NEW COMPOUNDS OF UREA-FORMALDEHYDE CONDENSATION PRODUCTS.

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Although many reports concerning urea-formaldehyde condensation products have been published by many investigators since Hölzer(1), of these condensation products, there are only two whose constitutional formulae have been accounted for to this day. They are namely, monomethylol-urea(2) ($H_2N-CO-NH-CH_2OH$) and dimethylol-urea(3) ($HOCH_2-NH-CO-NH-CH_2OH$). They are soluble crystalline compounds. It has been observed that urea-formaldehyde condensation products contain, besides crystalline compounds, insoluble amorphous compounds and resinous compounds. Of these, resinous compound is so-called urea resin, and is also termed " organic glass,"(4) being one of the important synthetic resins. The present author(5) has, for the past few years, been investigating methods of manufacture of this resin, and especially, most recently, investigated the chemical constitution and the mechanism of formation of this resin and fortunately succeeded in obtaining the expected results.

In this paper the author wishes to report on the thirty new compounds (given in Table 1) out of the condensation products of urea or urea derivatives with formaldehyde, which the author succeeded in synthesizing in the course of his research.

Methylenediurea (I, Table 1) was obtained, in the presence of acid, by the action of 1 mol of formaldehyde on 8 mol of urea. In the past, in the production of urea-formaldehyde condensation products, we had some instances in which formaldehyde was used as (raw) material considerably in excess. However, in the case of urea, 1.33 mol of urea on 1 mol of formaldehyde, as used by Dixon(6), was the maximum, and the use of any greater excess has never been reported. But the present author succeeded in obtaining methylenediurea as the result of experiment with a great excess of urea as (raw) material. Generally speaking, when urea is reacted upon formaldehyde in

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(1) Hölzer, *Ber.*, **17** (1884), 659.
(2) (3) Einhorn and Hamburger, *Ber.*, **41** (1908), 21.
(4) There are other names besides "organic glass."
(5) Kadowaki, *Repts. Imp. Ind. Research Laboratory, Osaka, Japan*, **7** (1926), No. 6; **13** (1932), No. 3, No. 6; **14** (1933), No. 6; **14** (1934), No. 11; **16** (1935), No. 6.
(6) Dixon, *J. Chem. Soc.*, **113** (1918), 233.

Table 1.

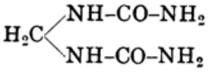
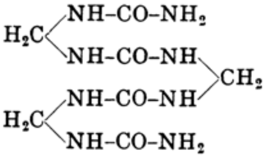
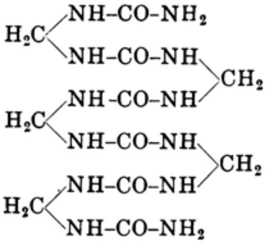
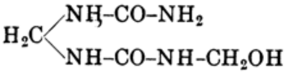
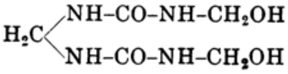
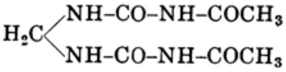
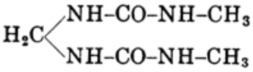
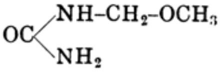
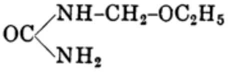
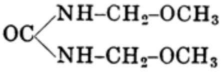
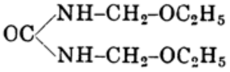
No.	Name	Constitutional formula	Properties	Photogram
I	Methylenediurea	 $H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH_2\\NH\text{-}CO\text{-}NH_2\end{array}\right.$	Needle-crystals m.p. 218°C. (effervesces)	Fig. 1 500×
II	Trimethylenetetraurea	 $\begin{array}{ll}H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH_2\\NH\text{-}CO\text{-}NH\end{array}\right. & \\ & \rangle CH_2\\ H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH\\NH\text{-}CO\text{-}NH_2\end{array}\right. & \end{array}$	White powder, at 230°C. turns yellow.	Fig. 2 500×
III	Pentamethylenehexaurea	 $\begin{array}{ll}H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH_2\\NH\text{-}CO\text{-}NH\end{array}\right. & \\ & \rangle CH_2\\ H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH\\NH\text{-}CO\text{-}NH\end{array}\right. & \\ & \rangle CH_2\\ H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH\\NH\text{-}CO\text{-}NH_2\end{array}\right. & \end{array}$	White powder, at 236°C. turns yellow.	Fig. 3 500×
IV	Methylolmethylenediurea	 $H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH_2\\NH\text{-}CO\text{-}NH\text{-}CH_2OH\end{array}\right.$	White powder.	Fig. 4 500×
V	Methylenebismethylolurea	 $H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH\text{-}CH_2OH\\NH\text{-}CO\text{-}NH\text{-}CH_2OH\end{array}\right.$	White powder m.p. 228°C. (effervesces)	Fig. 5 500×
VI	Methylenebisacetylurea	 $H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH\text{-}COCH_3\\NH\text{-}CO\text{-}NH\text{-}COCH_3\end{array}\right.$	Needle-crystals m.p. 156°C.	Fig. 6 20×
VII	Methylenebismethylurea	 $H_2C\left\langle\begin{array}{l}NH\text{-}CO\text{-}NH\text{-}CH_3\\NH\text{-}CO\text{-}NH\text{-}CH_3\end{array}\right.$	Prism-crystals m.p. 184°C.	Fig. 7 20×
VIII	Monomethylolureamethylether	 $OC\left\langle\begin{array}{l}NH\text{-}CH_2\text{-}OCH_3\\NH_2\end{array}\right.$	Plate-crystals m.p. 91°C.	Fig. 8 16×
IX	Monomethylolureaethylether	 $OC\left\langle\begin{array}{l}NH\text{-}CH_2\text{-}OC_2H_5\\NH_2\end{array}\right.$	Needle-crystals m.p. 111°C.	Fig. 9 40×
X	Dimethylolureadimethylether	 $OC\left\langle\begin{array}{l}NH\text{-}CH_2\text{-}OCH_3\\NH\text{-}CH_2\text{-}OCH_3\end{array}\right.$	Needle-crystals m.p. 101°C.	Fig. 10 40×
XI	Dimethylolureadiethylether	 $OC\left\langle\begin{array}{l}NH\text{-}CH_2\text{-}OC_2H_5\\NH\text{-}CH_2\text{-}OC_2H_5\end{array}\right.$	Plate-crystals m.p. 124°C.	Fig. 11 40×

Table 1. (*Continued*)

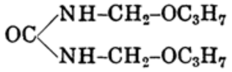
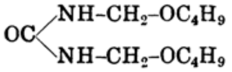
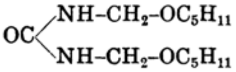
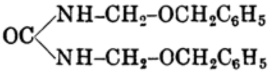
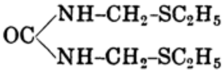
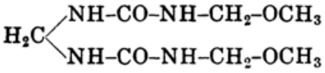
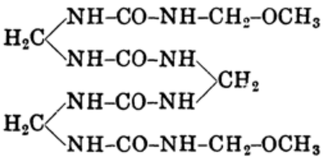
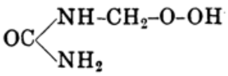
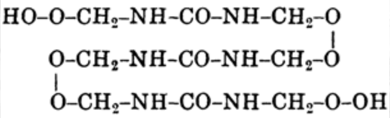
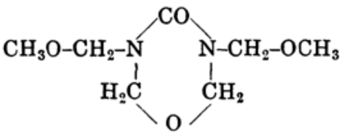
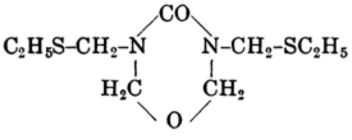
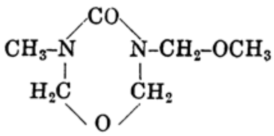
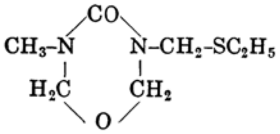
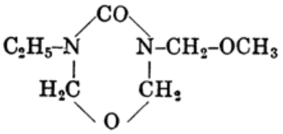
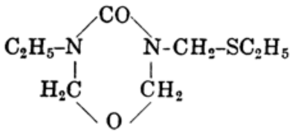
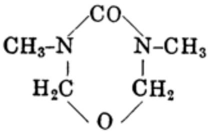
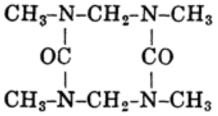
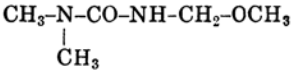
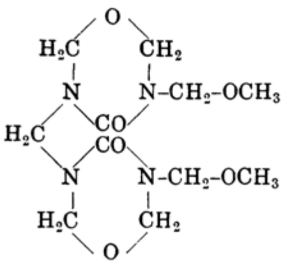
No.	Name	Constitutional formula	Properties	Photogram
XII	Dimethylolurea-di-*n*-propylether	 $\mathrm{OC}\begin{cases}\mathrm{NH\text{-}CH_2\text{-}OC_3H_7}\\ \mathrm{NH\text{-}CH_2\text{-}OC_3H_7}\end{cases}$	Prism-crystals m.p. 95°C.	Fig. 12 57.5×
XIII	Dimethylolurea-di-*n*-butylether	 $\mathrm{OC}\begin{cases}\mathrm{NH\text{-}CH_2\text{-}OC_4H_9}\\ \mathrm{NH\text{-}CH_2\text{-}OC_4H_9}\end{cases}$	Needle-crystals m.p. 93°C.	Fig. 13 40×
XIV	Dimethylolurea-di-*n*-amylether	 $\mathrm{OC}\begin{cases}\mathrm{NH\text{-}CH_2\text{-}OC_5H_{11}}\\ \mathrm{NH\text{-}CH_2\text{-}OC_5H_{11}}\end{cases}$	Plate-crystals m.p. 84°C.	Fig. 14 80×
XV	Dimethylolurea-dibenzylether	 $\mathrm{OC}\begin{cases}\mathrm{NH\text{-}CH_2\text{-}OCH_2C_6H_5}\\ \mathrm{NH\text{-}CH_2\text{-}OCH_2C_6H_5}\end{cases}$	Needle-crystals m.p. 112°C.	Fig. 15 57.5×
XVI	Dimethylolurea-diethylthioether	 $\mathrm{OC}\begin{cases}\mathrm{NH\text{-}CH_2\text{-}SC_2H_5}\\ \mathrm{NH\text{-}CH_2\text{-}SC_2H_5}\end{cases}$	Pillar-crystals m.p. 108.5°C.	Fig. 16 30×
XVII	Methylenebis-methylolurea-methylether	 $\mathrm{H_2C}\begin{cases}\mathrm{NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}OCH_3}\\ \mathrm{NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}OCH_3}\end{cases}$	Plate-crystals, at 240°C. turns yellow.	Fig. 17 30×
XVIII	Dimethyloltri-methylene-tetraurea-dimethylether	 $\mathrm{H_2C}\begin{cases}\mathrm{NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}OCH_3}\\ \mathrm{NH\text{-}CO\text{-}NH}\diagdown\end{cases}\mathrm{CH_2}\quad \mathrm{H_2C}\begin{cases}\mathrm{NH\text{-}CO\text{-}NH}\diagup\\ \mathrm{NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}OCH_3}\end{cases}$	White powder.	
XIX	Monomethylol-urea peroxide	 $\mathrm{OC}\begin{cases}\mathrm{NH\text{-}CH_2\text{-}O\text{-}OH}\\ \mathrm{NH_2}\end{cases}$	Needle-crystals m.p. 153°C.	
XX	Hexamethylol-triurea peroxide	 $\mathrm{HO\text{-}O\text{-}CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}O}$ $\mathrm{O\text{-}CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}O}$ $\mathrm{O\text{-}CH_2\text{-}NH\text{-}CO\text{-}NH\text{-}CH_2\text{-}O\text{-}OH}$	Amorphous powder.	
XXI	*N,N'*-Dimethylol-urondimethyl-ether		Colourless transparent liquid, b.p. 82–83°C. (0.1 mm.)	
XXII	*N,N'*-Dimethylol-urondiethyl-thioether		Pillar-crystals m.p. 59°C.	Fig. 19 20×

Table 1. (*Concluded*)

No.	Name	Constitutional formula	Properties	Photogram
XXIII	*N*-Methyl-*N'*-methyloluron-methylether		Colourless transparent liquid, b.p. 89–90°C. (0.2 mm.)	
XXIV	*N*-Methyl-*N'*-methyloluron-ethylthioether		Colourless transparent liquid, b.p. 122–125°C. (1.0 mm.)	
XXV	*N*-Ethyl *N'*-methyloluron-methylether		Colourless transparent liquid, b.p. 91–93°C. (1.0 mm)	
XXVI	*N*-Ethyl-*N'*-methyloluron-ethylthioether		Needle-crystals m.p. 15.5°C.	
XXVII	*N*,*N'*-Dimethyl-uron		Prism-crystals m.p. 38.5°C.	
XXVIII	Tetramethyl-dimethylene-diureid		Needle-crystals m.p. 258°C.	Fig. 20 40×
XXIX	*N*,*N*-Dimethyl-*N'*-methylolurea-methylether	 $CH_3{-}\underset{\displaystyle CH_3}{\underset{\vert}{N}}{-}CO{-}NH{-}CH_2{-}OCH_3$	Prism-crystals m.p. 65°C.	
XXX	Methylenebis-methyloluron-methylether		Colourless transparent sticky substance.	

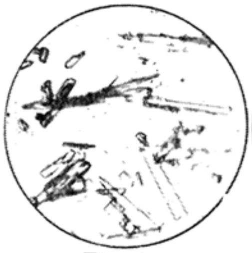


Fig. 1.

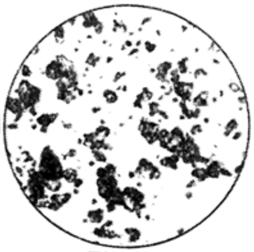


Fig. 2.

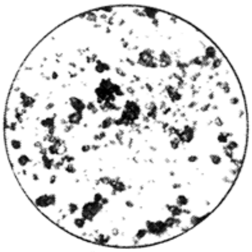


Fig. 3.

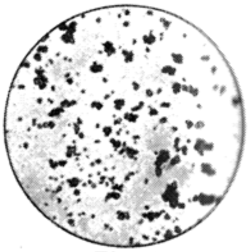


Fig. 4.

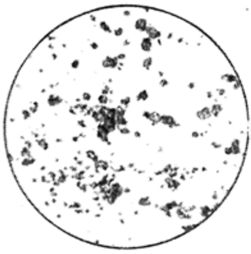


Fig. 5.


Fig. 6.


Fig. 7.

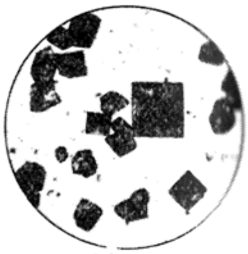


Fig. 8.


Fig. 9.

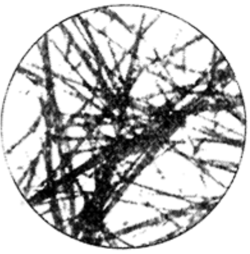


Fig. 10.

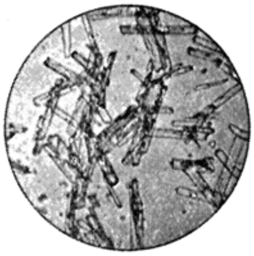


Fig. 11.


Fig. 12.


Fig. 13.

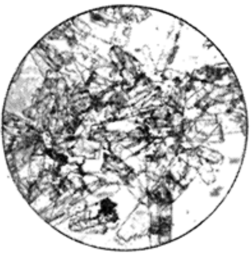


Fig. 14.


Fig. 15.


Fig. 16.


Fig. 17.


Fig. 18.

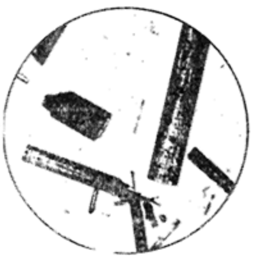


Fig. 19.

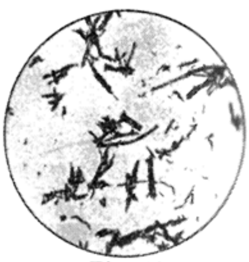


Fig. 20.

the presence of acid, there is a strong tendency to form polymer, and as the existence of acid is necessary for the formation of methyleneurea in water solution, if lower methyleneurea alone is desired to be obtained, special conditions of experiment must be prepared. According to the author's observation, insoluble methyleneurea(7) heretofore known, should be regarded as the mixture of higher methyleneurea.

It is noteworthy that such a soluble crystalline methyleneurea as methylenediurea was obtained, while methyleneurea heretofore known is insoluble. The author, by taking advantage of the solubility of methylenediurea, was enabled to know the nature and the formation characteristics(8) of methyleneurea, and consequently was able to know also the formation characteristics(9) of methylolurea. This new knowledge of the formation characteristics of methyleneurea and methylolurea would surely be most useful in the manufacture of resin.

In the next place trimethylenetetraurea (II) and pentamethylenehexaurea (III) were obtained in the following method: The precipitate which was formed by the addition of a small quantity of acid to the aqueous solution of methylenediurea, was subjected to a fractional extraction by means of hot water and boiling water, and each was obtained as the precipitate from the extract. These are interesting compounds for the purpose of observation of the constitution of the higher methyleneurea.

Methylolmethylenediurea (IV) and methylenebismethylolurea (V) were obtained, by the action of formaldehyde, in the presence of alkali, upon methylenediurea. Of these, compound V yields colourless, transparent, hard resin when it is heated under pressure. This resin is highly water-proof, and does not crack even when it is soaked in boiling water for several hours. Since, up to this time, the defect of urea-resin for practical use has been its lack of water-proof quality, it is noteworthy that a kind of resin with water-proof quality in a high degree, was obtained.

Methylenebisacetylurea (VI) was obtained by acetylation of methylenediurea, using acetic anhydride.

Methylenebismethylurea (VII) was obtained by the action of 1 mol of formaldehyde on 2 mol of methylurea (in the presence of acid). Since, in the

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(7) Hölzer, *Ber.*, **17** (1884), 659; **18** (1885), 3302 (Anm.). Lüdy, *Monatsh.*, **10** (1889), 297. Hemmelmayer, *Monatsh.*, **12** (1891), 94. Tollens, *Ber.*, **29** (1896), 2751. Dixon, *J. Chem. Soc.*, **113** (1918), 233. Scheibler, Trostler und Scholz, *Z. angew. Chem.*, **41** (1928), 1305.

(8) Kadowaki, *Repts. Imp. Ind. Research Laboratory, Osaka, Japan*, **13** (1932), No. 6, 15–41.

(9) Kadowaki, *ibid.*, **14** (1933), No. 6, 16–29.

case of methylurea, one of the hydrogen atoms of amido-radical of urea has been replaced by a methyl-radical, condensation products formed by the reaction with formaldehyde is considerably simpler, compared with the case of urea.

Monomethylolureamethylether (VIII) was obtained by making methyl alcohol act upon monomethylolurea, in the presence of acid. Again, this compound can be obtained simply by heating monomethylolurea with methyl alcohol somewhat longer. So far as the present author knows no research has been made concerning the reaction of alcohol upon monomethylhlurea and dimethylolurea. The author experimented upon the reaction of monomethylolurea, dimethylolurea and methylenebismethylolurea on alcohol or mercaptane, for the purpose of investigating the character of methylolurea, and by using the similar method as used in obtaining the compound VIII, succeeded to obtain compounds from IX to XVII. Of these, compounds formed by the reaction of dimethylolurea upon alcohol yields, on heating, colourless, transparent, hard resin. Above all, resins obtained from XIII, XIV, and XV have been observed to possess a greater degree of water-proof quality.

Next, dimethyloltrimethylenetetraureadimethylether (XVIII) was obtained as precipitate by the action of 8 mol of formalin, in the presence of acid, on 1 mol of urea at about –5°C. On this occasion, the formation of methylether was due to the reaction of methyl alcohol contained in formalin.

Monomethylolurea peroxide (XIX) and hexamethyloltriurea peroxide (XX) were obtained by the reaction of hydrogen peroxide (slightly acidic to litmus) on monomethylolurea and dimethylolurea. Moreover, the author obtained a liquid peroxide by using hydrogen peroxide which was neutralized beforehand. The author also obtained an insoluble crystalline peroxide $(C_3H_6N_2O_3)_n$ (Fig. 18) by adding acid to the mixture of dimethylolurea and hydrogen peroxide. The above-mentioned crystalline peroxide is different in its process of preparation from those which have been formerly obtained, but as its characteristics and analytical results are alike, it must be related to them.(10)

N,N'-Dimethylolurondimethylether (XXI) was obtained, first by the action of 1 mol of urea on 4 mol of formaldehyde, by heating in the presence of alkali (or by the reaction through concentration at room temperature), and then, by the action of methyl alcohol in the presence of acid. This compound contains, in its constitution, one dimethyleneetherurea-ring. Although this ring is an important one, frequently appearing in urea-formaldehyde condensation products, it is an unknown ring. Therefore, the author gave the name

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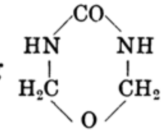
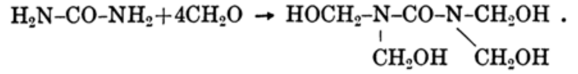
(10) Girsewald and Siegens, *Ber.*, **47** (1914), 2464. Bois de Chesne, *Kolloid Beihefte*, **36** (1932), 418.

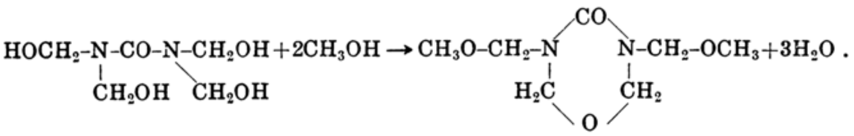
of " uron " to the normal constitution of this ring  . This uron ring is a stable ring and does not easily decompose when it is acted on by dilute acid.

That which is formed by the reaction of urea on formaldehyde by heating, first in the presence of alkali, in the process of manufacture of compound XXI is undoubtedly tetramethylolurea:



$$H_2N\text{-}CO\text{-}NH_2+4CH_2O \rightarrow HOCH_2\text{-}\underset{CH_2OH}{N}\text{-}CO\text{-}\underset{CH_2OH}{N}\text{-}CH_2OH\ .$$

That the compound XXI was formed in the treatment with methyl alcohol in the presence of acid, could be considered due to the process that, out of the two methylol-radical which were united with each urea amido-radical, one first reacting upon methyl alcohol, formed methylether, and then the other, mutually reacting, formed uron ring:



N-Methyl-*N'*-methyloluronmethylether (XXIII), *N*-ethyl-*N'*-methyloluronmethylether (XXV), *N,N'*-dimethyluron (XXVII)(11), tetramethyldimethylenediureid (XXVIII)(12), *N,N'*-dimethyl-*N'*-methylolureamethylether (XXIX) and methylenebismethyloluronmethylether (XXX) were obtained by the similar method as used in obtaining compound XXI, by the use of methylurea, ethylurea, *N,N'*-dimethylurea, *N,N*-dimethylurea and methylenediurea, in place of urea. All these are compounds whose three or four hydrogen atoms of urea-amidoradical are replaced by methylene-radical or alkyl-radical, and they have a very important place in our observation of the conditions of the union of urea with formaldehyde.

N,N'-Dimethylolurondiethylthioether (XXII) was obtained by the action of ethylmercaptane in the presence of acid on compound XXI. *N*-Methyl-*N'*-methyloluronethylthioether (XXIV) and *N*-ethyl-*N'*-methyloluronethylthioether (XXVI) were obtained by the action of ethylmercaptane, in the presence of acid, on compound XXIII and compound XXV.

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(11) (12) *N,N'*-Dimethyluron and tetramethyldimethylenediureid can also be obtained simply by the reaction of *N,N'*-dimethylurea and formaldehyde through heating in the presence of acid.

Experimental.

(1) **Methylenediurea** $C_3H_8N_4O_2$. Urea (1540 g.) was dissolved in the equal weight of water. When 22.5 c.c. of conc. hydrochloric acid and 250 c.c. of 38.37% formalin were added some white turbidity appeared in a few minutes. After leaving the mixture to stand for two days, it was neutralized with potassium hydroxide, and the precipitate from it was scooped out. The precipitate was treated with alcohol, and after urea contained in it was removed, it was recrystallised from water. (Yield: 279.6 g. Found: C, 26.89; H, 6.21; N, 41.98%; mol. wt., 117.6; CH_2O, 23.24%. Calculated for $C_3H_8N_4O_2$: C, 27.25; H, 6.12; N, 42.42%; mol. wt., 132. Calculated for $CH_2O/C_3H_8N_4O_2$: CH_2O, 22.73%.)

(2) **Trimethylenetetraurea** $C_7H_{16}N_8O_4$ **and Pentamethylenehexaurea** $C_{11}H_{24}N_{12}O_6$. Methylenediurea (10 g.) was dissolved in 200 c.c. of water, and when one drop of conc. hydrochloric acid was added to the solution, white turbidity appeared after a few minutes. After leaving the solution to stand for one day, the precipitate was scooped out and was thoroughly washed with water, and then was heated together with 1 l. of water at 95°C., and the solution was filtered while still warm, and when the filtrate was cooled, precipitate was separated. (Yield: 2.97 g. Found: C, 30.52; H, 6.00; N, 40.72; CH_2O, 31.78. Calculated for $C_7H_{16}N_8O_4$: C, 30.41; H, 5.84; N, 40.59. Calculated for $3CH_2O/C_7H_{16}N_8O_4$: CH_2O, 32.61%.) Then, the residue, together with 1 l. of water, was boiled, and was filtered while still warm, and when the filtrate was cooled, precipitate separated out. (Yield: 0.71 g. Found: C, 31.26; H, 5.90; N, 40.11; CH_2O, 34.17. Calculated for $C_{11}H_{24}N_{12}O_6$: C, 31.41; H, 5.76; N, 40.00. Calculated for $5CH_2O/C_{11}H_{24}N_{12}O_6$: CH_2O, 35.71%.)

(3) **Methylolmethylenediurea** $C_4H_{10}N_4O_3$. Methylenediurea (5 g.) was dissolved in 150 c.c. of water, and 0.1 g. of barium hydroxide and 2.96 g. of 38.37% formalin were added to the solution, and after leaving it to stand for 55 minutes, it was neutralized by passing a current of carbon dioxide and was filtered. The filtrate was evaporated and dried. The dried substance was extracted by heating with 60% alcohol. Then, this extract separated out a precipitate when it was cooled. This precipitate contains a small quantity of methylenebismethylolurea. (Yield: 0.58 g. Found: C, 30.57; H, 6.30; N, 32.72. Calculated for $C_4H_{10}N_4O_3$: C, 29.63; H, 6.22; N, 34.59%.)

(4) **Methylenebismethylolurea** $C_5H_{12}N_4O_4$. Methylenediurea (10 g.) was dissolved in 200 c.c. of water and 0.4 g. of barium hydroxide and 11.9 g. of 38.37% formalin were added, and the solution was left to stand for ten minutes, and then, it was neutralized by passing a current of carbon dioxide, and filtered. The filtrate was evaporated and dried. This dried substance was heated with 60% alcohol. The extract separated out precipitate when it was left to cool. (Yield: 2.9 g. Found: C, 31.79; H, 6.25; N, 30.10. Calculated for $C_5H_{12}N_4O_4$: C, 31.23; H, 6.30; N, 29.17%.)

(5) **Methylenebisacetylurea** $C_7H_{12}N_4O_4$. To 6 g. of methylenediurea 20 c.c. of acetic acid, 70 c.c. of acetic anhydride, and 1.5 c.c. of conc. sulphuric acid were added, and when the solution was left to cool after it was boiled for ten minutes, crystals were separated out. The crystals were scooped out, and were recrystallized from water. (Yield: crude 2.4 g. Found: CH_3CO, 59.3. Calculated for $CH_3CO_2H/C_7H_{12}N_4O_4$: CH_3CO, 55.5%.)

(6) **Methylenebismethylurea** $C_5H_{12}N_4O_2$. Methylurea (5.64 g.) was dissolved in 3 c.c. of 37.57% formalin and when one drop of conc. hydrochloric acid was added, the solution generated intense heat, and its temperature rose. When left to cool, crystals were separated out. These crystals were scooped out, and were recrystallized from alcohol. (Yield: crude 4.55 g. Found: N, 35.16. Calculated for $C_5H_{12}N_4O_2$: N, 35.00%.)

(7) **Monomethylolureamethylether** $C_3H_8N_2O_2$. Methyl alcohol (5 g.) and one drop of 5 N hydrochloric acid were added to 0.85 g. of monomethylolurea and were dissolved, and after allowing the solution to stand for one minute, it was neutralized with silver carbonate, and was filtered, and when the filtrate was evaporated, there remained crystals. These crystals were recrystallized from methyl alcohol. (Yield: crude 0.96 g. Found: C, 34.75; H, 7.58; N, 26.94. Calculated for $C_3H_8N_2O_2$: C, 34.58; H, 7.76; N, 26.91%.)

(8) **Monomethylolureaethylether** $C_4H_{10}N_2O_2$. Ethyl alcohol (15 g.) and 3 drops of 5 N hydrochloric acid were added to 1.9 g. of monomethylolurea and were dissolved. After leaving the solution to stand for 7 minutes, it was neutralized with silver carbonate, and was filtered. When this filtrate was concentrated, crystals separated out. These crystals were recrystallized from alcohol. (Yield: crude 1.37 g. Found: N, 23.84. Calculated for $C_4H_{10}N_2O_2$: N, 23.72%.)

(9) **Dimethylolureadimethylether** $C_5H_{12}N_2O_3$. Methyl alcohol (100 c.c.) and one drop of 5 N hydrochloric acid were added to 10 g. of dimethylolurea, and were dissolved, and the solution was left to stand for 5 minutes, and then, it was neutralized with silver carbonate, and was filtered. When the filtrate was concentrated, crystals separated out. The crystals were scooped out and were recrystallized from methyl alcohol. (Yield: 10.6 g. Found: C, 40.36; H, 8.33; N, 19.13%; mol. wt., 138; CH_2O, 40.61%. Calculated for $C_5H_{12}N_2O_3$: C, 40.51; H, 8.17; N, 18.91%; mol. wt., 148. Calculated for $2CH_2O/C_5H_{12}N_2O_3$: CH_2O, 40.54%.)

(10) **Dimethylolureadiethylether** $C_7H_{16}N_2O_3$. Ethyl alcohol (100 c.c.) and one drop of 5 N hydrochloric acid were added to 10 g. of dimethylolurea, and were dissolved. After allowing the solution to stand for 7 minutes, it was neutralized with silver carbonate and was filtered. When the filtrate was evaporated crystals remained. These crystals were recrystallized from alcohol. (Yield: crude 11.9 g. Found: N, 15.96; CH_2O, 34.83. Calculated for $C_7H_{16}N_2O_3$: N, 15.90. Calculated for $2CH_2O/C_7H_{16}N_2O_3$: CH_2O, 34.83%.)

(11) **Dimethylolureadi-*n*-propylether** $C_9H_{20}N_2O_3$. Dimethylolurea (1 g.) was dissolved by the addition of 5 g. of *n*-propyl alcohol and one drop of N hydrochloric acid. After leaving the solution to stand for 10 minutes, it was neutralized with silver carbonate, and was filtered. Through the concentration of the filtrate, crystals separated out. The crystals were scooped out and were recrystallized from ether. (Yield: crude 1.45 g. Found: N, 13.92. Calculated for $C_9H_{20}N_2O_3$: N, 13.72%.)

(12) **Dimethylolureadi-*n*-butylether** $C_{11}H_{24}N_2O_3$. Dimethylolurea (1 g.) was dissolved by the addition of 5 g. of *n*-butyl alcohol and one drop of N hydrochloric acid. After the solution was left to stand for 20 minutes, it was neutralized with silver carbonate, and was filt red. The filtrate was strongly cooled, and then crystals separated out. The crystals were scooped out and were recrystallized from ether. (Yield: crude 1.06 g. Found: N, 12.08. Calculated for $C_{11}H_{24}N_2O_3$: N, 12.07%.)

(13) **Dimethylolurea-*n*-amylether** $C_{13}H_{28}N_2O_3$. *n*-Amyl alcohol (5 g.) and one drop of 5 N hydrochloric acid were added to 1 g. of dimethylolurea and were dissolved. After allowing the solution to stand for 20 minutes, it was neutralized with silver carbonate, and was filtered. The filtrate was evaporated and dried. The dried substance was heated and extracted with ether. When the extract was cooled, crystals separated out. The crystals were scooped out and were recrystallized from ether. (Yield: crude 1.0 g. Found: N, 10.80. Calculated for $C_{13}H_{28}N_2O_3$: N, 10.76%.)

(14) **Dimethylolureadibenzylether** $C_{17}H_{20}N_2O_3$. Dimethylolurea (1 g.) was dissolved by adding 5 g. of benzyl alcohol and one drop of 5 N hydrochloric acid. After the solution was allowed to stand for 5 minutes, it was neutralized with silver carbonate and was filtered. When the filtrate was strongly cooled, crystals separated out. The crystals were scooped out and were dissolved in benzene. On adding ether to this solution, crystals separated out. (Yield: 1.0 g. Found: N, 9.24, Calculated for $C_{17}H_{20}N_2O_3$: N, 9.33%.)

(15) **Dimethylolureadiethylthioether** $C_7H_{16}N_2S_2O$. When 5 g. of dimethylolurea was added to 13 g. of ethylmercaptane, to which 10 drops of 5 N hydrochloric acid had been added beforehand, a soft lump was produced. After washing it thoroughly with water, it was heated with alcohol and dissolved. When the solution was cooled, crystals separated out. The crystals were scooped out and were recrystallized from alcohol. (Yield: 5.5 g. Found: C, 41.84: H, 7.78; N, 13.25; S, 30.76. Calculated for $C_7H_{16}N_2S_2O$: C, 40.33; H, 7.74; N, 13.45; S, 30.78%.)

(16) **Methylenebismethylolureadimethylether** $C_7H_{16}N_4O_4$. Methyl alcohol (100 c.c.) and 0.5 c.c. of 5 N hydrochloric acid were added to 3.77 g. of methylenebismethylolurea, and after allowing it to stand for 10 minutes, it was neutralized with silver carbonate, and was heated at 60°C., and was filtered. When the filtrate was cooled, crystals separated out. The crystals were scooped out and were recrystallized from methyl alcohol. (Yield: 2.71 g. Found: C, 37.88; H, 7.34; N, 25.76%; mol. wt., 223.9; CH_2O, 41.13%. Calculated for $C_7H_{16}N_4O_4$: C, 38.15; H, 7.33; N, 25.45; mol. wt., 220.2. Calculated for $3CH_2O/C_7H_{16}N_4O_4$: CH_2O, 40.90%.)

(17) **Dimethyloltrimethylenetetraureadimethylether** $C_{11}H_{24}N_8O_6$. Urea (95 g.) was dissolved in 1000 c.c. of 38% formalin, and the solution was filtered. Then the filtrate was cooled to -6.5°C., and when 10 c.c. of conc. hydrochloric acid was added, in 10 minutes, it yielded white turbidity. Leaving it to stand for one hour the precipitate was scooped out and was washed with alcohol. (Yield: 39.4 g. Found: C, 36.09; H, 6.63; N, 30.68; CH_2O, 43.45. Calculated for $C_{11}H_{24}N_8O_6$: C, 36.25; H, 6.60; N, 30.75. Calculated for $5CH_2O/C_{11}H_{24}N_8O_6$: CH_2O, 41.20%.)

(18) **Monomethylolurea peroxide** $C_2H_6N_2O_3$. Monomethylolurea (2.2 g.) was dissolved in 66 c.c. of 3% hydrogen peroxide (slightly acidic to litmus). The solution was dried by evaporation. This dried substance was dissolved in a small quantity of water by heating. When this solution was cooled, crystals separated out. The crystals were scooped out and were recrystallized from 50% alcohol. (Yield: 1.92 g. Found: C, 22.33; N, 26.63%; mol. wt., 98.8; avail. O, 15.30%. Calculated for $C_2H_6N_2O_3$: C, 22.64; N, 26.42%; mol. wt., 106.0. Calculated for $O/C_2H_6N_2O_3$: avail. O, 15.09%.)

(19) **Hexamethyloltriurea peroxide** $C_9H_{20}N_6O_{11}$, **Crystalline peroxide** $(C_3H_6N_2O_3)_n$ **and Liquid peroxide.** (A) *Hexamethyloltriurea peroxide.* Dimethylolurea (20 g.) was dissolved

in 500 c.c. of 3% hydrogen peroxide (slightly acidic to litmus), and when the solution was evaporated, there remained liquid. This was washed with carbon tetrachloride and ether, and then was dissolved in alcohol. Next, when a portion of insoluble substance was removed, and the solution was evaporated, solid remained. This solid was again dissolved in alcohol, ether was added to the solution, and precipitate separated out. (Yield: crude 5 g. Found: N, 21.30%; mol. wt., 383.2. Calculated for $C_9H_{20}N_6O_{11}$: N, 21.60%; mol. wt., 388.2.)

(B) *Crystalline peroxide.* When 2.5 g. of dimethylolurea was dissolved in 50 c.c. of 3% hydrogen peroxide, and 0.5 c.c. of 5 N hydrochloric acid was added to it, crystals separated out. (Yield: 2.06 g. Found: C, 30.48; H, 5.29; N, 23.65; avail. O, 13.73. Calculated for $C_3H_6N_2O_3$: C, 30.49; H, 5.12; N, 23.73. Calculated for $O/C_3H_6N_2O_3$: avail. O, 13.55%.)

(C) *Liquid peroxide.* Dimethylolurea (12 g.) was dissolved in 500 c.c. of 3% hydrogen peroxide which had been neutralized with barium hydroxide, and when the solution was evaporated, there remained liquid. This liquid was dissolved in alcohol, and a small quantity of the insoluble substance was removed, and the solution was evaporated, and liquid was obtained. When this liquid was poured into ether, it became slightly turbid. The turbidity was filtered, and then the filtrate was evaporated, there remained liquid.

(20) **N,N′-Dimethylolurondimethylether** $C_7H_{14}N_2O_4$. Barium hydroxide (5 g.) and 60 g. of urea were dissolved in 320 c.c. of 38% formalin, and when the solution was heated in boiling water for 10 minutes, and was evaporated, there remained slightly sticky liquid. This was dissolved in the mixture of 1 l. of methyl alcohol and 6 c.c. of conc. hydrochloric acid, and after leaving the solution to stand for 15 minutes, it was neutralized with barium hydroxide, and was filtered. A slightly fluid liquid remained when the filtrate was evaporated. After the inorganic salt was removed by treating it with chloroform, and dimethylolureadimethylether also was removed by treating it with ether, it was subjected to vacuum distillation for refining. (Yield: crude 126 g. Found: C, 43.86; H, 7.73; N, 14.74%; mol. wt., 188.5; CH_2O, 59.32%. Calculated for $C_7H_{14}N_2O_4$: C, 44.19; H, 7.42; N, 14.72%; mol. wt., 190.1. Calculated for $4CH_2O/C_7H_{14}N_2O_4$: CH_2O, 63.16%.)

(21) **N,N′-Dimethylolurondiethylthioether** $C_9H_{18}N_2S_2O_2$. *N,N′*-Dimethylolurondimethylether (10 g.) was dissolved in 14 g. of ethylmercaptane, and when 3 drops of conc. hydrochloric acid were added thereto, heat generated, and the temperature of the solution rose. After cooling, it was neutralized with barium hydroxide, and inorganic salt was removed by the treatment with ether, and when it was evaporated, there remained transparent liquid. When this liquid was subjected to vacuum distillation, the greater part distilled at 125–134°C. (0.1 mm.), and when left to stand, it crystallized. The crystals were dissolved in a small quantity of alcohol, and crystals were separated out by adding water to the solution. (Yield: crude 14.8 g. Found: C, 43.19; H, 7.37; N, 11,16; S, 25.33%; mol. wt., 240.6. Calculated for $C_9H_{18}N_2S_2O_2$: C, 43.15; H, 7.25; N, 11.19; S, 25.62%; mol. wt., 250.3.)

(22) **N-Methyl-N′-methylolurонmethylether** $C_6H_{12}N_2O_3$. Barium hydroxide (3 g.) and 10 g. of methylurea were dissolved in 42.7 c.c. of 38% formalin, and after the solution was heated in boiling water for 10 minutes, it was evaporated. Then, a slightly sticky liquid remained. This was dissolved in the mixture of 100 c.c. of methyl alcohol and 2.5 c.c. of conc. hydrochloric acid. After leaving it to stand for 15 minutes, it was

neutralized with barium hydroxide, and was filtered. When the filtrate was evaporated, there remained slightly fluid liquid. This was treated with chloroform in order to remove inorganic salt, and then, was subjected to vacuum distillation for refinement. (Yield: crude 15.0 g. Found: C, 44.28; H, 7.93; N, 17.43%; mol. wt., 162.5; CH_2O, 53.27%. Calculated for $C_6H_{12}N_2O_3$: C, 44.97; H, 7.56; N, 17.50%; mol. wt., 160.1. Calculated for $3CH_2O/C_6H_{12}N_2O_3$: CH_2O, 56.25%.)

(23) **N-Methyl-N′-methyloluronethylthioether** $C_7H_{14}N_2SO_2$. *N*-Methyl-*N′*-methyloluronmethylether (6.2 g.) was dissolved in 12.4 g. of ethylmercaptane, and when 3 drops of conc. hydrochloric acid were added thereto, the temperature of the solution rose, heat being generated. After cooling, it was neutralized with barium hydroxide, and again was treated with ether to remove inorganic salt. On evaporation, a transparent liquid remained. This liquid was washed with water, and was refined through vacuum distillation. (Yield: crude 5.8 g. Found: C, 43.91; H, 7.65; N, 14.52%; mol. wt., 186.4. Calculated for $C_7H_{14}N_2SO_2$: C, 44.16; H, 7.42; N, 14.73%; mol. wt., 190.2.)

(24) **N-Ethyl-N′-methyloluronmethylether** $C_7H_{14}N_2O_3$. Barium hydroxide (4 g.) and 22 5 g. of ethylurea were dissolved in 81 c.c. of 38% formalin, and the solution was heated in boiling water for 10 minutes. After evaporation, there remained a slightly sticky liquid. This liquid was dissolved in the mixture of 200 c.c. of methyl alcohol and 5 c.c. of conc. hydrochloric acid. After leaving it to stand for 15 minutes, it was neutralized with barium hydroxide, and was filtered. The filtrate was evaporated, and then slightly fluid liquid remained. This liquid was treated with chloroform in order to remove inorganic salt contained in it. Then, it was refined by vacuum distillation. (Yield: crude 41 g. Found: C, 47.72; H, 8.44; N, 16.23%; mol. wt., 174.1; CH_2O, 46.77%. Calculated for $C_7H_{14}N_2O_3$: C, 48.24; H, 8.10; N, 16.09%; mol. wt., 174.1. Calculated for $3CH_2O/C_7H_{14}N_2O_3$: CH_2O, 51.72%.)

(25) **N-Ethyl-N′-methyloluronethylthioether** $C_8H_{16}N_2SO_2$. *N*-Ethyl-*N′*-methyloluronmethylether (6.6 g.) was dissolved in 12.4 g. of ethylmercaptane. On adding 3 drops of conc. hydrochloric acid to the solution, it generated heat, and its temperature rose. After it was left to cool, it was neutralized with barium hydroxide and was again treated with ether to remove the inorganic salt contained therein. There remained slightly fluid liquid when it was evaporated. Washing it with water, it was subjected to vacuum distillation. It distilled mostly at 110–113°C. (1.0 mm.) and when the distillate was cooled strongly, crystals separated out. (Yield: crude 7.7 g. Found: C, 46.82; H, 8.32; N, 13.62%; mol. wt., 204.6. Calculated for $C_8H_{16}N_2SO_2$: C, 47.01; H, 7.90; N, 13.72%; mol. wt., 204.2.)

(26) **N,N′-Dimethyluron** $C_5H_{10}N_2O_2$ **and Tetramethyldimethylenediureid** $C_8H_{16}N_4O_2$. Barium hydroxide (1.5 g.) and 8.8 g. of *N,N′*-dimethylurea were dissolved in 24 c.c. of 38% formalin, and after heating the solution in boiling water for 5 minutes, it was evaporated. Then, a slightly sticky liquid remained. This liquid was dissolved in the mixture of 150 c.c. of methyl alcohol and 1.5 c.c. of conc. hydrochloric acid. Leaving it to stand for 15 minutes, it was neutralized with barium hydroxide, and was filtered. Through evaporation of the filtrate, there remained a slightly fluid liquid. Removing the inorganic salt contained therein by treatment with chloroform, it was subjected to vacuum distillation. Then, the greater part distilled, leaving crystals. The crystals were recrystallized from alcohol. (Yield: 1.3 g. Found: C, 47.78; H, 8.43; N, 28.00%;

mol. wt., 190.4; CH_2O, 30.07%. Calculated for $C_8H_{16}N_4O_2$: C, 47.95; H, 8.08; N, 27.99%; mol. wt., 200.2. Calculated for $2CH_2O/C_8H_{16}N_4O_2$: CH_2O, 29.99%.)

The distillate was refined by the treatment with the mixture of ethylmercaptane and hydrochloric acid, and was subjected to vacuum distillation. The best part distilled at 64°C. (0.1 mm.). When the distillate was strongly cooled, it formed crystals. These were recrystallized from ether. (Yield: crude 3.5 g. Found: C, 46.96; H, 7.83; N, 21.63%; mol. wt., 131.5; CH_2O, 46.21%. Calculated for $C_5H_{10}N_2O_2$: C, 46.12; H, 7.75; N, 21.53; mol. wt., 130.1. Calculated for $2CH_2O/C_5H_{10}N_2O_2$: CH_2O, 46.14%.)

(27) **N,N-Dimethyl-N′-methylolureamethylether** $C_5H_{12}N_2O_2$. Barium hydroxide (4 g.) and 8.8 g. of *N,N*-dimethylurea were dissolved in 24 c.c. of 38% formalin, and when the solution was heated in boiling water for 10 minutes, and was evaporated, a slightly sticky liquid remained. This liquid was dissolved in the mixture of 100 c.c. of methyl alcohol and 2.8 c.c. of conc. hydrochloric acid, and leaving it to stand for 15 minutes it was neutralized with barium hydroxide, and was filtered. When the filtrate was evaporated a transparent liquid remained. Removing the inorganic salt contained in it by treating it with chloroform, it was left to stand at room temperature. Then, crystals separated out. The crystals were scooped out, and were recrystallized from ether. (Yield: 7 g. Found: C, 45.51; H, 9.29; N, 21.32%; mol. wt., 128.7; CH_2O, 22.78%. Calculated for $C_5H_{12}N_2O_2$: C, 45.42; H, 9.16; N, 21.21%; mol. wt., 132.1. Calculated for $CH_2O/C_5H_{12}N_2O_2$: CH_2O, 22.72%.)

(28) **Methylenebismethyloluronmethylether** $C_{11}H_{20}N_4O_6$. Barium hydroxide (1 g.) and 13.2 g. of methylenediurea were dissolved in 50 c.c. of 38% formalin, and when the solution was heated in boiling water for 10 minutes, and was evaporated, colourless, transparent sticky substance remained. This was dissolved in the mixture of 200 c.c. of methyl alcohol and 1 c.c. of conc. hydrochloric acid. Leaving it to stand for 15 minutes, it was neutralized with barium hydroxide and was evaporated. Then, sticky liquid remained. Removing inorganic salt contained therein by the treatment of chloroform, it was refined with ether. (Yield: crude 27.0 g. Found: C, 42.67; H, 7.84; N, 18.92%; mol. wt., 273.3; CH_2O, 63.73%. Calculated for $C_{11}H_{20}N_4O_6$: C, 43.39; H, 6.63; N, 18.42%; mol. wt., 304.2. Calculated for $7CH_2O/C_{11}H_{20}N_4O_6$: CH_2O, 69.03%.)

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