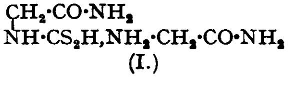
439. *The Conversion of Carbamates into Dithiocarbamates.*

By D. O. Holland.

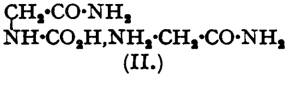
Carbon disulphide reacts with carbamylmethylammonium carbamylmethylcarbamate (II) at room temperature in aqueous alcohol to yield the corresponding dithiocarbamic derivative (I). Benzylammonium benzylcarbamate similarly yields benzylammonium benzyldithiocarbamate.

During an investigation of the preparation of carbamylmethylammonium carbamylmethyldithiocarbamate (I) (Cook, Heilbron, and Levy, *J.*, 1948, 201) by treating salts of aminoacetamide with bases and carbon disulphide, attempts were made to use sodium hydrogen carbonate as the base. By analogy with the compound formed by 2-aminooctanoamide hydrochloride under similar conditions (Erlenmeyer and Sigel, *Annalen*, 1875, **177**, 130) the reaction would have been expected to yield the carbamate (II). In fact, it was possible, by repeated extraction of the reaction mixture with alcohol (95%) and acetone and treatment of each extract with carbon disulphide, to obtain successive small quantities of the dithiocarbamate (I).



$$\begin{array}{l}\mathrm{CH_2{\cdot}CO{\cdot}NH_2}\\ |\\ \mathrm{NH{\cdot}CS_2H,NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2}\end{array}$$

(I.)



$$\begin{array}{l}\mathrm{CH_2{\cdot}CO{\cdot}NH_2}\\ |\\ \mathrm{NH{\cdot}CO_2H,NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2}\end{array}$$

(II.)

On the assumption that the carbamate (II) was first formed it was apparent that either (*a*) it had decomposed to aminoacetamide during the extraction, or (*b*) had itself been slowly extracted, yielding (I) on the subsequent addition of carbon disulphide.

$$R{\cdot}NH{\cdot}CO_2H,NH_2R + CS_2 \longrightarrow R{\cdot}NH{\cdot}CS_2H,NH_2R + CO_2 \qquad (R = CH_2{\cdot}CO{\cdot}NH_2)$$

It has now been found that the carbamate (II), formed in good yield by the action of carbon dioxide on an alcoholic solution of aminoacetamide, reacts readily with carbon disulphide in aqueous alcohol at room temperature to give the dithiocarbamate (I). The above reaction thus takes course (*b*). This is believed to be the first example of the conversion of a carbamate into the corresponding dithiocarbamate, although Inghilleri (*Gazzetta*, 1909, **39**, 634) described the reaction of carbon disulphide with ammonium carbonate under pressure at 100° to form ammonium thiocyanate, which might well have involved the initial conversion of the ammonium carbonate into ammonium carbamate followed by reaction with carbon disulphide and subsequent decomposition of the dithiocarbamate.

Benzylammonium benzylcarbamate (Wright and Moore, *J. Amer. Chem. Soc.*, 1948, **70**, 3865) similarly gives a good yield of the corresponding dithiocarbamate, but there has been no opportunity to extend the reaction to other carbamates.

The carbamate (II), m. p. 124·5° (decomp.) (uncorr.), is probably identical with the compound, m. p. 126° (decomp.), which is formed when aminoacetamide is exposed to air (Heintz, *Annalen*, 1868, **148**, 195; Koenigs and Mylo, *Ber.*, 1908, **41**, 4429; Cook, Heilbron, and Levy, *loc. cit.*) and was suspected of being a carbonate.

EXPERIMENTAL.

(All m. p.s are uncorrected.)

Carbamylmethylammonium Carbamylmethylcarbamate (II).—To a stirred suspension of aminoacetamide hydrochloride (39·0 g.) in absolute alcohol (180 ml.) at –5° 30% aqueous potassium hydroxide was added drop-wise till the reaction mixture was faintly alkaline (phenolphthalein). The mixture was filtered and the potassium chloride washed with a little absolute alcohol. Carbon dioxide was passed in a fairly rapid stream through the filtrate and washings, the temperature of the solution being conveniently kept at about 0° by the addition of small pieces of solid carbon dioxide. A practically colourless oil separated after a short time and separation appeared to be complete after about 2 hours. The oil crystallised when scratched, and the solid was filtered off, washed with alcohol and ether, and dried (14·38 g.); it had m. p. 124·5° (decomp.). The filtrate, on storage in the ice-chest overnight, yielded a further crop (9·42 g.), m. p. 123·5° (decomp.). *Carbamylmethylammonium carbamylmethylcarbamate* (10 g.) was recrystallised by dissolution in water (20 ml.) and addition of alcohol (75 ml.) followed by refrigeration, but the m. p. remained unchanged (Found: C, 31·2; H, 6·3. $C_5H_{12}O_4N_4$ requires C, 31·25; H, 6·25%). An aqueous solution gave no precipitate with barium chloride until warmed.

Reaction of Carbon Disulphide with Carbamylmethylammonium Carbamylmethylcarbamate.—To a solution of the carbamate (II) (5 g.) in water (10 ml.) and alcohol (20 ml.), carbon disulphide (2 ml.) was added. Slow evolution of carbon dioxide soon commenced and began to decrease after approx. 1·5 hours, when all the carbon disulphide had dissolved. Colourless crystals of carbamylmethylammonium carbamylmethyldithiocarbamate (I) rapidly separated at this point, and after a further hour at room temperature the mixture was cooled in the ice-chest and the solid (4·13 g., 71%) removed and washed with alcohol and ether. It had m. p. 139° (decomp.), not depressed on admixture with an authentic specimen; its identity was confirmed by conversion into 2-mercaptothiazolone by hydrochloric acid (Cook, Heilbron, and Levy, *loc. cit.*).

Reaction of Carbon Disulphide with Benzylammonium Benzylcarbamate.—Benzylammonium benzylcarbamate (5 g.) (Wright and Moore, *loc. cit.*) similarly gave the dithiocarbamate (4·42 g., 78·7%), m. p. 115° (decomp.) (heating from 110°), not depressed on admixture with an authentic specimen, m. p. 115° (decomp.) (heating from 110°), prepared from carbon disulphide and benzylamine in alcohol [Salkowski, *Ber.*, 1891, **24**, 2725, gave m. p. about 119° (decomp.)] (Found: C, 62·2; H, 6·2; N, 9·6; S, 22·8. Calc. for $C_{15}H_{18}N_2S_2$: C, 62·1; H, 6·2; N, 9·7; S, 22·1%).

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