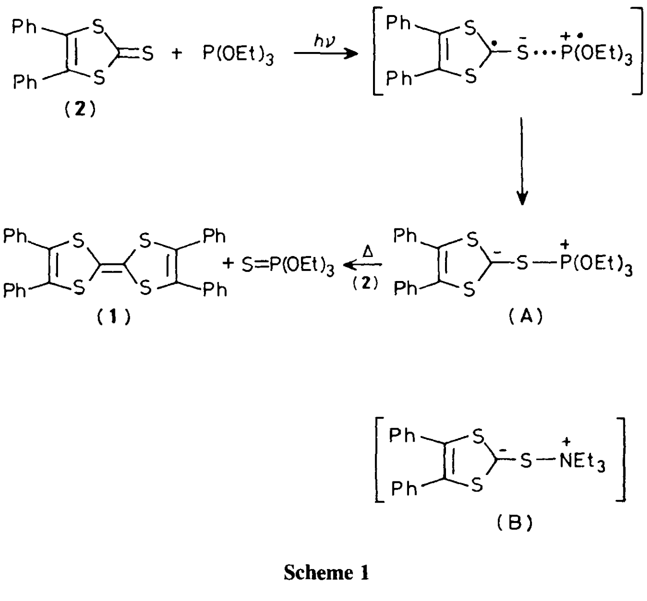
Photochemical reactions of 4,5-diphenyl-2-thioxo-1,3-dithiole in the presence of an electron donor produce tetraphenyltetrathiafulvalene.

We report in this communication that tetraphenyltetrathiafulvalene (**1**) is efficiently produced by photochemical reaction of a synthetic intermediate, 4,5-diphenyl-2-thioxo-1,3-dithiole (**2**), which is photochemically synthesized from diphenylacetylene and ethylene trithiocarbonate as previously reported.[1]

Thermal reactions of 2-thioxo-1,3-dithioles with phosphite normally produce the corresponding tetrathiafulvalenes (TTF). However, this method is limited to preparation of TTF bearing electron withdrawing substituents.[2] Thus (**1**) could not be synthesized by this method from (**2**). Ueno *et al.* have reported that the photochemical reaction of (**2**) in the presence of hexabutyldistannane gave (**1**) in reasonable yield.[3] We have found that (**2**) gives (**1**) in good yield on irradiation with a medium pressure mercury arc lamp in acetonitrile in the presence of an electron donor such as triethylamine or triethyl phosphite. The mechanism of this reaction is different from the one proposed by Ueno.

Irradiation of (**2**) (0.5 g) in acetonitrile (200 ml) in the presence of triethyl phosphite (0.6 ml) with a 10 W medium pressure mercury arc lamp for 16 h under nitrogen gave (**1**), m.p. 261—263 °C, in 91% yield together with recovered (**2**) (192 mg) and a substantial amount of triethyl thiophosphate.



Scheme 1

A similar irradiation of (**2**) (104 mg) in acetonitrile (70 ml) in the presence of triethylamine (0.1 ml) for 21 h gave (**1**) in 53% yield (conversion 81%). Even in the absence of electron donors irradiation of (**2**) in acetonitrile gave (**1**) in 27% yield. However, an electron acceptor such as 1,2,4,5-tetracyanobenzene quenched the photochemical reaction and no (**1**) was obtained after similar irradiation of (**2**) for 12 h.

From these results it may be concluded that photoinduced electron transfer from the phosphite to (**2**) apparently accelerates the formation of the zwitterion intermediate (A), which has previously been proposed as an intermediate in the thermal phosphite-promoted coupling of 2-thioxo-1,3-dithioles,[4] and then promotes the desulphurization–coupling reaction of (**2**) to give (**1**), as shown in Scheme 1. When triethylamine is used as an electron donor, a similar intermediate (B) may be postulated. Our findings open another photochemical synthetic route to TTF derivatives.

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