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PHOTOCHEMICAL AND THERMAL REACTIONS OF THIONES WITH SUBSTITUTED ALKYNES

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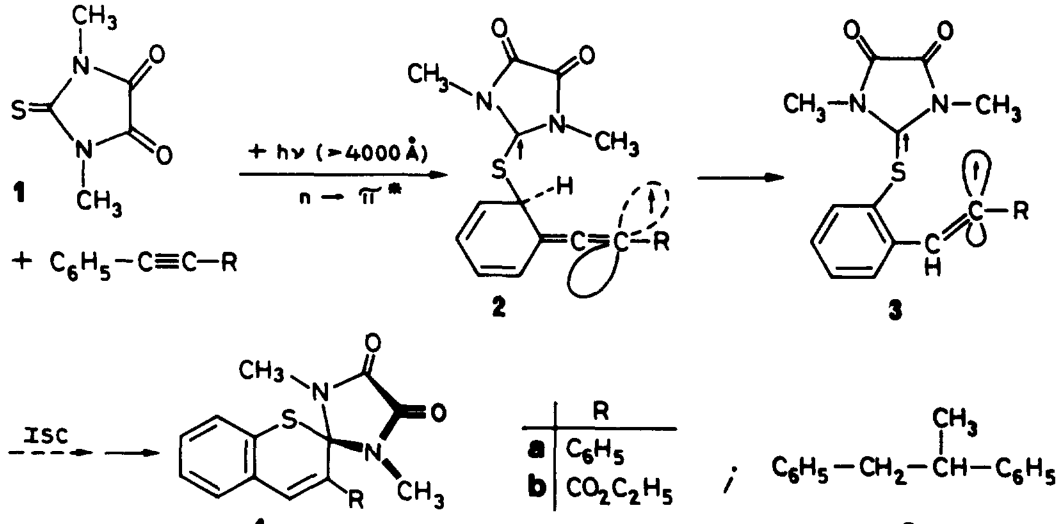
The light-induced reactions of 2-thioparabanates or xanthione with olefins offer a synthetically valuable entry into the thietane series[1,2]. Although the chemistry of thiones is going through a period of rapid growth[3], there exist only few studies concerned with the chemical behavior of thiones towards alkynes[4,5]. In this communication we wish to report on some new excited and ground state reactions of thiones with alkynes.

It is known that the photoreaction of thiobenzophenone with phenylacetylene produces 1,4-diphenyl-1,2-dihydro-2-thianaphthalene[4]. In the case of electron-rich alkynes a second type of reaction, namely the formation of α, ß-unsaturated thiocarbonyl compounds, has been observed recently[5]. Surprisingly, we found that the above-mentioned thiones react under n → π* excitation with diphenylacetylene in a different manner.



1 + $C_6H_5-C\equiv C-R$

2

3

4

	R
a	C_6H_5
b	$CO_2C_2H_5$

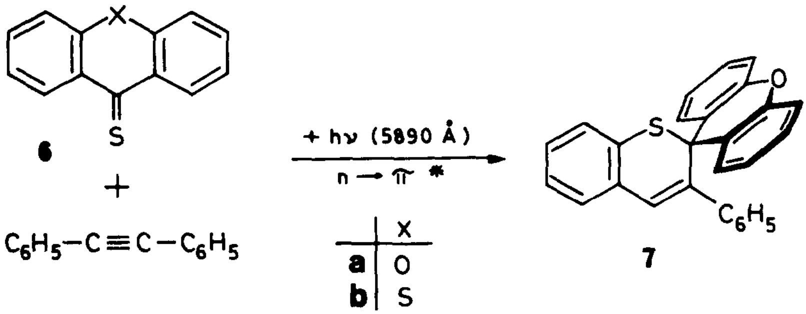
$C_6H_5-CH_2-\overset{CH_3}{\overset{|}{C}}H-C_6H_5$

5

When a degassed benzene solution of 1,3-dimethyl 2-thioparabanate (**1**) and diphenylacetylene is irradiated with blue light ($\lambda > 4000$ Å), light-yellow crystals of the spiro compound, **4a**, are obtained in 57% yield (**4a**: mp 203-204.5°; ir, 1748, 1726 (C=O), 1623, 1595 cm^{-1} (C=C); uv (dioxane), λ_{max} (lgε) = 242.5 (4.60), 348 nm (3.94); NMR (60 MHz, CDCl$_3$), τ = 6.76 (s, 2CH$_3$), 3.01-2.39 (m, 10 H); ms (70 eV), m/e = 336 (100%, M$^+$), 178 (71, $C_{14}H_{10}^+$)). The addition direction of the C=S chromophore in **4a** is supported by the results of several reduction steps. Thus, on treatment with lithium aluminum hydride, hydrochloric acid, Raney nickel, and hydrogen/palladium, **4a** is converted into 1,2-diphenylpropane (**5**), identical with an authentic sample[6].

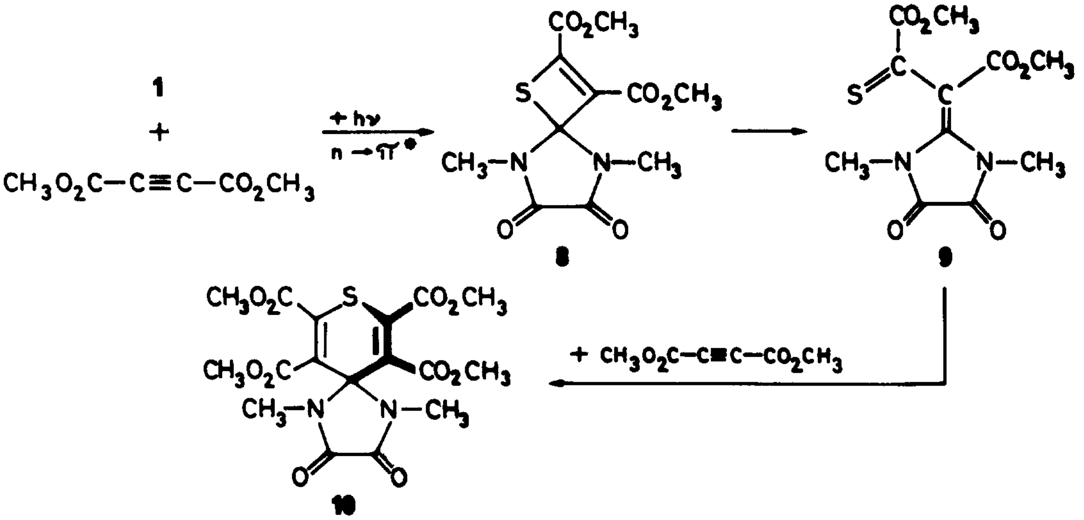
The analogous photoreaction of **1** with ethyl phenylpropiolate affords **4b**, pale yellow crystals (**4b**: mp 175-178°; ir, 1750, 1728, 1690 (C=O), 1599, 1592 cm^{-1} (C=C); NMR, τ = 8.79 (t, J = 7.1 Hz, CH$_3$), 6.80 (s, 2 CH$_3$), 5.80 (q, J = 7.1 Hz, OCH$_2$), 2.68-2.27 (m, 3H), 1.92-1.70 (m, 2H)).

We assume that the formation of **4** proceeds via the $^3(n,\pi^*)$ state of **1**, the diradical **2**, which rearranges to **3** by way of a [1,3]hydrogen shift.



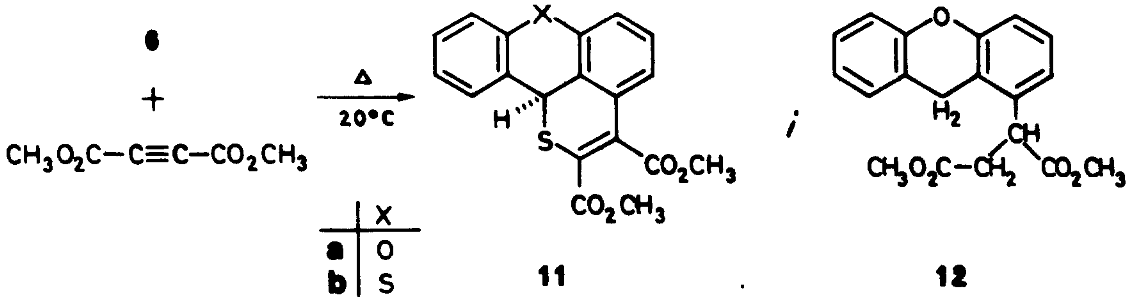
Similarly, the light-induced reaction of xanthione (**6a**) with diphenylacetylene using sodium light produces **7** in 91% yield, after recrystallization from methanol (**7**: mp 181.5-182.5°; uv (dioxane), λ_{max}(lgε) = 240 (4.56), 310 (4.06), 344 nm (3.95); NMR, τ = 3.17-2.15 (m); ms, m/e = 390 (100%, M$^+$), 313 (23, M$^+$-C$_6$H$_5$), 212 (23, M$^+$-C$_{14}$H$_{10}$), 180 (14, M$^+$-C$_{14}$H$_{10}$S)).

On the other hand, the photochemical reaction of **1** in the presence of dimethyl acetylenedicarboxylate leads to formation of the 1:2-adduct **10** in 63% yield (**10**: colorless needles, mp 183-184.5°; ir, 1753, 1740, 1728 (C=O), 1620, 1594 cm^{-1} (C=C); NMR, τ = 7.04 (s, 2 NCH$_3$), 6.25 (s, 2 OCH$_3$), 6.07 (s, 2 OCH$_3$);



ms, <u>m/e</u> = 442 (100%, M^+)).

The mechanism of formation of **10** presumable involves the $^3(n,\pi^*)$ state of **1**, which adds to the substrate with formation of a diradical intermediate, followed by ring-closure to the unstable thiete **8**. Electrocyclic ring-opening of **8** leads to the α,β-unsaturated thioketone **9**, which in turn reacts with a second molecule of acetylenic ester in a [4+2]cycloaddition step. Similar rearrangements of intermediate thietes to α,β-unsaturated dithioesters and thioamides have recently been observed^5.



Furthermore, **6** shows an interesting ground state reaction. Thus, the dark reaction of xanthione (**6a**) in the presence of dimethyl acetylenedicarboxylate proceeds at room temperature with formation of the polycyclic compound **11a** as a result of a nucleophilic attack of the sulfur at the electron-poor alkyne, followed by a nucleophilic substitution of the aromatic ring (11a: 48% pale orange plates, mp 168-169°; ir, 1730, 1720 cm^{-1} (C=O); uv (dioxane), λ_{max} ($lg\varepsilon$) = 252 (4.15), 288 (3.82), 353 nm (3.87); NMR, τ = 6.19, 6.10 (2s, 2 OCH_3), 4.50 (s, CH), 3.18-2.46 (m, 7 H); ms, m/e = 354 (100%, M^+)). Structure assignment of 11a is based on the conversion to 12.

Finally, the ground state reaction of 6b with dimethyl acetylenedicarboxylate yields 11b (21%, mp 145-146°; ir 1740, 1718 cm^{-1} (C=O); NMR, τ = 6.14, 6.06 (2s, 2 OCH_3), 4.56 (s, CH), 2.98-2.16 (m, 7H)).

These last results are somewhat surprising because in a recent communication it has been reported that the thermal reaction of 6a with 1-diethylamino-1-propyne leads to an α,β-unsaturated thioamide[5]. An explanation of this distinct behavior in the ground state reactions of 6 is provided by the different kind of electron density at the alkyne carbon. Electron-rich aminoalkynes prefer the attack with the β-carbon at the thiocarbonyl carbon atom[5].

All new described compounds gave satisfactory analytical results.

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