

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2220—2221(1972)

Reactions of Thiobenzophenones with Benzenediazonium-*o*-carboxylate, and Salicyloyl and *o*-Mercaptobenzoyl Chlorides as 1,4-Dipolar Reagents

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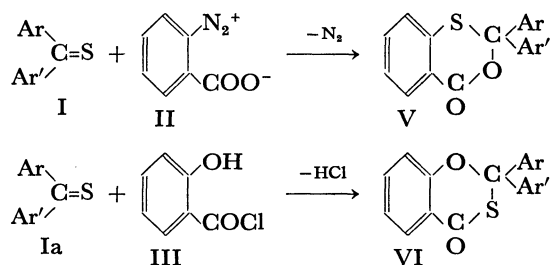
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(Received January 18, 1972)

Recently cycloaddition of *o*-carboxybenzenediazonium chloride to thiobenzophenone has been reported.¹⁾ It has been known that salicyloyl chloride reacts with ketones as a 1,4-dipolar reagent.²⁾

In order to obtain heterocycles containing sulfur atom by 1,4-cycloaddition, we carried out reactions of substituted thiobenzophenones (I) with benzenediazonium-*o*-carboxylate (II), and salicyloyl (III) and *o*-mercaptobenzoyl chlorides (IV).

Reactions of II and III with I gave 2,2-diarylbenzo-*[d]*[1,3]oxathian-6-one (V) and 2,2-diarylbenzo-*[e]*[1,3]oxathian-4-one (VI), respectively (see Table).

a: Ar=Ar'=Ph; b: Ar=Ph, Ar'=p-MeC₆H₄;c: Ar=Ph, Ar'=p-ClC₆H₄; d: Ar=Ar'=p-MeC₆H₄;e: Ar=Ar'=p-ClC₆H₄

The structures of V and VI were confirmed on the basis of the elemental analyses, and the MS and IR spectra.

1) D. C. Dittmer and E. S. Whitman, *J. Org. Chem.*, **34**, 2004 (1969).

2) E. Ziegler and H. D. Hanus, *Monatsh. Chem.*, **95**, 1053 (1964).

TABLE. 2,2-DIARYL-BENZOXATHIAN-6- AND 4-ONES (V AND VI)

	Yield (%)	Mp (°C)	Elemental analyses			
				C(%)	H(%)	S(%)
Va	40	182.3—182.8 (lit ¹⁾ , 185)	Found	75.75	4.66	10.06
Vb	32	136.3—138.3	Found	75.95	5.18	9.54
			Calcd	75.88	4.85	9.65
Vc	31	88—90	Found	68.29	3.73	9.14
			Calcd	68.08	3.71	9.09
Vd	30	101—102	Found	76.24	5.21	9.41
			Calcd	76.27	5.24	9.26
Ve	10	119.5—120.0	Found	61.79	2.99	8.09
			Calcd	62.03	3.12	8.28
VIa	80	119.5—121.0	Found	75.21	4.59	10.13
			Calcd	75.45	4.43	10.07
VIb	55	128.3—129.7	Found	75.84	4.65	9.95
			Calcd	75.88	4.85	9.65
VIc	57	113.2—114.3	Found	68.26	3.56	8.93
			Calcd	68.08	3.71	9.09
VId	60	120.0—121.5	Found	76.07	5.13	8.98
			Calcd	76.27	5.24	9.26

On the contrary, treatment of IV with Ia did not evolve hydrogen chloride, but gave oily products (A). Treatment of A with aniline gave bis[*o*-(phenylcarbamoyl)phenyl] disulfide (VII) (65%), diphenylmethylenedianiline (VIII) (40%) and aniline hydrochloride (99%). Similar treatment with pyridine gave Ia (70%) and pyridine hydrochloride (94%). On heating A afforded benzo-*[d]*[1,2]dithiolan-3-one (IX) (60%) and diphenylmethyl chloride (X) (80%). Moreover,

9) G. Reddelien, *ibid.*, **46**, 2718 (1913).