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PHOTOCHEMICAL REACTION OF PHENYLACETYLENES WITH ETHYLENE TRITHIOCARBONATE. PHOTOCHEMICAL PREPARATION OF 2-THIOXO-1,3-DITHIOLES

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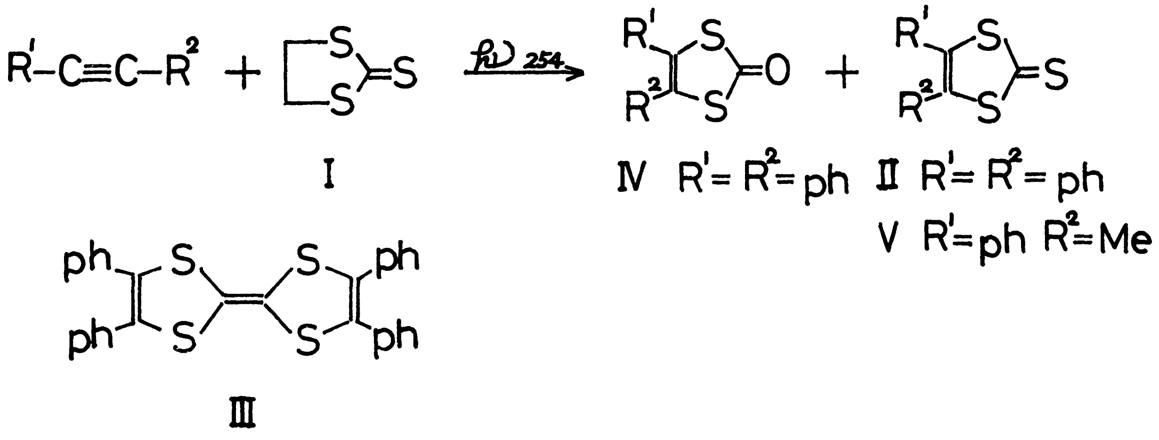
On irradiation diphenyl- and methylphenylacetylene react with ethylene trithiocarbonate to give 4,5-diphenyl- and 4-methyl-5-phenyl-2-thioxo-1,3-dithiole, respectively. Selective excitation of the acetylenes is essential to this reaction.

It has been well documented that 2-thioxo-1,3-dithioles are excellent starting materials for preparations of tetrathiafulvalenes(TTF), components of organic metals.[1)] Most acetylenes bearing electron-withdrawing substituents react with ethylene trithiocarbonate(I) to yield 2-thioxo-1,3-dithioles. However, methyl-, phenyl-, and diphenylacetylene do not react with I by heating and thus these reactions have been applicable only to preparations of TTF derivatives bearing electron-withdrawing substituents.[2)] We now report that diphenylacetylene in the excited state does react with I to give 4,5-diphenyl-2-thioxo-1,3-dithiole(II) which is, in turn, readily converted to tetraphenyl-TTF(III).[3,4)]

A solution of diphenylacetylene(9.8x10^{-3} M) and I(3.2x10^{-3} M) in acetonitrile (300 ml) was irradiated with a 12 W low pressure mercury lamp for 14 h under nitrogen. The solvent was removed *in vacuo* and the residue was chromatographed on alumina(100 g), eluting with hexane, to give II, mp 120°C(lit.[3)] 119-120°C), M^+ m/e 286, in 22% yield together with a trace amount of 4,5-diphenyl-2-oxo-1,3-dithiole(IV),[5)] an oxidation product of II.

The UV absorption spectrum of the starting mixture exhibited the sum of the individual absorption bands of both components.[6)] When the mixture was irradiated at 327 nm by means of a spectro-irradiator,[7)] intensity of the absorption bands of I decreased gradually, but those of the acetylenes did not change. On the contrary when the mixture was irradiated at 275 nm, the absorption bands of both compounds decreased simultaneously. Taking account that alkylacetylenes do not absorb ultraviolet light in the region longer than 220 nm, a mixture of 2-butyne or 3-hexyne and I in acetonitrile was irradiated by means of a medium pressure mercury arc. Consequently I was consumed, but the corresponding 2-thioxo-1,3-dithiole derivative was not obtained.8) These experiments indicate that selective excitation of the acetylenes is essential to this new photochemical reaction. Since the fluorescence of diphenylacetylene was quenched by I, a singlet state of the acetylene is possibly involved in the reaction.

A similar reaction occurred when 1-phenylpropyne was irradiated in the presence of I with a low pressure mercury arc, where 4-methyl-5-phenyl-2-thioxo-1,3-dithiole(V)9) was obtained in 39% yield. The above mentioned photochemical reaction may open a new simple synthetic route to TTF derivatives from I and phenylacetylenes.



I

IV R¹=R²=ph

II R¹=R²=ph

V R¹=ph R²=Me

III

References and Notes

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6) UV absorption maxima in acetonitrile: I, 296(sh), 315(log ε 4.21)nm; diphenylacetylene, 263(4.33), 270(4.37), 278(4.50), 287(4.34), and 295(4.45)nm.
7) A JASCO CRM-FA spectro-irradiator was used for selective excitation.
8) Photochemical reactions of excited I with olefins have been reported; R. Okazaki, F. Ishii, K. Okawa, K. Ozawa, and N. Inamoto, J. Chem. Soc., Perkin Trans. 1, 1975, 270; Chem. Lett., 1972, 9.
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