*Anal.* Calcd. for $C_9H_{14}N_4O$: N, 28.86. Found: N, 28.40.

**5,5-Dimethyl-2,4-dithiohydantoin.**—A yield of 535 g. of 5,5-dimethyl-2,4-dithiohydantoin (m. p. 143°) was obtained from 420 g. of carbon disulfide and 925 g. of α-aminoisobutyronitrile (see ref. 8). *Anal.* Calcd. for $C_5H_8N_2S_2$: C, 37.50; H, 5.00; S, 40.00. Found: C, 37.44; H, 5.00; S, 40.16.

**Acknowledgment.**—The author wishes to express his indebtedness to Dr. N. E. Searle of the Chemical Department of E. I. du Pont de Nemours & Company for proving that the compound derived from carbon disulfide and α-aminoisobutyronitrile is 5,5-dimethyl-2,4-dithiohydantoin.

## Summary

1. A number of N-substituted α-aminoisobutyronitriles have been conveniently prepared from acetone cyanohydrin and amines, usually in good yields. α-Dicyclohexylaminoisobutyronitrile and α-(β-hydroxyethylamino)-isobutyronitrile have not been previously described.

2. Several new derivatives have been prepared from α-aminoisobutyronitrile. These include the methacrylyl derivative ($CH_2{=}C(CH_3)CONHC(CH_3)_2CN$), N-(α-cyanoisopropyl)-N′-phenyl-urea, ($C_6H_5NHCONHC(CH_3)_2CN$), and 1,3-bis-(α-cyanoisopropyl)-urea ($NCC(CH_3)_2NHCONHC(CH_3)_2CN$).

3. 5,5-Dimethyl-2,4-dithiohydantoin has been prepared from α-aminoisobutyronitrile and carbon disulfide.

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[CONTRIBUTION NO. 169 FROM THE CHEMICAL DEPARTMENT, E. I. DU PONT DE NEMOURS & COMPANY]

# Methacrylylurea and N-Phenyl-N′-methacrylylurea

BY RALPH A. JACOBSON

The preparation of monosodium urea and its reactions with esters to obtain acyl ureas were described in a preceding paper.[1] Methacrylylurea has now been prepared from monosodium urea and methyl methacrylate. The methacrylyl derivatives of phenylurea, aniline and phenylhydrazine have also been obtained by reaction of their respective sodium derivatives with methyl methacrylate.[2]

At 5 to 10° methyl methacrylate reacts with monosodium urea in the presence of acetone to yield methacrylylurea, $CH_2{=}C(CH_3)CONHCONH_2$. N-Phenyl-N′-methacrylylurea is obtained in an analogous manner from methyl methacrylate and N-sodium-N′-phenylurea. The monosodium urea and sodium phenylurea required as intermediates are easily obtained by the reaction of metallic sodium upon urea and phenylurea in liquid ammonia. In fact, the sodium derivatives need not be isolated since the subsequent reaction with methyl methacrylate goes well in liquid ammonia.

Methacrylylurea is soluble in water, alcohol and other organic solvents. It readily polymerizes when heated in alcohol solution in the presence of benzoyl peroxide. The polymeric form of methacrylylurea is an amorphous white powder, insoluble in water, alcohol and in the common organic solvents but soluble in dilute alkali. Since methacrylylurea polymerizes rather easily even in the absence of catalysts, any method of preparation involving high temperatures is unsuitable. The method here described has the advantage that only the mildest of experimental conditions are required. N-Phenyl-N′-methacrylylurea does not polymerize so readily as methacrylylurea.

The preparation of the methacrylyl derivatives of aromatic amines through their sodium derivatives is also feasible. Methyl methacrylate reacts, for example, with sodium aniline and with sodium phenylhydrazine to yield methacrylylaniline and N-methacrylyl-N′-phenylhydrazine, respectively. These compounds also polymerize, although less readily than methacrylylurea.

## Experimental

**N-Sodium-N′-phenylurea.**—To a solution of 45 g. of phenylurea (0.33 mole) dissolved in 1 liter of liquid ammonia was slowly added 7.66 g. (0.33 mole) of sodium. Reaction proceeded smoothly and after each addition of sodium, the blue color was quickly discharged. The ammonia was allowed to evaporate overnight and the product was obtained as a white reactive powder; yield 51 g. (96%). The following analytical data were obtained on this crude product.

*Anal.* Calcd. for $C_7H_7N_2ONa$: N, 17.72; Na, 14.55. Found: N, 16.76; Na, 13.75.

**Methacrylylurea.**—A mixture of 2400 g. (24 moles) of methyl methacrylate, 656 g. (8 moles) of monosodium urea,[1] and 600 cc. of acetone was mechanically stirred for three hours at 5–10°. The thick yellow mixture was stirred, and 1520 cc. of 18% hydrochloric acid added at such a rate that the temperature of the mixture did not exceed 25°. The mixture was cooled to 2°, filtered with suction, and the excess methyl methacrylate recovered as the upper layer (1980 g.) of the filtrate. Crystallization of the solid material from alcohol yielded 384 g. (38%) of methacrylylurea, m. p. 133–134°.

*Anal.* Calcd. for $C_5H_8N_2O_2$: N, 21.87. Found: N, 21.39.

Methacrylylurea was also prepared by treating a solution of 200 g. (2 moles) of methyl methacrylate and 120 g. (2 moles) of urea in 1 liter of liquid ammonia with 46 g. (2 moles) of sodium; yield 112 g. (43.7%).

**N-(α,β-Dichloroisobutyryl)-urea.**—Chlorine was passed into a suspension of 32 g. (0.25 mole) of methacrylylurea in 150 cc. of carbon tetrachloride. The heat of reaction caused the carbon tetrachloride to boil. The reaction product at first dissolved in the solvent but in half an hour it separated as a crystalline mass. The mixture was diluted

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(1) Jacobson, THIS JOURNAL, 58, 1984 (1936).

(2) Jacobson, U. S. Patents 2,090,592, 2,090,594 and 2,090,596.

with 50 cc. of carbon tetrachloride, filtered and the product recrystallized from dilute alcohol; yield 49 g. (quantitative), m. p. 99–101°.

*Anal.* Calcd. for $C_5H_8N_2O_2Cl_2$: Cl, 35.67. Found: Cl, 35.75.

**N-Phenyl-N′-methacrylylurea.**—A solution of 25 cc. of methyl methacrylate in 30 cc. of acetone was treated with 15.8 g. (0.1 mole) of sodium phenylurea. Considerable heat was liberated with the formation of a transparent semi-solid mass. After twelve hours a small amount of water was added and the white crystalline precipitate filtered. Upon crystallization from alcohol, beautiful white crystals, m. p. 130–131°, were obtained; yield 8.8 g. (43%).

*Anal.* Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.70; H, 5.88; N, 13.72. Found: C, 64.40; H, 5.97; N, 14.09.

N-Phenyl-N′-methacrylylurea was also conveniently prepared by slowly treating a solution of 90 g. (0.66 mole) of phenylurea in 1 liter of liquid ammonia with 15.2 g. of sodium. The sodium phenylurea remained in solution, in contrast to sodium urea, which is only slightly soluble in liquid ammonia. A solution of 90 g. of methyl methacrylate in 50 cc. of acetone was then added by means of a dropping funnel. The ammonia was allowed to evaporate and the residue treated as described above; yield 80 g. (58.8%).

**Methacrylylaniline.**—Sodium aniline was prepared[3] by treating 31 g. (0.33 mole) of aniline with 13 g. (0.33 mole) of powdered sodamide. A solution of 40 g. of methyl methacrylate in 100 cc. of benzene was slowly added and this mixture gently refluxed for one hour, cooled, diluted with water, and the upper benzene layer separated. Concentration of the solution on a steam-bath yielded methacrylylaniline (22 g.) which upon crystallization from ligroin melted at 84–85°. Although white at first, the crystals darkened somewhat on standing.

*Anal.* Calcd. for $C_{10}H_{11}NO$: C, 74.53; H, 6.83; N, 8.69. Found: C, 74.08; H, 6.63; N, 9.00.

**N-Methacrylyl-N′-phenylhydrazine.**—A suspension of sodium phenylhydrazine in benzene was prepared[3] by treating a solution of 27 g. of phenylhydrazine in 200 cc. of benzene with 10 g. of powdered sodamide. The mixture was refluxed for one hour and 35 g. of methyl methacrylate slowly added. The mixture was cooled, diluted with water, and acidified with hydrochloric acid. The mixture was filtered and the solid material crystallized from dilute alcohol. N-Phenyl-N′-methacrylylhydrazine was obtained as scale-like crystals, m. p. 130.5–131.5°, yield 10 g. (22%). The compound is soluble in hydrochloric acid but reprecipitated by sodium hydroxide.

*Anal.* Calcd. for $C_{10}H_{12}N_2O$: C, 68.18; H, 6.81; N, 15.90. Found: C, 68.67; H, 7.29; N, 15.25.

## Summary

1. Methacrylylurea and N-phenyl-N′-methacrylylurea have been prepared by the reaction of methyl methacrylate with monosodium urea and monosodium phenylurea, respectively. The latter is easily prepared by the action of sodium upon the urea in liquid ammonia.

2. Methacrylylurea polymerizes readily when heated in alcohol solution in the presence of benzoyl peroxide. The polymer is insoluble in water and in organic solvents.

3. Methacrylylaniline and N-methacrylyl-N′-phenylhydrazine have been obtained from methyl methacrylate and the sodium derivatives of aniline and phenylhydrazine, respectively.

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[3] Titherley, *J. Chem. Soc.*, **71**, 460 (1897).

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# The Mannich Reaction: β-Aminoketones from Diisopropyl Ketone

BY RALPH A. JACOBSON

This paper deals with the preparation of several new β-aminoketones[1] from diisopropyl ketone by means of the Mannich reaction.

The reaction of diisopropyl ketone with aqueous formaldehyde and methylamine hydrochloride yielded methylamino-*t*-butyl isopropyl ketone (I) and a diketone having the empirical formula $C_{19}H_{38}N_2O_2$. The method of preparation and analytical data suggest that the diketone has the structure (II) and was formed from two molecules each of methylamine and diisopropyl ketone and three molecules of formaldehyde. A small amount of non-distillable sirupy resin was also obtained, indicating that further condensation had proceeded to a limited extent.

$CH_3NHCH_2C(CH_3)_2COCH(CH_3)_2$ (I)

$CH_3NHCH_2C(CH_3)_2COC(CH_3)_2CH_2N(CH_3)CH_2C(CH_3)_2$-
$COCH(CH_3)_2$ (II)

It is of interest that the same aminoketone (I) was obtained when ammonium chloride was substituted for methylamine hydrochloride in the above condensation. The explanation lies in the fact that ammonium chloride and aqueous formaldehyde yield substantial amounts of methylamine when heated.[2] The equivalence of the monomeric products from the two reactions was indicated by the similarity of their physical constants and demonstrated by the preparation of identical hydrochlorides. While the high-boiling fraction obtained from ammonium chloride, formaldehyde and diisopropyl ketone appeared to contain more than one compound, at least one of them was identical with II. This fact was established by the preparation of identical aminodiketone hydrochlorides from the high-boiling fractions of both reactions.

The formation of diketones analogous to II is obviously precluded in the case of a secondary amine. Dimethylamine hydrochloride and diethylamine hydrochloride yielded the aminoketones, dimethylamino-*t*-butyl isopropyl ketone (III) and diethylamino-*t*-butyl isopropyl ketone (IV), respectively, upon condensation with form-

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[1] Jacobson, U. S. Patent 2,179,215.

[2] Werner, *J. Chem. Soc.*, **111**, 844 (1917).