[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

STEARAMIDOMETHYL ETHERS

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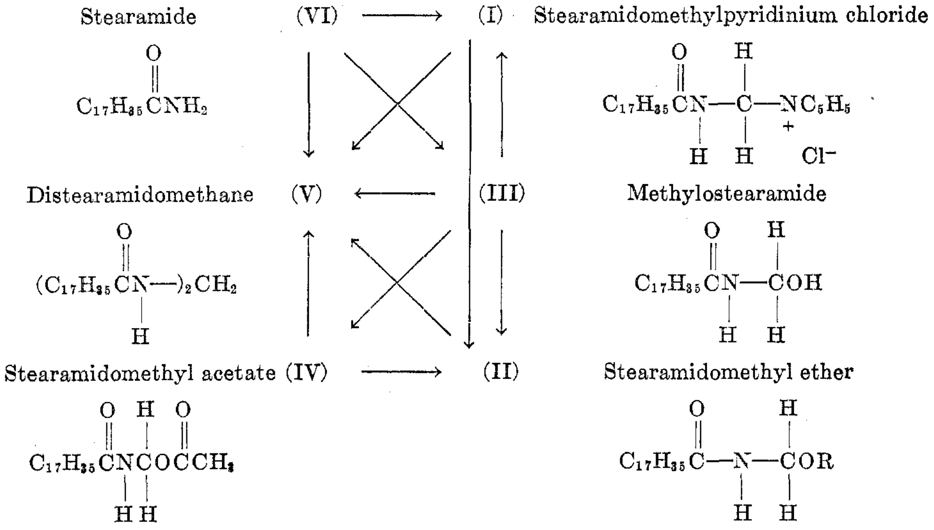
Long-chain amidomethyl compounds, such as stearamidomethylpyridinium chloride (I), have been patented (1–5) and have found wide application in the textile finishing industry. Their use to produce water repellency (6), especially with cotton cloth, has been discussed extensively in the literature. In most of these discussions (7–10) it is either claimed or suggested that in imparting water repellency an ether of cellulose (II) is formed.

During the course of study of the possible etherification of cotton by the stearamidomethylpyridinium chloride type of compound several simple ethers were prepared and characterized.

The preparation of such simple ethers from the reaction between methylolstearamide (III) and an alcohol in the presence of a catalyst has been patented (11, 12). We have found that the reaction between stearamidomethyl acetate (IV) and alcohols will produce such ethers in good yields, as will the reaction between stearamidomethylpyridinium chloride and alcohols.

The relationship between the various compounds mentioned is best illustrated as follows:



All of the amidomethyl compounds considered here condense with the elimination of formaldehyde to give distearamidomethane (V) when subjected to heat or boiled with dilute aqueous solutions of strong acids.

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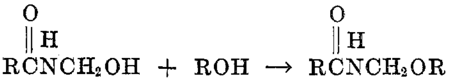
While $RC(O)NHCH_2OR$ is referred to here as an ether (primarily because it has been so named in previous literature) it should be pointed out that it does not possess the stability of true ethers, but more closely resembles the acetals. The following comparison will illustrate this point:



$$\mathrm{R\overset{\overset{O}{\|}}{C}\overset{H}{N}CH_2OH + ROH \rightarrow R\overset{\overset{O}{\|}}{C}\overset{H}{N}CH_2OR}$$

Unstable in dilute aqueous strong acid

$$\mathrm{ROCH_2OH + ROH \rightarrow (RO)_2CH_2}$$

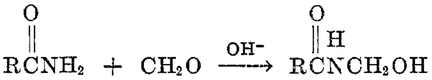
Unstable in acid

The amidomethyl compounds may be looked upon as acetals in which one of the —O— groups has been replaced by —C(O)NH—. This has the effect of stabilizing the remaining —O— linkage to some extent, but boiling with dilute mineral acid will still split formaldehyde between two molecules with the formation of distearamidomethane (V). This compound can be considered as an acetal in which both —O— groups have been replaced by —C(O)NH— and the stability has been increased to the point that boiling with concentrated mineral acid is required to split out the methylene group.

Further comparisons are:

AMIDO COMPOUNDS

ACETALS

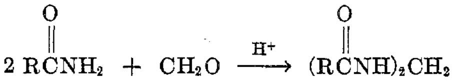


$$\mathrm{R\overset{\overset{O}{\|}}{C}NH_2 + CH_2O \xrightarrow{OH^-} R\overset{\overset{O}{\|}}{C}\overset{H}{N}CH_2OH}$$

Stable

$$\mathrm{ROH + CH_2O \xrightarrow{OH^-} ROCH_2OH}$$

Exists in solution only



$$\mathrm{2\,R\overset{\overset{O}{\|}}{C}NH_2 + CH_2O \xrightarrow{H^+} (R\overset{\overset{O}{\|}}{C}NH)_2CH_2}$$

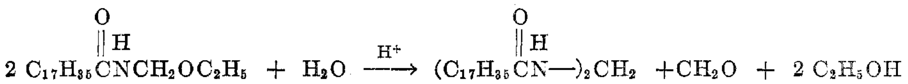
Stable in alkali
Unstable in conc'd strong acid

$$\mathrm{2\,ROH + CH_2O \xrightarrow{H^+} (RO)_2CH_2}$$

Stable in alkali
Unstable in acid

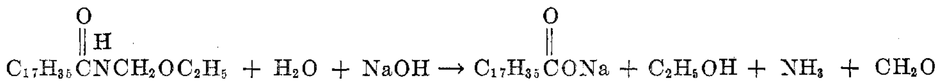
The amidomethyl ethers are stable under ordinary conditions, but decompose readily at elevated temperatures. The plots of time at a fixed temperature *vs.* the melting point of the decomposition residue, shown in Figure 1, illustrate the stability of the stearamidomethyl ethyl ether (II). The ultimate melting point for the decomposition product of stearamidomethyl ethyl ether should be that of distearamidomethane (V, m.p. 147°).

These ethers decompose in boiling 5% sulfuric acid to yield the theoretical amount of formaldehyde (13) in accordance with:



$$\mathrm{2\,C_{17}H_{35}\overset{\overset{O}{\|}}{C}\overset{H}{N}CH_2OC_2H_5 + H_2O \xrightarrow{H^+} (C_{17}H_{35}\overset{\overset{O}{\|}}{C}\overset{H}{N}\text{—})_2CH_2 + CH_2O + 2\,C_2H_5OH}$$

Refluxing in 50% sodium hydroxide will decompose them quantitatively to yield ammonia.



$$C_{17}H_{35}\overset{O}{\overset{\|}{C}}\overset{H}{N}CH_2OC_2H_5 + H_2O + NaOH \rightarrow C_{17}H_{35}\overset{O}{\overset{\|}{C}}ONa + C_2H_5OH + NH_3 + CH_2O$$

They are soluble in most organic solvents and are easily crystallized from acetone.

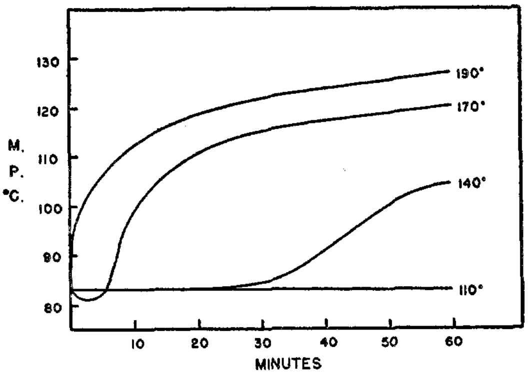


FIGURE 1. DECOMPOSITION OF STEARAMIDOMETHYL ETHYL ETHER

EXPERIMENTAL

Materials. Commercial stearamide (93% stearamide) was recrystallized twice from alcohol to yield a white material, m.p. 107° [Lit. 109° (14)]. Preliminary comparison between derivatives of this stearamide with derivatives of pure stearamide showed no perceptible difference in chemical or physical properties.

Methods. (a) *Formaldehyde determination.* Formaldehyde yield was determined by digestion at reflux for one hour with 5% aqueous sulfuric acid followed by steam-distillation with the tip of the condenser below the surface of the liquid in the receiver. The colorimetric method of Hoffpauir (15) was employed for the determination of formaldehyde content of the distillate.

(b) *Ammonia determination.* Samples of ethers (0.1 g.) were placed in 200-ml. flasks attached to a semi-micro Kjeldahl apparatus. Then 25 ml. of 50% sodium hydroxide was run in and steam was passed through the mixture until 200 ml. had distilled into the receiver containing 10 ml. of 40% boric acid according to the Kjeldahl method of Cole and Parks (16). The volume of liquid in the reaction flask was kept constant by the application of heat. The ammonia in the distillate was titrated with 0.03 *N* hydrochloric acid using the mixed indicator of Cole and Parks.

(c) *Thermal decomposition.* Samples of the ethers in melting-point capillaries were placed in a mechanical convection oven previously heated to the desired temperature. At regular intervals a sample was removed, allowed to cool, and the melting point determined. The melting point was considered as that point where a clear homogeneous liquid was formed. Similar series were run at various temperatures and the melting points of the residues plotted *versus* the time at the prescribed temperature.

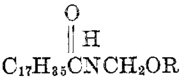
(d) *Molecular weight determination.* Molecular weights were determined by the ebullioscopic method of Menzies and Wright (17) using the differential water thermometer of Menzies (18).

Methylolstearamide. Methylolstearamide was prepared by the reaction of stearamide with paraformaldehyde in benzene in the presence of potassium carbonate (2) but the reaction sometimes failed to proceed, and the method was abandoned in favor of the following modification of the method of Pikl (19, 20):

Stearamide (182 g.) was dissolved in 3.5 liters of alcohol at 70°. To this was added 250 ml. of 40% formalin and enough sodium hydroxide to just make the solution basic to litmus. The solution was stirred at 70° for 3 hours during which the product began to crystallize. The mixture was cooled and filtered, yielding 83% of methylolstearamide. Recrystallization from methanol gave m.p. 115° (Lit. 115°).

TABLE I

STEARAMIDOMETHYL ETHERS



$C_{17}H_{35}\overset{O}{\overset{\|}{C}}\overset{H}{N}CH_2OR$

R	METHOD	YIELD, %	M.P., °C. (UNCORR.)		ANALYSIS[a]						
					C		H		N		
										Found	
			Found	Lit.	Calc'd	Found	Calc'd	Found	Calc'd	Kjeldahl	Hydrolysis
CH_3	A	85	87	88–89 (11–12)	73.33	73.28	12.62	12.47	4.28	4.19	4.27
C_2H_5	A	64	85		73.84	74.02	12.69	12.72	4.10	4.08	4.07
C_2H_5	B	84									
C_2H_5	C	66									
C_2H_5	D	76									
C_2H_5	E	54									
C_2H_5	F	69									
C_2H_5	G	84									
C_2H_5	H	40									
i-C_3H_7	A	85	72–73		74.30	74.51	12.76	12.76	3.94	3.97	3.98
C_4H_9	A	—	82–83		74.73	73.51	12.82	12.53	3.79	3.90	—
C_8H_{17}	A	56	82–83	81 (11–12)	76.17	75.62	13.02	12.94	3.29	3.51	3.58
C_6H_5	A	50	116–117		77.07	77.18	11.12	11.30	3.60	3.57	—

[a] Carbon hydrogen analyses were conducted by L. E. Brown; Kjeldahl nitrogen determination by E. R. McCall.

Anal. Calc'd for $C_{19}H_{39}NO_2$: N, 4.47; Mol. wt., 313; CH_2O, 4.78.
Found: N, 4.44; Mol. wt., 308; CH_2O, 4.43.

Stearamidomethyl acetate. Stearamidomethyl acetate may be prepared by the acetylation of methylolstearamide or directly from stearamide (21). Stearamide (200 g.) and 25 g. of paraformaldehyde were dissolved in 200 ml. of acetic anhydride and 400 ml. of glacial acetic acid. The solution was heated at 70° for 4 hours, cooled, filtered, and recrystallized from acetone. The yield was 66% and the product melted at 92–93°.

Anal. Calc'd for $C_{21}H_{41}NO_3$: CH_2O, 4.21; Sapon. equiv., 355.
Found: CH_2O, 4.09; Sapon. equiv., 353.

Stearamidomethylpyridinium chloride. Stearamide (141 g., 0.5 mole) and 20 g. of paraformaldehyde were added to 0.5 mole of pyridine hydrochloride in 2 liters of pyridine. The mixture was heated at 80° for 10 hours, cooled, and filtered (2). An equal volume of cold acetone was added to the filtrate and the precipitate recovered and added to the original crop. The combined solids were recrystallized from acetone to yield 160 g. (78%) melting at 135°. The material sintered about 92° and the final melting point varied with the rapidity of heating, probably because of partial conversion to distearamidomethane.

Anal. Calc'd for $C_{24}H_{43}ClN_2O$: N, 6.81; Cl, 8.63; CH_2O, 3.65.

Found: N, 6.33; Cl, 8.53; CH_2O, 3.99.

Stearamidomethyl ethyl ether. (a) Methylolstearamide (5 g.) was dissolved in 40 ml. of ethanol at 60°. Concentrated sulfuric acid (1 ml.) was added and heating was continued for five hours. The solution was cooled and the solids recrystallized from ethanol (11, 12). The product weighed 3.5 g. (65%) and melted at 85°.

(b) Stearamidomethylpyridinium chloride (10 g.) was added to 100 ml. of absolute ethanol. The mixture was refluxed for three hours, cooled, filtered, and the solids recrystallized from ether. The yield was 84%.

(c) As in method (b), with the addition of 5 ml. of pyridine. The yield was 66%.

(d) As in method (b), with the addition of 3 g. of potassium hydroxide. The yield was 76%.

(e) Stearamidomethyl acetate (10 g.) was dissolved in 100 ml. of ethanol and refluxed for three hours. Water was added to precipitate the solids which were recrystallized from ethanol. The yield was 54%.

(f) As in method (e), with the addition of 5 ml. of pyridine. The yield was 69%.

(g) As in method (e), with the addition of 3 g. of potassium hydroxide. The yield was 84%.

(h) As in method (e), with the addition of 2 ml. of concentrated hydrochloric acid. The yield was 40%.

Other ethers. Stearamidomethyl ethers of propanol-2, *n*-butanol, octanol, and phenol were prepared from methylolstearamide and the appropriate alcohol in accordance with method (a). The results are given in Table I.

Acid decomposition of stearamidomethyl ethyl ether. Hydrolysis with 5% sulfuric acid as described above yielded 97.7% of the theoretical formaldehyde (0.5 mole of CH_2O per mole of the ether). The residue isolated from the reaction mixture was distearamidomethane.

Basic decomposition of stearamidomethyl ethyl ether. Decomposition with 50% sodium hydroxide, as described above, gave a nitrogen content of 4.09% compared to a calculated value of 4.10%.

SUMMARY

The stearamidomethyl ethers of methanol, ethanol, propanol-2, *n*-butanol, octanol, and phenol have been prepared and characterized. The ethyl, isopropyl, butyl, and phenyl derivatives are new compounds. It has been shown that their properties do not resemble those of ethers, but rather resemble those of acetals as would be predicted.

New Orleans 19, La.

REFERENCES

(1) Baldwin, Evans, and Salkeld, U. S. Patents 2,278,417 and 2,278,418 April 1942.
(2) Baldwin and Walker, British Patent 475,170 Nov. 1937.
(3) Baldwin and Walker, U. S. Patent 2,146,392 Feb, 1939.
(4) Imperial Chemical Industries, Ltd., French Patent 821,856 Dec. 1937.
(5) Pikl, U. S. Patent 2,306,185 Dec. 1942.
(6) Schuyten, Reid, Weaver, and Frick, *Textile Research J.*, **18**, 408 (1948).
(7) Mullin, *Textile Colorist*, **60**, 96 (1938).
(8) Bonnet, *Ind. textile*, **57**, 219, 254 (1940).
(9) Chwala, *Melliand Textilber.*, **19**, 905 (1928).
(10) Burnand, *Teintex*, **4**, 27 (1939).

(11) Engelmann and Pikl, U. S. Patent 2,313,741 March 1943.
(12) Engelmann and Pikl, U. S. Patent 2,361,185 Oct. 1944.
(13) Davis, *J. Soc. Dyers Colourists*, **63**, 260 (1947).
(14) Lange, *Handbook of Chemistry*, 5th Ed. (1944).
(15) Hoffpauir, Buckaloo, and Guthrie, *Ind. Eng. Chem., Anal. Ed.*, **15**, 605 (1943).
(16) Cole and Parks, *Ind. Eng. Chem., Anal. Ed.*, **18**, 61 (1946).
(17) Menzies and Wright, *J. Am. Chem. Soc.*, **43**, 2314 (1921).
(18) Menzies, *J. Am. Chem. Soc.*, **43**, 2309 (1921).
(19) Pikl, U. S. Patent 2,477,346 July 1949.
(20) Einhorn, *et al.*, *Ann.*, **343**, 207 (1905).
(21) Shipp, U. S. Patent 2,232,485 Feb. 1941.