(123 g., 1.15 moles) was added in the same manner as described previously to a mixture of glacial methacrylic acid (150 g.), dimethylformamide (150 g.), and hydroquinone (5 g.). At the reflux temperature of the solution, chloromethyltrimethylsilane (123 g., 1 mole) was added slowly over a period of one hour. After refluxing for an additional two hours, the solids were filtered off (Wt. 62 g.; theory for NaCl 58.5 g.). The filtrate was washed first with water and then with dilute sodium bicarbonate solution. The product was dried over sodium sulfate. After the addition of hydroquinone (5 g.), distillation yielded methacryloxymethyltrimethylsilane, b.p. 98° at 75 mm.; n_D^{25} 1.4282; d_4^{25} 0.883; in 62% yield.

Anal. Calc'd for $C_8H_{16}O_2Si$: R_D, 0.2905; Si, 16.30. Found: R_D, 0.2915; Si, 16.10.

The monomer was polymerized to give a clear, hard acetone-soluble polymer which in appearance was very similar to polymethylmethacrylate.

Methacryloxymethyldimethylphenylsilane. Chloromethyldimethylphenylsilane[8] (92.3 g., 0.5 mole), sodium methacrylate (59 g., 0.55 mole), methacrylic acid (70 g., 0.82 mole), hydroquinone (7 g.), and dimethylformamide (150 g.) were heated at 60–70° for 18 hours and refluxed for one-half hour. Filtration yielded 27 g. of solids (theory for NaCl, 29 g.). The filtrate after dilution with benzene was washed with water until neutral and distilled in a still of ten plates to give 23 g. (0.13 mole) of chloromethyldimethylphenylsilane (26% recovery) and methacryloxymethyldimethylphenylsilane, b.p. 103° at 10 mm.; n_D^{25} 1.5045; d_4^{25} 0.991, in 84% yield based on unrecovered chloromethyl compound.

Anal. Calc'd for $C_{13}H_{18}O_2Si$; R_D, 0.2984; Si, 11.99. Found: R_D, 0.2990; Si, 11.86.

Polymerization yielded a hard, slightly yellow polymer which was insoluble in both acetone and benzene.

1,3-Bis(acryloxymethyl)tetramethyldisiloxane. Dry sodium acrylate (71 g., 0.75 mole) prepared from glacial acrylic acid practical grade, was dissolved, as described previously, in a mixture of practical glacial acrylic acid (200 g.) and hydroquinone (5 g.). Over a period of one half hour 1,3-bis(chloromethyl)tetramethyldisiloxane (77 g., 0.33 mole) was added at the reflux temperature of the reaction mixture. Refluxing was maintained for three hours. After cooling, the reaction mixture was mixed with an equal volume of benzene and then washed with water and sodium bicarbonate solution until neutral. The benzene solution was dried over sodium sulfate and the benzene was evaporated to give a residue of 97 g. (theory for product is 99.6 g., 0.33 mole).

The residue was distilled on a still of about ten plates at 1–2 mm. pressure using hydroquinone as an inhibitor; 56 g. of distillate was obtained in five cuts. The two middle cuts were combined, washed with sodium hydroxide to remove the hydroquinone that had distilled over, and dried over sodium sulfate to yield 1,3-bis(acryloxymethyl)-tetramethyldisiloxane, b.p. 123° at 1 mm.; n_D^{25} 1.4418, d_4^{25} 1.008.

Anal. Calc'd for $C_{12}H_{22}O_5Si_2$: R_D, 0.2615; Si, 18.57. Found: R_D, 0.2624; Si, 18.24.

Acryloxymethylpentamethyldisiloxane. This was prepared in the manner previously described for its methacrylate analog using a 6.5/1 molar ratio of hexamethyldisiloxane to 1,3-bis(acryloxymethyl)tetramethyldisiloxane. Acryloxymethylpentamethyldisiloxane was obtained by distillation at reduced pressure b.p. 113° at 50 mm.; n_D^{25} 1.4165; d_4^{25} 0.906.

Anal. Calc'd for $C_9H_{20}O_3Si_2$: R_D, 0.2758; Si, 24.15. Found: R_D, 0.2772; Si 24.48.

Polymerization yielded a clear, elastic high polymer which was soluble in acetone or benzene.

Polymerization. The monomers were polymerized in bulk by heating the sample at 70° using as a catalyst 0.05 to 0.1% by wt. of α,α'-azodi-iso-butyronitrile or benzoyl peroxide. A nitrogen atmosphere was maintained over the sample during the polymerization which required from 4 to 24 hours. Copolymerizations of methyl methacrylate (MMA) and methacryloxymethylpentamethyldisiloxane (SMA) corresponding to the monomer compositions shown in Table I were carried out at 70° under a nitrogen atmosphere for a period of 16 hours using 0.1% by wt. of α,α'-azodi-iso-butyronitrile.

Acknowledgment. The authors wish to thank Dr. O. K. Johannsen for the molecular weight determination of polymethacryloxymethylpentamethyldisiloxane.

CORNING GLASS AND DOW CORNING MULTIPLE FELLOWSHIP
MELLON INSTITUTE
PITTSBURGH, PENNA.

---

[8] J. E. Noll, J. L. Speier, and B. F. Daubert, *J. Am. Chem. Soc.*, **73**, 3867 (1951).

Reactions of *unsym*-Dimethylhydrazine with Acrylonitrile and with Chloroacetamide

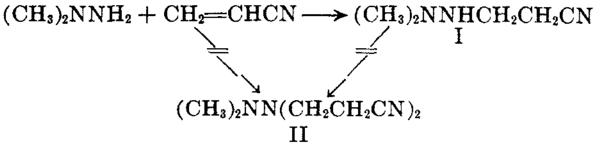
RICHARD L. HINMAN AND JAMES ROSENE

Received August 10, 1956

1,1-Dimethyl-2,2-hydrazino-diacetic and -dipropionic acids were desired for study as possible chelating agents. This paper reports two approaches, which, though unsuccessful, are of some interest in their own right.

The method selected for the preparation of 1,1-dimethyl-2,2-hydrazinodipropionic acid was cyanoethylation of *unsym*-dimethylhydrazine, followed by hydrolysis of the nitrile group. Monocyanoethylation of *unsym*-dimethylhydrazine was readily effected by refluxing an aqueous solution of the reactants for two hours. The product, 1,1-dimethyl-2-(β-cyanoethyl)hydrazine (I) was isolated in 87% yield. It is particularly interesting that the reaction occurred only when water was present. In another experiment the reactants were recovered unchanged from refluxing in wet ether which contained a few pellets of sodium hydroxide.

Various attempts were made to introduce two cyanoethyl groups into *unsym*-dimethylhydrazine. However, 1,1-dimethyl-2-(β-cyanoethyl)hydrazine (I) was the only product isolated from reactions in which the following sets of conditions were employed: (1) 4:1 molar ratio of acrylonitrile to dimethylhydrazine; (2) 4:1 molar ratio of acrylonitrile to hydrazine at 170° and 300 p.s.i.; (3) use of sodium hydroxide as a catalyst; (4) use of acetic acid as a solvent.



$$(CH_3)_2NNH_2 + CH_2{=}CHCN \longrightarrow (CH_3)_2NNHCH_2CH_2CN$$

I

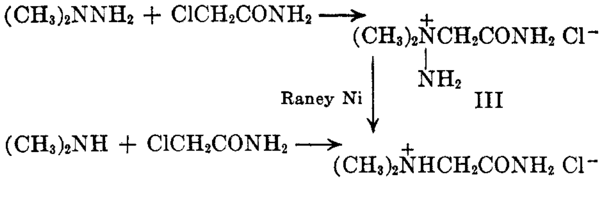
$$(CH_3)_2NN(CH_2CH_2CN)_2$$

II

In another attempt to prepare II, an aqueous solution of compound I was refluxed with excess acrylonitrile for 36 hours, but the starting materials were recovered.

The failure of *unsym*-dimethylhydrazine to undergo double cyanoethylation can be compared to the difficulty with which methylamine and ethylamine react with a second mole of acrylonitrile.[1] The amines do yield dicyanoethylated products, however, under conditions in which only monocyanoethylation of *unsym*-dimethylhydrazine occurs.

Although it is known that alkylhydrazines undergo alkylation on the nitrogen which already bears an alkyl group,[2,3] the reaction of chloroacetamide and *unsym*-dimethylhydrazine was examined as a possible route to the desired acetic acid derivative.



$$(CH_3)_2NNH_2 + ClCH_2CONH_2 \longrightarrow \underset{\textstyle NH_2}{(CH_3)_2\overset{+}{N}}CH_2CONH_2\ Cl^- \quad \text{III}$$

$$\Big\downarrow \text{Raney Ni}$$

$$(CH_3)_2NH + ClCH_2CONH_2 \longrightarrow (CH_3)_2\overset{+}{N}HCH_2CONH_2\ Cl^-$$

The product isolated was 1-carbamylmethyl-1,1-dimethylhydrazinium chloride (III) as shown by the following observations. Hydrogenolysis of the nitrogen-nitrogen bond with Raney nickel in ethanol[4] produced a crystalline solid which did not depress the melting point of an authentic specimen of N,N-dimethylaminoacetamide hydrochloride. The latter compound was prepared by passing dimethylamine into a solution of monochloroacetamide in dioxane.

Although no attempt was made to hydrolyze III, the hydrolysis of I was tried using the barium hydroxide method which has been employed in the hydrolysis of β-aminopropionitrile to β-alanine.[5] No identifiable material was isolated. Hydrolysis with concentrated hydrochloric acid was also unsuccessful. From an attempt to convert the nitrile to the corresponding amide using polyphosphoric acid[6] only resinous materials were isolated. An attempt was also made to convert I directly to the ester by refluxing with an ethanolic solution of hydrogen chloride, but again only tars were obtained.

EXPERIMENTAL[7]

1,1-Dimethyl-2-(β-cyanoethyl)hydrazine. Acrylonitrile (17.5 g., 0.33 mole) was added slowly to a refluxing solution of 30 g. (38 ml., 0.5 mole) of *unsym*-dimethylhydrazine in 40 ml. of water. After an additional two hours of heating the reaction mixture was distilled under reduced pressure. The principal fraction distilled at 80–90° (3 mm.) and weighed 33 g. (87%). The product was a colorless, odorless oil, n_D^{25} 1.441, d_4^{20} 0.92, which slowly turned red on standing.

1,1-Dimethyl-2-(β-cyanoethyl)-4-phenylthiosemicarbazide. Equal amounts of 1,1-dimethyl-2-(β-cyanoethyl)hydrazine and phenyl isothiocyanate were heated together for three minutes. The mixture solidified on cooling and was recrystallized three times from 95% ethanol. The pale yellow crystalline solid melted at 104–105°.

Anal. Calc'd for $C_{12}H_{16}N_4S$: C, 58.03; H, 6.49; N, 22.56. Found: C, 58.56; H, 6.39; N, 22.48.

1,1-Dimethyl-2-(β-cyanoethyl)hydrazine hydrochloride. A dioxane solution of 1,1-dimethyl-2-(β-cyanoethyl)hydrazine reacted with dry hydrogen chloride gas to form an insoluble oil which, after separation from the dioxane by decantation, solidified to a pale yellow wax. Three recrystallizations from a mixture of absolute ethanol and petroleum ether (b.p. 60–70°) (2:1) yielded a white crystalline deliquescent solid melting at 90–92°.

Anal. Calc'd for $C_5H_{12}ClN_3$: C, 40.12; H, 8.08. Found: C, 39.91; H. 8.40.

1-Carbamylmethyl-1,1-dimethylhydrazinium chloride. Dry monochloroacetamide (9.3 g., 0.10 mole) was mixed with 7.5 g. (0.13 mole) of *unsym*-dimethylhydrazine. After the initial exothermic reaction the mixture cooled and solidified. Three crystallizations of the solid from absolute ethanol yielded 7.5 g. (48%) of white crystals, m.p. 145–148°.

Anal. Calc'd for $C_4H_{12}ClN_3O$: C, 31.27; H, 7.87. Found: C, 31.09; H, 7.31.

N,N-Dimethylaminoacetamide hydrochloride. (*A*). A one-gram sample of 1-carbamylmethyl-1,1-dimethylhydrazinium chloride was subjected to Ainsworth's method[4] for hydrogenolysis of the nitrogen-nitrogen bond with Raney nickel. A few milligrams of crystalline material was obtained, which melted at 195–196° and did not depress the m.p. of the authentic specimen prepared as described below. (*B*). Dry dimethylamine gas was passed through a dioxane solution of monochloroacetamide. The white crystals which separated were removed by filtration and recrystallized from absolute ethanol. The product melted at 195–196°.

Anal. Calc'd for $C_4H_{11}ClN_2O$: C, 34.65; H, 8.01; N, 20.24. Found: C, 35.02; H, 8.01; N, 19.64.

DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

---

[1] H. A. Bruson in R. Adams, *Org. Reactions*, **5**, 79 (1949).

[2] C. D. Harries and T. Haga, *Ber.*, **31**, 58 (1898).

[3] O. Westphal, *Ber.*, **74**, 759 (1941).

[4] C. Ainsworth, *J. Am. Chem. Soc.*, **78**, 1635 (1956).

[5] J. H. Ford, *J. Am. Chem. Soc.*, **67**, 876 (1945).

[6] H. R. Snyder and C. T. Elston, *J. Am. Chem. Soc.*, **76**, 3039 (1954).

[7] Melting points and boiling points are uncorrected.

Some N-Substituted-5-oxo-2-pyrrolidinecarboxamides

R. B. ANGIER AND V. K. SMITH

Recieved August 13, 1956

The detection of a very slight anti-neoplastic activity[1] in N-benzyl-5-oxo-2-pyrrolidinecarboxamide (Ib)[2] led to the preparation of a number of its derivatives and analogs. This report describes a series of N-substituted derivatives of 5-oxo-2-pyrrolidinecarboxamide (Ia).

Several N-aryl derivatives of Ia have been de-

---

[1] Private communication from S. Halliday and D. McKenzie of this laboratory.

[2] Angier, U. S. Patent 2,651,639 (Sept. 8, 1953).