tained. This product was washed with a hot solution of sodium carbonate. Recrystallization from benzene–petroleum ether (b.p. 40–60°) gave (Ib), 1.7 g., 22.3% as yellow crystals, m.p. 168–169°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 78.94; H, 4.69.

Ib was rearranged quantitatively to the corresponding β-diketone (IIb) on treatment with sodium methoxide solution[1] (melting point and mixture melting point).

The product which was insoluble in petroleum ether (b.p. 70–80°) was recrystallized from benzene (charcoal) to give IIb, 2.9 g., (40%); as orange needles, m.p. 220–222°.

Anal. Calcd. for: $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.85; H, 4.84.

The product was soluble in a cold dilute solution of sodium hydroxide or sodium carbonate.

Reaction of naphthalic anhydride with o-chlorophenylacetic acid. A mixture of naphthalic anhydride (5 g.), *o*-chlorophenylacetic acid (4.3 g.) (prepared in a manner similar to that for *p*-fluorophenyl acetic),[7] and fused sodium acetate (0.5 g.) was treated as described before.

Recrystallization of the product extracted with petroleum ether (b.p. 70–80°) from ethyl alcohol gave Id, 1.1 g. (13%), as yellow needles, m.p. 185–186°.

Anal. Calcd. for $C_{19}H_{11}O_2Cl$: C, 74.39; H, 3.6; Cl, 10.44. Found: C, 74.09; H, 3.49; Cl, 11.21.

When Id was treated with alcoholic sodium methoxide solution a chlorine free yellow product was obtained, m.p. 195–97°.

Anal. Found: C, 83.51; H, 3.85.

The product which was insoluble in petroleum ether (b.p. 70–80°) proved to be naphthalic anhydride (melting point and mixture melting point). No β-diketone was isolated.

Reaction of naphthalic anhydride with p-chlorophenylacetic acid. A mixture of naphthalic anhydride (5 g.), *p*-chlorophenylacetic acid (*cf.* ref. 7) (4.3 g.), and fused sodium acetate (0.3 g.) was treated as described before.

Recrystallization of the product extracted with petroleum ether (b.p. 70–80°) from ethyl alcohol gave Ic, 0.7 g. (9%), as orange yellow needles, m.p. 178–79°.

Anal. Calcd. for $C_{19}H_{11}O_2Cl$: C, 74.39; H, 3.6; Cl, 10.44. Found: C, 74.32; H, 3.52; Cl, 11.16.

The product was rearranged quantitatively to the corresponding β-diketone on treatment with alcoholic sodium methoxide solution (melting point and mixture melting point).

The product which was insoluble in petroleum ether (b.p. 70–80°) was recrystallized from ethyl alcohol to give IIc, 1.0 g. (13%), as orange crystals, m.p. 272–273°.

Anal. Calcd. for $C_{19}H_{11}O_2Cl$: C, 74.39; H, 3.60; Cl, 10.44. Found: C, 73.74; H, 3.59; Cl, 10.99.

The product (IIc) was soluble in a cold dilute solution of sodium hydroxide or sodium carbonate.

Reaction of naphthalic anhydride with quinaldine. A mixture of naphthalic anhydride (1.0 g.), quinaldine (1.5 g.), and a catalytic amount of fused zinc chloride or sodium acetate (0.3 g.) was heated rapidly to 230–240° for 3 hr. The reaction mixture was then poured on cold water, whereby a dark solid mass was obtained. Recrystallization of the product so obtained from ethyl alcohol gave IV, 1 g. (62%), as deep red needles, m.p. 254–255°. The product separated from benzene solution as deep violet rosets and from concentrated benzene solution as olive green crystals.

Anal. Calcd. for $C_{22}H_{13}O_2N$: C, 81.72; H, 4.05; N, 4.33. Found: C, 81.98; H, 3.98; N, 4.50.

Reaction of naphthalic anhydride with α-picoline. A mixture of naphthalic anhydride (2 g.), α-picoline (3 ml.), and a catalytic amount of fused zinc chloride was heated in a sealed tube at 200° for 4 hr. The reaction product was poured on cold water and the solid mass so obtained was washed with a little methyl alcohol, then allowed to dry. The crude product was dissolved in dry benzene and chromatographed over silica gel. On elution with dry benzene, a colorless fraction (0.9 g.) was obtained which proved to be naphthalic anhydride (melting point and mixture melting point). An orange fraction was also obtained, which on concentration gave V, 0.8 g. (30%), as orange needles, m.p. 268–269°. It was soluble in dilute solution of sodium hydroxide or sodium carbonate.

Anal. Calcd. for $C_{18}H_{11}O_2N$: C, 79.11; H, 4.06; N, 5.13. Found: C, 79.17; H, 4.04; N, 5.10.

Reaction of naphthalic anhydride with γ-picoline. Naphthalic anhydride (2 g.), γ-picoline (3 ml.), and catalytic amount of fused zinc chloride was treated as discussed above. Naphthalic anhydride was also isolated here and VI, 0.60 g. (23%), was isolated as orange needles, m.p. 258–59°. It was soluble in a dilute solution of sodium hydroxide or sodium carbonate.

Anal. Calcd. for $C_{18}H_{11}O_2N$: N, 5.13. Found: N, 4.57.

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(7) F. L. M. Patisson and B. C. Saunders, *J. Chem. Soc.*, 2745(1949).

[CONTRIBUTION FROM THE YERKES RESEARCH LABORATORY, E. I. DU PONT DE NEMOURS & CO., INC., FILM DEPARTMENT]

Carbamates. IV. The Reactions of Disubstituted Carbamates with Alcohols

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The reaction of ethyl *N,N*-disubstituted carbamates with alcohols in the presence of the sodium alkoxide of the alcohol yields either carbamates or carbonates, apparently as a function of the relative base strengths of the disubstituted amine and the alkoxide. Thus, the reactions of isobutyl alcohol with ethyl *N,N*-diethyl- and *N*-ethyl-*N*-phenylcarbamates, and benzyl alcohol with ethyl *N*-ethyl-*N*-phenylcarbamate and *N*-*N'*-dicarbethoxypiperazine yield the corresponding carbamates. The reaction of isobutyl alcohol with ethyl *N,N*-diphenylcarbamate yields principally diisobutyl carbonate and diphenylamine, while the reaction of benzyl alcohol with ethyl *N,N*-diphenylcarbamate yields dibenzyl ether, by decarboxylation of the carbonate, and diphenylamine.

It has previously been reported[2] 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,

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[2] N. G. Gaylord and C. E. Sroog, *J. Org. Chem.*, 18, 1632 (1953).

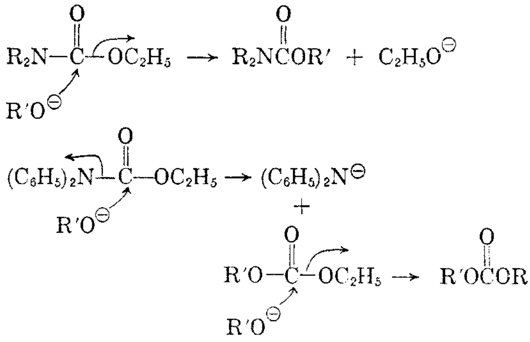
without catalysis, yield the corresponding carbamates, probably by an ester exchange mechanism. The reaction of ethyl *N*-monosubstituted carbamates with benzyl alcohol yields the corresponding benzyl carbamate by what is probably a decomposition of the initial carbamate to an isocyanate followed by reaction with benzyl alcohol. Isobutyl alcohol does not react with the monosubstituted carbamate even with acid catalysis.

Whereas the attempted reactions of isobutyl alcohol with ethyl *N,N*-diethyl- and *N,N*-diphenylcarbamates, in the presence of sulfuric acid, of benzyl alcohol with ethyl *N,N*-diethyl-, *N,N*-dibutyl- and *N,N*-diphenylcarbamates, in the absence of sulfuric acid, of benzyl alcohol with ethyl *N,N*-diphenylcarbamate, in the presence of sulfuric acid, failed to yield any ethanol,[2] it was observed that the uncatalyzed reaction of benzyl alcohol with ethyl *N*-ethyl-*N*-phenylcarbamate yielded the theoretical amount of ethanol after 125 hours, with the subsequent isolation of benzyl *N*-ethyl-*N*-phenylcarbamate in 85% yield. As no satisfactory explanation for this behavior could be set forth, the latter reaction was repeated with a new batch of purified reagents. In this case no ethanol was obtained even after refluxing for eight days. The single, irreproducible success, probably due to the presence of an impurity, indicated that an ester exchange reaction was possible with a disubstituted carbamate, and prompted an investigation of the base-catalyzed reaction of disubstituted carbamates with alcohols.

The reaction of ethyl *N*-ethyl-*N*-phenylcarbamate with benzyl alcohol in the presence of the sodium alkoxide of the alcohol gave the theoretical amount of ethanol in 2.6 hours. An 82% yield of benzyl *N*-ethyl-*N*-phenylcarbamate was obtained. The reaction with isobutyl alcohol gave a 94% yield of the isobutyl analog. This was noteworthy, as the only previously observed successful reaction with isobutyl alcohol had occurred with the unsubstituted ethyl carbamate in the presence of sulfuric acid. The reaction of ethyl *N,N*-diethylcarbamate with isobutyl alcohol in the presence of the alkoxide gave an 87% yield of isobutyl *N,N*-diethylcarbamate.

The reaction of ethyl *N,N*-diphenylcarbamate with isobutyl alcohol in the presence of the sodium alkoxide gave only a 5% yield of isobutyl *N,N*-diphenylcarbamate, accompanied by 87% of didiphenylamine and 62% of diisobutyl carbonate. Similarly, reaction with benzyl alcohol gave 5% of the benzyl carbamate, 94% of diphenylamine, and 77% of dibenzyl ether. The ether undoubtedly arose through decarboxylation of dibenzyl carbonate. It has been shown[3] that at elevated temperatures α-polydecamethylene carbonate undergoes scission to give carbon dioxide and decamethylene oxide radicals which combine to form the polymeric ether.

The mechanism of the alkoxide catalyzed reactions undoubtedly involves a nucleophilic attack of the anion on the carbonyl carbon atom:



$$R_2N{-}\overset{O}{\overset{\|}{C}}{-}OC_2H_5 \;(+\,R'O^{\ominus}) \longrightarrow R_2N\overset{O}{\overset{\|}{C}}OR' + C_2H_5O^{\ominus} \qquad (1)$$

$$(C_6H_5)_2N{-}\overset{O}{\overset{\|}{C}}{-}OC_2H_5 \;(+\,R'O^{\ominus}) \longrightarrow (C_6H_5)_2N^{\ominus} + R'O{-}\overset{O}{\overset{\|}{C}}{-}OC_2H_5 \;(+\,R'O^{\ominus}) \longrightarrow R'O\overset{O}{\overset{\|}{C}}OR' \qquad (2)$$

Whether the reaction follows path (1) or (2) is determined by the relative base strengths of the secondary amine and the alkoxide ion. The fact that the diethylamine and ethylaniline derivatives follow path (1) indicates that these compounds are stronger bases than the alkoxide. On the other hand, diphenylamine is a much weaker base than the other amines and probably weaker than the alkoxide ion, resulting in the elimination of the amine grouping. This is in line with the mechanism of the acetoacetic ester type of condensation which will proceed when a base is formed which is weaker than that used as the condensing agent.[4]

The reaction of *N,N'*-dicarbethoxypiperazine with benzyl alcohol in the presence of the alkoxide followed path (1) to yield the dicarbamate.

The attempted reactions of ethyl carbamate with isobutyl alcohol or *t*-butyl alcohol in the presence of the sodium alkoxide resulted in the recovery of ethyl carbamate.

The reaction between *N*-carbethoxyimidazole and ethanol in the absence of a catalyst is reported to give a 70% yield of diethyl carbonate.[5] *N,N'*-Biscarbethoxy-1,*n*-diamines are reported[6] to undergo a base-catalyzed selfcondensation to yield polyureas, ethanol, and diethyl carbonate. However, no reaction reportedly took place when bisurethanes prepared from *N,N*-disubstituted amines were heated under the same conditions.

EXPERIMENTAL

Reaction of ethyl N-ethyl-N-phenylcarbamate and benzyl alcohol. A. Uncatalyzed. A mixture of 38.6 g. (0.2 mole) of the carbamate was heated with 64.8 g. (0.6 mole) of benzyl alcohol under a Vigreux column topped by a partial takeoff reflux head. After 125 hr. the theoretical amount of ethanol was collected. The reaction mixture was distilled and 43.1 g. (84.6% yield) of benzyl *N*-ethyl,*N*-phenylcarbamate was

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(3) J. W. Hill, *J. Am. Chem. Soc.*, **57**, 1131 (1935).

(4) C. R. Hauser and B. E. Hudson, Jr., *Org. Reactions*, I, 270 (1942).

(5) H. A. Staab, *Ann.*, **609**, 83 (1957).

(6) T. M. Laakso and D. D. Reynolds, *J. Am. Chem. Soc.*, **79**, 5717 (1957); D. D. Reynolds and T. M. Laakso, U. S. Patent **2,784,163** (March 5, 1957).

collected at 155–158° (4 mm.). On redistillation the product boiled at 130–133° (0.3 mm.), n_D^{25} 1.5545, d_4^{25} 1.0960.

Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.29; H, 6.67; N, 5.49. Found: C, 75.20; H, 6.70; N, 5.45.

Numerous attempts to repeat this reaction have been unsuccessful.

The structure of the product was proved by hydrolysis and decarboxylation in the presence of methanolic potassium hydroxide. The carbamate, 12.7 g., was heated under reflux for 17 hr. with 14 g. of potassium hydroxide and 25 ml. of methanol. Work-up of the reaction mixture gave 2.5 g. of benzyl alcohol, identified as the 1-naphthylurethane, and 6.7 g. of *N*-ethylaniline, identified as the benzoyl derivative after purification of the base through the hydrochloride.

B. Catalyzed. Sodium metal, 0.46 g. (0.02 mole) was dissolved in 64.8 g. (0.6 mole) of benzyl alcohol and heated, under a Vigreux column topped by a partial takeoff reflux head, with 38.6 g. (0.2 mole) of ethyl *N*-ethyl,*N*-phenylcarbamate. The theoretical amount of ethanol was collected in 157 min. The reaction mixture was diluted with ether, washed with water until neutral and dried over anhydrous sodium sulfate. On distillation there was collected 41.6 g. (82%) of benzyl *N*-ethyl-*N*-phenylcarbamate, b.p. 120–125° (0.2 mm.). On redistillation the product boiled at 145–146° (0.8 mm.) and its physical constants were identical with those of the product obtained in the uncatalyzed reaction.

Reaction of ethyl N-ethyl-N-phenylcarbamate and isobutyl alcohol. Under the same conditions as above, the reaction of 38.6 g. (0.2 mole) of the carbamate with the alkoxide from 0.46 g. (0.02 mole) of sodium and 44.4 g. (0.6 mole) of isobutyl alcohol gave the theoretical amount of ethanol in 4 hr. A total of 41.4 g. (94%) of isobutyl *N*-ethyl,*N*-phenylcarbamate was collected at 80–88° (1 mm.). On redistillation the product boiled at 75–78° (0.2 mm.), n_D^{25} 1.4908, d_4^{25} 1.0062.

Anal. Calcd. for $C_{13}H_{19}NO_2$: C, 70.59; H, 8.60; N, 6.33. Found: C, 70.25; H, 8.30; N, 6.34.

Reaction of ethyl N,N-diethylcarbamate and isobutyl alcohol. The reaction of 29 g. (0.2 mole) of the carbamate with the alkoxide from 0.46 g. (0.02 mole) of sodium and 44.4 g. (0.6 mole) of isobutyl alcohol gave the theoretical amount of ethanol in 5.5 hr. A total of 31 g. (87%) of isobutyl *N*,*N*-diethylcarbamate was collected at 90–100° (31 mm.). On redistillation the product boiled at 95–98° (31 mm.).

Anal. Calcd. for $C_9H_{19}NO_2$: N, 8.09. Found: N, 8.27, 7.81.

Reaction of ethyl N,N-diphenylcarbamate and isobutyl alcohol. The reaction of 48.2 g. (0.2 mole) of the carbamate with the alkoxide from 0.46 g. (0.02 mole) of sodium and 44.4 g. (0.6 mole) of isobutyl alcohol gave the theoretical amount of ethanol in 3.75 hr. Ether was added to the reaction mixture and the precipitate was filtered. The precipitate was dissolved in water, acidified with dilute hydrochloric acid, made alkaline with 10% sodium hydroxide, and extracted with ether. The dried ether extract was combined with the original ether filtrate. Gaseous hydrogen chloride was bubbled through the ethereal solution and the resultant white precipitate filtered. This was repeated twice. The precipitated hydrochloride, 37.6 g., was treated with sodium hydroxide to liberate 29.4 g. (87%) of diphenylamine, m.p. 51–53° (reported[7] m.p., 54°).

Anal. Calcd. for $C_{12}H_{11}N$: N, 8.28. Found: N, 8.27.

The benzamide of diphenylamine, prepared in the usual manner, melted at 180–181° (reported[7] m.p. 180°) and showed no depression on a mixed melting point with authentic material.

The filtrate from the hydrogen chloride treatment was neutralized with solid sodium bicarbonate and dried over magnesium sulfate. Distillation gave two fractions, 21.7 g. (62%), b.p. 67–71° (10 mm.) and 2.6 g. (4.8%), b.p. 140–145° (0.6 mm.).

The lower boiling fraction on redistillation boiled at 184–186°, n_D^{25} 1.4060, d_4^{25} 0.9050, and was identified as diisobutyl carbonate by analysis and by the liberation of carbon dioxide on heating a methanol solution in the presence of concd. hydrochloric acid.

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.07; H, 10.35. Found: C, 62.11; H, 10.44.

The higher boiling fraction, isobutyl *N*,*N*-diphenylcarbamate, had n_D^{29} 1.5538 and after standing for several months solidified to m.p. 50–50.5°.

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.63; H, 7.00; N, 5.32.

Reaction of ethyl N,N-diphenylcarbamate and benzyl alcohol. The reaction of 0.2 mole of the carbamate with 0.6 mole of benzyl alcohol in the presence of 0.02 mole of sodium gave the theoretical amount of ethanol in 2 hr. and 52 min. The reaction mixture was worked up and treated with gaseous hydrogen chloride as above to yield 38.5 g. (94%) of diphenylamine hydrochloride, m.p. 174–175°, which was converted to the free base, m.p. 51–53°, in quantitative yield.

The filtrate from the hydrogen chloride treatment was neutralized, dried, and distilled to yield 23.5 g. (36%) of benzyl alcohol, 30.3 g. (77%) of dibenzyl ether, b.p. 108–112° (0.5 mm.), and 6.0 g. of b.p. 150–166° (0.5 mm.). The lower boiling fraction on redistillation boiled at 108–109° (0.8 mm.), n_D^{25} 1.5606, and was identified as dibenzyl ether by the analysis and by the failure to evolve carbon dioxide on heating a methanolic solution with concd. hydrochloric acid.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.83; H, 7.07. Found: C, 84.52; H, 7.08.

The higher boiling fraction solidified on standing, was combined with the solidified distillation residue, 1.6 g., and on recrystallization twice from petroleum ether (b.p. 120–135°) and once from benzene gave 3.0 g. (5%) of benzyl *N*,*N*-diphenylcarbamate, m.p. 112–113.5°.

Anal. Calcd. for $C_{20}H_{17}NO_2$: C, 79.21; H, 5.61; N, 4.62. Found: C, 79.34; H, 5.80; N, 4.64.

N,N'-Dicarbethoxypiperazine. A solution of 38.8 g. (0.2 mole) of piperazine hexahydrate in 50 ml. of water was stirred in a three necked flask at 3°. A solution of 19.2 g. (0.48 mole) of sodium hydroxide in 90 ml. of water was placed in one dropping funnel and a solution of 52.1 g. (0.48 mole) of ethyl chloroformate in 50 ml. of ether was placed in a second dropping funnel. The two solutions were added dropwise, simultaneously, over a period of 2.5 hr. while maintaining the temperature below 8°. Upon the completion of the addition the reaction mixture was transferred to a separatory funnel, 50 ml. of ether was added, and the aqueous layer was saturated with sodium chloride. The ether layer was dried and evaporated to yield 48.5 g. of crude product. Upon distillation, 40.8 g. (89%) of pure product was collected at 128–129° (1 mm.), m.p. 44–45° (reported m.p. 45°[8] and 49°[9]).

Reaction of N,N'-dicarbethoxypiperazine and benzyl alcohol. The reaction of 5.75 g. (0.025 mole) of the carbamate with the alkoxide from 0.115 g. (0.005 mole) of sodium and 16.21 g. (0.15 mole) of benzyl alcohol gave the theoretical amount of ethanol in 3 hr. The reaction mixture was diluted with ether, washed with water until neutral and dried over magnesium sulfate. On distillation 7.0 g. of benzyl alcohol was collected at 55° (1 mm.). Addition of ether to the distillation residue resulted in crystallization to yield 2.9 g. (33%) of the benzyl carbamate, m.p. 97–103°. Recrystallization from petroleum ether (b.p. 120–135°) gave 2.15 g., m.p. 107–109°.

Anal. Calcd. for $C_{20}H_{22}N_2O_4$: N, 7.91. Found: N, 7.85.

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