dence it may be surmised that biurea forms a triclinic crystal.

X-ray pictures of *p*-urazine were also prepared by Dr. Russell. A rotation picture and a zero layer picture of this substance seems to indicate an orthorhombic crystal with the following cell dimensions: a_0 = 5.58 Å; b_0 = 5.39 Å; c_0 = 6.63 Å.

On microscopic examination biurea appears as diamond-shaped crystals and shows inclined extinction, whereas *p*-urazine appears as rectangular-shaped crystals and these exhibit parallel extinction.

In the reaction of ammonia with the chlorinated urea product, ammonia may be acting as a dehydrohalogenating agent, exclusively, or may play a more important role in the reaction. If the former is the true situation, ethylamine should also produce biurea when it is treated with the chlorinated urea product. In the latter reaction a white solid was obtained that melted at 247–250° and gave a mixed melting point of 239–244° with biurea. Its properties and analysis indicates that it is diethylbiurea, $C_2H_5NHCONHNHCONHC_2H_5$.[6]

The above results would make one suspect that some intermediate product, such as oxycyanogen (O=C=N—N=C=O) is formed in a Hofmann type rearrangement. The latter product then reacts with ammonia and amines to form biurea and the dialkylbiurea, respectively.

We were unable to isolate either biurea or *p*-urazine from the solution resulting from the reaction of concentrated ammonium hydroxide with monochlorourea prepared by the method of Chalsty and Israelstam.[7] From these latter results one might suspect that monochlorourea is not the reactive species present in the chlorinated urea product.

EXPERIMENTAL

Preparation of the chlorourea products. The method of Chattaway[3] was employed to prepare a product corresponding closely in composition to monochlorourea.

Sixty grams (1 mole) of urea was dissolved in a minimum amount of water. To the resulting solution was added 120 g. (1.5 moles) of zinc oxide.[8] Chlorine gas was then slowly bubbled into the stirred reaction mixture. The temperature was maintained at or very nearly 0° during the addition of the chlorine. As chlorine was added the reaction mixture became momentarily clear. Then a white precipitate began to form and the reaction vessel became filled with a thick mass of crystals. The addition of chlorine was then stopped, but the agitation was continued a while longer to allow the dissolved chlorine to react with the unchanged urea. The white flake-like precipitate was then removed by filtration. Various samples prepared by the above procedure showed from 20 to 35% available chlorine (determined by an addition of excess potassium iodide-starch reagent and titration with standard thiosulfate). Calcd. for monochlorourea (CH_3ON_2Cl): Cl, 37.4. Maximum yield obtained: about 65%.

A product corresponding closely in composition to dichlorourea was obtained by direct chlorination of an aqueous solution of the product obtained above. A soft white solid product was obtained that showed 53.5% available chlorine. Calcd. for dichlorourea ($CH_2ON_2Cl_2$): Cl, 55.1. This product also reacted with an excess of concentrated aqueous ammonia to form biurea.

Biurea (*$H_2NCONHNHCONH_2$*). The chlorinated urea product (20–35% available chlorine) obtained above was dissolved in approximately 25 volumes of water. The resulting solution was slowly poured into an excess of concentrated aqueous ammonia. A vigorous evolution of gas occurred and the solution became yellow in color. On cooling a white precipitate formed. The resulting solid was separated by filtration and was crystallized from hot water, m.p. 255° dec.; yield 16%.

Method of Curtius and Heidenreich. Six grams (0.1 mole) of urea was heated with 2.5 g. (0.05 mole) of hydrazine hydrate in a closed tube at 130° for 1 hr. The residue was recrystallized from hot water. The yield of biurea was about 20% based upon the amount of urea employed.

Anal. Calcd. for biurea, $C_2H_6N_4O_2$; C, 20.38; H, 5.08; N, 47.4. Calcd. for *p*-urazine, $C_2H_4N_4O_2$: C, 20.7; H, 3.45; N, 48.3. Found for the ammoniated chlorourea product: C, 20.51, 20.47; H, 5.00, 5.01; N, 46.80, 46.53. Found for biurea prepared by the method of Curtius and Heidenreich[4]: C, 20.51; H, 5.06; N, 46.51. Found for *p*-urazine prepared by the method of Curtius and Heidenreich[4]: C, 20.85; H, 3.12; N, 47.54.

Diethylbiurea (*$C_2H_5NHCONHNHCONHC_2H_5$*). Five grams of the dichlorourea (53.5% available chlorine) prepared above was dissolved in 100 ml. of ice water. This solution was gradually poured into 10 g. of a 70% solution of ethylamine. A vigorous reaction ensued and much heat was generated. The white solid that formed melted at 247–250° and gave a depression of the melting point when mixed with biurea. Yield about 2 g. or 60% of the theory.

Anal. Calcd. for $C_6H_{14}N_4O_2$: C, 41.4; H, 8.05; N, 32.1. Found: C, 41.65, 41.80; H, 8.56, 8.26; N, 31.90, 31.99.

Stollé[9] has prepared diethylbiurea by the reaction of ethylamine on hydrazodicarbonazide ($N_3CONHNHCON_3$) and reported a melting point. of 255°. Mauguin[10] reported its melting point at 250°.

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[6] G. F. Grillot and R. C. Chang, U.S. Patent 2,855,435 (Oct. 7, 1958). Assigned to W. R. Grace & Co.

[7] J. S. Chalsty and S. S. Israelstam, *Chem. & Ind. (London)*, November 1954, page 1452.

[8] Lime (calcium oxide) can replace the zinc oxide in this preparation.

[9] R. Stollé, *Ber.*, **43**, 2470 (1910).

[10] C. Mauguin, *Ann. de chemie et de phys.* (8), **22**, 318 (1911).

The Dialkylation of Cyanoacetic Ester with Chloromethylmethylethoxysilanes

Omar W. Steward[1] and Leo H. Sommer

Received February 6, 1961

Sommer *et al.*[2] reported an attempt to introduce a second trimethylsilylmethyl group into malonic ester using chloromethyltrimethylsilane and diethyl sodiotrimethsilylmethylmalonate. The only product obtained was trimethylsilylmethyl ethyl ether, the product of a Williamson type reaction.

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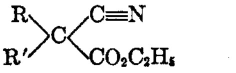
[1] Dow Corning Corp., Midland, Mich.

[2] L. H. Sommer, G. M. Goldberg, G. H. Barnes, and L. S. Stone, Jr., *J. Am. Chem. Soc.*, **76**, 1609 (1954).

Using the more reactive bromomethyltrimethylsilane, Eberson[3] was able to prepare diethyl bis-(trimethylsilylmethyl)-malonate in a 38.5% yield.

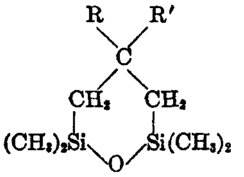
As it has been observed that cyanoacetic ester forms dialkylation products much more readily than malonic ester,[4,5] it was thought that dialkylation of cyanoacetic ester with chloromethylmethylethoxysilanes might be possible. Addition of chloromethyldimethylethoxysilane to ethyl sodiomethyldiethoxysilylmethylcyanoacetate gave ethyl (methyldiethoxysilylmethyl)-(dimethylethoxysilylmethyl)cyanoacetate (I) in a 55% yield.



I. R = $C_2H_5O(CH_3)_2SiCH_2$: R′ = $(C_2H_5O)_2(CH_3)SiCH_2$
II. R = H; R′ = $C_2H_5O(CH_3)_2SiCH_2$
III. R = R′ = $C_2H_5O(CH_3)_2SiCH_2$

Two dimethylethoxysilylmethyl groups can also be introduced into cyanoacetic ester simultaneously. When chloromethyldimethylethoxysilane was added to ethyl cyanoacetate dissolved in ethanol containing two moles of sodium ethoxide per mole of ester, a 34.5% yield of ethyl dimethylethoxysilylmethylcyanoacetate (II) and a 30% yield of ethyl bis(dimethylethoxy-silylmethyl)cyanoacetate (III) were obtained.

Hydrolysis of ethyl bis(dimethylethoxysilylmethyl)cyanoacetate (III) under acidic or basic conditions gave six-ring disiloxanes.[6]



IV. R = H R′ = CO_2H
V. R = C≡N R′ = $CO_2^-K^+$
VI. R = C≡N R′ = CO_2H

Refluxing compound III with a mixture of glacial acetic acid and concentrated hydrochloric acid gave 3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylic acid (IV) in an 80% yield. Addition of a solution of potassium hydroxide to compound III in ethanol gave a white crystalline precipitate which was identified as potassium 1-cyano-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylate (V), a 77% yield. Acidification of compound V gave 1-cyano-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylic acid (VI). The infrared spectra of the above disiloxanes showed the siloxane absorption maxima between 9.8–10.1 μ indicating the six-membered ring structure.[6] The position of the absorption band seemed to vary somewhat with the polarity of the groups on the ring.

EXPERIMENTAL

Starting materials. Ethyl cyanoacetate was obtained from the Eastman Kodak Co. Chloromethyldimethylethoxysilane[7] was prepared by the reaction of the corresponding chlorosilane with absolute ethanol. The preparation of ethyl methyldiethoxysilylmethylcyanoacetate has been reported previously.[8]

Preparation of ethyl (methyldiethoxysilylmethyl)(dimethylethoxysilylmethyl)cyanoacetate (I). Ethyl methyldiethoxysilylmethylcyanoacetate (92.6 g., 0.35 mole) was added rapidly to a sodium ethoxide solution, prepared from sodium (8.2 g., 0.35 g.-atom mole) and absolute ethanol (200 ml.). The mixture was heated to reflux, and chloromethyldimethylethoxysilane (55.2 g., 0.35 mole) was added over a period of 0.5 hr. The resulting mixture was refluxed with stirring for 72 hr. The reaction mixture was filtered, and the filtrate was distilled through a Claisen heat separating the ethanol from the higher boiling material. Fractional distillation of the higher boiling material gave compound I, b.p. 170° (7 mm.), n_D^{20} 1.4384, d_{20}^{D} 0.9982, a 55% yield.

Anal. Calcd. for $C_{16}H_{33}NO_5Si_2$: Si, 14.95; MR_D, 99.3; sap. equiv., 375. Found: Si, 15.2; MR_D, 98.8; sap. equiv., 376, 381.

Very mild conditions were used to determine the saponification equivalent in order to prevent hydrolysis of the cyano group. Samples were added to 1*N* potassium hydroxide in Butyl Cellosolve and allowed to stand at room temperature for approximately 1 hr.

Preparation of ethyl dimethylethoxysilylmethylcyanoacetate (II) *and ethyl bis(dimethylethoxysilylmethyl)cyanoacetate* (III). Ethyl cyanoacetate (113.1 g., 1.0 mole) was added to a sodium ethoxide solution, prepared from sodium (46.0 g., 2.0 g.-atoms) and ethanol (1 l.). Sodium iodide (10 g.) was added followed by addition of chloromethyldimethylethoxysilane (305.2 g., 2.0 moles) over a period of 2.5 hr. The resulting mixture was refluxed for 42 hr. The reaction mixture was filtered, and the filtrate was distilled through a Claisen head separating the ethanol from the higher boiling material. Fractional distillation of the higher boiling material gave: Compound II (79.2 g., 0.43 mole), b.p. 123° (6 mm.), n_D^{20} 1.4340, d_D^{20} 0.9868, a 34.5% yield.

Anal. Calcd. for $C_{10}H_{19}NO_3Si$: Si, 12.2; MR_D, 60.34. Found: Si, 12.4; MR,, 60.50. Compound III (104.0 g., 0.30 mole), b.p. 159° (6 mm.), n_D^{20} 1.4430, d^{20} 0.9805, a 30.1% yield.

Anal. Calcd. for $C_{15}H_{31}NO_4Si_2$: Si, 16.25; MR_D, 93.88. Found: Si, 16.25; MR_D, 93.39.

Reactions of ethyl bis(dimethylethoxysilylmethyl)cyanoacetate (III).

A. *With acetic acid–concentrated hydrochloric acid.* Compound III (83.4 g., 0.24 mole), acetic acid (120 g., 2.0 moles) and concd. hydrochloric acid (35 ml.) were placed in a 500-ml. flask connected to a glass packed column. The mixture was heated to reflux, and the ethyl acetate formed by transesterification was removed at various times. When no more ethyl acetate was formed, the remaining acetic acid and water were removed under reduced pressure leaving a white crystalline solid. This solid was dissolved in a mixture of water (100 ml.) and ether (100 ml.). The layers were separated, and the water layer was extracted with 50 ml. of ether. Benzene (50 ml.) was added to the combined ether layer. The ether was removed through a column followed by the benzene-water azeotrope and benzene. A white crystalline solid remained which was dried under reduced pressure. On recrystallization from petroleum ether (b.p. 35–60°),

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[3] L. Eberson, *Acta. Chem. Scand.*, 8, 1083 (1954).

[4] A. C. Cope, H. L. Holmes, and H. O. House, *Org. Reactions*, 9, 121 (1957).

[5] F. C. B. Marshall, *J. Chem. Soc.*, 2754 (1930).

[6] L. H. Sommer, J. M. Masterson, O. W. Steward, and R. H. Leitheiser, *J. Am. Chem. Soc.*, **78**, 2010 (1956).

[7] H. Freiser, M. V. Eagle, and J. Speier, *J. Am. Chem. Soc.*, 75, 2824 (1953).

the product, 3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylic acid (IV),[8] 42.2 g., 0.193 mole, m.p. 143–144°, was obtained in an 80% yield. The infrared spectra of the two acids in carbon tetrachloride were identical and showed strong siloxane absorption bands with the maxima at 10.07 ± 0.02 μ.

B. *With potassium hydroxide.* Potassium hydroxide (10.9 g., 0.195 mole), dissolved in 38 ml. of water, was added with stirring to compound III (66.8 g., 0.193 mole), dissolved in 150 ml. of ethanol. A white crystalline solid precipitated almost immediately. The solid was recrystallized from 95% ethanol and dried by heating on the steam bath at a pressure of less than 1 mm. for 3 days. The product, potassium 1-cyano-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylate (V), 41.8 g., 0.148 mole, a 77% yield, crystallized in the form of white needles which sublimed on heating.

Anal. Calcd. for $C_9H_{16}KNO_3Si_2$: Si, 19.95. Found: Si, 19.7.

The infrared spectrum (potassium bromide plate) showed the siloxane absorption maximum at 9.94 ± .02 μ.

Compound V (41.6 g., 0.148 mole) was dissolved in 900 ml. of water. The solution was filtered, and concd. hydrochloric acid was added until no more precipitate formed. The precipitate was filtered, washed four times with 50-ml. portions of water, and was dried at a pressure of less than 1 mm. overnight. The product, 1-cyano-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylic acid (VI), 31.4 g., 0.140 mole, m.p. 128.5–129.5°, was obtained in a 94.7% yield.

Anal. Calcd. for $C_9H_{17}NO_3Si_2$: Si, 23.1; neut. equiv., 243. Found: Si, 23.1; neut. equiv., 241.

The infrared spectrum in carbon tetrachloride showed the siloxane absorption maximum at 9.93 ± .02 μ (potassium bromide plate—9.88 ± .02 μ).

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[8] 3,3,5,5-Tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylic acid (IV), m.p. 145°, was prepared previously by saponification and decarboxylation of diethyl 3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1,1-dicarboxylate, obtained by the malonic ester synthesis using bis(chloromethyl)tetramethyldisiloxane.[6]

The Reaction Product of Hydroxypivalaldehyde and Ammonia

ROBERT H. HASEK AND JAMES C. MARTIN

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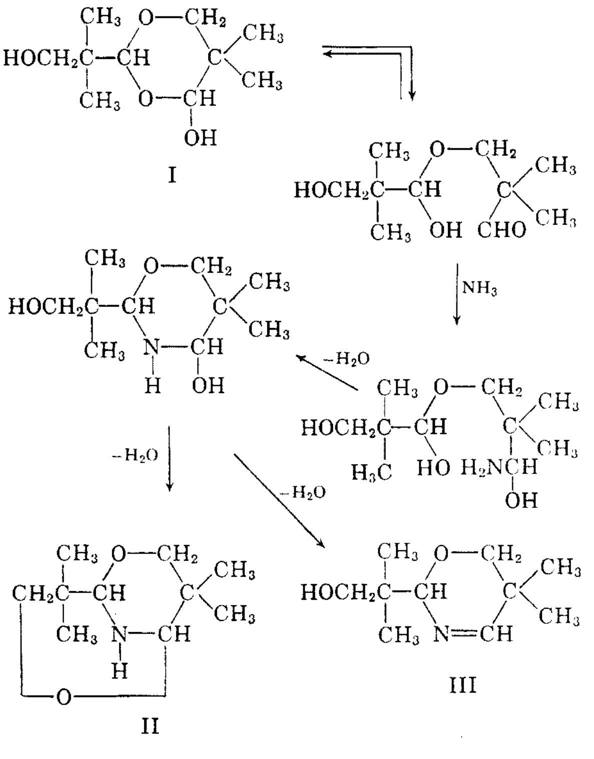
Späth and Szilagyi obtained a crystalline compound, $C_{10}H_{19}NO_2$, from the treatment of 4-hydroxy-β,β,5,5-tetramethyl-2-*m*-dioxaneethanol (hydroxypivalaldehyde dimer, I) with ammonia, and proposed the bicyclic structure II as the formula of this compound.[1]

During recent work on ammonia derivatives of tertiary aldehydes, we prepared Späth and Szilagyi's compound and examined its infrared and NMR spectra. The infrared spectrum showed strong absorption at 3.1 μ [—OH]; 6.1 μ [>C=N—]; 7.25, 7.35 μ [>C(CH_3)$_2$]; and 9.2, 9.4 μ [C—O—C]. The NMR spectrum[2] showed one —CH=N— proton at −100 c.p.s.,[3] one —OH proton at 8 c.p.s., CH and CH_2 protons at 55 c.p.s., and CH_3 protons at 150 c.p.s.[4] No N—H proton peak was detected. These spectra indicated that a more likely formulation of the compound is 5,6-dihydro-β,β,5,5-tetramethyl-2H-1,3-oxazine-2-ethanol (III). This conclusion was strengthened by the infrared spectrum of the phenylisocyanate derivative which still showed strong absorption at 6.1 μ [>C=N—], indicative of the phenylurethane of III rather than the phenylurea of II.

The reaction of I and ammonia presumably takes the course suggested by Späth and Szilagyi, except in the last step, where elimination of water results in the formation of the dihydrooxazine ring rather than the bicyclic structure II. Apparently, III is the first recognized example of the 5,6-dihydro-2H-1,3-oxazine ring system.[5]



Destructive distillation of III gave, after removal of formaldehyde, isobutyraldehyde, and other volatile products, a tarry residue from which a low yield of 4,4,8,8,12,12-hexamethyl-2,6,10-trioxa-13-azatricyclo[7.3.1.0^{5,13}]tridecane (IV) was iso-

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(1) E. Späth and I. V. Szilagyi, *Monatsh. Chem.*, **76**, 77 (1946).

(2) NMR spectra were obtained by means of a Varian V4300B NMR spectrometer operating at 40 mc. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of water.

(3) R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 1822 (1961).

(4) Spectrum determined on a 50% solution of III in carbon tetrachloride.

(5) N. H. Cromwell, *Heterocyclic Compounds*, Vol. 6, R. C. Elderfield, ed., Wiley, New York, 1957, p. 534.