

PHOTOCYCLOADDITION OF THIOCARBONYL COMPOUNDS TO MULTIPLE BONDS. VI  
THE REACTION OF THIOBENZOPHENONE WITH ACETYLENIC COMPOUNDS.

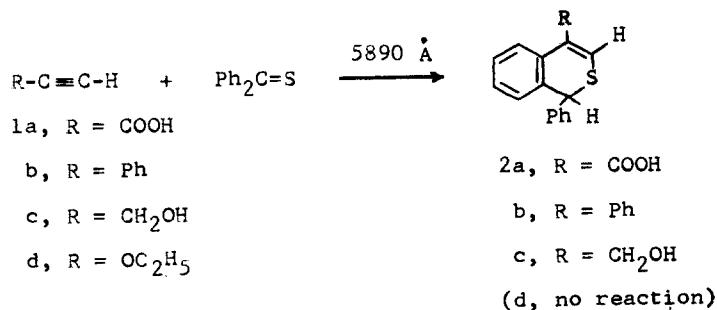
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(Received in Japan 6 April 1970; received in UK for publication 21 April 1970)

Recently, we have reported that the photocycloaddition of  $n, \pi^*$  triplet state of thiobenzophenone to electron-rich olefins affords either 1,4-dithiane or thietane derivatives depending on the substituent on the olefin(1,2). The same reaction with benzophenone is well known to give oxetane derivatives(3, 4). The detailed studies on mechanisms of both reactions have revealed that the difference in reactivities of sulfur- and oxygen-compounds is responsible for the difference in the reaction courses(1-3). This fact has stimulated us to study on the photocycloaddition of thiobenzophenone to carbon-carbon triple bonds and in this communication we would like to report the reaction has different feature from those with olefins, as shown below.



Thiobenzophenone(2.5 g) and acetylene carboxylic acid, 1a(10 g), was dissolved in tetrahydrofuran (33 ml) and the solution was irradiated for 10 days

with 5890 Å light from sodium lamps(480 W). After the color of thiobenzophenone had completely disappeared, the solvent was evaporated at a reduced pressure remaining white crystals and oily material. The latter was subjected to silica-gel column chromatography and more crystals were obtained (total 0.81 g, 24 %).

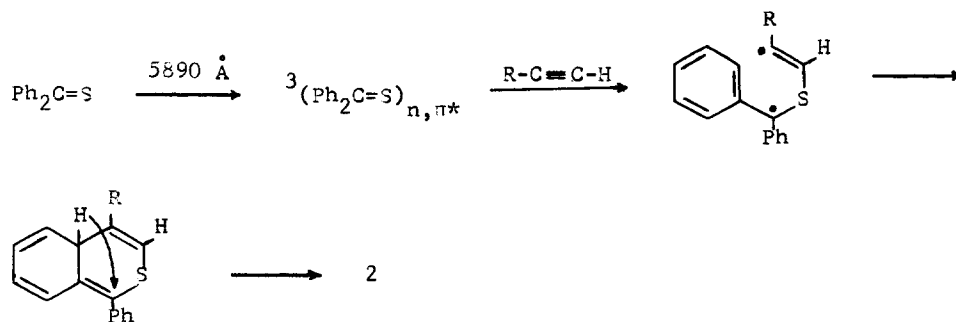
The product thus obtained was identified to be 4-phenyl-3-thia-3,4-dihydro-1-naphthoic acid, 2a(mp 164 - 6°), by the following evidence: ir(KBr) 3050 - 2560, 1660, 1420, and 1250  $\text{cm}^{-1}$ ; nmr( $\text{CDCl}_3$ )  $\delta$ (TMS) 5.13(d, 1H, J = 1.5 Hz), 7.90(d, 1H, J = 1.5 Hz), 6.90 - 7.44 and 8.00 - 8.12(m, 9H); ms( $\underline{m/e}$ , species, %) 268( $\text{M}^+$ , 100), 250( $\text{M}^+$ -  $\text{H}_2\text{O}$ , 10), 235( $\text{M}^+$ - SH, 14), 223( $\text{M}^+$ -  $\text{CO}_2\text{H}$ , 16), 221(250 - CHO, 24), 191( $\text{M}^+$ - Ph, 134), 178( $\text{M}^+$ -  $\text{C}_7\text{H}_5$ , 11), 145(191 -  $\text{CO}_2\text{H}_2$ , 13), and 36(-, 28); Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}$ : C, 71.64; H, 4.48; S, 11.94. Found: C, 71.61; H, 4.56; S, 11.94; MW: Calcd, 268. Found, 265.

The same reaction with phenylacetylene, 1b, resulted in the formation of 2b in 54 % yield; ir 3050 - 2850, 1600, 1490, and 1450  $\text{cm}^{-1}$ ; nmr 4.96(d, 1H, J = 1 Hz), 6.19(d, 1H, J = 1 Hz), and 6.85 - 7.20(m, 14H); ms 300( $\text{M}^+$ , 100), 267( $\text{M}^+$ - SH, 27), and 223( $\text{M}^+$ - Ph, 103); Anal. Calcd for  $\text{C}_{21}\text{H}_{16}\text{S}$ : C, 84.00; H, 5.33; S, 10.67. Found: C, 83.08; H, 5.71; S, 9.96; MW: Calcd, 300. Found, 275.

Since 2b is glassy and hardly purified even by repeated column and thin-layer chromatographies, the elemental analyses and molecular-weight determination did not give satisfactory results. Then the structure of 2b was further confirmed by the fact that the reductive desulfurization with Raney Ni(W-2) yielded 1,3-diphenyl indane(mp 157 - 9°; lit(5), 156 - 7°). The presence of a double bond was confirmed by titration with bromine.

Similarly, the reaction of 1c afforded 2c (28 %) as a glassy material, which was prepared alternatively by the reduction of 2a with lithium aluminum tetrahydride (89 %): ir 3600 - 3100, 3050 - 2850, 1600, 1490, 1450, 1380, and 1210  $\text{cm}^{-1}$ ; nmr 1.65(broad s, 1H), 4.54(d, 2H), 5.06(d, 1H), 6.38(d, 1H), 6.80 - 7.60(m, 9H); ms 254( $\text{M}^+$ , 100), 221( $\text{M}^+$ - SH, 20), 177( $\text{M}^+$ - Ph, 156), 166( $\text{Ph}_2\text{CH}$ , 18), and 115(166 -  $\text{C}_3\text{H}_3$ , 34).

Since it is evident that the reaction is initiated by the attack of n, $\pi^*$  triplet state of thiobenzophenone to acetylenic compounds(1), the most reasonable mechanism for the reaction seems to be:



The intra-molecular hydrogen-migration has been proved by using deuterated solvents. Thus, no deuterium was incorporated in the product even when the reaction was carried out in perdeuterated isopropanol or in deuterated chloroform as a solvent.

The difference in reactions of olefins and acetylenes could be interpreted in terms of reactivities of  $\pi$ - and  $\sigma$ -radicals, that are formed by the addition of thiobenzophenone to an olefin and to an acetylene, respectively. Aromatic substitution is favored by a  $\sigma$ -radical(6,7), while the attack to the thiocarbonyl-sulfur is preferred by easily ionizable  $\pi$ -radical(8). The fact that the reaction with ethoxyacetylene does not proceed, despite of the expectation that the addition of  $n,\pi^*$  triplet state of thiobenzophenone to carbon-carbon triple bond might be fast(1), supports this idea. That is, an  $\alpha$ -oxygen reduces the electronegativity of an orbital, which contains an odd electron, with sacrifice of its facility to attack the aromatic ring. However, since the electronegativity of such an orbital is not so small as that of p-orbital in a  $\pi$ -radical, it cannot attack the thiocarbonyl-sulfur either.

Carbonyl compounds are known to undergo photocycloaddition to acetylenic compounds yielding oxetene derivatives, which decompose subsequently to  $\alpha,\beta$ -unsaturated ketones(9,10). Although we have no concrete evidence to discuss factors that result in combination of two radical centers in carbonyl compound and aromatic substitution in thiocarbonyl compound, one possible explanation is longer bond length and smaller bond angle in C-S-C moiety than in C-O-C make it favor for the sulfur-containing biradical to cyclize over the oxygen-containing

species. It should be noted that the attack to an aromatic ring takes place from the side of out-of-plane of the ring but not from in-plane. An alternative possibility is the responsibility of  $n, \pi^*$  singlet state to the reaction of carbonyl compounds(11).

It is unlikely to expect larger reactivity to an ortho-position of sulfur-containing biradical than that of oxygen-containing one because spin densities at both positions are almost the same(12).

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