Tetrahedron. Vol 26, pp. 4247 to 4249. Pergamon Press 1970. Printed in Great Britain

REACTION OF THIOBENZOYLDISULPHIDES WITH BASES SYNTHESIS OF THION-ESTERS

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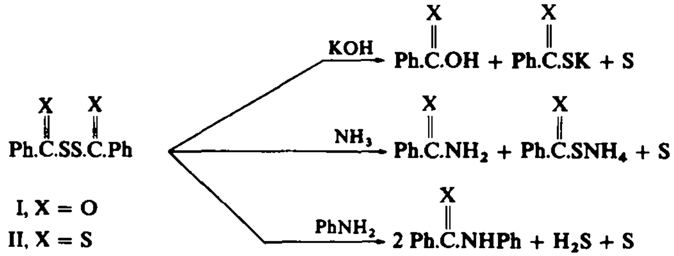
(*Received in the UK* 28 *October* 1969; *Accepted for publication* 9 *February* 1970)

Abstract—Evidence has been put forward in support of a mechanism for the cleavage of thiobenzoyldisulphides in basic medium with rupture of the C—S bond in preference to the S—S bond. Reaction of Na-alkoxides with thiobenzoyldisulphides affords a new and convenient method for the synthesis of thion-esters.

ANALOGOUS compounds of oxygen and sulphur sometimes show marked differences in physical and chemical properties. Benzoyldisulphide (I, Ph.CO.SS.CO.Ph) and thiobenzoyldisulphide (II, Ph.CS.SS.CS.Ph) are the S analogues of benzoylperoxide. The latter is known to react with alkali[1] to give salts of perbenzoic and benzoic acids but its S analogues I and II react with bases in a different way.

Fromm,[2] in explaining the action of alcoholic potassium hydroxide and ammonia on I and II, postulated a mechanism for the addition of the base to the carbonyl or thiocarbonyl group and cleavage of the C—S bond according to the following scheme:



It was also mentioned that with two molecules of organic amines two molecules of amide (from I) or thioamide (from II) are formed, although nothing had been reported about the formation of the second molecule. Latif and Azim[3] studied the reaction of benzoyldisulphide and its substituted derivatives with Na-alkoxides—but under the conditions used, instead of obtaining the S analogue of perbenzoic acid, the reaction followed the course shown above.

The present work was undertaken to study the reaction of bases with thiobenzoyldisulphide and its derivatives.

When thiobenzoyldisulphide (II) was allowed to react with an equivalent amount of NaOMe, methylthionbenzoate (Ph.CS.OMe), Na-dithiobenzoate and sulphur were obtained almost quantitatively. The same compound with NaOEt gave ethylthionbenzoate (Ph.CS.OEt). Reaction of bis-*p*-methoxythiobenzoyldisulphide (III, *p*-MeO-C_6H_4.CS.SS.CS.C_6H_4-OMe-*p*) with NaOMe and NaOEt took place similarly producing methyl-*p*-methoxythionbenzoate (*p*-MeO-C_6H_4.CS.OMe) and ethyl-*p*-methoxythionbenzoate (*p*-MeO-C_6H_4.CS.OEt), respectively. With excess of alcoholic ammonia both II and III gave thiobenzamide and *p*-methoxythiobenzamide respectively together with NH_4-salts of dithioacids and sulphur. However, no dithioacid could be isolated when II and III were allowed to react with alcoholic aniline. In this case two molecules of corresponding thioamides were obtained together with H_2S and sulphur. With excess of dimethylamine only a small amount of dithioacid was isolated. In the cases we have investigated no compound derived from the S analogue of perbenzoic acid could be isolated.

These results indicate that in the reaction of thiobenzoyldisulphides with organic amines, the second molecule of thioamide is formed by elimination of H_2S from the dithioacid salt. Similar observations had also been reported by Wuyts *et al.*[4] The reaction of thiobenzoyldisulphides with Na-alkoxides yields about 90% of thion-esters.

These thion-esters are known and have been prepared by various methods[5–8] but the yields obtained were not satisfactory. Difficulties were also encountered due to transformation of the thion-esters into the thiol-form during the synthesis.[9] The present workers have been able to obtain thion-esters in about 45% overall yield in a three step synthesis starting from the corresponding dithioacids. About 97% of the esters were isolated in the thion-form depending on the method used for the determination of thion-structure. Moreover, the reactions were clean and the products easily isolated.

EXPERIMENTAL

All evaporations were carried out under reduced pressure. Thion-sulphur content of the esters was determined approximately by precipitating the sulphur as Ag_2S according to Karjala and McElvain.[9]

Preparation of thiobenzoyldisulphides. These were prepared by oxidizing the Na-salts of the corresponding dithioacids with I_2 in KI soln or $K_3Fe(CN)_6$ in 50% alcoholic soln[10,11] (yield 55–60%). The dithioacids were prepared by reacting the corresponding aldehydes with ammonium-polysulphide of the approximate composition $(NH_4)_2S_2$ in alcoholic soln by a modification[12] of the method of Bruni and Levi[11] (yield 25–40% of the aldehyde). Dithioacids were also prepared by adding the corresponding arylmagnesium bromides to a slight excess of CS_2[10] (yield 90%).

Thiobenzoyldisulphide (II) was obtained as a red powder, m.p. 87–90° (lit[10] 92·5°). (Found: S, 41·50. Calc for $C_{14}H_{10}S_4$: S, 41·83%). *Bis-p-methoxythiobenzoyldisulphide* (III) was obtained as a red powder, crystallized from acetone, m.p. 160° (lit[11] 150°). (Found: S, 34·55. Calc for $C_{16}H_{14}O_2S_4$: S, 34·97%).

Reaction of thiobenzoyldisulphade wiyh NaOMe. A soln of 7·65 g thiobenzoyldisulphide in 30 ml $CHCl_3$ was cooled to −5° and Na (0·6 g) dissolved in 20 ml MeOH, cooled to 0°, was added (10 min) with shaking. The temp was not allowed to rise above 10°. An immediate ppt of S was formed and the mixture stirred for 20 min at the same temp. The ppt of S was then filtered off, washed with alcohol and dried 0·6 g, m.p. 117°.

The filtrate was treated with about 75 ml water and the two layers separated. The aqueous layer was treated with I_2 in KI soln. A deep-red ppt of II was obtained, 3·25 g (85%).

The chloroform layer was dried over Na_2SO_4 and the solvent evaporated. The residual viscous liquid was distilled under reduced pressure. Methylthionbenzoate was obtained as a yellow liquid, 3·1 g (81·5%), b.p. 114°/12 mm. (Found: S, 20·67. Calc for C_8H_8OS: S, 21·05%). Thion-structure 96·9%.

Reaction of thiobenzoyldisulphide with NaOEt. Under similar conditions ethylthionbenzoate was obtained as a yellow liquid (86%), b.p. 125°/5 mm. (Found: S, 18·93. Calc for $C_9H_{10}OS$: S, 19·27%). Thion-structure 96·4%.

Reaction of bis-p-methoxythiobenzoyldisulphide with NaOMe *and* NaOEt. About 300 ml of solvent had to be used for each 4·6 g of substance; otherwise the procedure and isolation of the products were the same. *Methyl-p-methoxythionbenzoate* was obtained as a yellow liquid, 1·9 g (83%), b.p. 127°/25 mm. (Found: S, 17·07. Calc for $C_9H_{10}O_2S$: S, 17·59%). Thion-structure 96·2%.

Ethyl-p-methoxythionbenzoate is a yellow oil, 2·1 g (85%), b.p. 128°/4 mm. (Found: S, 15·85. Calc for $C_{10}H_{12}O_2S$: S, 16·33%). Thion-structure 95·9%.

Reaction of thiobenzoyldisulphide with ammonia. To 1·5 g II in 15 ml EtOH, 6 ml conc ammonia were added and the mixture warmed at 50° for 30 min and then allowed to stand overnight. A resinous substance was precipitated and found to be unreacted II.

The alcoholic soln was evaporated. The residue was dissolved in ether and washed with water to remove dithiobenzoic acid as a NH_4-salt. The aq soln yielded 0·5 g (66%) II after treatment with I_2 in KI soln. The ethereal soln was evaporated and thiobenzamide was crystallized from water as yellow needles, m.p. 116°. (Found: S, 22·82. Calc for C_7H_7NS: S, 23·36%).

Reaction of bis-p-methoxythiobenzoyldisulphide with ammonia. This reaction was performed as above using 1·5 g III. After standing overnight the undissolved material was filtered off. The residue gave sulphur and unreacted III (0·5 g, 33%). The alcoholic soln was treated similarly. The aq soln yielded 0·4 g III on treatment with I_2 in KI soln. *p*-Methoxythiobenzamide was obtained as yellow flakes from water, m.p. 148°. (Found: S, 18·61. Calc for C_8H_9NOS: S, 19·16%).

Reaction of thiobenzoyldisulphide with aniline. To 1·5 g II in 30 ml abs EtOH, 0·9 g aniline was added. The mixture was refluxed for 1 hr. After standing overnight the resinous ppt of unreacted II and sulphur was filtered off. The alcoholic soln gave no evidence of the presence of dithiobenzoic acid. This was evaporated and thiobenzanilide was crystallized from ether, 1·0 g (50%), m.p. 101·5°. (Found: S, 14·47. Calc for $C_{13}H_{11}NS$: S, 15·02%).

Reaction of bis-p-methoxythiobenzoyldisulphide with aniline. To 1·5 g of III in 30 ml abs EtOH, 0·5 g aniline was added and the mixture warmed to 50° for 30 min. After standing overnight, sulphur and 1·0 g (66%) unreacted III were isolated. The alcoholic soln gave *p*-methoxythiobenzanilide as yellow crystals, m.p. 154°. (Found: S, 12·73. Calc for $C_{14}H_{13}NOS$: S, 13·7%).

This reaction was also performed using excess aniline and the mixture was refluxed for 1 hr. In this case 60% conversion took place.

Reaction of thiobenzoyldisulphide with dimethylamine. II (1·5 g) was dissolved in 20 ml abs EtOH and the soln cooled to 0°. 5 ml Me_2NH was added with shaking and cooling so that the temp did not rise above 10°. A yellow ppt of sulphur was obtained. After 30 min the soln was concentrated, the residue dissolved in ether and washed with water to separate dithiobenzoic acid. The aqueous soln yielded 0·2 g (13%) II on treatment with I_2 in KI soln. The ethereal soln was evaporated and N,N-dimethylthiobenzamide was crystallized, 1·0 g, m.p. 67°. (Found: S, 18·87. Calc for $C_9H_{11}NS$: S, 19·39%).

Reaction of bis-p-methoxythiobenzoyldisulphide with dimethylamine. This reaction was performed as above using 1·5 g of III. The aqueous soln yielded 0·3 g (20%) III. The ethereal soln gave 0·8 g N,N-dimethyl-*p*-methoxythiobenzamide, m.p. 69°. (Found: S, 15·95. Calc for $C_{10}H_{13}NOS$: S, 16·41%).

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