Thermolysis of Trimethylamine-β-carboxypropionimide and Its Derivatives

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Received January 15, 1973

Thermolysis of trimethylamine-β-carboxypropionimide gave carbon dioxide, water, formaldehyde, trimethylamine, methanol, ammonium bicarbonate, 1-methylene-2,2-dimethylhydrazine, methyl succinate, *N*-methylsuccinimide, and *N*-dimethylaminosuccinimide. The sodium salt in the same reaction gave polymeric material. The methyl ester gave trimethylamine, methanol, methyl acrylate, trimer of methyl isocyanate, methyl β-carbomethoxyaminopropionate, methyl β-succinimidopropionate, *N*-dimethylaminosuccinimide, and 1,2,3,4,5,6-hexahydro-2,4-dioxopyrimidine. The *N*-phenyl- and *N*-ethylamides gave mainly the corresponding 1,2,3,4,5,6-hexahydro 3-substituted 2,4-dioxopyrimidines and *N*-substituted succinimides. Reactions schemes are presented for the formation of abnormal products in these reactions.

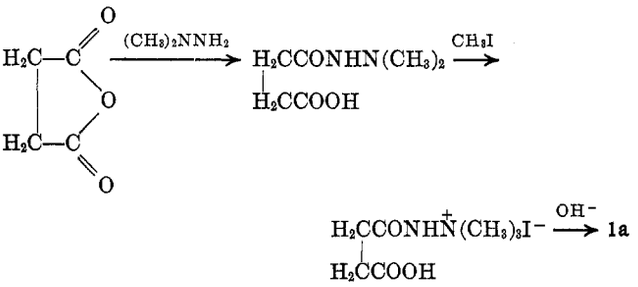
The generation of isocyanato groups in molecules containing an adjacent carboxyl or amide group is useful synthetically for the formation of heterocyclic compounds. 2-Carboxy-3-nitrobenzazide, for example, on heating gave 3-nitroisatoic anhydride.[2] *N*-Methylphthalamide when treated with potassium hypobromite gave 1,2,3,4-tetrahydro-3-methyl-2,4-dioxoquinazoline.[3]

In the present work this type of reaction has been investigated with monoaminimides derived from succinic acid and its derivatives (**1**); aminimides on thermolysis give isocyanates.[4]

$(CH_3)_3\overset{+}{N}\overset{-}{N}COCH_2CH_2COR$

1a, R = ONa
b, R = OH
c, R = OCH_3
d, R = NHC_6H_5
e, R = NHC_2H_5

Sodium trimethylamine-β-carboxylatepropionimide (**1a**) was prepared from succinic anhydride using the following series of reactions.

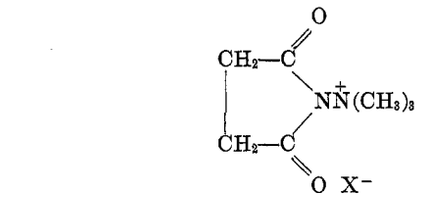


The acid **1b** was prepared from the salt **1a** by the addition of hydrochloric acid. Evidence for the structure of **1b** were infrared absorptions at 1540 cm^{-1} for the aminimide group and 1710 cm^{-1} for the acid. The methyl ester **1c** was synthesized from β-carbomethoxypropionyl chloride using similar reactions to that for the sodium salt **1a**. The amides **1d** and **1e** were prepared by treating the acid **1b** with phenyl isocyanate and ethyl isocyanate, respectively.

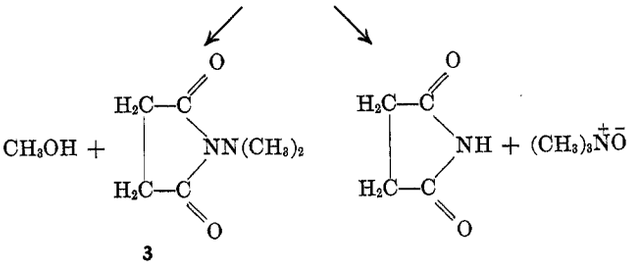
Thermolysis of the sodium salt **1a** neat occurred at a temperature of 250° and proceeded almost explosively. The product was a brittle brown solid which could not be characterized. A similar product was obtained by heating the salt in tetramethylene glycol dimethyl ether.

The thermolysis of the acid **1b** occurred at a lower temperature than that of the salt **1a** and gave the following products: carbon dioxide, water, formaldehyde, trimethylamine, methanol (26.3%), ammonium bicarbonate (3.22%), 1-methylene-2,3-dimethylhydrazine (5.37%), methyl succinate (1.51%), *N*-methylsuccinimide (4.75%), *N*-dimethylaminosuccinimide (49%), methyl β-succimidopropionate (10.4%), and polymeric material.

The formation of *N*-dimethylaminosuccinimide (**3**) in the largest amount suggests that the aminimide **1b** cyclizes during the thermolysis to the quaternary ammonium hydroxide **2a**, which would behave thermally



2a, X^- = OH^-
b, X^- = $^-OOCCH_2CH_2CO\overset{-}{N}\overset{+}{N}(CH_3)_3$
c, X^- = OCH_3^-



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like tetramethylammonium hydroxide and form *N*-dimethylaminosuccinimide (**3**), methanol, succinimide, and trimethylamine oxide.

The base **2a** can also react with the aminimide **1b** and form a salt **2b** which thermally can act as a methylating agent similar to other quaternary ammonium salts,[5] and form the methyl ester of the aminimide **1c** and *N*-dimethylaminosuccinimide (**3**). Salts between **2a** and succinimide and trimethylamine oxide in a similar reaction would lead to *N*-methylsuccinimide and the methoxytrimethylammonium ion which is the source of the formaldehyde isolated.[6] The methyl ester of the aminimide **1c** thus formed decomposes normally and forms β-carbomethoxyethyl isocyanate, which can undergo either an elimination reaction with the formation of methyl acrylate and isocyanic acid or hydrolysis

(1) Abstracted in part from the Ph.D. Thesis of J. N. K., June 1973.
(2) T. Curtius and A. Semper, *Ber.*, **46**, 1162 (1913).
(3) F. S. Spring and J. C. Woods, *J. Chem. Soc.*, 625 (1945).
(4) S. Wawzonek and R. C. Gueldner, *J. Org. Chem.*, **30**, 3031 (1965); M. S. Gibson and A. W. Murray, *J. Chem. Soc.*, 880 (1965); R. F. Smith and P. C. Briggs, *Chem. Commun.*, 120 (1965).
(5) A. T. Lawson and N. Collie, *J. Chem. Soc.*, **53**, 624 (1888).
(6) J. Meishenheimer, *Justus Liebigs Ann. Chem.*, **397**, 273 (1913).

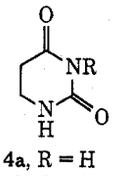
to methyl β-aminopropionate and carbon dioxide. The methyl acrylate thus produced converts a portion of the succimide present to *N*-β-carbomethoxyethylsuccinimide and may be also the basis of the polymer isolated. The isocyanic acid is the precursor of the ammonium bicarbonate isolated.

The source of the small amount of methyl succinate isolated may be the action of base on *N*-dimethylaminosuccinimide (**3**) followed by alkylation *via* **2a**. The yield of 1,1-dimethylhydrazine, the precursor of the methylenedimethylhydrazine isolated, actually is slightly higher (5.31%) than that of methyl succinate (1.51%) and suggests that a portion of the latter may be involved in the formation of *N*-β-carbomethoxyethylsuccinimide.

The thermolysis of **1b** in dimethylformamide gave **3** (52.8%), methyl succinate (5.6%), *N*-methylsuccinimide (5.6%), methyl β-succinimidopropionate (17.6%), and methyl *N*,*N*-dimethylsuccinamate (18.5%). The last compound would be derived from dimethylformamide, since the corresponding acid, for example, can be made from succinic anhydride and dimethylformamide in a 90% yield.[7]

The attempt to confirm the intermediacy of **2a** in the thermolysis of **1b** by synthesis from *N*-dimethylaminosuccinimide (**3**) was not successful. Alkylation of **3** could only be carried out with dimethyl sulfate. Hydrolysis of the salt with barium hydroxide required 3 weeks at steam-bath temperatures and gave a glassy material which upon treatment with hydriodic acid gave trimethylhydrazinium iodide as the only identifiable product.

The decomposition of the methyl ester of the aminimide **1c**, which is extremely hygroscopic, gave products which confirmed its intermediacy in the decomposition of **1b**. The following compounds were isolated: trimethylamine, methanol (11.9%), methyl acrylate (24.8%), trimethyl-*s*-triazine(1*H*,3*H*,5*H*)trione (trimer of methyl isocyanate) (1.3%), methyl β-carbomethoxyaminopropionate (3.6%), methyl β-succinimidopropionate (1.7%), *N*-dimethylaminosuccinimide (**3**) (20.8%), and 1,2,3,4,5,6-hexahydro-2,4-dioxopyrimidine (**4a**) (7.1%). Approximately one half of the products can be explained by the thermolysis of the ester **1c** to β-carbomethoxyethyl isocyanate, which can either eliminate isocyanic acid and form acrylate, or react with methanol and give the carbamate.



4a, R = H
b, R = C_6H_5
c, R = C_2H_5

The formation of *N*-dimethylaminosuccinimide (**3**) is indicative of a cyclization reaction of **1c** to a similar intermediate (**2c**) to that formed from the acid **1b**. This intermediate (**2c**) would react with isocyanic acid and form a salt which on thermolysis would give **3**, methanol, and methyl isocyanate. The last compound forms the trimer isolated. Thermolysis of **2c** to succinimide must also occur to a small extent, since the methyl acrylate adduct was formed.

β-Carbomethoxyethyl isocyanate is also the precursor of the pyrimidine. Hydrolysis with traces of water would lead to methyl β-aminopropionate, which after reaction with isocyanic acid would give a urea that would cyclize thermally to **4a**.

The thermolysis of trimethylamine-β-(phenylcarbamoyl)propionimide (**1d**) paralleled that of the ester **1c** and gave *N*-dimethylaminosuccinimide (**3**) (6%), 1,2,3,4,5,6-hexahydro-3-phenyl-2,4-dioxopyrimidine (**4b**) (8.5%), methylaniline (7.1%), aniline (25.7%), and *N*-phenylsuccinimide (29.4%). The first four products would be formed by steps similar to those shown for the ester **1c**. The formation of *N*-phenylsuccinimide must proceed by the displacement of trimethylamine imine from **1d**.

Trimethylamine-β-(ethylcarbamoyl)propionimide (**1e**) in the same reaction gave only 1,2,3,4,5,6-hexahydro-3-ethyl-2,4-dioxopyrimidine (**4c**) (81.6%) and *N*-ethylsuccinimide (14.1%).

Experimental Section[8]

***N*,*N*-Dimethylaminosuccinamic Acid.**—A solution of succinic anhydride (50.2 g) in acetonitrile (300 ml) when treated at its boiling point dropwise with 1,1-dimethylhydrazine (38 g) gave a white, insoluble precipitate. The resulting mixture was refluxed for an additional 0.5 hr, cooled, and filtered. The resulting white solid (63.2 g) upon recrystallization from ethanol melted at 158.5–159.0°: ir (Nujol) 3300 (NH), 3200–2500 (COOH), 1715, 1640 cm^{-1} (CO); nmr (D_2O) δ 2.64 [s, 6, $N(CH_3)_2$] and 2.52 (m, 4, CH_2CH_2).

Anal. Calcd for $C_6H_{12}N_2O_3$: C, 44.99; H, 7.55; N, 17.49. Found: C, 44.69; H, 7.84; N, 17.56.

1,1,1-Trimethyl-2-(β-carboxypropionyl)hydrazinium Iodide.—A solution of *N*-dimethylaminosuccinamic acid (120 g) in a mixture of acetonitrile (550 ml) and water (90 ml) was treated dropwise at its boiling point with methyl iodide (137.0 g). The resulting solution was refluxed for 2 hr and the solvent was removed under reduced pressure. The solid obtained was recrystallized from a mixture of methanol and ether: yield 172 g; mp 137–138.5°; ir (Nujol) 3280 (NH), 3000–2500 (COOH), 1698 cm^{-1} (CO); nmr (D_2O) δ 3.78 [s, 9, $N(CH_3)_3$], 2.70 (s, 4, CH_2-CH_2).

Anal. Calcd for $C_7H_{15}N_2O_3I$: C, 27.83; H, 5.01; N, 9.27. Found: C, 27.71; H, 5.07; N, 9.27.

Sodium Trimethylamine-β-Carboxylatepropionimide (1a).—A solution of the hydrazinium iodide (46.0 g) in water (200 ml) was neutralized with 1 *N* sodium hydroxide. Removal of the water under reduced pressure gave a solid which was mixed with sand and extracted with dry acetone for 2 weeks to remove the sodium iodide. The resulting mixture was dissolved in methanol and filtered. Removal of the methanol gave a solid which was recrystallized from a methanol–ethyl acetate mixture: yield 26.1 g; mp 246° dec; ir (Nujol) 1610–1540 cm^{-1} (CO); nmr (D_2O) δ 3.40 [s, 9, $N(CH_3)_3$], 2.37 (m, 4, CH_2CH_2).

Anal. Calcd for $C_7H_{13}N_2O_3Na$: C, 42.85; H, 6.69; N, 14.28. Found: C, 42.65; H, 6.95; N, 14.32.

Trimethylamine-β-carboxypropionimide (1b).—A solution of the sodium salt (13.27 g) in 50% methanol (100 ml) was treated with 50 ml of 1.3535 *N* hydrochloric acid. Removal of the solvent followed by extraction with hot chloroform gave a solid which was recrystallized from methanol–ether: yield 10.6 g; mp 150.5–151.5° dec; ir (Nujol) 3000–2500 (COOH), 1710, 1540 cm^{-1} (CO); nmr (D_2O) δ 3.48 [s, 9, $N(CH_3)_3$], 2.42 (s, 4, CH_2-CH_2).

Anal. Calcd for $C_7H_{14}N_2O_3$: C, 48.31; H, 8.37; N, 16.23. Found: C, 48.26; H, 8.10; N, 16.08.

(7) G. M. Coppinger, *J. Amer. Chem. Soc.*, **76**, 1372 (1954).

(8) Melting points were corrected; boiling points were not corrected. Infrared spectra were obtained using a Perkin-Elmer 137B infrared spectrophotometer and nmr spectra were recorded with a Varian A-60 nmr spectrometer. Mass spectra were measured using a Hitachi RMU6E mass spectrometer. Gas chromatographic analysis were carried out with a Hewlett-Packard Model 5750B research gas chromatograph.

Pyrolysis of Trimethylamine-β-carboxypropionimide (1b). A. Solid.—The aminimide (0.8 g) was heated in a distilling flask at 180–190° until the evolution of trimethylamine ceased. The volatile products were a liquid and a white solid which was partially soluble in the liquid. The white solid (0.35 g) from its chemical behavior and ir and nmr spectra was identified as ammonium bicarbonate.

The liquid, which gave a positive chromotropic acid test for formaldehyde, was neutralized with hydrochloric acid and the solution was extracted with benzene. Neutralization of the acid extract followed by glc analysis indicated the presence of ammonia, 1,1-dimethylhydrazine, and trimethylamine.

Direct analysis of the original distillate by gas chromatography and nmr indicated the presence of the following compounds: ammonium bicarbonate (0.45 g), water (0.28 g), methanol (1.49 g), and 1-methylene-2,2-dimethylhydrazine (0.55 g).

The residue (20.9 g) from the pyrolysis was dissolved in benzene and filtered from an insoluble solid (3.96 g), and was found on the basis of gas chromatography using a silicone rubber W98 column and tlc on silica to consist of four components. Chromatography using a silica gel column and eluting with benzene and benzene–ethyl acetate (19:1) gave the following compounds: methyl succinate (0.39 g), *N*-methylsuccinimide (0.95 g), *N*-dimethylaminosuccinimide (**3**) (12.2 g), and methyl β-(*N*-succinimido)-propionate (3.4 g). The first three compounds were identified by comparison with authentic samples. The last compound was identical with a sample synthesized from methyl β-aminopropionate.

The residue insoluble in benzene was polymeric in nature and was not investigated further.

B. Solution in Dimethylformamide.—A solution of the aminimide (2.42 g) in dimethylformamide (10 ml) was refluxed until the evolution of trimethylamine ceased. Removal of the dimethylformamide under reduced pressure gave a black, oily residue (1.98 g) which upon the basis of gas chromatographic analysis using a 10% silicone rubber W98 column contained dimethyl succinate (5.6%), *N*-methylsuccinimide (5.6%), *N*,*N*-dimethylaminosuccinimide (**3**) (52.8%), methyl *N*,*N*-dimethylsuccinamate (18.5%), and methyl β-succinimidopropionate (17.6%) in the relative percentages listed. Ammonium bicarbonate (0.3 g) was also isolated as a sublimate in the condenser used in the pyrolysis.

Methyl β-Succinimidopropionate.—A mixture of methyl β-aminopropionate hydrochloride (21.0 g) in benzene (500 ml) was treated at room temperature dropwise with succinyl chloride (23.3 g) and then refluxed for 12 hr. The resulting dark brown solution was filtered and gave upon removal of the benzene and fractional distillation a colorless liquid: bp 143–145° (1 mm); n^{26}D 1.4794; yield 15.6 g; ir (neat) 1775, 1715 (imide), 1760 cm^{-1} ($COOCH_3$); nmr ($CDCl_3$) δ 3.77 (t, 2, NCH_2), 3.66 (s, 3, OCH_3), 2.72 (s, 4, CH_2CH_2), 2.58 (t, 2, CH_2C); mol wt 185 (mass spectrum).

Anal. Calcd for $C_8H_{11}NO_4$: C, 51.89; H, 5.99; N, 7.57. Found: C, 51.78; H, 5.99; N, 7.45.

Methyl *N*,*N*-Dimethylaminosuccinamate Hydrochloride.—*N*,*N*-Dimethylaminosuccinamic acid (40.0 g) was refluxed with a solution of hydrogen chloride (23.0 g) in methanol (400 ml) for 17 hr. Removal of the solvent gave a liquid which separated into two layers. The smaller layer (5.7 g) was dimethyl succinate. The larger layer (44.2 g) was purified by crystallization from methanol–ether and gave white crystals melting at 109.5–11.5°: ir (Nujol) 3420 (NH), 2770 (NH^+), 1750, 1710 cm^{-1} (CO); nmr (D_2O) δ 3.65 (s, 3, CH_3O), 3.20 [s, 6, $NH(CH_3)_2$], 2.65 (s, 4, CH_2CH_2).

Anal. Calcd for $C_7H_{15}N_2O_3Cl$: C, 39.91; H, 7.18; N, 13.30. Found: C, 39.91; H, 7.09; N, 13.21.

Methyl *N*,*N*-Dimethylaminosuccinamate. A.—A suspension of the hydrochloride (17.5 g) in ether (400 ml) was treated with triethylamine (10.1 g). Filtration of the resulting mixture followed by removal of the ether gave a white solid which was recrystallized from benzene–hexane, yield 4.1 g, mp 93–95°.

B.—A solution of β-carbomethoxypropionyl chloride (37.6 g) in ether (200 ml) at 10–20° was treated with a mixture of dimethylhydrazine (16.0 g) and trimethylamine (50 g) in ether (300 ml). The reaction mixture was stirred at room temperature for 4 hr and filtered. The filtrate upon removal of the solvent gave a pale yellow solid (11.0 g). More of this solid was obtained by extracting the precipitate of amine hydrochlorides with three 300-ml portions of ethyl acetate. Recrystallization of the solid from toluene gave white crystals melting at 93–95°: yield 36.2 g; ir (Nujol) 3290, 3190 (NH), 1740, 1680 cm^{-1} (CO); nmr (D_2O) δ 3.75 (s, 3, CH_3O), 2.62 (m, 4, CH_2CH_2), 2.58 [s, 6, $N(CH_3)_2$].

Anal. Calcd for $C_7H_{14}N_2O_3$: C, 48.26; H, 8.10; N, 16.08. Found: C, 47.94; H, 8.26; N, 15.95.

1,1,1-Trimethyl-2-β-carbomethoxypropionylhydrazinium Iodide.—A solution of methyl *N*,*N*-dimethylaminosuccinamate (30.0 g) and methyl iodide (32 g) in acetonitrile (500 ml) was refluxed for 3.5 hr. Removal of the acetonitrile gave a solid which was recrystallized from methanol–ether: yield 49.9 g; mp 132.5–3.5°; ir (Nujol) 3205 (NH), 1735, 1690 cm^{-1} (CO); nmr (D_2O) δ 3.88 [s, 12, $N(CH_3)_3$, CH_3O], 2.83 (m, 4, CH_2CH_2).

Anal. Calcd for $C_8H_{17}N_2O_3I$: C, 30.39; H, 5.42; N, 8.86. Found: C, 30.21; H, 5.38; N, 8.80.

1,1,1-Trimethyl-2-β-carbomethoxypropionylhydrazinium Chloride.—This compound was prepared in a similar fashion to the iodide by heating the ester and methyl chloride in a Paar bomb at 100° for 16 hr. The chloride was recrystallized from methanol–ether and melted at 165.0° dec: yield 82.5%; ir (Nujol) 3010 (NH), 1745, 1695 cm^{-1} (CO); nmr (D_2O) δ 3.77 [s, 9, $N(CH_3)_3$], 3.75 (s, 3, CH_3O), 2.72 (s, 4, CH_2CH_2).

Anal. Calcd for $C_8H_{17}N_2O_3Cl$: C, 42.76; H, 7.62; N, 12.47. Found: C, 42.89; H, 7.87; N, 12.67.

Trimethylamine-β-carbomethoxypropionimide (1c).—A solution of the hydrazinium chloride (44.9 g) in water (100 ml) was neutralized with 1 *N* sodium hydroxide. Removal of the water gave a solid which was extracted with hot ethyl acetate (400 ml). The ethyl acetate solution gave upon evaporation of the solvent a white solid, which upon crystallization from ethyl acetate melted at 114–6.5°; yield 33.1 g; ir (Nujol) 1740 ($COOCH_3$), 1580 cm^{-1} (CON); nmr (D_2O) δ 3.64 (s, 3, CH_3O), 3.39 [s, 9, $N(CH_3)_3$], 2.42 (m, 4, CH_2CH_2).

Anal. Calcd for $C_8H_{16}N_2O_3$: C, 51.05; H, 8.57; N, 14.89. Found: C, 50.68; H, 8.65; N, 14.83.

The hydrazinium iodide in the same reaction gave a mixture of the aminimide and sodium iodide which could only be separated by preparative thin layer chromatography.

Pyrolysis of Trimethylamine-β-carbomethoxypropionimide (1c).—Pyrolysis of the solid aminimide (10.4 g) was carried out in a distillation flask at 190–200°. The liquid collected consisted of trimethylamine (0.09 g), methanol (0.21 g), and methyl acrylate (1.18 g).

A chloroform extract of the residue (4.92 g) in the distilling flask upon separation by chromatography on silica gel using benzene and benzene–ethyl acetate as eluting solvents gave trimethyl-*s*-triazine(1*H*,3*H*,5*H*)trione (1.20 g), mp 174–176° (lit.[9] mp 176°), methyl β-carbomethoxyaminopropionate (0.32 g), mp 29–31° (lit.[10] mp 33.5°), methyl β-succinimidopropionate (0.17 g), *N*-dimethylaminosuccinimide (**3**) (1.63 g), and 1,2,3,4,5,6-hexahydro-2,4-dioxopyrimidine (**4a**) (0.45 g), mp 273–277° dec (lit.[11] mp 275°). Identification in all cases was made by comparison with authentic samples.

The remainder of the pyrolysis residue (1.15 g) was a black, viscous oil which was not investigated further.

Trimethylamine-β-phenylcarbamoylpropionimide (1d).—This compound was prepared from trimethylamine-β-carboxypropionimide and phenyl isocyanate in a 48.2% yield by slight modification of the procedure used for the ethyl derivative. The original product obtained was dissolved in water to remove diphenylurea: mp 169–170.5°; ir (Nujol) 3220 (NH), 1680 (CONH), 1550 cm^{-1} (CON); nmr (D_2O) δ 7.22 (m, 5, C_6H_5), 3.18 [s, 9, $N(CH_3)_3$], 2.43 (m, 4, CH_2CH_2).

Anal. Calcd for $C_{13}H_{19}N_3O_2$: C, 62.63; H, 7.68; N, 16.86. Found: C, 62.83; H, 7.68; N, 16.53.

Trimethylamine-β-(ethylcarbamoyl)propionimide (1e).—A solution of trimethylamine-β-carboxypropionimide (20.0 g) and ethyl isocyanate (16.0 g) in chloroform (400 ml) was refluxed for 2.5 hr. Removal of the solvent gave a solid, which was triturated with ether and then refluxed in acetonitrile (50 ml) with decolorizing carbon for 1 hr. Filtration followed by removal of the solvent gave a white solid which was recrystallized from acetonitrile: yield 12.9 g; mp 167.5–169.5°; ir (Nujol) 3360 (NH), 1660 (CONH), 1580 cm^{-1} (CON); nmr ($CDCl_3$) δ 3.40 [s, 9, $N(CH_3)_3$], 3.20 (q, 2, $-CH_2N$), 2.40 (m, 4, CH_2-CH_2), 1.11 (t, 3, CH_3).

(9) A. W. Hofmann, *Ber.*, **19**, 2061 (1880).
(10) F. Lengfeld and J. Stieglitz, *Amer. Chem. J.*, **15**, 215 (1893).
(11) E. Fischer and G. Roeder, *Ber.*, **34**, 3751 (1901).

Anal. Calcd for $C_9H_{19}N_3O_2$: C, 53.71; H, 9.52; N, 20.88. Found: C, 53.97; H, 9.71; N, 21.06.

Pyrolysis of Trimethylamine-β-phenylcarbamoylpropionimide (1d).—Pyrolysis of the aminimide (5.22 g) at 200–220° gave a liquid which distilled and a solid residue. The liquid, based upon chromatographic analysis using a silicone rubber W98 column, consisted of aniline (0.5 g), *N*-methylaniline (0.16 g), and *N*-dimethylaminosuccinimide (**3**) (0.18 g).

The residue upon chromatography using a silica gel column and ethyl acetate as the eluting solvent gave *N*-phenylsuccinimide (1.08 g), mp 152.5–154.5° (lit.[12] mp 155°), and 1,2,3,4,5,6-hexahydro-3-phenyl-2,4-dioxopyrimidine (**4b**) (0.34 g), mp 233.5° (lit.[13] mp 231–234°). Identification was made by comparison with authentic samples.

Pyrolysis of Trimethylamine-β-ethylcarbamoylpropionimide (1e).—Decomposition of the aminimide (5.02 g) at 200–220° gave a dark solid (3.51 g) which upon vacuum sublimation at 120° (16 mm) gave a white solid (3.34 g). Analysis by gas chromatography at 220° using a silicone rubber W98 column showed two compounds in a 12:1 ratio. The first component was identified by its migration as *N*-ethylsuccinimide. The second component was isolated by recrystallizing the mixture from ethanol and was identified as 1,2,3,4,5,6-hexahydro-3-ethyl-2,4-dioxopyrimidine (**4c**) by comparison with a sample synthesized from *N*-ethylsuccinamide, yield 2.89 g, mp 113–114.5°.

1,2,3,4,5,6-Hexahydro-3-ethyl-2,4-dioxopyrimidine (4c).—A solution of *N*-ethylsuccinamide (3.3 g) and lead tetraacetate (10.5 g) in dimethylformamide (30 ml) was heated with stirring at 60–70°. Removal of the dimethylformamide gave a solid which was extracted with ether. Removal of the ether followed by recrystallization from ethanol gave white crystals melting at 113.4–114.5°: yield 0.94 g; ir (Nujol) 3285, 3120 (NH), 1720, 1650 cm^{-1} (CO); nmr ($CDCl_3$) δ 7.32 (s, 1, NH), 3.80 (q, 2, NCH_2CH_3), 3.40 (t, 2, CH_2NH), 2.68 (t, 2, CH_2CO), 1.13 (t, 3, CH_3); mol wt 142 (mass spectrum).

Anal. Calcd for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.89; H, 7.24; N, 19.92.

***N,N,N*-Trimethyl-*N*-(*N'*-succinimido)ammonium Methyl Sulfate.**—A solution of *N*-dimethylaminosuccinimide (20.0 g) and methyl sulfate (20.2 g) in benzene (400 ml) was refluxed for 24 hr. The solid (12.4 g) formed upon cooling was filtered. The filtrate upon refluxing for an additional 24 hr gave more of the product (16.6 g). Recrystallization of the combined solids from methanol–ether gave white crystals melting at 147.5–149.5°: yield 21.0 g; ir (Nujol) 1895, 1740 (cm^{-1} (CO); nmr (D_2O) δ 4.20 [s, 9, $N(CH_3)_3$], 3.90 (s, 3, CH_3OSO_3), 3.12 (s, 4, CH_2CH_2).

Anal. Calcd for $C_8H_{16}N_2O_6S$: C, 35.81; H, 6.01; N, 10.44. Found: C, 35.80; H, 6.07; N, 10.24.

Reaction of *N,N,N*-Trimethyl-*N*-(*N'*-succinimido)ammonium Methyl Sulfate with Barium Hydroxide.—A solution of the methyl sulfate (5.36 g) and barium hydroxide octahydrate (6.31 g) in water (100 ml) was heated in a sealed flask on a steam bath for 3 weeks. The solution was filtered periodically to remove the barium sulfate. After this period the theoretical amount of barium sulfate was isolated. The resulting solution was saturated with carbon dioxide, filtered, and concentrated to dryness. The resulting product (3.51 g) was a glassy material which was extremely hygroscopic and could not be crystallized. A portion (1.41 g) of this material, when treated in water (50 ml) with 0.0650 *N* hydriodic acid (7.31 ml) gave after removal of the solvent a solid which melted at 229–230° after one recrystallization from methanol, yield 1.1 g. The ir spectrum was identical with that of 1,1,1-trimethylhydrazinium iodide and a mixture melting point was not depressed.

Registry No.—**1a**, 39267-13-5; **1b**, 39267-14-6; **1c**, 39267-15-7; **1d**, 39267-16-8; **1e**, 39267-17-9; **3**, 10574-06-8; **4c**, 39267-19-1; *N,N*-dimethylaminosuccinamic acid, 1596-84-5; succinic anhydride, 108-30-5; 1,1-dimethylhydrazine, 57-14-7; 1,1,1-trimethyl-2-(β-carboxypropionyl)hydrazinium iodide, 39267-21-5; methyl iodide, 74-88-4; methyl β-succinimidopropionate, 39267-22-6; methyl β-aminopropionate hydrochloride, 3196-73-4; succinyl chloride, 543-20-4; methyl *N,N*-dimethylaminosuccinamate hydrochloride, 39267-24-8; methyl *N,N*-dimethylaminosuccinamate, 28402-64-4; β-carbomethoxypropionyl, 1490-25-1; trimethylamine, 75-50-3; 1,1,1-trimethyl-2-β-carbomethoxypropionylhydrazinium iodide, 39267-27-1; 1,1,1-trimethyl-2-β-carbomethoxypropionylhydrazinium chloride, 39477-74-2; methyl chloride, 74-87-3; phenyl isocyanate, 103-71-9; *N*-ethylsuccinimide, 2314-78-5; *N,N,N*-trimethyl-*N*-(*N'*-succinamido)ammonium methyl sulfate, 39267-28-2; barium hydroxide, 12230-71-6; 1,1,1-trimethylhydrazinium iodide, 3288-80-0.

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3-Substituted Oxetanes

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Received February 23, 1972

3-Allyloxyoxetane was rearranged to 3-propenoxyoxetane in 85–90% yield. The *t*-BuOK-catalyzed isomerization was essentially stereospecific, yielding 96% cis isomer. The propenyl ether was cleaved by acid hydrolysis to produce 3-oxetanol in 84% yield. Esterification of oxetanol with tosyl chloride gives crystalline oxetyl tosylate in 90–95% yield. Oxetanone is formed either by mild oxidation of oxetanol with chromic oxide–pyridine complex or by heating oxetyl tosylate in dimethyl sulfoxide. Heating oxetyl tosylate above 150° with alkali halides in triethylene glycol gave 75–85% yields of 3-halo oxetanes as overhead product in about 95% purity. A lower yield (10–20%) of 3-chlorooxetane was obtained when 3-oxetanol was treated with thionyl chloride. Reaction of iodooxetane with diethylamine at 200° gave 3-dimethylaminooxetane. Oxetyl acetate was prepared in 84% yield by transesterification of oxetanol with allyl acetate. Transesterification of oxetanol with ethyl acrylate gave a low yield of oxetyl acrylate; the main product was ethyl 3-(3′-oxetoxy)propionate. The acetate and acrylate esters were also prepared by acylation of oxetanol. Attempts to prepare oxetene by dehydrotosylation of oxetyl tosylate, dehydroacetoxylation of oxetyl acetate, or dehydrohalogenation of chloro- and iodooxetanes were unsuccessful.

The synthesis of 3-allyloxyoxetane[2] afforded an intermediate from which a variety of monosubstituted oxetanes could be prepared.

The work which is presented in this article deals with the isomerization of allyloxyoxetane to propenoxyoxetane followed by cleavage of the propenyl ether to 3-oxetanol[3] and conversion of the latter to halo oxetanes[4] and other new oxetanes.

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