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Hydrophobic Compounds and Polymers from Long Chain Alkanamide-Formaldehyde Condensation Reactions

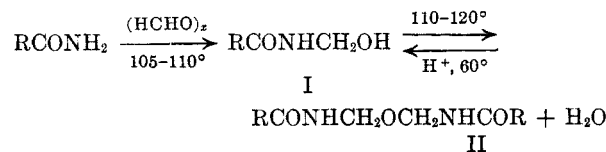
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N,N'-Oxydimethylenebisalkanamides were obtained by thermal or acid-catalyzed dehydration between two higher *N*-hydroxymethylalkanamides. At a higher temperature and with acid catalysts the self-ethers split out formaldehyde and gave the hydrophobic *N,N'*-methylenebisalkanamides. *N*-Hydroxymethylalkanamides and acrylamide gave polymerizable *N*-(alkanamidomethyl)acrylamides. In analogy to the *N,N'*-methylenebisalkanamides, polymers having side chains twelve to twenty carbons long were high-melting, hydrophobic, and their side chains showed paraffinic crystallinity by x-ray analysis; those with shorter side chains were not crystalline or hydrophobic.

Reactions of formaldehyde with alkanamides were first studied in 1905 by Einhorn,¹ who prepared *N*-hydroxymethylpropanamide and related compounds. Ugelstad and De Jonge² showed by kinetic methods that the reaction to give the *N*-hydroxymethyl compound is reversible.

We were surprised to discover that by simply heating a melt of a pure higher alkanamide such as octadecanamide and polymeric formaldehyde at 105–110°, the *N*-hydroxymethylamide (I) was formed. No acid or alkaline catalyst was added to the mixture, as is required at lower temperatures in solution.



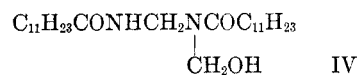
R = C₁₁ to C₂₁

As heating was continued (alkali being absent), dehydration of I to the long chain *N,N'*-oxydimethylenebisalkanamide (II) also occurred; removal of water drove the latter reaction to completion. No other products were produced, and II was stable to several hours of heating at 120°. Under very carefully controlled conditions II was also prepared from I in nonhydroxylic solvents at 60–80° by acid catalysis.^{3,4} The reaction was reversed by addition of water at a pH of 3–4. Heating a solution of I or II in an alcohol other than *t*-butyl alcohol at a pH of 3–4 gave the *O*-alkyl ethers^{5,6} (*N*-alkoxymethylalkanamides). Preparations of II are described in Table I. Further heating of II at

120–140° or treatment with strong acid at a pH below 3 in solution converted the self-ether to the *N,N'*-methylenebisalkanamide (III), irreversibly. This sequence, I ⇌ II → III, was observed previously by Arbusova⁷ in the case of *N*-hydroxymethylmethacrylamide. The technical significance of this process is that it provides an efficient means for depositing the effective hydrophobizing agent *N,N'*-methylenebisoctadecanamide *in situ* on a fabric or fiber surface.⁴ II, itself, is not particularly hydrophobic.

Treatment of I with aqueous alkali or with pyridine and benzoyl chloride gave the parent amide rather than II. Lower alkyl or aryl analogs of II have been obtained in this way by Einhorn¹ and later by Zigeuner,⁸ who showed them to be true ethers having no free hydroxyl group.

Recently Petterson and Brownell⁹ isolated a dehydration product from *N*-hydroxymethyldodecanamide, the infrared spectrum of which was identical with those of II. These latter workers⁹ were apparently unaware of Zigeuner's work and discarded structure II in favor of IV.



The correctness of structure II as demonstrated by Zigeuner for lower alkyl analogs, however, is further supported by our results. We observed no absorption due to the hydroxyl group in the infrared spectrum of II (when free of I) and derivatives of II contain only the RCONHCH₂-moiety.⁸ Unlike I, which slowly reverts to the amide and formaldehyde, samples of II have been kept several years without change. Efforts to isolate IV have failed in the past because such structures are too unstable to be obtained directly from reaction of I with form-

(1) A. Einhorn, *Ann.*, **343**, 204 (1905).

(2) J. Ugelstad and J. De Jonge, *Rec. trav. chim.*, **76**, 919 (1957).

(3) J. Pikl, U. S. Patent 2,509,649, April 25, 1950.

(4) N. O. Brace, U. S. Patent 2,793,182, May 21, 1957.

(5) M. Englemann and J. Pikl, U. S. Patent 2,361,185, October 24, 1942.

(6) J. M. Weaver, H. A. Schuyten, J. G. Frick, Jr., and J. D. Reid, *J. Org. Chem.*, **16**, 1111 (1951). The amount of acid catalyst previously used was too much to give ethers alone. We found that a pH of 3–4 was satisfactory, however.

(7) J. A. Arbusova, *et al.*, *J. Gen. Chem. (U.S.S.R.) (Eng. Transl.)*, **28**, 1322 (1958).

(8) G. Zigeuner, W. Knierzinger, and K. Voglar, *Monatsh. Chem.*, **82**, 817 (1951); G. Zegeuner, *Kunststoffe*, **41**, 221 (1951).

(9) R. C. Petterson and H. R. Brownell, *J. Org. Chem.*, **25**, 843 (1960).

TABLE I
SYNTHESIS OF LONG CHAIN *N,N'*-OXYDIMETHYLENEBISALKANAMIDES (II)
METHOD A. ACID-CATALYZED DEHYDRATION OF I
METHOD B. FUSION AND DISTILLATION OF WATER

Compound II R	Method	Yield, %	M.P.	Calcd., %			Found, %		
				C	H	N	C	H	N
C ₁₁ H ₂₃ ^a	A	70	95-96	—	—	6.5	—	—	6.0
C ₁₇ H ₃₅ ^b	A	92	108-110	74.42	12.48	4.82	73.9	12.5	4.48
C ₁₇ H ₃₅ ^c	A	—	110-112	75.00	12.58	4.60	74.45	12.4	64.45
C ₁₇ H ₃₅ ^b	B	95	100-105 ^d	74.42	12.48	4.82	74.8	12.6	4.6
C ₂₁ H ₄₃ ^e	A	90	111.5-112.5	—	—	3.87	—	—	3.92

^a From a technical grade of *N*-hydroxymethyldecanamide, m.p. 102-104.5°, containing also *N*-hydroxymethyldecan- and -tetradecanamide. ^b From a mixture of about 55% of *N*-hydroxymethyloctadecanamide, m.p. 112-114° and 45% of *N*-hydroxymethylhexadecanamide. ^c From *N*-hydroxymethyloctadecanamide, m.p. 117°; contained about 93% of C₁₇H₃₅-CONHCH₂OH. ^d Crude product recrystallized from isopropyl acetate; it had m.p. and infrared spectrum identical with II. ^e From *N*-hydroxymethyldocosanamide, m.p. 119.5-120.5°; experiment done by Dr. J. Píkl.

TABLE II
N-(ALKANAMIDOMETHYL)ACRYLAMIDES AND -METHACRYLAMIDES
RCONHCH₂NHCOCH=CH₂

R	Yield, %	M.P.	Calcd, %			Found, %		
			C	H	N	C	H	N
CH ₃ - ^a	69	166-167	50.63	7.09	19.7	50.1	7.1	19.7
<i>n</i> -C ₅ H ₁₁ - ^b	85	152.3	60.6	9.1	14.1	60.6	9.3	14.0
<i>n</i> -C ₇ H ₁₅ - ^c	81	155.6	63.7	9.7	12.4	64.1	9.93	11.9
<i>n</i> -C ₁₁ H ₂₃ - ^d	85	153.4	68.08	10.71	9.96	68.4	10.5	9.4
<i>n</i> -C ₁₇ H ₃₅ - ^e	87	152.3	71.58	11.44	7.95	70.3	11.5	7.5
RCONHCH ₂ NHCOC(CH ₃)=CH ₂								
<i>n</i> -C ₁₇ H ₃₅ - ^{e,f}	81	111-113	72.10	11.55	7.65	71.0	11.5	7.3

^a From equimolar amounts of *N*-hydroxymethylacetamide and acrylamide; see Experimental part for details. ^b From *N*-hydroxymethylhexanamide, m.p. 55-75° (dec. on heating). ^c From *N*-hydroxymethyloctanamide, m.p. 90-92°. ^d From *N*-hydroxymethyldecanamide, m.p. 102-104.5°. ^e From a mixture, m.p. 112°, containing about 55% of *N*-hydroxymethyloctadecanamide and 45% of *N*-hydroxymethylhexadecanamide. ^f Recrystallized from 2-butanone and acetone.

aldehyde¹⁰; an excess of paraformaldehyde with III gave the *N,N'*-bishydroxymethyl^{10,11} and the *N,N'*-bischloromethyl^{11,12} derivatives under more vigorous conditions than those which give II and III from I.

ω-Trifluorotridecanamide derivatives. The formaldehyde condensation products of 13,13,13-trifluorotridecanamide (V) showed unexpected properties. Despite the wide separation of its *ω*-trifluoromethyl group and amide function, *N*-hydroxymethyl-13,13,13-trifluorotridecanamide (VI) melted some 50° lower than the hydrocarbon analog and in the presence of acid or alkali very readily reverted to V. *N,N'*-methylenebis-13,13,13-trifluorotridecanamide (VII) could be obtained only by careful heating of VI with a trace of acid in 2-butanone solution.

N-(Alkanamidomethyl)acrylamides and -methacrylamides. Acid-catalyzed condensation of I with acrylamide (or methacrylamide) gave the "mixed" *N,N'*-methylenebisamide in good yield. Preferably

an excess was used of the water-soluble reactant, which could be readily removed by washing from the reaction product. Thus, *N*-(octadecanamido-methyl)acrylamide (VIII) was prepared in 87% yield from one mole of I and two moles of acrylamide with hydrochloric acid catalyst.¹³ Alternatively, *N*-hydroxymethylacrylamide and a higher alkanamide could be used, from which *N,N'*-methylenebisacrylamide could be extracted. Preparations of VIII and analogous compounds are listed in Table II.

Tetradecyl mercaptan was added with alkaline catalyst in a 1,4- manner to VIII to give a new *N,N'*-methylenebisamide having two long chains.



(13) Reaction of acrylonitrile and I in concentrated sulfuric acid [F. R. Benson and J. J. Ritter, *J. Am. Chem. Soc.*, **71**, 4128 (1949)] gave only III, even though these conditions have been used to give *N*-(benzamidomethyl)acrylamide [E. E. Magat and L. F. Salisbury, *J. Am. Chem. Soc.*, **73**, 1035 (1951)] and methylenebisacrylamides from the lower aliphatic dinitriles and formaldehyde [D. T. Mowry and E. L. Ringwald, *J. Am. Chem. Soc.*, **72**, 4439 (1950); E. E. Magat, L. B. Chandler, B. A. Faris, J. E. Reith, and L. F. Salisbury, *J. Am. Chem. Soc.*, **73**, 1031 (1951)].

(10) J. Píkl, U. S. Patent 2,306,185, December 22, 1942.

(11) M. Hunt and H. W. Bradley, U. S. Patent 2,493,068, January 3, 1950.

(12) M. A. T. Rogers, U. S. Patent 2,386,140, October 2, 1945.

Hydrophobic polymers and copolymers of VIII. The structure of a polymer of VIII bears a close analogy to that of long chain methylenebisamides (III), in that a multiplicity of long side chains attached to the strongly polar methylenebisamide grouping are present. For this reason polymers of VIII and its analogs were prepared and their hydrophobic properties determined. Those polymers of this type having side chains of twelve to eighteen carbons softened above 200°, were markedly crystalline by x-ray analysis (paraffinic identity period of 4.17 Å), and were extremely hydrophobic¹⁴; while polymers of *N*-(alkanamidomethyl)acrylamides having short side chains (one to eight carbons) softened above 250°, showed no paraffinic crystallinity, and were not hydrophobic. Copolymers of VIII with several common monomers were prepared (Table III). The softening range and x-ray paraffinic crystallinity were affected primarily by the nature of the comonomer and, to a lesser extent, by the amount present. Copolymers containing an equimolar amount of small comonomers such as methyl methacrylate or styrene showed crystallinity and melted above 120°. All were soluble; however, those containing 2,3-epoxypropyl methacrylate or *N*-hydroxymethylacrylamide were readily cross-linked by heating to give an insoluble solid and in this way were irreversibly deposited on a fabric or solid surface. A copolymer containing an equimolar amount of *n*-tetradecyl methacrylate and VIII softened near 100° and was not crystalline. It was apparent that the dissimilar long chain ester repeating unit interfered with side chain orientation of the amide groups. Only those copolymers containing a major amount of VIII gave hydrophobic coatings, whereas the noncrystalline copolymer containing an equal number of long chains both of *n*-tetradecyl methacrylate and of VIII was not hydrophobic.¹⁵ We conclude that oriented long side chains and a highly polar polymer chain "backbone" are together responsible for

(14) N. O. Brace, U. S. Patent 2,966,481 (1960). Analogous polymers having long hydrocarbon side chains, such as polyvinyl octadecanoate [D. Swern, W. S. Port, J. E. Hansen, E. F. Jordan, J. W. O'Brien, and T. J. Dietz, *J. Am. Chem. Soc.*, **69**, 2439 (1940); **70**, 2334 (1949); **71**, 2377 (1952)], poly-*p*-octadecylstyrene [C. G. Overberger, C. Frazier, J. Mandelman, and H. F. Smith, *J. Am. Chem. Soc.*, **75**, 3326 (1953)], or poly-*n*-hexadecyl acrylate [C. E. Rehberg and C. H. Fisher, *J. Am. Chem. Soc.*, **66**, 1203 (1944); H. S. Kaufman, A. Sacher, T. Alfrey, and I. Fankuchen, *J. Am. Chem. Soc.*, **70**, 3147 (1948)] also show paraffinic crystallinity by x-ray examination [H. Mark, *Annals N. Y. Acad. of Sci.*, **57**, (4), 445 (1953)] but have much lower melting points. Polyvinyl octadecanoate and poly-*n*-hexadecyl acrylate, moreover, do not exhibit a degree of hydrophobicity comparable to poly-*N*-(octadecanamidomethyl)acrylamide.

(15) See ref. 4 and 14 for method of application to textiles and testing of hydrophobicity. It is interesting to note that VIII (before polymerization) was ineffective as a hydrophobic coating on textiles, as was octadecanamide itself. III (R = C₁₇H₃₅), however, was an excellent hydrophobe.

TABLE III
COPOLYMERS OF *N*-(OCTADECANAMIDOMETHYL)ACRYLAMIDE^a

Comonomer	Charged Mol. Ratio	Polymer Softening Range	X-Ray Cryst., ^b Å.
Vinyl acetate	1:1	195-205 ^c	Yes 4.17
Methyl methacrylate	1:1	132-140	Yes 4.17
Styrene	1:1	120-130 ^d	Yes 4.17
<i>n</i> -Tetradecyl methacrylate	1:1	90-108	No ^e
2,3-Epoxypropyl methacrylate	20:1	196-202	Yes 4.15
<i>N</i> -(Hydroxymethyl)acrylamide	10:1	192-201	Yes 4.15

^a All polymerizations done under nitrogen atmosphere in benzene solution at 60-80° with 0.3 to 1.5% of α, α' -azobisisobutyronitrile initiator. See Experimental part. ^b Peak of sharp band; x-ray spectra taken of powder or pressed plug in North American Philips x-ray spectrometer. ^c Analysis showed that not all the vinyl acetate was incorporated into the polymer. ^d Polymer precipitated in methanol from benzene solution. ^e Broad band only (4.10-5.0 Å).

the hydrophobic properties of these film-forming polymers.

Infrared techniques proved most valuable for identifying individual compounds and determining the amount of each present in mixtures. Elementary analyses and melting points were frequently ineffective because only minor differences exist among different compounds. Characteristic absorption bands are listed in the Experimental part.

EXPERIMENTAL

N,N'-Oxydimethylenebisalkanamides (II). *N*-Hydroxymethyloctadecanamide.^{5,6} An equimolar amount of paraformaldehyde was added in three portions to an isopropyl alcohol solution of technical grade stearamide (containing about 55% of octadecanamide and 45% of hexadecanamide) at 60°. Potassium hydroxide (10% aqueous) solution was added dropwise to maintain the reaction mixture just alkaline when tested with phenolphthalein paper. After 1 hr. at 60° the mixture was cooled to 30°, acidified with acetic acid, and filtered. I, m.p. 110-111°, was obtained in 85-90% yield. A Zerewitinoff determination showed 0.65% active hydrogen (calcd., 0.67%). The infrared spectrum was that given in ref. 9; bands at 3.05 (NH), 3.15 (OH), 6.45 (NHCH₂-) and 8.95, 9.90, 13.74, 13.94, and 14.30 μ were useful for identification.

Thermal dehydration of I. Equimolar amounts of paraformaldehyde and octadecanamide were heated at 105-110°. Infrared spectra of known mixtures of I and II (see below) were used to determine quantitatively the amount of each present. A series of samples removed from the hot melt contained the following percentages of II, the remainder being I.

Time (hr.)	1	3	5	7	23
% II	55	72	80	89	100

The infrared spectrum of the final product was identical to that of II. The process was completed in 2 to 3 hr. when the water was removed under reduced pressure at 120°. II was stable to long heating at 120°. Analyses are listed in Table I; a Zerewitinoff determination gave 0.37% active hydrogen (calcd., 0.34%).

Acid-catalyzed dehydration of I to II. I (390 g., 1.3 moles; containing about 55% of *N*-hydroxymethyloctadecanamide and 45% of *N*-hydroxymethylhexadecanamide, m.p. 112–114°) in 500 cc. of 2-butanone was stirred, heated to 60°, and made just barely acid to Congo red indicator paper by the addition of 6.0 cc. of 24% isopropyl alcoholic hydrogen chloride solution. The mixture grew thicker and 1000 cc. of 2-butanone was added during the course of the reaction. A sample was removed after 1 hr., m.p. 109–111°; 2 hr., m.p. 103–104.5°; 4 hr., m.p. 106–107°; and 5 hr., m.p. 107–108°. The slurry was filtered at 30°. The white solid was washed with a quantity of fresh cold solvent and air dried. The product weighed 350 g. (92% yield); m.p. 107.5°. An infrared spectrum of this material showed no bands attributable to I, octadecanamide or III; bands at 3.00 (NH), 6.00 (C=O), 9.75 (CH₂OCH₂), and 13.90 μ were useful for identification. There was no absorption band at 3.15 μ when I was absent. A comparison of absorbance values at 14.30 and 13.90 μ was used to calculate the relative amounts of I and II in a mixture of only I and II. This method was developed by F. W. Blodgett.

At higher temperatures (120–140°) II, in the presence of tartaric acid, or a trace of mineral acid, or at pH of 1–4 as shown on indicator paper in solution at 60–80°, yielded quantitatively formaldehyde and III; m.p. 148–149°.

Stearamidomethyl alkyl ethers. The amount of acid used in preparing *N*-alkoxymethyloctadecanamides (*i.e.*, methyl, ethyl, isopropyl, *n*-propyl, *n*-butyl, phenyl ether derivatives of I) by previous workers^{5,6} was critical. In our hands, just enough acid to give a pH of 3 (about 1 to 2 drops sulfuric acid) sufficed to give the *O*-alkyl ether and did not cause further decomposition to III, which we observed when the recommended 1 ml.^{5,6} was used. *N*-*n*-Propoxymethyloctadecanamide, m.p. 81.5–83°, was prepared in this way in 70% yield by reaction of I or II with *n*-propyl alcohol.

Anal. Calcd. for C₂₁H₄₁NO₂: C, 73.95; H, 12.68; N, 4.10; mol. wt., 341.57. Found: C, 73.9; H, 12.6; N, 4.10; mol. wt., 360.

Infrared spectra of the various *N*-alkoxymethyloctadecanamides were distinctive (different from II) and were used to identify the individual compounds. There was no absorption band at 9.75 μ in these *O*-alkyl ethers.

N-Hydroxymethyl-13,13,13-trifluorotridecanamide (VI). From 5.3 g. (0.014 mole) of amide V¹⁶ (mp. 103°), 0.70 g. (0.02 mole) of paraformaldehyde, 1.0 g. of potassium carbonate, and 30 cc. of benzene, heated for 2 hr. at 50°, and the benzene allowed to evaporate, was obtained 5.5 g. (100%) of VI, m.p. (sinter 64°) 65–66°. Attempted recrystallization of 1.0 g. in 10 cc. methanol gave 0.01 g. of the amide V, m.p. (sinter 99.5°) 102–105°, and mixtures of V and VI. VI was too soluble and unstable in methanol to be crystallized.

Anal. Calcd. for C₁₄H₂₅F₃O₂N: C, 56.6; H, 8.82; F, 19.6; N, 4.71. Found: C, 56.6; H, 8.95; F, 20.2; N, 4.7.

VI could not be prepared in alcohol by the procedure used for I.

N,N'-Methylenebisalkanamides (III). *N,N'*-Methylenebis tridecanamide. A mixture of 1.0 g. of tridecanamide, 10 cc. of 37% aqueous formaldehyde solution, and 1.0 cc. of concd. hydrochloric acid was heated at 68–70° for 1 hr. The white thick paste was collected on a Büchner funnel, neutralized with ammonium hydroxide, and washed with water. The air dried solid, 1.0 g. (100%); m.p. (sinter 138°) 142–146°; was recrystallized from 10 cc. of boiling isopropyl alcohol (insoluble in boiling ether or ethyl acetate); m.p. 154–154.6°; 0.70 g.

Anal. Calcd. for C₂₇H₅₂O₂N₂: C, 73.3; H, 12.0; N, 6.32. Found: C, 74.4; H, 12.5; N, 6.2.

The identical procedure gave a quantitative yield of *N,N'*-methylenebis dodecanamide,⁹ m.p. 148.9°. The same yield resulted from reaction of I or II in 2-butanone made strongly

acid with hydrochloric acid. The infrared spectrum of III showed an NH band at 3.05 μ , C=O at 6.10 μ , N—CH₂N— at 8.86 μ and bands at 13.75, 13.90, and 14.40; μ ; its presence in a mixture could be readily detected.

N,N'-Methylenebis-13,13,13-trifluorotridecanamide (VII).

(1) *From V and aqueous formaldehyde.* Reaction of 1.0 g. (0.0375 mole) of V with 10 cc. of 37% formalin and 1 cc. of concd. hydrochloric acid at 72–80° for 1 hr. gave an oil, rather than the expected high-melting solid. It was extracted with ether, the ether solution washed with water, and the ether evaporated. The oil partly congealed to a soft semisolid which was completely soluble in petroleum ether (b.p. 30–60°) containing a drop or two of methanol. Various solvents gave only solution at room temperature or deposition of a soft gel.

(2) *From VI in 2-butanone.* A solution of 0.5 g. (0.0017 mole) of VI in 10 cc. of 2-butanone was heated to about 60° and made strongly acid by the addition of one drop of concd. hydrochloric acid. Gas evolution occurred. The solution was kept at a gentle boil for 5 hr. After 1 hr., 3 drops of concd. hydrochloric acid was added. The solution (10.0 cc.) when cooled deposited a soft solid (0.11 g.); m.p. (sinter 132°) 138–143.3°; a second crop of VII was a white soft powder (0.05 g.); m.p. 140.1–140.3°.

Anal. Calcd. for C₂₇H₄₈F₆N₂O₂: C, 60.4; F, 19.36; H, 9.01. Found: C, 58.9; F, 19.3; H, 9.0.

Its infrared spectrum was similar at characteristic points to III.

Subsequent fractions of solid separated from solution consisted of VII mixed with V [0.35 g., m.p. (sinter 99°) 106–123°]; and V, m.p. 95–100° and 97.5–100° (0.06 g.).

N-(Alkanamidomethyl)acrylamides. (a) *N-(Octadecanamidomethyl)acrylamide (VIII).* A slurry of 300 g. (1 mole) of I (m.p. 110–111°), 142 g. (2.0 moles) of acrylamide, 0.5 g. of sodium nitrite (polymerization inhibitor), 20 cc. of concd. hydrochloric acid, and 20 cc. of water in 1.7 l. of 2-butanone was stirred at 50–55° for 2 hr. The thick white slurry was cooled to 30° and neutralized with sodium hydroxide solution. The solid was collected on a Büchner funnel, washed with water, and reslurried twice. After drying VIII weighed 310 g.; m.p. 150–150.4°. A mixed melting point with III, a possible product from this reaction, was 141–144.5°, showing nonidentity. Analyses of VIII and homologs are listed in Table II. The infrared spectrum of VIII was very similar to III, but the vinyl stretching band at 6.15 μ was present, though poorly resolved.

VIII decolorized dilute permanganate solution and reacted with *n*-tetradecylmercaptan in pyridine solution with potassium hydroxide catalyst to give *N*-(octadecanamidomethyl)-[2-(tetradecylthio)]-propanamide, m.p. 141–142.5°. Recrystallized from alcohol solution, it had m.p. 142–145°.

Anal. Calcd. for C₃₅H₇₂O₂N₂S: C, 71.90; H, 12.4; N, 4.79; S, 5.48. Found: C, 70.5; H, 11.7; N, 4.8; S, 4.08.

(b) *Polymerization of VIII.* The method described is typical for all polymerizations with this monomer alone or with other monomers.

A slurry of 11.0 g. of VIII and 250 cc. of analytical reagent benzene was heated under a nitrogen atmosphere to 80° while stirring until a clear solution was formed. A solution of α,α' -azobisisobutyronitrile ABN in benzene (see table below) was added and stirring continued for 4 hr. Benzene was removed by vacuum distillation during the last 2 hr. Alternatively, the polymer was precipitated by addition of ace-

Mol. % ABN Initiator	Polymer Yield, %	Intrinsic Viscosity (Chloroform 30°)	Softening Range
8.8		0.15	220–233°
5.1	75	0.26	
2.55	82	0.32	
0.64	79	0.37	

(16) G. Gavlin and R. G. Maguire, *J. Org. Chem.*, **21**, 1342 (1956).

tone and collected on a filter. The residue (or filter cake) was extracted with boiling ethyl acetate and air dried. The following data show the intrinsic viscosity of solutions to be inversely proportional to the α, α' -azobisisobutyronitrile concentration used.

(c) *N*-(Acetamidomethyl)acrylamide. *N*-Hydroxymethylacetamide was prepared from 177.0 g. (3.0 moles) of acetamide and 93.0 g. (3.1 moles) of 94% paraformaldehyde in 300 cc. of ethyl acetate at 50–54°, using 4 cc. of 25% alcoholic potassium hydroxide as catalyst. After 0.5 hr. an additional 2.0 cc. of catalyst solution was added and stirring was continued for 2 hr. A layer of *N*-hydroxymethylamide separated on standing overnight. Stirring was resumed while 213 g. (3.0 moles) of acrylamide and 6.0 cc. of concd. hydrochloric acid were added. After 3 hr. at 53°, 4.0 cc. of concd. hydrochloric acid was added to lower the pH to 1–2. After 2 hr. the solution began to thicken, and crystalline product

separated. The slurry was cooled to 30°, 1.0 g. of sodium nitrite was added, and the solid collected on a Büchner funnel. The filter cake was washed with 100 cc. of ethyl acetate and air dried; its weight was 143.1 g. and m.p. (sinter 148°) 152–156°. Recrystallization from 1:1 ethyl acetate–methanol raised the m.p. to 166–167°. Polymerization occurred in a heated capillary tube at the melting point. Analyses are listed in Table II. The mother liquors gave 164 g. of less pure product (total yield 69%).

(d) *Polymerization of N*-(acetamidomethyl)acrylamide. Polymerization occurred readily in a 10% solution in water with 1% hydrogen peroxide at 40–60°. The polymer invariably formed a gel which was soluble in alcohol–water mixtures, but was insoluble in acetone. The dried polymer was a white, brittle solid which did not melt at 300°.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE MELLON INSTITUTE¹]

The Reaction of Alkyl Halides with Carboxylic Acids and Phenols in the Presence of Tertiary Amines

ROBERT L. MERKER AND MARY JANE SCOTT

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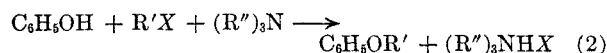
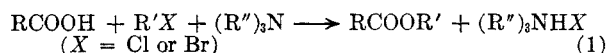
The preparation of a number of esters of aliphatic and aromatic carboxylic acids and of mixed aromatic-aliphatic ethers has been carried out through the reaction of tertiary amine salts of carboxylic acids or phenolic compounds with alkyl halides. In addition to other advantageous factors, the rather large solubility of the amine carboxylates in a variety of organic solvents leads to a wide possible choice of solvent systems and reaction temperatures which are not always obtainable when employing conventional esterification methods.

The use of pyridine to discourage side reactions in the preparation of esters from acid chlorides and alcohols has been reported by Norris and Rigby.² In a variation of this procedure Mills³ carried out this reaction in the presence of excess pyridine in an inert solvent.

The preparation of some *p*-phenylphenacyl esters through reaction of methylammonium carboxylates with *p*-phenylphenacyl bromide has been reported by Drake and Bronitsky.⁴ In a similar reaction Cromwell and Starks⁵ reported the synthesis of α -acetoxy- β -piperidinobenzylacetophenone from α -bromo- β -piperidinobenzylacetophenone and triethylamine acetate in benzene solution. More recently Moreland⁶ has described the preparation of a number of esters from phenacyl bromide, *p*-phenylphenacyl bromide, and *p*-nitrobenzyl chloride through reaction with triethylamine carboxylates.

Concurrent with the above work, a number of silylmethyl esters⁷ were synthesized in this labora-

tory through reaction of chloromethylsilicon compounds with various triethylamine carboxylates. This present paper gives examples of the extension of this general method of esterification to halogen compounds in which the halogen is not activated by an adjacent carbonyl group or aromatic ring as well as its application for the preparation of mixed aliphatic-aromatic ethers.



In general, the procedure for conducting these reactions consisted of adding stoichiometric quantities of the reactants either to an excess of the particular carboxylic acid reactant or an appropriate solvent. The reaction mixture was then refluxed or held at some other temperature for a suitable period of time after which the tertiary amine hydrohalide was either filtered or washed from the reaction mixture. The products were isolated by distillation. Yields varied from about 50 to 93%. Full investigation of variables leading to optimum yields for each reaction system was not attempted, but the results of the reactions carried out proved the method to be most attractive.

Using triethylamine as the tertiary amine in

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(3) J. A. Mills, *J. Chem. Soc.*, 2332, 1951.

(4) N. L. Drake and J. Bronitsky, *J. Am. Chem. Soc.*, **52**, 3715 (1930).

(5) N. H. Cromwell and F. W. Starks, *J. Am. Chem. Soc.*, **72**, 4108 (1950).

(6) W. T. Moreland, *J. Org. Chem.*, **21**, 820 (1956).

(7) R. L. Merker, U. S. Patent 2,833,802, May, 1958.