

Photochemical Reactions of Phenylacetylenes with Ethylene Trithiocarbonate. Synthesis of Phenyl-substituted 2-Thioxo-1,3-dithioles

Shuzo Yamada, Norihisa Mino, Noboru Nakayama, and Mamoru Ohashi*

Department of Materials Science, The University of Electro-Communications, Chofu, Tokyo 182, Japan

A novel photochemical synthetic route to phenyl-substituted 2-thioxo-1,3-dithioles (TDT), intermediates in the synthesis of tetrathiafulvalenes (TTF), starting from ethylene trithiocarbonate (ETC) and phenylacetylenes is described. Phenyl- and diphenyl-acetylene and 1-phenylpropyne reacted with ETC derivatives in reasonable yields. The fluorescence of the acetylenes was quenched by ETC *via* a trivial process: sensitization with benzophenone and quenching with air suggested that the reaction proceeded mainly through the triplet excited states of the acetylenes. Irradiation of ETC alone with light of longer wavelength and quenching experiments suggested that the excited singlet state of ETC also participated in the reaction, in a minor process.

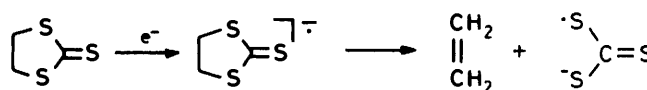
Molecular charge-transfer complexes of TTF with electron acceptors have high and anisotropic conductivities and have attracted great interest as organic metals.¹ One of the typical synthetic routes to TTF derivatives is *via* TDT derivatives, from the thermal reactions of ETC with acetylenes.² This convenient method, however, is limited in the case of TTF derivatives bearing only electron-withdrawing substituents such as CN or CO₂Me; thus, acetylene itself, and alkyl-, and diphenyl-acetylene hardly react on being heated with ETC.

In contrast with the thermal reactions, we found that with irradiation phenylacetylene (**1b**) and diphenylacetylene (**1a**) reacted with ETC to give 4-phenyl-TDT (**2b**) and 4,5-diphenyl-TDT (**2a**), respectively. Goodman and Chambers report that on electrochemical reduction, the radical anion of ETC decomposed to give the trithiocarbonate radical anion as shown in Scheme 1.³ We therefore assumed that the photoinduced electron-transfer from the acetylene to ETC might take place to give the corresponding TDT, but we have not succeeded in obtaining any evidence for such a process. We report here these novel photochemical reactions of phenylacetylenes with ETC to give the corresponding TDT derivatives.⁴

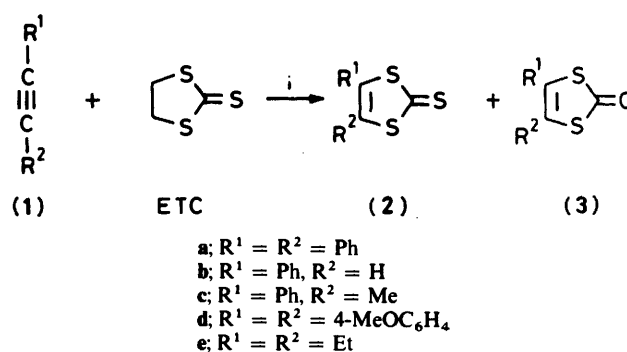
Results and Discussion

U.v. Spectral Change.—The u.v. absorption spectrum of the starting mixture of ETC and compound (**1a**) exhibits the sum of the individual absorption bands of both components. No charge-transfer absorption bands in the ground state were observed. When the mixture was irradiated at 325 nm, exciting only ETC, with a spectroirradiator, the intensity of the absorption bands of ETC decreased gradually, but those of compound (**1a**) only slightly. In contrast, when the mixture was irradiated at 275 nm, exciting mainly compound (**1a**), the absorption bands of both components decreased simultaneously suggesting the possibility of a reaction taking place. These experiments indicated that the selective excitation of the acetylene was more effective than that of ETC for the photochemical reaction.

Photochemical Reactions.—Table 1 summarizes the results of the photochemical reactions. The yields of the TDT depended on the solvent and the wavelength of incident light. The use of light of shorter wavelength (254 rather than 366 nm) and a polar solvent (acetonitrile rather than hexane) were favourable for the reaction. The formation of 2-oxo-1,3-dithioles (ODT) is attributed to oxidation of the resulting TDT (Scheme 2). Alkylacetylenes, however, do not absorb light of wavelength 254 nm, and irradiation of a mixture of hex-3-yne (**1e**) and ETC



Scheme 1.



Scheme 2. Reagents: i, *hν*, N₂

Table 1. Photo-induced reactions of acetylenes with ETC (*cf.* Scheme 2)

Compound	λ (nm)	Solvent	Yield (%) ^a	
			TDT	ODT
(1a)	245	MeCN	22	Trace
		CH ₂ Cl ₂	11	
		C ₆ H ₁₄	5	
		MeOH-MeCN (1:1)	6	3
		MeOH		
(1a)	366	MeCN	7	
(1b)	254	MeCN	22	Trace
(1c)	254	MeCN	39	Trace
(1d)	254	MeCN		
(1e)	366	MeCN		

^a Yields are calculated based on the acetylene consumed for (**1a**) and (**1c**), and on the consumed ETC for (**1b**)

with a medium-pressure mercury arc resulted only in consumption of the ETC and formation of S₈. Therefore, this method can not be used for the synthesis of alkyl substituted TDT.

Table 2. Sensitization of the reaction with benzophenone

Concentration (M)	E_T (kcal mol ⁻¹)	PhCOPh (M)	λ (nm)	TDT (% Yield) ^a
(1a) 1×10^{-2}	63		366	(2a) (6.7)
1×10^{-2}		1×10^{-2}	366	(2a) (26.0)
(1b) 8×10^{-2}	72		366	(2b) (4.6)
8×10^{-2}		8×10^{-2}	366	(2b) (2.9)

^a See the footnote,^a Table 1.

Reactive Species.—Several mechanistic experiments were carried out to establish the reactive species. First, *fluorescence quenching* was examined. The fluorescence of compound (1c) was quenched by ETC. The critical concentration was found to be $ca. 3 \times 10^{-5}$ M. Using this value we were able to calculate the critical distance⁵ to be $ca. 240 \text{ \AA}$, which is too large for singlet-singlet energy transfer. Since compound (1c) fluoresces at 298 nm and ETC absorbs at 315 nm, the quenching mechanism must be a so-called trivial process. The fluorescence of ETC at 360 nm was not quenched by compound (1c) indicating that the primary step of the reaction may not involve an exciplex between ETC and (1c) in the singlet state.

Secondly, *sensitization* was investigated. Irradiation of compound (1a) in the presence of benzophenone, which absorbed more than 90% of the incident light at 366 nm, gave the product (2a) in 26% yield, while without benzophenone present a similar experiment gave (2a) in only 7% yield. Since the E_T values of benzophenone and compound (1a) are 68 and 63 kcal mol⁻¹ respectively,^{6,*} energy transfer from benzophenone to (1a) is exothermic and must be diffusion controlled. On the other hand, in the (1b)-ETC-benzophenone system, energy transfer from benzophenone to (1b) (E_T 72 kcal mol⁻¹)⁶ is endothermic and a similar experiment showed (see Table 2) such a transfer to be inefficient. The results of these experiments with benzophenone sensitization suggest that the energy transfer from benzophenone to ETC is not important, and that the acetylene triplet state must participate in the reaction. Furthermore, the reaction of compound (1a) with ETC was partially quenched by air, giving the product (2a) in 8.8% yield, compared with 22.4% yield when the reaction was carried out under nitrogen. This observation implies that a triplet state or a radical species participates in the reaction.

Although the triplet state of acetylenes plays an important role, the excitation of ETC alone can also give the same products, although in poor yields. For instance, irradiation of a mixture of ETC with compound (1a) or (1b) at 366 nm and longer wavelengths (absorbed only by ETC) gave the products (2a) and (2b) in 7 and 5% yields respectively. In the case of the (1b)-ETC system, sensitization with benzophenone did not improve the yield of (2b), and even on quenching of the (1a)-triplet system by air, (2a) was obtained in 8.8% yield; thus the excited singlet state of ETC must also participate in the reaction, in a minor process.

As far as the results of Goodman and Chambers³ are concerned, we have tried to find evidence for the occurrence of photoinduced electron transfer. The solvent dependency of the product yield is in accord with the electron-transfer mechanism, *i.e.* more polar solvents (*e.g.* acetonitrile) favour the reaction, while protic solvents (*e.g.* methanol) quench it; however, this trend does not necessarily indicate the occurrence of electron transfer, but only the participation of a polar species in the course of reaction. All efforts to find any direct evidence of

electron transfer, such as charge-transfer absorption, exciplex emission, and electron-transfer quenching of fluorescence, failed. Furthermore, the lack of reactivity of bis(4-methoxyphenyl)acetylene (1d) is definitely in conflict with an electron-transfer mechanism according to Weller's equation.⁷ We conclude, therefore, that the proposed electron-transfer mechanism should be discarded; thus, although the direct attack of the singlet excited ETC on the acetylenes, as in the photochemical reaction of 1,2,4-dithiazole-3-thione with olefins,⁸ takes place to a minor extent, the direct attack of the triplet acetylenes on the ground state ETC must be the major process in this novel reaction.

Experimental

General Procedures.—M.p.s were determined with a Kofler hot-stage apparatus. T.l.c. was performed with silica gel GF-254 (Merck). I.r. spectra were taken with a JASCO model IRA-1 instrument, u.v. spectra were obtained with a Hitachi 124 spectrophotometer, and n.m.r. spectra were recorded with Hitachi R-24 and R-20B instruments with tetramethylsilane as internal standard. Mass spectra were recorded with a Hitachi RMU-6MG instrument equipped with a direct/in-beam ion source; ionizing energy 20 eV, source temperature *ca.* 200 °C. Irradiation with a monochromatic light was carried out with a JASCO CRM-FA spectroirradiator.

ETC purchased from Eastman Co. was recrystallized twice from chloroform. Compounds (1b), (1c), and (1e) were purchased from Tokyo Kasei Co. and distilled before use. Compound (1a) purchased from the same company was recrystallized twice from ethanol. Compound (1d)⁹ was prepared as in ref. 10.

Photochemical Reactions of Phenylacetylenes with ETC.—(a) A solution of diphenylacetylene (1a) (521 mg) and ETC (132 mg) in acetonitrile (300 ml) was irradiated with a 12-W low-pressure mercury lamp for 15 h under nitrogen. The solvent was removed under reduced pressure and the residue was chromatographed on alumina (Merck, neutral grade). Elution with hexane gave 4,5-diphenyl-2-thioxo-1,3-dithiole (2a)¹¹ (25 mg, 22%), m.p. 120 °C (lit.,¹¹ 119–120 °C). A trace amount of 4,5-diphenyl-2-oxo-1,3-dithiole (3a)¹² was detected by mass spectrometry; m/z 270, 242, 210, and 178. Compound (1a) (381 mg, 73%) and ETC (25 mg, 19%) were also recovered.

(b) A similar irradiation of phenylacetylene (1b) (0.82 ml) and ETC (339 mg) in acetonitrile (350 ml) gave 4-phenyl-2-thioxo-1,3-dithiole (2b) (26 mg, 22%), m.p. 117 °C (lit.,¹³ 117–118 °C). A trace amount of 4-phenyl-2-oxo-1,3-dithiole (3b)¹² was detected by mass spectrometry; m/z 194 and 166. ETC (182 mg, 54%) was recovered.

(c) A similar irradiation of a solution of 1-phenylpropyne (1c) (1.0 ml) and ETC (349 mg) in acetonitrile (350 ml) gave 4-methyl-5-phenyl-2-thioxo-1,3-dithiole (2c)¹³ (82 mg, 39%) and a trace amount of 4-methyl-5-phenyl-2-oxo-1,3-dithiole (3c),¹⁴ m/z 208, 193, and 148. ETC (109 mg, 31%) and compound (1c) (156 mg, 16%) were recovered.

(d) Similar irradiations of ETC with diphenylacetylene (1a) in dichloromethane, hexane, methanol, and methanol-acetonitrile (1:1) gave compounds (2a) and (3a) (Table 1). Similar irradiations of ETC with compound (1d) and (1e) in acetonitrile did not give the corresponding TDT in detectable amounts.

Sensitization.—(a) A solution of diphenylacetylene (1a) (537 mg), ETC (369 mg), and benzophenone (549 mg) in acetonitrile (300 ml) was irradiated through a filter solution [composed of CuSO₄ (250 ml) and CoSO₄ (240 mg) in water (1 l), transparent only for 366 nm light]¹⁵ with a 100-W medium-pressure mercury lamp for 10 h under nitrogen. The products were

* 1 kcal is 4.184 kJ.

separated by alumina chromatography. Compound (**2a**) (24 mg, 26%) was obtained after recrystallization from acetone, and starting compound (**1a**) (479 mg, 89%) was recovered. A similar irradiation but without benzophenone gave the products (**2a**) (15 mg, 7%) and recovered (**1a**) (398 mg, 74%).

(b) A solution of compound (**1b**) (0.148 ml), ETC (61 mg), and benzophenone (246 mg) was irradiated through the same filter solution with a 300-W medium-pressure mercury lamp for 12 h under nitrogen. After chromatographic separation on alumina, compound (**2b**) (2.2 mg, 3%) was obtained, and ETC (12.3 mg, 20%) was recovered. A similar irradiation but without benzophenone gave the product (**2b**) (3.2 mg, 4.6%) and recovered ETC (15.3 mg, 25%).

Quenching.—(a) The fluorescence of compound (**1c**) (emission max. 298 nm, c 1.1×10^{-3} M) in acetonitrile was quenched by ETC at a concentration of 2.0×10^{-5} — 8.1×10^{-5} M. However, the fluorescence of ETC (360—410 nm, c 1.6×10^{-4} M) in acetonitrile was not quenched by (**1c**) at concentrations of 2.0×10^{-2} and 4.0×10^{-2} M.

(b) A solution of compound (**1a**) (278 mg) and ETC (63 mg) in acetonitrile (80 ml) was irradiated with a 6-W low-pressure mercury lamp for 10 h while air was bubbled through. The reaction products were separated by chromatography on alumina, and compound (**2a**) (7.2 mg, 8.8%) was obtained, together with recovered (**1a**) (235 mg, 84%) and ETC (23 mg, 37%). A similar irradiation with nitrogen in place of the air gave compound (**2a**) (9.0 mg, 22.4%), together with recovered (**1a**) (251 mg, 90%) and ETC (39 mg, 64%).

(c) A solution of compound (**1a**) (502 mg), ETC (127 mg), and triethylamine (1 ml) in acetonitrile (350 ml) was irradiated with a 12-W low-pressure mercury lamp for 13 h under nitrogen. The reaction mixture was separated by chromatography on alumina; no product (**2a**) was detected, but ETC (8.0 mg) and starting compound (**1a**) (286 mg) were recovered.

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