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THE REACTION OF α-DIAZOKETONES WITH THIOBENZOPHENONE

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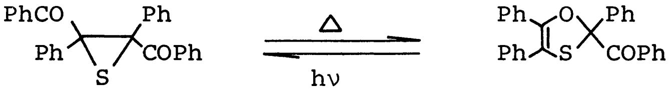
The reaction of azibenzil (1) and α-diazophenanthrone (2) with thiobenzophenone (4) gave the corresponding 1,3-oxathioles 5 and 8 in 31 and 73% yields, respectively, whereas α-diazoacenaphthenone 3 gave diphenylmethylideneacenaphthenone 9 in 97% yield.

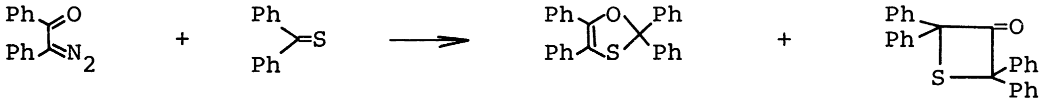
Recently, the interconversion between trans-1,2-dibenzoyl-1,2-diphenylepisulfide and the corresponding 1,3-oxathiole was reported.1)



The reaction of diazo compounds with thioketones, which proceeds via episulfide intermediate, is extensively explored and known to be useful for olefin synthesis.2) Even on the reaction of α-diazoester with thioketone, in which the formation of 1,3-oxathiole via α-ketoepisulfide could be expected, only α,β-unsaturated carbonyl compounds were isolated.2) Up to the present time, no paper has reported on the 1,3-oxathiole formation by the reaction of α-diazoketones with thioketones.

We now report the first examples of 1,3-oxathiole formation by the reaction of azibenzil (1) and α-diazophenanthrone (2) with thiobenzophenone (4).

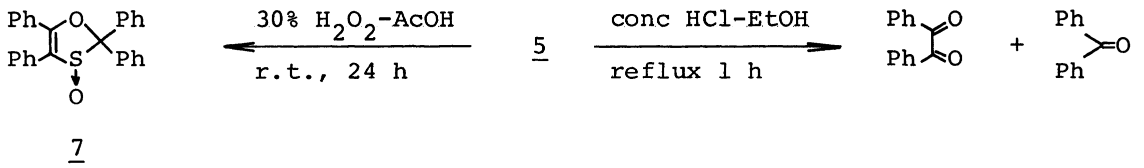
The equimolecular mixture of 1 and 4 in benzene was heated at reflux for 30 min. After removal of the solvent *in vacuo*, the residue was columnchromatographed on alumina using benzene as an eluent, affording 2,2,4,5-tetraphenyl-1,3-oxathiole (5) and the 1:1-adduct (6)3) of diphenylketene and 4 in 31 and 8% yields, respectively.



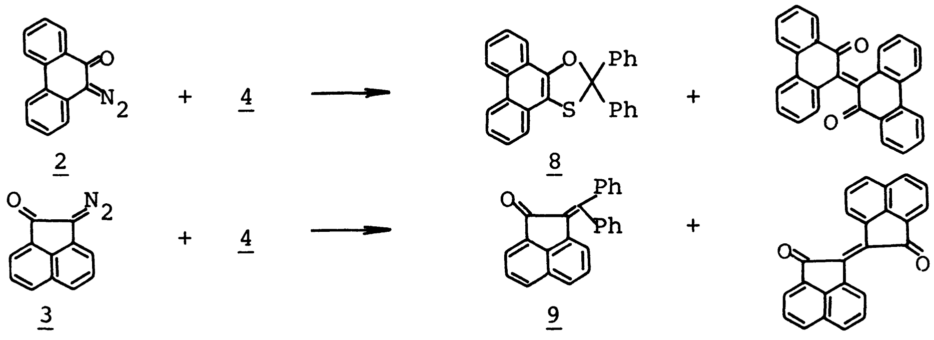
1 4 5 6

When anhydrous cuprous sulfate was added to the mixture of 1 and 4 in order to surpress the Wolff rearrangement of 1, vigorous gas evolution was observed even at room temperature. No formation of 5 was observed and only a large amount of the intractable resinous materials was obtained. This suggests that not ketocarbene but 1 itself might participate in the formation of 5.

The structure of 5 was deduced from the comparison of its spectral data4) with those of the 1,3-oxathioles1) hitherto known as well as from its chemical conversion; the hydrolysis gave benzophenone and benzil, and hydrogen peroxide oxidation afforded the corresponding S-oxide (7)5) in 47% yield.

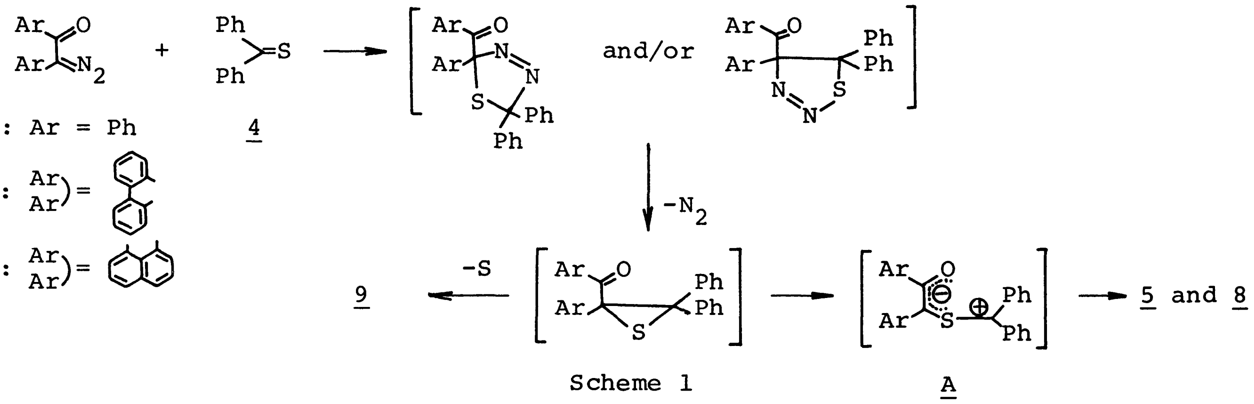


The reaction of 2 with 4 in refluxing toluene for 4 h gave the corresponding 1,3-oxathiole (8)[6] in 73% yield together with 4% yield of diphenanthrylidenedione, whereas α-diazoacenaphthenone (3) gave no 1,3-oxathiole but diphenylmethylidene-acenaphthenone (9), mp 194° of yellow prisms, and diacenaphtylidenedione in 97 and 3% yields, respectively.



These results are rationalized in scheme 1 and the formation of 9 in the reaction of 3 with 4 may well be understood in terms of the unfavorable ring strain which might be caused by the carbon-carbon double bond in the intermediate A.

The reaction of other α-diazoketones with thiocarbonyls are now in progress.



Scheme 1

References and Notes

1) U. Jacobson, T. Kempe and T. Norin, J. Org. Chem., 39, 2722 (1974).

2) A. Schönberg and E. Frese, Chem. Ber., 96, 2420 (1963), and the references cited therein.

3) H. Staudinger, Helv. Chim. Acta., 3, 862 (1920).

4) 5; pale yellow prisms. Mp 146-146.5°. IR (KBr-Disk); $\nu_{C=C}$ 1610 cm^{-1}. CMR ($CDCl_3$); δ 99.7 (C_2), 111.4 (C_4), 143.8 (C_5) ppm. UV (EtOH); λmax 343 nm (ε=7550).

5) 7; colorless prisms. Mp 192-193°. IR (KBr-Disk); $\nu_{C=C}$ 1610, $\nu_{S\rightarrow O}$ 1070 cm^{-1}. CMR ($CDCl_3$); δ 106.5 (C_2), 119.4 (C_4), 159.3 (C_5) ppm.

6) 8; pale yellow plates. Mp 164.5-165.5°. CMR ($CDCl_3$); δ 104.3 (C_2), 115.2 (C_4), 146.3 (C_5) ppm.

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