of Nunn and Smedley-Maclean.[5] The product was separated into a fraction insoluble in petroleum ether (6.3 g.; neut. equiv. 307; iodine value 5.3; OCH_3 7.74%; OH 6.2%) and a fraction soluble in petroleum ether (7.0 g.; neut. equiv. 285; iodine value 7.7; OCH_3 5.95%). The latter fraction contained most of the 9(10)-ketostearic acid present in the original residue. The fraction insoluble in petroleum ether (5.5 g.) was cleaved with periodic acid, and the products were oxidized to carboxylic acids by the method of King.[6] The carboxylic acids were separated into a fraction insoluble in petroleum ether (0.6 g.; neut. equiv. 160; OCH_3 5.5%) and a fraction soluble in petroleum ether (2.1 g.; neut. equiv. 219; OCH_3 5.6%).

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[7] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

The Preparation and Stabilities of Some β-Dialkylaminopropionamides

BY JOHN G. ERICKSON[1]

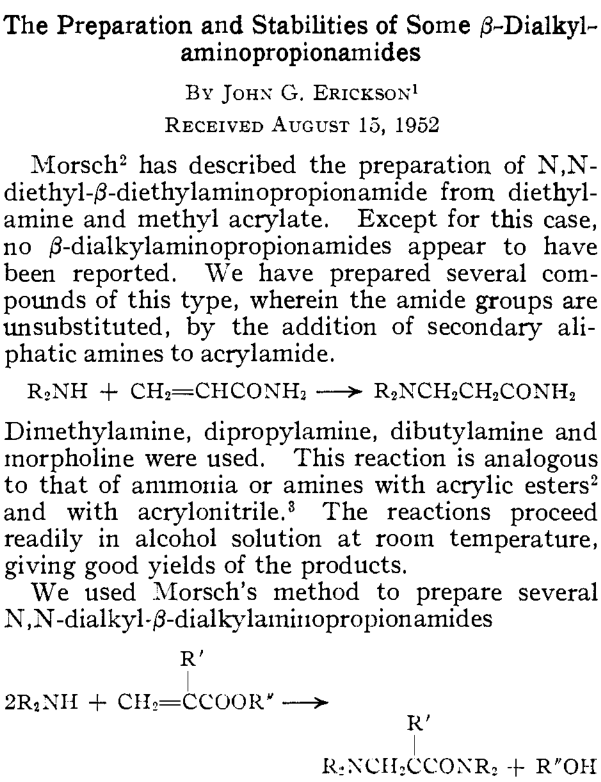
RECEIVED AUGUST 15, 1952

Morsch[2] has described the preparation of N,N-diethyl-β-diethylaminopropionamide from diethylamine and methyl acrylate. Except for this case, no β-dialkylaminopropionamides appear to have been reported. We have prepared several compounds of this type, wherein the amide groups are unsubstituted, by the addition of secondary aliphatic amines to acrylamide.

$$R_2NH + CH_2{=}CHCONH_2 \longrightarrow R_2NCH_2CH_2CONH_2$$

Dimethylamine, dipropylamine, dibutylamine and morpholine were used. This reaction is analogous to that of ammonia or amines with acrylic esters[2] and with acrylonitrile.[3] The reactions proceed readily in alcohol solution at room temperature, giving good yields of the products.

We used Morsch's method to prepare several N,N-dialkyl-β-dialkylaminopropionamides



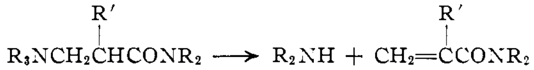
$$2R_2NH + CH_2{=}\overset{R'}{\overset{|}{C}}COOR'' \longrightarrow R_2NCH_2\overset{R'}{\overset{|}{C}}CONR_2 + R''OH$$

II

Dimethylamine was heated with ethyl acrylate to give N,N-dimethyl-β-dimethylaminopropionamide and with methyl methacrylate to give N,N-di-methyl-β-dimethylaminoisobutyramide. Morsch's preparation of N,N-diethyl-β-diethylaminopropionamide from diethylamine and methyl acrylate was repeated. Dibutylamine and methyl acrylate were heated together to give a low yield of N,N-dibutyl-β-dibutylaminopropionamide and much N,N-dibutylacrylamide. This latter compound was apparently formed by decomposition of the aminopropionamide during distillation.

Several interesting observations were made regarding the thermal stabilities of these compounds. Several persons have noted that β-aminopropionic derivatives tend to be rather unstable. For instance, Whitmore and co-workers,[4] Buc, Ford and Wise,[5] and Wiedeman and Montgomery[6] have commented on the instability of β-aminopropionitrile at room temperature. Whitmore and his co-workers also observed that the higher β-dialkylaminopropionitriles are unstable at elevated temperatures. Elderfield and his colleagues[7] state that ethyl β-*p*-anisidinopropionate is not stable and decomposes readily to the amine and ethyl acrylate. McElvain and Stork[8] found that the addition of ammonia to ethyl acrylate, yielding ethyl β-aminopropionate, ethyl β,β′-iminodipropionate and ethyl β,β′,β″-nitrilotripropionate, constitutes a series of reversible reactions.

We found that the N,N-dialkyl-β-dialkylaminopropionamides show a striking gradation in the ease with which they decompose, when heated, to dialkylamines and N,N-dialkylacrylamides



$$R_2NCH_2\overset{R'}{\overset{|}{C}}HCONR_2 \longrightarrow R_2NH + CH_2{=}\overset{R'}{\overset{|}{C}}CONR_2$$

N,N-Dimethyl-β dimethylaminopropionamide (II, $R = CH_3$, $R' = H$) is about 65% decomposed after being refluxed for four hours at 210–215°; no noticeable decomposition occurs at 200°. N,N-Diethyl-β-dibutylaminopropionamide is decomposed to about the same extent upon being heated for 15 minutes at 180–200°. N,N-Dibutyl-β-dibutylaminopropionamide, as has been said, is much less stable; it undergoes much decomposition merely upon being distilled under reduced pressure at 125°.

It will be noted that the stability of these N,N-dialkyl-β-dialkylaminopropionamides decreases with increasing length of carbon chains in the substituent alkyl groups. This increasing instability is not a result only of greater loading upon the amino nitrogen atoms. β-Dibutylaminopropionamide (I, $R = C_4H_9$) distills undecomposed at 167° while N,N-dibutyl-β-dibutylaminopropionamide (II, $R = C_4H_9$, $R' = H$) is mostly decomposed by distillation at 125°. Clearly, the presence of butyl groups on amide nitrogen atoms has a considerable effect on the stability of the molecule.

Another factor which decreases the stability of these β-aminopropionamides is the presence of an alpha methyl group on the propionamide chain. This is shown by a comparison of N,N-dimethyl-β-dimethylaminopropionamide with N,N-dimethyl-β-dimethylaminoisobutyramide (II, $R = R' = CH_3$). The latter compound is the less stable and breaks down to some extent, merely upon distillation, to give dimethylamine; this is shown by the poor yield in which it was obtained, its poor nitrogen analysis, and the persistent odor of dimethylamine over the distilled product.

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Acknowledgment.—Members of the Analytical and Microanalytical groups performed the analyses here.

Experimental

β-Dimethylaminopropionamide.—A mixture of dimethylamine (49.5 g., 1.10 moles) and acrylamide (71.0 g., 1.00 mole) in methanol (300 ml.) stood for three days at room temperature. It was then distilled to give 73.0 g. (63%) of product, b.p. 107–110° (3.5 mm.). It was distilled again, b.p. 96° (0.5 mm.), m.p. 39.8–40.3°.

Anal. Calcd. for $C_5H_{12}N_2O$: C, 51.69; H, 10.42; N, 24.12. Found: C, 51.51, 51.66; H, 10.50, 10.60; N, 23.27.

β-Dipropylaminopropionamide.—A mixture of dipropylamine (110.0 g., 1.09 moles) and acrylamide (71.0 g., 1.00 mole) in 95% alcohol (85 ml.) stood at room temperature for two weeks. It was then distilled, giving 138.4 g. (80%) of product, b.p. 154–157° (3.5 mm.).

Anal. Calcd. for $C_9H_{20}N_2O$: N, 16.27. Found: N, 16.09.

β-Dibutylaminopropionamide.—A mixture of dibutylamine (142.0 g., 1.10 moles) and acrylamide (71.0 g., 1.00 mole) in 95% alcohol (85 ml.) stood for eight days at room temperature. It was then distilled to give 148.8 g. (74%) of product, b.p. 162–167° (3 mm.).

Anal. Calcd. for $C_{11}H_{24}N_2O$: C, 65.95; H, 12.08; N, 13.99. Found: C, 65.97, 65.94; H, 11.70, 11.77; N, 14.07, 14.38.

β-4-Morpholinylpropionamide.—Morpholine (98.0 g., 1.12 moles) was added to a solution of acrylamide (71.0 g., 1.00 mole) in 95% alcohol (85 ml.). The reaction was more vigorous than were the preceding three, and cooling with a water-bath was necessary to hold the temperature at 35–40°. After several hours, the solution was evaporated to a volume of 200 ml., then chilled. The crystallized product was filtered off and dried; wt. 78.2 g. (49%), m.p. 97.5–100°. After two recrystallizations from benzene, the m.p. was 98–100°.

Anal. Calcd. for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71. Found: C, 53.29, 53.20; H, 8.81, 9.02; N, 17.49, 17.67.

N,N-Dimethyl-β-dimethylaminopropionamide.—A mixture of ethyl acrylate (50.0 g., 0.50 mole) and dimethylamine (67.5 g., 1.50 moles) was heated for 18 hours at 200°. Distillation gave 58.2 g. (81%) of product, b.p. 111–114° (15 mm.). It was distilled again, b.p. 112° (15 mm.), $n^{25}D$ 1.4590.

Anal. Calcd. for $C_7H_{16}N_2O$: C, 58.30; H, 11.18; N, 19.43. Found: C, 58.16, 58.21; H, 11.40, 11.27; N, 18.83.

Decomposition Experiment.—A mixture of N,N-dimethyl-β-dimethylaminopropionamide (50.0 g., 0.35 mole) and hydroquinone (1.0 g.) was heated at 200° for 20 minutes. No change was noticed at this temperature so the mixture was heated to 210–215°, when it boiled vigorously. After having been refluxed for four hours at this temperature, the mixture had lost 10.2 g. of weight. Distillation of the mixture gave 13.0 g. (38%) of N,N-dimethylacrylamide, b.p. 96–104° (35 mm.). The mixture became very viscous during distillation; apparently extensive polymerization of the acrylamide occurred.

Anal. Calcd. for C_5H_9NO: N, 14.13; I_2 no. (cg. of I_2 per g. of sample), 256. Found: N, 14.44; I_2 no., 226.

The iodine numbers of substituted acrylamides are difficult to determine precisely because of the uncertainty in judging the end-point.

N,N-Dimethyl-β-dimethylaminoisobutyramide.—A mixture of methyl methacrylate (50.0 g., 0.50 mole) and dimethylamine (67.5 g., 1.50 moles) was heated 16 hours at 200°. Distillation of the product gave 28.5 g. (36%) of product, b.p. 108–117° (15 mm.). The material appeared to decompose to some extent during distillation and a sharper boiling point could therefore not be taken. The distilled material had a pronounced odor of dimethylamine.

Anal. Calcd. for $C_8H_{18}N_2O$: N, 17.71. Found: N, 16.94.

Decomposition Experiment with N,N-Diethyl-β-diethylaminopropionamide.—A mixture of the amide (100.0 g., 0.50 mole) and hydroquinone (1.0 g.) was heated in a flask to which was attached a six-inch column packed with glass beads. Heating was continued for 15 minutes at 180–200° while diethylamine (18.1 g.) was condensed and drawn off at the top of the column. The residue weighed 78.7 g. It was fractionated to yield 46.6 g. of N,N-diethylacrylamide, b.p. 95–99° (18 mm.).

Anal. Calcd. for $C_7H_{13}NO$: N, 11.02; I_2 no., 200. Found: N, 10.58; I_2 no., 179.

N,N-Dibutyl-β-dibutylaminopropionamide.—A mixture of methyl acrylate (251 g., 2.92 moles) and dibutylamine (920 g., 7.13 moles) was refluxed under a short column attached to a take-off head. The temperature of the refluxing mixture was kept high by removal of the methanol formed through the head. After 40 hours of heating, the formation of methanol had ceased. The mixture was distilled under reduced pressure to give unreacted dibutylamine, 334.4 g. of N,N-dibutylacrylamide, b.p. 95–102° (1 mm.), and 138.5 g. of N,N-dibutyl-β-dibutylaminopropionamide, b.p. 120–138° (1 mm.). That this product decomposes during distillation is indicated by the fact that the 138.5 g., redistilled, gave only 40.0 g. of material, b.p. 120–125° (1 mm.). There was a substantial forerun from this redistillation. Complete purification for analysis appeared impossible because of the ease with which decomposition took place.

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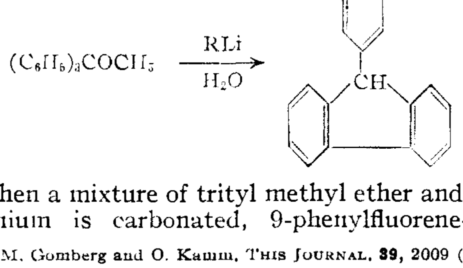
The Reaction of Trityl Methyl Ether with Phenyllithium and with *n*-Butyllithium

BY HENRY GILMAN, WILLIAM J. MEIKLE AND JOHN W. MORTON, JR.

RECEIVED JULY 1, 1952

A number of reactions of trityl ethers and halides with organometallic compounds have been studied. Trityl methyl, ethyl and phenyl ethers react with phenylmagnesium bromide under forcing conditions to yield varying amounts of tetraphenylmethane.[1] The same hydrocarbon is obtained, together with triphenylmethane and a large amount of diphenyl-*p*-xenylmethane, from the reaction of trityl chloride with phenylmagnesium bromide.[2] Small amounts of higher molecular weight hydrocarbons, such as phenyldi-*p*-xenylmethane, are also formed.[3] Trityl chloride reacts with *n*-butyllithium in petroleum ether to produce 1-tritylbutane,[4] while the reaction with phenyllithium in diethyl ether leads to *p*-benzohydryltetraphenylmethane.[5]

We have found that trityl methyl ether reacts with phenyllithium under forcing conditions, and with *n*-butyllithium under mild conditions, to produce a scarlet mixture which yields 9-phenylfluorene on hydrolysis.



When a mixture of trityl methyl ether and phenyllithium is carbonated, 9-phenylfluorene-9-car-

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