anhydrous sodium acetate with diphenyldichlorosilane in diethyl ether with a yield of 68.4% (mean).

A concentrated solution of freshly prepared diphenyldiacetoxysilane was easily supercooled to 0°, and vigorous stirring or shaking with or without seeding resulted in an exothermic crystallization, producing an acicular crystal. Further purification was effected by recrystallization from diethyl ether, and a large prismatic crystal was obtained thereby.

The product melted at 66.8–67.0° (uncorrected), and contained 37.8% acetoxy groups (calcd. acetoxy groups: 39.3%), and its density determined indirectly by suspending a clean crystal specimen in aqueous calcium of matched density was 1.2740 (at 13°).

Phenyltriacetoxysilane melting at 29°[12] (uncorrected) and containing 61.2% acetoxy groups was obtained similarly.

The x-ray powder pattern data and the infrared absorption spectra data for these acetoxysilanes were recorded satisfactorily. They are listed in Table I.

These acetoxysilanes dissolved readily and endothermically in a variety of organic solvents but not in aliphatic hydrocarbons such as *n*-hexane, heptane, octane, and ligroin.

Some reactions of diphenyldiacetoxysilane. I. Hydrolysis. Neutralization of an ethanolic solution containing 30 g. (0.1 mole) of diphenyldiacetoxysilane, with $0.1N$ aqueous sodium hydroxide gave a white precipitate from which 20 g. (92%) of pure diphenylsilanediol was obtained by recrystallization from methyl acetate.

Another hydrolysis made at refluxing temperature without adding the alkali solution gave a crude mixture of diphenylsilanediol and hexaphenylcyclotrisiloxane as product.

II. *Reaction with diphenyldichlorosilane.* Addition of 25 g. (0.1 mole) of diphenyldichlorosilane to a refluxing solution containing 30 g. (0.1 mole) of diphenyldiacetoxysilane and 200 ml. of methyl acetate as diluent, gave crude crystalline material after 90 hr. of heating. Recrystallization of the above product yielded 24 g. (44%) of hexaphenylcyclotrisiloxane melting at 187–188°.

III. *Reaction with dipotassium diphenylsilanolate.* Addition of 30 g. (0.1 mole) of dipotassium diphenylsilanolate dissolved in 150 ml. of ethanol to a stirred solution containing 30 g. (0.1 mole) of diphenyldiacetoxysilane and 300 ml. of methyl acetate gave potassium acetate as a white precipitate. After 10 min. of refluxing the precipitate was removed by filtration. Usual treatment of the filtrate gave 33 g. of mixture of hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane.

IV. *Reaction with gaseous ammonia.* When gaseous ammonia, produced from concentrated aqueous ammonia upon heating, was bubbled into a flask in which 40 g. (0.14 mole) of phenyltriacetoxysilane and 400 ml. of diethyl ether had been placed, a white precipitate was formed gradually and after the formation of precipitate was complete, the resultant mixture was filtered by suction. After the filtrate was concentrated to about 100 ml. under reduced pressure, 500 ml. of purified *n*-hexane was added.

On evaporating the mixture under vacuum in a clean quartz crystallizing dish, there appeared characteristic shiny platelets mixed with a slightly colored oily product. The oily product was removed by filtration from the mixture and the platelets were washed with *n*-hexane and then with cold water. The x-ray powder pattern[13] and infrared spectra[14] for the product were identical with those of phenylsilanetriol.

Anal. Calcd. for $C_6H_8SiO_3$: C, 46.13; H, 5.10; Si, 17.98; OH/molecule, 3.00. Found: C, 45.7; H, 5.0; Si, 18.6; OH/molecule, 2.9.

The powdered sample melted at 127–129°. Recrystallization from methyl acetate-hexane always led to the loss of most of the sample unless the temperature was kept below 10°.

Many runs under modified conditions were always accompanied by formation of oily condensation products together with phenylsilanetriol, the yield of which did not exceed 15%. A similar procedure with diphenyldiacetoxysilane as sample gave diphenylsilanediol almost quantitatively.

With phenylsilanetriol, another attempt which involved direct hydrolysis of phenyltriacetoxysilane in a buffer solution also failed to obtain phenylsilanetriol because of its extreme instability.

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(12) H. H. Anderson and Thomas C. Hager, *J. Am. Chem. Soc.*, 81, 1584 (1949).

(13) T. Takiguchi, *J. Am. Chem. Soc.*, **81**, 2359 (1959).

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Derivatives of 2-Amino-1,3-propanediol

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Some time ago Pfeiffer and co-workers[2] demonstrated the central nervous system stimulating effect of 2-dimethylaminoethanol—a compound believed to be a precursor of acetylcholine.

As part of an investigation dealing with central nervous system active materials it seemed of interest to prepare ethanolamines—preferably substituted by hydrophilic as well as aromatic moieties—which might act as acetylcholine precursors or, alternately, as antagonists.

Our major effort was directed toward the synthesis of derivatives of 2-amino-1,3-propanediol. The following reaction sequence was explored and carried to completion in the case of the diethylaminoethyl derivative (IV. $R'' = R''' = C_2H_5$).

Condensation of tris(hydroxymethyl)nitromethane with a number of aldehydes and ketones led to the hydroxymethylnitrodioxane (I).[3] The ketals derived from acetone and cyclohexane proved to be most suitable for subsequent reactions. The *n*-butyraldehyde condensation product could be separated into its two isomers melting at 32–33° and 100–101°, respectively.[4]

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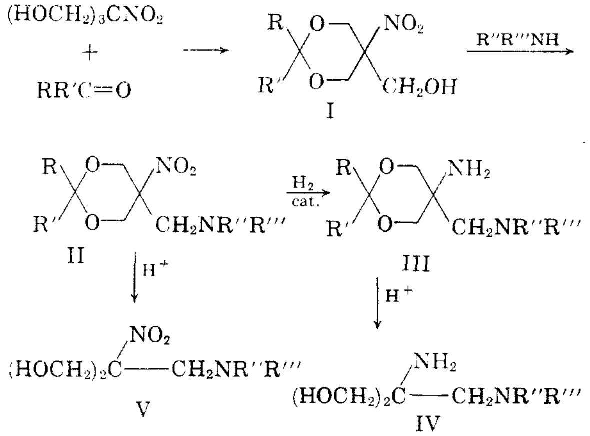
(1) (a) Present address: Wm. H. Rorer Inc., Philadelphia, Pa. (b) Present address: Celanese Corp. of America, Summit, N. J.

(2) (a) C. C. Pfeiffer, E. H. Jenney, W. Gallagher, R. P. Smith, W. Bevan, Jr., K. F. Killam, E. K. Killam, and W. Blackmore, *Science*, **126**, 610 (1957). (b) D. P. Groth, J. A. Bain, and C. C. Pfeiffer, *J. Pharm. Exptl. Therap.*, **124**, 290 (1958).

(3) M. Senkus, *J. Am. Chem. Soc.*, **63**, 2635 (1941).

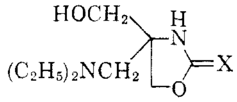
(4) Senkus (ref. 3) reports a single product, m.p. 69.5°, from the reaction of *n*-butyraldehyde and tris(hydroxymethyl)nitromethane.

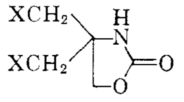
Compounds of type I were converted smoothly by the action of amines to the aminomethylnitrodioxanes (II)[5] which in several instances were hydrolyzed to derivatives of 2-nitro-2-aminomethyl-1,3-propanediol (V); these compounds resisted all attempts at catalytic hydrogenation. On the other hand, several of the ketals (II) could be reduced to the corresponding diaminodioxanes (III) by employing a Raney nickel catalyst at elevated pressures. Noble metal catalysis proved less useful and frequently led to incomplete reduction (hydroxylamine formation) or reductive cleavage of the nitro group.



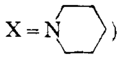
Acid hydrolysis of 3 - amino - 3 - diethylaminomethyl-1,5-dioxaspiro[5.5]undecane [III. R and R' = —$(CH_2)_5$—, R'' = R''' = C_2H_5] resulted in the cleavage of the ketal linkage and furnished the desired diaminodiol (IV. R'' = R''' = C_2H_5). Unfortunately, this reaction could not be extended to compounds of type III possessing secondary instead of tertiary amino groups.

The diaminodiol (IV. R'' = R''' = C_2H_5) was allowed to react with ethyl carbonate to give the oxazolidone (VI. X = O) which polymerized readily; reaction with carbon disulfide yielded the stable thiooxazolidone (VI. X = S).


VI

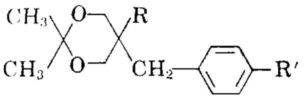

VII

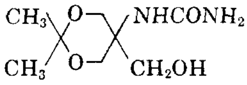
Another pathway expected to lead to the desired ethanolamines was explored briefly: 4,4-bis(hydroxymethyl)oxazolidone-2[6] (VII. X = OH) was converted by the action of thionyl chloride to the bischloromethyl derivative (VII. X = Cl), which, in turn was treated with piperidine to give the bispiperidinomethyloxazolidone

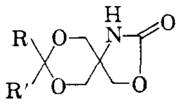
(VII. X = ).

Preliminary studies of the hydrolysis of the latter compound were unpromising.

In search of suitable precursors for certain aromatic derivatives of ethanolamine the readily accessible 2,2-dimethyl-5-nitro-5-*p*-nitrobenzyl-*m*-dioxane[7] (VIII. R = R' = NO_2) was subjected to catalytic reduction. Depending upon the reaction conditions the nitroamine (VII. R = NO_2, R' = NH_2) or the desired diamine (VIII. R = R' = NH_2) could be isolated; however, hydrolytic cleavage of these compounds did not lead to the desired diols and this experimental approach was not explored further.


VIII


IX


X

Finally, the synthesis of a number of spirooxazolidones was undertaken. Fusion of 2,2-dimethyl-5-amino-5-hydroxymethyl-*m*-dioxane[8] with nitrourea, led to the urea (IX); treatment with ethyl carbonate, however, yielded the desired oxazolidone(X. R = R' = CH_3). The corresponding dispiro derivative (X. R and R' = —$(CH_2)_5$—) was obtained by the condensation of 4,4-bis(hydroxymethyl)oxazolidone-2[6] (VII. X = O) and cyclohexanone in the presence of boron trifluoride etherate.[9]

EXPERIMENTAL[10]

Acetalization and ketalization of 2-nitro-2-hydroxymethyl-1,3-propanediol. The following compounds were prepared by the procedure of Senkus[3]: 2-*n*-hexyl-5-nitro-5-*m*-dioxanemethanol[3](I. R = H, R' = C_6H_{13}), 2,2-dimethyl-5-nitro-5-*m*-dioxanemethanol[5] (I. R = R' = CH_3) and 3-hydroxymethyl-3-nitro-1,5-dioxaspiro[5.5]undecane[11] (I. R and R' = —$(CH_2)_5$—).

2-n-Propyl-5-nitro-5-m-dioxanemethanol (I. R = H, R' = *n*-C_4H_9). The procedure of Senkus[3] was followed and the reaction residue (after washing out the acid catalyst and evaporating the reaction solvent) was extracted with hot pentane. The pentane insoluble portion was recrystallized several times from a 1 : 10 mixture of absolute ethanol and hexane; m.p. 100–101°; yield of isomer A, 44%.

Anal. Calcd. for $C_8H_{15}NO_5$: C, 46.82; H, 7.37; N, 6.83. Found: C, 47.21; H, 7.25; N, 6.70.

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[5] S. Malinowski and T. Urbanski, *Roczniki Chem.*, **25**, 183 (1951).

[6] J. Cason and F. S. Prout, *J. Am. Chem. Soc.*, **71**, 1218 (1949).

[7] Z. Eckstein and T. Urbanski, *Roczniki Chem.*, **30**, 1163 (1956).

[8] M. Senkus, U. S. Patent **2,370,586** (Feb. 27, 1945).

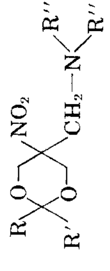
[9] G. B. Linden and M. H. Gold, *J. Org. Chem.*, **21**, 1175 (1956).

[10] (a) All melting points are uncorrected. (b) Analyses by Mr. E. Hoffmann and staff.

[11] F. F. Blicke and E. L. Schumann, *J. Am. Chem. Soc.*, **76**, 3153 (1954).

TABLE I

5-AMINOMETHYL-5-NITRO-*m*-DIOXANES



R	R′	R″	R‴	Formula	M.P.	Yield, %	Solvent of Recrystallization	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
H	*n*-C_6H_{13}	H	*n*-C_4H_9	$C_{15}H_{31}ClN_2O_4$[a]	156–159	68	Ether-ethanol	53.16	53.29	9.22	9.18	8.27	8.07
H	*n*-C_6H_{13}	H	$CH_2CH_2N(C_2H_5)_2$	$C_{17}H_{37}Cl_2N_3O_4$[b]	164–167	31	Ethanol	48.80	49.08	8.92	8.93	10.04	10.00
CH_3	CH_3	H	*n*-C_4H_9	$C_{11}H_{23}ClN_2O_4$[a]	157–159	80	Ethanol	46.72	46.73	8.20	8.38	9.91	9.89
CH_3	CH_3	C_2H_5	C_2H_5	$C_{11}H_{22}N_2O_4$	70–71	79	Pentane	53.64	53.80	9.00	9.09	11.37	11.35
—$(CH_2)_5$—		H	*n*-C_4H_9	$C_{14}H_{27}ClN_2O_4$[a]	156–158	66	Ether-ethanol	52.08	52.12	8.43	8.29	8.68	8.53
—$(CH_2)_5$—		H	$CH_2CH_2N(C_2H_5)_2$	$C_{16}H_{33}Cl_2N_3O_4$[b]	165–167	46	Ethanol	47.76	47.53	8.27	8.42	10.44	10.50
—$(CH_2)_5$—		C_2H_5	C_2H_5	$C_{14}H_{26}N_2O_4$	38–39	88	Pentane	58.72	58.77	9.15	9.10	9.78	9.62

[a] Data given for hydrochloride. [b] Data given for dihydrochloride.

The pentane extract was cooled to −30° and the solid was collected by filtration: m.p. 32–33°; yield of isomer B, 8%.

Anal. Calcd. for $C_5H_{15}NO_5$: C, 46.82; H, 7.37; N, 6.83. Found: C, 46.98; H, 7.41; N, 7.06.

5-Aminomethyl-5-nitro-m-dioxanes (II). The compounds listed in Table I were prepared by the method of Malinowski and Urbanski.[5]

3-Amino-3-diethylaminomethyl-1,5-dioxaspiro[5.5]undecane (III. R and R′ = —$(CH_2)_5$—, R″ = R‴ = C_2H_5) *dihydrochloride.* A suspension of 230 g. of II [R and R′ = —$(CH_2)_5$—, R″ = R‴ = C_2H_5], 10 g. of freshly prepared Raney nickel catalyst,[12] and 600 ml. of absolute ethanol was subjected to hydrogenation at an initial pressure of 1000 lb. After completed reduction the catalyst was filtered off, the solvent was evaporated, and the residue was distilled: b.p. 100–103°/0.06 mm., yield, 188 g. (77%). The dihydrochloride after recrystallization from absolute ethanol melted at 197–198°.

Anal. Calcd. for $C_{14}H_{30}Cl_2N_2O_2$: C, 51.06; H, 9.18; N, 8.51. Found: C, 50.94; H, 9.32; N, 8.35.

3-Amino-3-n-butylaminomethyl-1,5-dioxaspiro[5.5]undecane (III. R and R′ = —$(CH_2)_5$—, R″ = H, R‴ = *n*-C_4H_9) *dihydrochloride.* The preceding directions were applied to 49.5 g. of II (R and R′ = —$(CH_2)_5$—, R″ = H, R‴ = *n*-C_4H_9): b.p. 135–136°/0.08 mm. n_D^{24}, 1.4857, yield, 28.4 g. (50%). The dihydrochloride after recrystallization from absolute ethanol melted at 188–190°.

Anal. Calcd. for $C_{14}H_{30}Cl_2N_2O_2$: C, 51.06; H, 9.18; N, 8.51. Found: C, 51.03; H, 9.07; N, 8.35.

When an initial pressure of 1700 lb. was employed there was obtained in addition to the above diamine (yield, 28%) the cleavage product *1,5-dioxaspiro[5.5]undecan-3-amine,* b.p. 90–91°/0.12 mm., yield, 26%.

Anal. Calcd. for $C_9H_{17}NO_2$: C, 63.13; H, 10.00; N, 8.18. Found: C, 63.13; H, 10.20; N, 8.16.

3-Hydroxylamino-3-(2-diethylaminoethylamino)methyl-1,5-dioxaspiro[5.5]-undecane trihydrochloride. A mixture of 12 g. of III [R and R′ = —$(CH_2)_5$—, R″ = H, R‴ = $CH_2CH_2N(C_2H_5)_2$], 0.5 g. of 5% platinum on charcoal catalyst, and 100 ml. of absolute ethanol was subjected to hydrogenation at an initial pressure of 60 lb. After hydrogen uptake had ceased, the catalyst and solvent were removed and the residue was taken up in ether and converted into a trihydrochloride. Yield, 9.5 g. (62%); m.p. 152–153° after recrystallization from methanol and ether.

Anal. Calcd. for $C_{16}H_{36}Cl_3N_3O_3$: C, 45.23; H, 8.64; N, 9.89. Found: C, 45.15; H, 8.50; N, 10.15.

2-Amino-2-diethylaminomethyl-1,3-propanediol (IV). A solution of 178 g. of III (R and R′ = —$(CH_2)_5$—, R″ = R‴ = C_2H_5) and 300 ml. of 3*N* hydrochloric acid was heated on a steam bath for 0.5 hr. The reaction mixture was washed with ether and the aqueous portion was reduced to one third of its original volume. The solution was made basic with 20% potassium hydroxide and extracted with three 500-ml. portions of chloroform. After drying and evaporation of the solvent, the residue was distilled: b.p. 135–138°/0.07 mm., yield, 52.9 g. (43%). The material solidified on standing; m.p. 57–59° after recrystallization from ether.

Anal. Calcd. for $C_8H_{20}N_2O_2$: C, 54.51; H, 11.44; N, 15.89. Found: C, 54.50; H, 11.32; N, 15.80.

2-Diethylaminomethyl-2-nitro-1,3-propanediol (V. R″ = R‴ = C_2H_5) *hydrochloride.* A solution of 10 g. of II [R and R′ = —$(CH_2)_5$—, R″ = R‴ = C_2H_5] hydrochloride and 100 ml. of 3*N* hydrochloric acid was heated on a steam bath for 15 min. The acid solution was washed with ether and evaporated to dryness. The gummy residue was triturated with a mixture of 20 ml. of ether and 5 ml. of absolute ethanol. The resulting crystalline mass was recrystallized from ether ethanol: m.p. 130–131°; yield, 6.3 g. (89%).

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[12] H. Adkins and H. R. Billica, *J. Am. Chem. Soc.,* **70,** 695 (1948).

Anal. Calcd. for $C_8H_{19}ClN_2O_4$: C, 39.59; H, 7.89; N, 11.54. Found: C, 39.38; H, 7.97; N, 11.31.

2-(2-Diethylaminoethylamino)methyl-2-nitro-1,3-propanediol (V. $R'' = H$, $R''' = CH_2CH_2N(C_2H_5)_2$) *dihydrochloride.* The preceding procedure was applied to 10 g. of II [R and $R' = —(CH_2)_5—$, $R'' = H$, $R''' = CH_2CH_2N(C_2H_5)_2$]. Yield, 6.6 g. (67%); m.p. 146–147°, after recrystallization from absolute ethanol.

Anal. Calcd. for $C_{10}H_{25}Cl_2N_3O_4$: C, 37.27; H, 7.82; N, 13.04. Found: C, 37.43; H, 7.67, N, 12.95.

4-Diethylaminomethyl-4-hydroxymethyloxazolidone-2 (VI. X = O). A mixture of 3.5 g. of IV, 10 ml. of dry ethyl carbonate, and 0.01 g. of sodium methoxide was stirred and heated at 120° for 0.5 hr., while ethanol was removed by distillation through a short column. The excess ethyl carbonate was removed *in vacuo* and the residue was distilled: b.p. 205–210°/0.08 mm.; yield, 2.4 g. (54%); m.p. 51–54°, after recrystallization from pentane.

Anal. Calcd. for $C_9H_{18}N_2O_3$: C, 53.44; H, 8.97; N, 13.85. Found: C, 53.68; H, 8.80; N, 13.75.

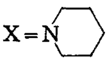
4-Diethylaminomethyl-4-hydroxymethyloxazolidine-2-thione (VI. X = S). In accordance with the procedure of Skulski *et al.*[13] there was added dropwise 7.1 g. of carbon disulfide and 10 ml. of ethanol to a stirred and cooled solution of 17.6 g. of IV in 75 ml. of ethanol. During the addition the temperature was maintained at 2–5°. The reaction mixture was refluxed for 16 hr., another portion of 3.5 g. of carbon disulfide was added, and refluxing was continued for 10 hr. The excess ethanol was evaporated and the residue was recrystallized from ether: m.p. 93–94°; yield, 19 g. (87%).

Anal. Calcd. for $C_9H_{18}N_2O_2S$: C, 49.52; H, 8.31; N, 12.84. Found: C, 49.80; H, 8.30; N, 12.72.

4,4-Bis(chloromethyl)oxazolidone-2 (VII. X = Cl). To a cooled and stirred solution of 14.7 g. of 4,4-bis(hydroxymethyl)oxazolidone-2[6] in 17 ml. of dry pyridine was added dropwise 24 g. of thionyl chloride. The mixture was stirred at room temperature for 48 hr. The solid mass was washed well with water, dried, and recrystallized from chloroform: m.p. 156–157°; yield, 11 g. (60%).

Anal. Calcd. for $C_5H_7Cl_2NO_2$: C, 32.63; H, 3.83; N, 7.61; Cl, 38.53; mol. wt., 184. Found: C, 32.88; H, 3.80; N, 7.69; Cl, 38.21; mol. wt., 182.

4,4-Bis(piperidinomethyl)oxazolidone-2

(VII. X=).

A solution of 20 g. of VII (X = Cl) and 100 ml. of piperidine was heated on a steam bath for 24 hr. The semisolid reaction product was acidified with 3*N* hydrochloric acid and the insoluble portion was filtered off. The filtrate was made basic with 10% potassium hydroxide and extracted with 100 ml. of ether. The extract was dried and diluted with three volumes of pentane. The solid was collected by filtration and recrystallized from 50% ethanol; m.p. 180–181°; yield, 17.4 g. (58%).

Anal. Calcd. for $C_{15}H_{27}N_3O_2$: C, 64.02; H, 9.67; N, 14.93. Found: C, 64.10; H, 9.44; N, 14.85.

2,2-Dimethyl-5-p-aminobenzyl-5-nitro-m-dioxane (VIII. $R = NO_2$, $R' = NH_2$). A suspension of 3 g. of 2,2-dimethyl-5-*p*-nitrobenzyl-5-nitro-*m*-dioxane[7] (VIII, $R = R' = NO_2$), 0.5 g. of 5% palladium on charcoal catalyst, and 100 ml. of 95% ethanol was subjected to hydrogenation at an initial pressure of 60 lb. After completed hydrogen consumption the catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The residue was triturated with ether and the ether-insoluble portion was recrystallized from ethanol; m.p. 195–196°; yield, 1.8 g. (67%).

Anal. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.70; H, 6.77; N, 10.54. Found: C, 58.72; H, 6.97; N, 10.30.

2,2-Dimethyl-5-amino-5-p-aminobenzyl-m-dioxane (VIII. $R = R' = NH_2$). A suspension consisting of 41 g. of VIII ($R = R' = NO_2$), 300 ml. of ethanol, and 10 g. of Raney nickel catalyst[12] was subjected to hydrogenation at an initial pressure of 1700 lb. and at a temperature of 180°. After completed reaction the catalyst was filtered off and the solvent evaporated. The residue was recrystallized from hexane; m.p. 96–97°; yield, 24 g. (74%).

Anal. Calcd. for $C_{13}H_{20}N_2O_2$: C, 66.07; H, 8.53; N, 11.86. Found: C, 66.17; H, 8.52; N, 11.62.

2,2-Dimethyl-5-hydroxymethyl-5-ureido-m-dioxane (IX). A solution of 5 g. of 2,2-dimethyl-5-amino-5-hydroxymethyl-*m*-dioxane,[8] 3.3 g. of nitrourea, 30 ml. of ethanol, and 60 ml. of water was heated and stirred at 70° for 1 hr. The volume was reduced by evaporation to 10 ml. and the solid was allowed to crystallize. Yield, 4.6 g. (73%), m.p. 173–174° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_8H_{16}N_2O_4$: C, 47.05; H, 7.90; N, 13.72. Found: C, 47.07; H, 7.90; N, 13.55.

8,8-Dimethyl-1-aza-3,7,9-trioxaspiro[4.5]decanone-2 (X. $R = R' = CH_3$). A mixture consisting of 5 g. of 2,2-dimethyl-5-amino-5-hydroxymethyl-*m*-dioxane[8] and 30 ml. of ethyl carbonate was heated at 120° while the ethanol formed in the reaction was allowed to distil slowly through a 1-ft. Vigreux column. The excess ethyl carbonate was removed *in vacuo* and the residue was recrystallized from ethyl acetate; m.p. 164–165°, yield, 3.6 g. (62%).

Anal. Calcd. for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.47. Found: C, 51.45; H, 7.03; N, 7.42.

1-Aza-3,7,14-trioxadispiro[4.2.5.2]pentadecanone-2 [X. R and $R' = —(CH_2)_5—$]. A suspension of 14.7 g. of 4,4-bis(hydroxymethyl)oxazolidone-2[6] and 35 ml. of cyclohexanone was heated and stirred on a steam bath for 15 min. The mixture was cooled to 20° and 13 ml. of boron trifluoride etherate was added to the manually stirred paste. The temperature rose to 50° and the reaction mixture was allowed to stand for 0.5 hr. The solid mass was poured onto 120 ml. of saturated bicarbonate and the paste was stirred for 1 hr. The solid was filtered, washed with water and dried. Yield, 21 g. (92%), m.p. 201–202° after recrystallization from acetone.

Anal. Calcd. for $C_{11}H_{17}NO_4$: C, 58.13; H, 7.54; N, 6 16. Found: C, 58.35; H, 7.72; N, 6.35.

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Chloroethylation of Sulfuric Acid

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The formation of bis(2-chloroethyl)sulfate by the simultaneous addition of chlorine and ethylene to sulfuric acid has been reported by Titov and Maklyaev.[1,2] In connection with another problem in this laboratory, we found it desirable to study the factors affecting the yield of bis (2-chloroethyl) sulfate from this reaction.

$$CH_2{=}CH_2 + Cl_2 + H_2SO_4 \longrightarrow ClCH_2CH_2OSO_3H + HCl$$

$$CH_2{=}CH_2 + Cl_2 + ClCH_2CH_2OSO_3H \longrightarrow (ClCH_2CH_2)_2SO_4 + HCl$$

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(1) A. I. Titov and F. L. Maklyaev, *Doklady Akad. Nauk S.S.S.R.*, 98, No. 5, 795–8 (1954).

(2) A. I. Titov and F. L. Maklyaev, *Zhur. Obshchei Khim.*, **24**, 1631–5 (1954).