iodide and triethyl-*n*-butylammonium iodide were used as reference compounds.

Diethylallylamine Hydrobromide.—This salt was prepared from diethylallylamine and dry hydrogen bromide. It was recrystallized from acetone. It was not especially hygroscopic and did decolorize a solution of bromine in carbon tetrachloride. It melted at 189–190°. When a sample was mixed with diethyltrimethyleneammonium bromide the mixture melted at 158–160°.

Anal. Calcd. for $C_6H_{16}NBr$: Br, 41.24. Found: Br, 41.17.

Summary

The bromopropyldialkylamines in which the alkyl groups are ethyl, *n*-propyl and *n*-butyl, respectively, have been found to undergo spontaneous intramolecular condensation to give the corresponding cyclic dialkyltrimethyleneammonium bromides. The reaction is of theoretical interest since the corresponding bromopropyldimethylamines condense to produce only linear polymers.

URBANA, ILL. RECEIVED DECEMBER 14, 1933

The Action of Sodium Ethoxide upon Phenyl Thiocyanate

BY JOHN ROSS

Examining the reaction between ethyl thiocyanate and the sodium enolates of certain keto-esters, Kohler[1] showed that the primary reaction was the formation of a metal mercaptide and a cyano substitution product of the keto ester. This result was the opposite of the transformations that occur when metallic sodium or alkali sulfides, hydroxides and mercaptides react with alkyl thiocyanates to eliminate the cyano group as the metallic cyanide or cyanate. In the previous investigations the reaction appears to follow one selected course only, but it would be expected that when the conditions are such as to favor the formation of a metal mercaptide or cyanide to an almost equal degree, then both the above modes of reaction might be found to proceed simultaneously.

Sodium ethoxide in alcohol reacts with phenyl thiocyanate to give sodium thiophenate, diphenyl disulfide and ethyl phenyl sulfide. In attempting to formulate a mechanism whereby these products could be obtained, the previous considerations suggest that both the above types of reaction had taken place to an unequal extent.

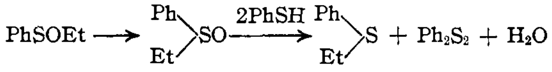
The main reaction (80%) is the production of sodium thiophenate and ethyl cyanate

$$PhSCN + NaOEt \longrightarrow PhSNa + EtOCN$$

The ethyl cyanate would isomerize to the isocyanate and combine with alcohol or sodium ethoxide to form ethyl ethyl carbamate EtNHCOOEt or its sodium enolate.

The secondary reaction (20%) follows the direct production of sodium cyanide and presumably ethyl benzenesulfenate

$$PhSCN + NaOEt \longrightarrow PhSOEt + NaCN$$



$$PhSOEt \longrightarrow \begin{matrix} Ph \\ Et \end{matrix}\!\!>\!SO \xrightarrow{2PhSH} \begin{matrix} Ph \\ Et \end{matrix}\!\!>\!S + Ph_2S_2 + H_2O$$

If the ethyl benzenesulfenate is transformed into the isomeric sulfoxide by migration of the ethyl group from oxygen to sulfur, then the sulfoxide might on reduction with thiophenol give ethyl phenyl sulfide and diphenyl disulfide. The amounts of ethyl phenyl sulfide and diphenyl disulfide isolated were approximately equivalent in accordance with the above equation.

It was found that thiophenol in the presence of a small amount of sodium ethoxide would reduce ethyl phenyl sulfoxide to give ethyl phenyl sulfide and diphenyl disulfide under conditions comparable with those of the reaction under discussion. Some ethyl benzenesulfenate was prepared, but it was found that this ester reacted vigorously with thiophenol (in the presence of a trace of sodium ethoxide) to give entirely diphenyl disulfide, presumably according to the reaction

$$PhSOEt + HSPh \longrightarrow PhSSPh + EtOH$$

This behavior would appear to preclude altogether the formation of free ethyl benzenesulfenate in the reaction. Although the conditions governing the transformation of ethyl benzenesulfenate into ethyl phenyl sulfoxide are not completely known, the above hypothetical reaction mechanism is open to several objections. Wheeler and Barnes,[2] Bettschart and Bistrzycki[3] and others have examined many cases of transformations in thiocarbamide derivatives where the hydrocarbon group is transferred from oxygen to sulfur under

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(1) E. P. Kohler, *Am. Chem. J.*, **22**, 67 (1899).

(2) Wheeler and Barnes, *Am. Chem. J.*, **22**, 141 (1899).

(3) Bettschart and Bistrzycki, *Helv. Chim. Acta*, **2**, 118 (1919).

the influence of alkyl halides and similar reagents, in which the fission of a fairly simple addition compound was considered the mechanism of the transference of the hydrocarbon group. From previous investigations[4,5,6] it is apparent that esters of sulfenic acids are very reactive compounds and also that certain reactions which should give these esters as products yield only a series of oxidation and reduction products which contain the alkyl group attached to the sulfur instead of the oxygen atom. The fission of a simple addition compound as postulated by Wheeler and Barnes might well explain these transformations, but in the particular case of the reaction between phenyl thiocyanate and sodium ethoxide the conditions are rather different. Similarity only exists in the products, the reagents used being of quite another type. There is no evidence to suppose the formation of a salt of benzenesulfenic acid or of the presence of an ethyl ester of the type required by the Wheeler and Barnes transformation that could perform the alkylation or the rearrangement.

Alternatively, if the hypothesis of transitory formation of ethyl benzenesulfenate followed by conversion into ethyl phenyl sulfoxide be rejected, then to account for the production of ethyl phenyl sulfide, there remains the not entirely satisfactory conclusion that ethyl phenyl sulfide and sodium cyanate are direct products of the reaction, thus

$$\mathrm{PhSCN} + \mathrm{NaOEt} \longrightarrow \mathrm{PhSEt} + \mathrm{NaOCN}$$

In this case it is doubtful whether the diphenyl disulfide would be formed by oxidation of the thiophenol by the sodium cyanate, since separate experiments have shown that this reaction takes place slowly and incompletely. By the action of potassium cyanate on thiophenol in boiling alcohol only a 15% yield of diphenyl disulfide could be obtained. Diphenyl disulfide could be formed by the action of sodium thiophenate upon phenyl thiocyanate, but in that case there would be no particularly significant relation in the equivalence of the yields of ethyl phenyl sulfide and diphenyl disulfide.

Alcohol-free sodium ethoxide in ether or benzene reacts with phenyl thiocyanate to give entirely diphenyl disulfide and no indication of the formation of ethyl phenyl sulfide was found.

Experimental

Action of Sodium Ethoxide on Phenyl Thiocyanate.—To a solution of 4.6 g. of sodium in 70 cc. of absolute alcohol, 27 g. of phenyl thiocyanate was added and mixed with rapid cooling in an ice-bath. A vigorous reaction occurred immediately which was indicated by an appreciable evolution of heat. After standing for twelve hours, the excess alcohol was removed under reduced pressure in a water-bath at 50°. The cold residue was treated with water and the neutral product taken up with ether. There was thus obtained after distillation 1.3 g. of ethyl ethyl carbamate, b. p. 65° (15 mm.), 5.1 g. of ethyl phenyl sulfide, b. p. 104° (15 mm.), and 7.8 g. of diphenyl disulfide, m. p. 60°. The aqueous extract upon acidifying gave 9.6 g. of thiophenol, b. p. 65° (15 mm.).

The ethyl phenyl sulfide was characterized by analysis, boiling point, odor, inactivity toward alkalies and acids and conversion to ethyl phenyl sulfone, m. p. 42°, by oxidation with chromic acid. The ethyl phenyl sulfone was in all respects identical with a sample prepared by the action of ethyl bromide on sodium benzenesulfenate.[7] Alcohol-free sodium ethoxide in benzene or ether with phenyl thiocyanate gave the theoretical yield of diphenyl disulfide only.

Reduction of Phenyl Ethyl Sulfoxide with Thiophenol.—A mixture of 5 g. of ethyl phenyl sulfoxide,[8] b. p. 124° (2 mm.), 7.5 g. of thiophenol, 10 cc. of absolute alcohol containing 2 drops of a dilute solution of sodium ethoxide was heated on the water-bath for six hours. The product was diluted with water and the neutral portion extracted with ether and distilled. There was obtained 4.0 g. of ethyl phenyl sulfide and 7.0 g. of diphenyl disulfide.

Action of Ethyl Benzenesulfenate upon Thiophenol.—Ethyl benzenesulfenate was prepared by the method described by Lecher[9] for the preparation of the methyl ester. It is a colorless liquid, b. p. 100° (4 mm.), with a not unpleasant ethereal odor.

Anal. Calcd. for $C_8H_{10}SO$: S, 20.82. Found: S, 20.55.

To a mixture of 5 g. of ethyl benzenesulfenate and 7.5 g. of thiophenol in 25 cc. of absolute alcohol 1 drop of sodium ethoxide solution was added. There was an immediate reaction as shown by a perceptible evolution of heat and on cooling diphenyl disulfide crystallized out. The product consisted of 6.8 g. of diphenyl disulfide together with 3.0 g. of thiophenol recovered unchanged.

Action of Potassium Cyanate upon Thiophenol.—A mixture of 4 g. of thiophenol and 2 g. of powdered potassium cyanate in 20 cc. of absolute alcohol was heated for six hours on the water-bath. The cyanate did not go completely into solution. The alcohol and some thiophenol was removed by distillation under reduced pressure and the residue was treated with 10% caustic potash. The solid diphenyl disulfide was filtered off, the yield being 0.6 g. or approx. 15%.

Summary

1. Sodium ethoxide in alcohol solution reacts with phenyl thiocyanate to give sodium thio-

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[4] Fromm, *Ber.*, **41**, 3405 (1909).

[5] Fries, *ibid.*, **45**, 2965 (1912); **52**, 2182 (1919).

[6] C. Courtot, M. Chaix and L. Nicholas, *Compt. rend.*, **194**, 1837 (1932).

[7] Otto, *Ber.*, **13**, 1275 (1880).

[8] Hepworth and Clapham, *J. Chem. Soc.*, **119**, 1192 (1921).

[9] H. Lecher, *Ber.*, **58**, 409 (1925).

phenate, ethyl phenyl sulfide and diphenyl disulfide.

2. An attempt has been made to formulate a mechanism through which the ethyl phenyl sulfide and diphenyl disulfide could be formed.

LONDON, ENGLAND RECEIVED DECEMBER 14, 1933

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Reactions of Certain Gamma Ketonic Acids. I. Ketonic Beta Lactones

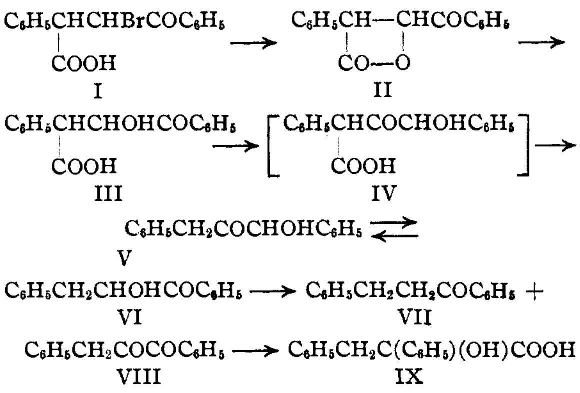
BY E. P. KOHLER AND R. H. KIMBALL

By brominating phenyl benzoyl propionic acid it is possible to obtain two stereoisomeric monobromo derivatives which have bromine as well as benzoyl in the beta position. These derivatives are excellent material for investigating the extent to which the properties of beta bromo acids are affected by their configuration. We are employing them for a study of beta lactones because, despite many excellent investigations, there still is much that is mysterious with respect to the mechanism by which these 4-ring compounds are formed and the manner in which they behave.

In this paper we deal only with the higher melting of the two beta bromo acids, and with the reactions which it was necessary to study before undertaking to determine the relative rates at which the two stereoisomers form lactones and the speed with which the lactone rings are opened. When this bromo acid is dissolved in dilute aqueous solutions of weak bases it is rapidly converted into a beta lactone which is precipitated almost as fast as it is formed, and a hydroxy acid which remains in solution. Of the three types of products that are commonly formed when beta bromo acids react with bases—beta lactone, hydroxy acid and ethylenic compound—this acid yields but two, no ethylenic compound—in this case benzalacetophenone—being formed under any conditions.

Only one of the two possible stereoisomeric beta lactones is formed from the higher melting bromo acid and this lactone constitutes more than 90% of the product, the remainder being a mixture of the two possible beta hydroxy acids. Since a similar mixture of hydroxy acids is formed very slowly by the action of weak bases on the lactone, rate measurements will be necessary to determine whether the acids are secondary products or whether the lactone and the hydroxy acids are formed concurrently from some common intermediate.

The action of strong bases is much more complicated; even in dilute solutions strong bases induce a series of reactions which end in secondary products that are only remotely related to the substances from which they arise



$$\underset{\text{I}}{\begin{array}{l}C_6H_5CHCHBrCOC_6H_5\\ |\\ COOH\end{array}} \longrightarrow \underset{\text{II}}{\begin{array}{l}C_6H_5CH{-}CHCOC_6H_5\\ \quad |\qquad\ \ |\\ \quad CO{-}O\end{array}} \longrightarrow$$

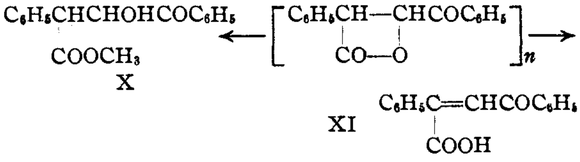
$$\underset{\text{III}}{\begin{array}{l}C_6H_5CHCHOHCOC_6H_5\\ |\\ COOH\end{array}} \longrightarrow \underset{\text{IV}}{\left[\begin{array}{l}C_6H_5CHCOCHOHC_6H_5\\ |\\ COOH\end{array}\right]} \longrightarrow$$

$$\underset{\text{V}}{C_6H_5CH_2COCHOHC_6H_5} \rightleftarrows$$

$$\underset{\text{VI}}{C_6H_5CH_2CHOHCOC_6H_5} \longrightarrow \underset{\text{VII}}{C_6H_5CH_2CH_2COC_6H_5} +$$

$$\underset{\text{VIII}}{C_6H_5CH_2COCOC_6H_5} \longrightarrow \underset{\text{IX}}{C_6H_5CH_2C(C_6H_5)(OH)COOH}$$

Another fertile cause of secondary products is polymerization. When the bromo acid is dissolved in concentrated aqueous solutions of bases, the solutions soon precipitate sparingly soluble, oily salts or insoluble and infusible solids which have the same composition as the readily soluble lactone. Similar polymers are formed with great rapidity when the lactone is dissolved in a polar solvent containing a trace of a weak base. These products are mixtures representing various degrees of polymerization. Some of them can be crystallized from acetone, many can be converted into the methyl ester of a monomeric hydroxy acid, and pyridine transforms all of them as well as the monomeric lactone into *cis* phenyl benzoyl acrylic acid



$$\underset{\text{X}}{\begin{array}{l}C_6H_5CHCHOHCOC_6H_5\\ |\\ COOCH_3\end{array}} \longleftarrow \left[\begin{array}{l}C_6H_5CH{-}CHCOC_6H_5\\ \quad |\qquad\ \ |\\ \quad CO{-}O\end{array}\right]_n \longrightarrow$$

$$\text{XI}\quad \begin{array}{l}C_6H_5C{=}CHCOC_6H_5\\ |\\ COOH\end{array}$$

In marked contrast to these involved effects of bases, the reactions between the lactone and