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

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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, $Ar' = p MeC_6H_4$;
- c: Ar=Ph, Ar'=p-ClC₆H₄; d: Ar=Ar'=p-MeC₆H₄;
- e: $Ar = Ar' = p ClC_6H_4$

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

Table. 2,2-Diaryl-benzoxathian-6and 4-ones (V and VI)

AND 4-ONES (V AND VI)						
	Yield	Мр (°С)	Elemental analyses			
	(%)			C(%)	H(%)	S(%)
Va	40	182.3—182.8	Found	75.75	4.66	10.06
		(lit ¹⁾ , 185)				
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	101102	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%), diphenylmethyleneaniline (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,

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).

A exhibited no absorptions due to thioester and SH groups in the IR spectrum. Therefore, A was assigned as the structure of o-(diphenylmethyldithio)benzoyl chloride (XI), although it was unsuccessful to obtain pure XI.

Benzophenone did not react with II and IV.

Experimental

Materials. Substituted thiobenzophenones were prepared by the method previously reported.³⁾ Benzenediazonium-o-carboxylate,⁴⁾ salicyloyl⁵⁾ (bp 57—58°C/0.5 mmHg) and o-mercaptobenzoyl chlorides⁶⁾ (bp 110—111°C/0.45 mmHg, mp 56—58°C) were prepared by the methods described in the literature.

Reactions with Benzenediazonium-o-carboxylate (II). A typical procedure is described for a reaction of p,p'-dimethylthiobenzophenone (Id).

To Id (3.3 g, 14.5 mmol) in dichloromethane (200 ml) was added II (5.4 g, 36 mmol), and the mixture was refluxed for 3 hr with stirring under nitrogen atmosphere. After removal of the solvent, the residual oil was chromatographed

on silica gel. Elution with benzene gave 1.5 g (30%) of Vd, mp 101—102°C (from ethanol-petroleum ether). IR (KBr disk): 1727 cm⁻¹ (–COO–); m/e: 346 (M+, 11%), 136 ([M—Tol₂CO]+, 100), 120 ([M—Tol₂CS]+, 11), 108 ([M—Tol₂COCO]+, 20), and 105 (PhCO+, 6), where Tol represents p-MeC₆H₄.

Other results were summarized in Table.

Reactions with Salicyloyl Chloride (III). A typical procedure is described for a reaction of thiobenzophenone (Ia).

A mixture of Ia (8.7 g, 44 mmol) and III (7.0 g, 45 mmol) was heated for 6 hr at 100—120°C under nitrogen atmosphere, until evolution of hydrogen chloride ceased. The cooled solution was extracted with 1 l of petroleum ether. Removal of the solvent from the extract gave 11.2 g (80%) of VIa, mp 119.5—121°C (from petroleum ether). IR (KBr disk): 1660 cm⁻¹ (-COS-); m/e: 318 (M+, 62%), 258 ([M-COS]+, 33), 198 (Ph₂CS+, 100), 165 ((C₆H₄)₂CH+, 84.5), 121 ([M-Ph₂CS+H]+, 67), and 77 (Ph+, 61).

Other results were summarized in Table.

Reaction with o-Mercaptobenzoyl Chloride (IV). a) A mixture of Ia (5.55 g, 28 mmol) and IV (4.86 g, 28 mmol) in benzene (200 ml) was stirred for 10 hr at room temperature, until the blue color of the mixture disappeared. After removal of the solvent, the residual oil, which could not be purified, was heated for 3 hr at 180—190°C, and then distilled in vacuo (bp 112—116°C/0.2 mmHg). After cooling, 2.8 g (60%) of yellow crystals (IX) thus obtained were recrystallized from petroleum ether, mp 76—78°C (lit,7) 77°C). After removal of IX, diphenylmethyl chloride (4.5 g, 80%) was detected in the distillate by gas chromatography.

b) To a similar reaction mixture from Ia (5.55 g, 28 mmol) and IV (4.86 g, 28 mmol) in benzene (200 ml) was added aniline (8.0 g, 86 mmol), and the mixture was stirred for 3 hr at room temperature. Hydrogen sulfide evolved and white precipitates appeared. The precipitates were washed with water and recrystallized from pyridine-petroleum ether to afford 4.2 g (65%) of disulfide (VII), mp 236—240°C (lit,8) 243°C). Concentration of the filtrate and the above aqueous washings gave 2.9 g (40%) of VIII, mp 104—110°C (from petroleum ether) (lit,9) 109°C) and aniline hydrochloride (3.6 g, 99%), respectively.

In the addition of pyridine instead of aniline, pyridine hydrochloride (1.5 g, 94%) and Ia (70%, by UV spectroscopy) were produced.

³⁾ H. Tokunaga, K. Akiba, and N. Inamoto, This Bulletin, 45, 506 (1972).

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⁵⁾ E. H. Wilson, U. S. 2899458 (1959).

⁶⁾ E. Ziegler and H. D. Hanus, Monatsh. Chem., 96, 411 (1965).

⁷⁾ M. McKibben and E. W. McClelland, *J. Chem. Soc.*, **123**, 170 (1923).

⁸⁾ A. Reissert and E. Manns, Ber., 61, 1308 (1928).

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