[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUQUESNE UNIVERSITY]

THE SYNTHESIS AND REACTIONS OF *p*-PHENYLMERCAPTOBENZALDEHYDE

H. HARRY SZMANT, MICHAEL J. SEGEDI, AND JOSEPH DUDEK

Received January 9, 1953

As part of the study of derivatives of phenyl sulfide (1) there was investigated the synthesis of *p*-phenylmercaptobenzaldehyde from phenyl sulfide. While the Gattermann-Koch reaction (2) and the formylation with N-methylformanilide and phosphorus oxychloride (3) failed in our hands, the desired aldehyde was prepared through the application of the Gattermann reaction as modified by Adams (4).

The structure of the aldehyde was proven by oxidation to the known *p*-phenylsulfonylbenzoic acid, and by conversion to the known *p*-phenylmercaptobenzoic acid in the course of the Cannizzaro reaction. A number of substituted chalcones were obtained when the aldehyde was condensed with acetophenone and related compounds.

In an attempt to prepare *p*-phenylmercaptobenzoyl chloride from phenyl sulfide, the latter was subjected to a Friedel-Crafts reaction with phosgene. The hope that the acid chloride-aluminum chloride complex might be insoluble in the reaction medium and thus be kept from reacting farther was not realized. Instead, there were isolated *p,p'*-diphenylmercaptobenzophenone and thiaxanthone. Both of these products were converted to the corresponding sulfones and the 2,4-dinitrophenylhydrazones of the sulfide and sulfone ketones were also prepared. It is believed that the reaction of phenyl sulfide with phosgene represents a novel synthesis of the thiaxanthone nucleus.

EXPERIMENTAL[1]

p-Phenylmercaptobenzaldehyde. A rapid stream of hydrogen chloride was passed into a stirred mixture of 76.5 g. of phenyl sulfide, 73.5 g. of zinc cyanide, and 200 ml. of tetrachloroethane for 3 hours, and then 197 g. of aluminum chloride was added over a period of ten minutes while the reaction mixture was cooled in an ice-bath. Upon removal of the ice-bath the temperature rose to 40° and the mixture was stirred for an additional 3.5 hours. The reaction mixture was poured on ice and after the addition of 25 ml. of concentrated hydrochloric acid it was allowed to stand overnight. After heating the mixture for 30 minutes the oily layer was separated and combined with an extract of the aqueous phase. The solvent was removed by steam-distillation and the residual oil was extracted with benzene. On removal of benzene the residue was distilled and the fraction boiling at 185–186° (at 5 mm.) was collected (36 g. or 45.7% yield since 10.7 g. of phenyl sulfide was recovered in the fore-run). On crystallization of the product from an acetic acid-water mixture there were obtained colorless crystals, m.p. 53–54°.

Anal. Calc'd for $C_{13}H_{10}OS$: C, 72.86; H, 4.74.
Found: C, 72.91; H, 5.01.

p-Phenylmercaptobenzaldehyde 2,4-dinitrophenylhydrazone. This compound was prepared

---

[1] All microanalyses were determined by Mr. Stragand of the Microanalytical laboratories of the University of Pittsburgh. All melting points are uncorrected.

in the conventional fashion and upon crystallization from glacial acetic acid had m.p 213–214°.

Anal. Calc'd for $C_{19}H_{16}N_4O_4S$: C, 57.71; H, 3.82.
Found: C, 57.66; H, 4.03.

p-Phenylsulfonylbenzoic acid. The oxidation of 2 g. of *p*-phenylmercaptobenzaldehyde with potassium permanganate under alkaline conditions gave a nearly quantitative yield of *p*-phenylsulfonylbenzoic acid, m.p. 271–273°. The m.p. was not depressed by admixture with a sample of the authenic acid.

p-Phenylmercaptobenzoic acid and p-phenylmercaptobenzyl alcohol. The aldehyde, 3.5 g., was shaken with 10 ml. of a 50% sodium hydroxide solution. After standing for one day the mixture was poured into 1000 ml. of H_2O, heated for one hour to approximately 95°, cooled, and extracted with benzene. The benzene solution was first extracted with a 30% sodium bisulfite solution, and then concentrated to give *p*-phenylmercaptobenzyl alcohol. The m.p. of the alcohol (49–51°, on crystallization from a benzene-petroleum ether mixture) was depressed by the admixture of the initial aldehyde.

Anal. Calc'd for $C_{13}H_{12}OS$: C, 72.18; H, 5.59.
Found: C, 71.97; H, 5.57.

TABLE I

$p\text{-}C_6H_5SC_6H_4\text{—}CH{=}CHCOR$

R	M.P., °C.	ANALYSES			
		C		H	
		Calc'd	Found	Calc'd	Found
p-Xenyl	175–177	82.62	82.59	5.14	5.28
p-Chlorophenyl	136–137	71.89	71.52	4.31	4.28
p-Phenylmercaptophenyl	119–120	76.38	76.50	4.75	5.01
2-Thienyl	124–125	70.77	70.88	4.38	4.50
5-Methyl-2-thienyl	135–138	71.36	71.20	4.79	4.95

The aqueous portion of the reaction mixture on acidification gave *p-phenylmercaptobenzoic acid*, m.p. 176–177°. Weedon and Doughty (5) reported m.p. 177° for this acid.

p-Phenylmercaptostyryl phenyl ketone. *p*-Phenylmercaptobenzaldehyde (3 g.) and acetophenone (1.7 g.) were dissolved in 30 ml. of 95% ethanol, and 2 cc. of a 10% sodium hydroxide solution was added to the stirred mixture. After 30 minutes there was obtained a nearly quantitative yield of yellow crystals which on crystallization from ethanol gave m.p. 87–89°.

Anal. Calc'd for $C_{21}H_{16}OS$: C, 79.71; H, 5.09.
Found: C, 79.73; H, 5.24.

In a similar fashion there were obtained the condensation products of *p*-phenylmercaptobenzaldehyde listed in Table I.

p,p'-Diphenylmercaptobenzophenone and thiaxanthone. To a cooled mixture (5°) of 21 g. of aluminum chloride and 250 cc. of carbon disulfide there was added 8 g. of phosgene in 75 cc. of carbon disulfide. To the resulting mixture there was then added over a period of 1.5 hours 24 g. of phenyl sulfide in 100 cc. of carbon disulfide. After stirring for 30 hours the mixture was hydrolyzed. The carbon disulfide layer was washed, dried, and upon removal of the solvent the residue was distilled at 1 mm. The first fraction, b.p. 110–120°, consisted of 8.3 g. of phenyl sulfide. The second fraction (2.5 g.) b.p. 130–180°, was recrystallized from alcohol to give thiaxanthone, m.p. 212–214°. The third fraction (5.2 g.) b.p. 210–250°, was recrystallized from alcohol and had m.p. 136–138°. It analyzed correctly for *p,p'-diphenylmercaptobenzophenone*.

Anal. Calc'd for $C_{25}H_{19}OS_2$: C, 75.35; H, 4.55.
Found:C, 75.19; H, 4.83.

The thiaxanthone obtained from this reaction was oxidized with peracetic acid in glacial acetic acid to thiaxanthone sulfone, m.p. 187° [lit. m.p. 187° (5)].

p,p'-Diphenylmercaptobenzophenone 2,4-dinitrophenylhydrazone. The ketone from the preceding reaction was converted to the 2,4-dinitrophenylhydrazone, m.p. 151–152°, in the usual fashion.

Anal. Calc'd for $C_{31}H_{22}N_4O_4S_2$: C, 64.34; H, 3.83.

Found: C, 64.27; H, 3.82.

p,p'-Diphenylsulfonylbenzophenone. The sulfide ketone was oxidized with an excess of peracetic acid in glacial acetic acid by warming the solution to 70°. A quantitative yield of the disulfone, m.p. 274–275°, was obtained.

Anal. Calc'd for $C_{25}H_{18}O_5S_2$: C, 64.91; H, 3.92.

Found: C, 64.76; H, 3.91.

p,p'-Diphenylsulfonylbenzophenone 2,4-dinitrophenylhydrazone. This compound prepared in the usual manner was crystallized from ethanol to give m.p. 262–263°.

Anal. Calc'd for $C_{31}H_{22}N_4O_8S_2$: C, 57.95; H, 3.45.

Found: C, 58.05; H, 3.26.

SUMMARY

The synthesis of *p*-phenylmercaptobenzaldehyde by means of the Gattermann reaction is described. It was shown that the aldehyde can be oxidized, and subjected to the Cannizzaro and condensation reactions.

The reaction of phenyl sulfide with phosgene and aluminum chloride is shown to give *p,p'*-diphenylmercaptobenzophenone as well as thiaxanthone.

PITTSBURGH 19, PENNA.

REFERENCES

(1) SZMANT AND PALOPOLI, *J. Am. Chem. Soc.*, **72,** 1757 (1950).
(2) CROUNSE IN *Org. Reactions*, **5,** 290 (1949).
(3) BUU-HOÏ AND HOÁN, *J. Am. Chem. Soc.*, **73,** 99 (1951).
(4) ADAMS AND LEVINE, *J. Am. Chem. Soc.*, **45,** 2373 (1923).
(5) WEEDON AND DOUGHTY, *Am. Chem. J.*, **33,** 424 (1905).
(6) ULMANN AND LEHNER, *Ber.*, **38,** 735 (1905).