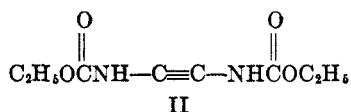
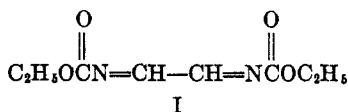


CARBAMATES. III. REACTIONS OF "ACETYLENE
BIS-CARBAMATES" (1)

NORMAN G. GAYLORD

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The reaction of glyoxal with ethyl carbamate in the presence of concentrated hydrochloric acid has been reported to yield an insoluble, microcrystalline powder named "glyoxal-bis(carbethoxy-imide)" (I) (2). However, the abstract literature refers to this compound as "diethyl N,N'-acetylenebis(carbamate)" (II).

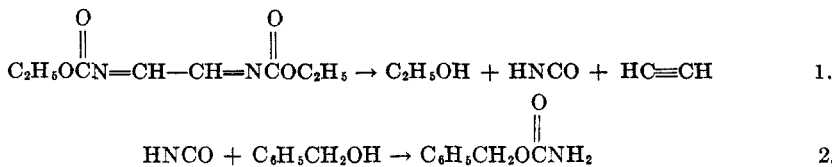


Due to the expected differences in behavior of I and II an investigation of the structure and reactions of this product, hereinafter referred to as I, was carried out.

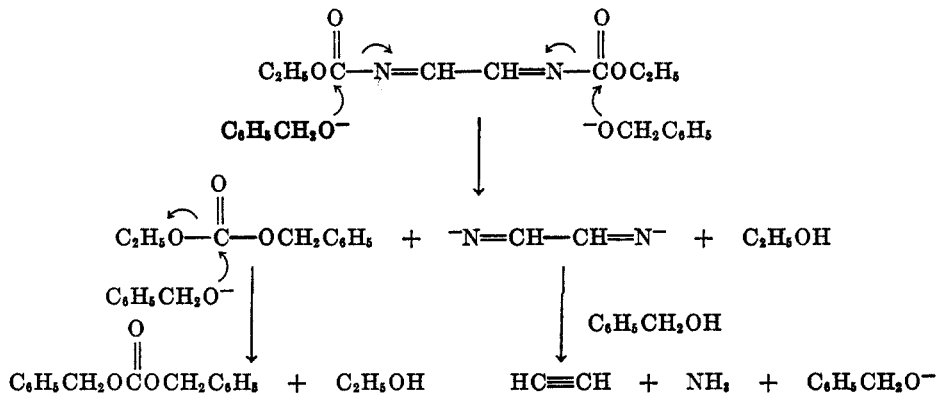
The preparation of I by the reported procedure (2) gave a solid, m.p. 286–287°, which although analytically pure, was at no time in the synthesis or purification in solution or capable of being dissolved in the usual solvents. The infrared spectra of this compound, obtained from a Nujol mull, clearly indicated the absence of an acetylenic linkage and led to the conclusion that I was the correct structure. In an attempt to obtain a more soluble compound, glyoxal-bis(carbo-benzyloxy-imide) was prepared from glyoxal and benzyl carbamate. This product was obtained in a toluene-soluble form, m.p. 180–185°, and an insoluble form, m.p. 275–280°, mixture melting point 195–210°. Both forms analyzed correctly for the benzyl compound and had identical spectra which indicated the absence of an acetylenic linkage.

Previous work (1a) has shown that the reactions of ethyl carbamate with low-boiling alcohols, *e.g.* isobutyl alcohol, with acid catalysis, or with high-boiling alcohols, *e.g.* benzyl alcohol, without catalysis, yields the corresponding carbamate, probably by an ester exchange mechanism. The reaction of ethyl N-monosubstituted carbamates with benzyl alcohol yields the corresponding benzyl carbamate by what is principally a decomposition of the initial carbamate to an isocyanate followed by reaction with the benzyl alcohol. Isobutyl alcohol does not react with the monosubstituted carbamate even with acid catalysis.

The reaction of I with benzyl alcohol gave ethanol acetylene, ammonia, benzyl carbamate, and dibenzyl carbonate. The ethanol, acetylene and benzyl carbamate probably arose by decomposition of I as follows:



The formation of carbonates by the reaction of alcohols with *N,N*-disubstituted carbamates has been previously observed (3) and can be accounted for as follows:



The decomposition postulated in equation 1 was verified by heating I with tetralin to yield acetylene and ethyl carbamate. The attempted reaction of I with isobutanol failed to yield any ethanol or carbamate other than I.

The reduction of carbamates with lithium aluminum hydride has been shown to yield *N*-methylamines and alcohols (4). The reduction of benzyl carbamate gave benzyl alcohol although no methylamine could be trapped in a dilute hydrochloric or acetic acid solution. The reduction of I with the complex hydride in tetrahydrofuran, by the Soxhlet extraction technique, gave *N,N'*-dimethylethylenediamine, identified by analysis and by the formation of a picrate. Here reduction of the carbon-nitrogen double bond accompanies reduction of the carbamate group.

EXPERIMENTAL

Glyoxal-bis(carboethoxy-imide) (I). The reaction of 193 g. (1 mole) of a 30% aqueous glyoxal solution with 178 g. (2 moles) of ethyl carbamate, in the presence of 135 ml. of concentrated hydrochloric acid, according to the procedure of Pauly and Sauter (2), after heating on a steam-bath for 12 hours gave a semi-solid reaction mixture. After filtration the solid residue was washed with 3 liters of water and triturated with 1.5 liters of acetone. After drying 115 g. (49%) of a white solid was obtained, m.p. 286–287°. I was insoluble in water, ethanol, ethyl acetate, dioxane, and hexane.

Anal. Calc'd for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_4$: N, 14.00. Found: N, 14.26.

Glyoxal-bis(carbobenzoxy-imide). The reaction of 31 g. (0.16 mole) of a 30% aqueous glyoxal solution with 48.3 g. (0.32 mole) of benzyl carbamate, in the presence of 23 ml. of concentrated hydrochloric acid, after heating on a steam-bath with stirring for 12 hours gave a dark-colored heterogeneous mixture. A tarry residue was obtained upon filtration and after washing with several liters of water and triturating with acetone, 7.2 g. of a light blue solid was obtained. This material was extracted from a Soxhlet thimble with refluxing toluene to yield 1.2 g. of a soluble fraction, m.p. 180–185°.

Anal. Calc'd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$: N, 8.64. Found: N, 8.92.

The insoluble portion, 6.0 g. had m.p. 275–280°.

Anal. Calc'd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$: N, 8.64. Found: N, 8.61.

A mixture melting point determination of the soluble and insoluble fractions had m.p. 195–210°.

Reaction of I with benzyl alcohol. A mixture of 45 g. (0.225 mole) of I and 146 g. (1.35 moles) of benzyl alcohol was heated for 30 minutes and then distilled, with partial take-off, through a Vigreux column. After 7 hours 21.5 ml. of ethanol had been collected. During

the reaction period ammonia and acetylene were generated and the latter was identified by the decolorization of bromine-carbon tetrachloride and aqueous potassium permanganate solutions and by the formation of the characteristic precipitate from an ammoniacal silver nitrate solution. A total of 2 g. of benzyl carbamate, m.p. 82°, sublimed in the lower end of the condenser during the heating cycle.

Vacuum-distillation of the reaction mixture gave 77.9 g. of benzyl alcohol (54% recovery), identified as the α -naphthylurethan, 34.7 g. of benzyl carbamate, b.p. 130–135° (0.5 mm.), m.p. 82–83° (total yield, 36.7 g., 54%), and 21.6 g. of dibenzyl carbonate, b.p. 156–160° (0.3 mm.) (20% yield).

The benzyl carbamate was identified by the absence of a depression in a mixture m.p. with authentic material, m.p. 84–85°, by analysis, and by the reduction with lithium aluminum hydride described below.

Anal. Calc'd for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.26.

Found: C, 63.81; H, 6.09; N, 9.13.

The dibenzyl carbonate was identified by analysis and by the evolution of carbon dioxide, precipitated as calcium carbonate by bubbling through lime water, upon heating an alcoholic solution in the presence of a few drops of hydrochloric acid.

Anal. Calc'd for $C_{16}H_{14}O_3$: C, 74.36; H, 5.84.

Found: C, 74.37; H, 5.88.

The attempted reaction of *I* with isobutanol failed to yield any ethanol after heating for 10 hours.

A heterogeneous mixture of *I* and tetralin was heated for 4 hours during which time no ethanol was collected but a great deal of foaming occurred and acetylene was generated. The mixture was filtered to yield 52% of *I* and the filtrate was distilled *in vacuo* to yield 85% of the tetralin. A small quantity of solid which sublimed in the apparatus during the course of the distillation was identified as ethyl carbamate, m.p. 47–49°.

Reduction of benzyl carbamate. A solution of 15.1 g. (0.1 mole) of benzyl carbamate in 200 ml. of ether was added over 1.25 hours to an ethereal solution of LAH prepared from 5.7 g. LAH and 150 ml. of ether. The mixture was refluxed for 45 minutes when the addition was completed. A white precipitate formed during the course of the reaction. The mixture was decomposed with ethyl acetate and water. The ether layer and the ethereal extract of the aqueous layer were concentrated to 100 ml., washed with a dilute sulfuric acid solution, dried over sodium sulfate and evaporated. The residual oil, 7.8 g. (72%), was identified as benzyl alcohol by conversion to the α -naphthylurethan, m.p. 133–134°, no depression on a mixture m.p. with authentic material.

Reduction of I. A solution of 15 g. of LAH in 500 ml. of tetrahydrofuran was refluxed under a Soxhlet thimble containing 23 g. of *I* for 7 days until all the *I* was transferred to the reaction flask. The mixture was decomposed with 15 ml. of water, 4–5 ml. of 20% sodium hydroxide, and 15 ml. of water, in that order. After filtration of the inorganic salts the tetrahydrofuran solution was dried several times over magnesium sulfate and distilled to yield 7 g. of *N,N'*-dimethylethylenediamine, b.p. 118–120° [reported (5) 120°], picrate, m.p. 214° [reported (6) 215°].

Anal. Calc'd for $C_4H_{12}N_2$: C, 54.50; H, 13.65; N, 31.90.

Found: C, 54.21; H, 13.59; N, 31.60.

BUFFALO 8, NEW YORK

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