yield 0.76 g. (95%). The infrared spectrum was identical with that of an authentic sample.[3]

(b) **In Hydrogen Fluoride.**—In a polyethylene bottle was placed 3.2 g. (0.01 mole) of the bromide [IV. $Z = (OCH_2)_2$] and a Teflon-coated magnetic stirring bar. Approximately 50 ml. of liquid hydrogen fluoride was added, and the mixture stirred magnetically for 1 hr. The mixture was allowed to remain in the hood until the hydrogen fluoride had evaporated. The residue was dissolved in 100 ml. of water and evaporated to dryness under reduced pressure (aspirator). The residue was dissolved in 250 ml. of methanol and passed through an Amberlite 401 anion exchange column loaded with bromide. The acridizinium bromide isolated from the eluate was less pure than that obtained in the hydrobromic acid cyclization; yield 1.71 g. (65%), m.p. 230–233°.

(c) **In Sulfuric Acid.**—A solution containing 3.22 g. (0.01 mole) of the bromide [IV. $Z = (OCH_2)_2$] in 30 ml. of concentrated sulfuric acid was stirred at 80–90° for 3 hr. The cooled solution was slowly poured with stirring into 300 ml. of cold ether (−10°). The yellow precipitate was collected on a sintered-glass funnel and then dissolved in 5 ml. of water. Addition of 35% perchloric acid caused the precipitation of acridizinium perchlorate which was purified by crystallization from methanol–ethyl acetate; yield 1.12 g. (40%), m.p. 205–206° (lit.,[3] 205–206°).

(d) **In Polyphosphoric Acid.**—The bromide [1.60 g.; IV. $Z = (OCH_2)_2$] was stirred for 4 hr. at 70–80° with 30 g. of polyphosphoric acid. The mixture was cooled to room temperature and diluted by the addition of about 60 g. of ice. To the resulting solution 35% perchloric acid was added dropwise until further addition caused no further precipitation. The resulting acridizinium perchlorate was collected; yield 1.08 g. (77%), m.p. 197–200°. A sample was recrystallized from methanol–ethyl acetate as light yellow prisms, m.p. 205–206° (lit.,[3] 205–206.2°). It gave no mixed melting point depression with an authentic sample.

2-(1,3-Dioxolan-2-yl)6-methylpyridine [**III.** $\mathbf{Z = (O{-}CH_2{-})_2}$] was prepared starting with 6-methyl-2-picolinaldehyde (III. Z = O) and following the procedure used in the preparation of the lower homolog [I. $Z = (O{-}CH_2{-})_2$] except that 3 molecular equivalents of ethylene glycol were used as well as a correspondingly greater quantity of benzene; yield 63%, b.p. 121–126° (6 mm.), $n^{25}\text{D}$ 1.5200.

Anal. Calcd. for $C_9H_{11}NO_2$: N, 8.48. Found: N, 8.54.

4-Methylacridizinium Bromide (IX. Y = Br).—A solution containing 4.95 g. (0.03 mole) of 2-(1,3-dioxolan-2-yl)-6-methylpyridine and 3.6 ml. (0.031 mole) of benzyl bromide was dissolved in 4 ml. of tetramethylene sulfone and the mixture allowed to stand for 1 month at room temperature. The addition of 100 ml. of ethyl acetate precipitated an oil which was washed with two other portions of ethyl acetate. The resulting oil, which could not be obtained in a crystalline form, was dissolved in hydrobromic acid, and refluxed for 3 hr. The acid was removed in the usual way, and the yellow residue crystallized from methanol–ethyl acetate; yield 0.73 g. (9%), m.p. 233–239°. The analytical sample formed fine yellow needles from the same solvents, m.p. 245–246°; λ_{max} (log ϵ), 200 (4.38), 243 (4.52), 250* (4.50), 364 (3.91), 381 (3.91), 400 (3.81); λ_{min} 214 (4.11), 313 (3.07), 372.5 (3.80), 391 (3.70).

Anal. Calcd. for $C_{14}H_{12}BrN\cdot{}^1/_2H_2O$: C, 59.38; H, 4.63; N, 4.95. Found: C, 59.45; H, 4.63; N, 5.12.

The perchlorate was obtained from methanol–ethyl acetate as bright yellow platelets, m.p. 180–180.5°.

Anal. Calcd. for $C_{14}H_{12}ClNO_4$: C, 57.23; H, 4.11; N, 4.76. Found[13]: C, 57.35; H, 4.03; N, 4.80.

The picrate crystallized from methanol–ethyl acetate as yellow needles, m.p. 199.5–201° (lit.,[4] 230–233°).[14]

Anal. Calcd. for $C_{20}H_{14}N_4O_7$: C, 56.87; H, 3.34; N, 13.27. Found[13]: C, 56.62; H, 3.87; N, 13.24.

2-(2-Methyl[1,3]dioxolan-2-yl)pyridine [**II.** $\mathbf{Z = (O{-}CH_2{-})_2}$].—The reaction of ethylene glycol (110 ml.) with 72.6 g. of 2-acetylpyridine (II. Z = O) was carried out essentially as in the case of the isomeric acetal [III. $Z = (O{-}CH_2)_2$]. The product was purified by vacuum distillation, b.p. 120–130° (12 mm.); yield 85.3 g. (86%). A sample was redistilled in a spinning band column at 6.2 mm. b.p. 106°, $n^{27}\text{D}$ 1.5093.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.45; H, 6.67; N, 8.48. Found: C, 65.76; H, 6.71; N, 8.54.

11-Methylacridizinium (VIII) Perchlorate.—The quaternization of 3.30 g. of 2-(2-methyl[1,3]dioxolan-2-yl)pyridine by reaction of 2.6 ml. of benzyl bromide in the presence of 4 ml. of dry tetramethylene sulfone was carried out at 64° in a sealed flask (5 days). The resulting viscous yellow oil was washed repeatedly with ethyl acetate and the solvent removed *in vacuo* on the steam bath. The residual oil was stirred for 15 hr. in polyphosphoric acid at 120–130°. The cooled reaction mixture was diluted by adding about 100 g. of ice. The diluted mixture was heated on the steam bath and filtered. To the cold filtrate, 35% perchloric acid was added. The precipitated 11-methylacridizinium perchlorate was recrystallized from methanol–ethyl acetate; yield 2.02 g. (35%), m.p. 237–238°. Recrystallized, it melted at 240–241° and was shown to be identical with a sample obtained *via* the ketone (reported, m.p. 243–244.5°).[7]

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(13) Analysis by Dr. C. Daessle, Montreal, P. Q., Canada.

(14) The compound, prepared earlier (ref. 4) and reported to be 4-methylacridizinium picrate, has been shown (by actual comparison of samples) to be acridizinium picrate, m.p. 238–239°. In view of the fact that only a 2.5% yield of a very crude product was obtained in the earlier work, it seems probable that the acridizinium picrate was derived from a small amount of picolinaldehyde present as an impurity in the 6-methylpicolinaldehyde.

Reaction of Cyanuric Acid with Epoxides

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Tris(2-hydroxyethyl) isocyanurate (Ib) of 95–99% purity was prepared in 98–100% yields by the uncatalyzed reaction of cyanuric acid (Ia) with ethylene oxide in dimethylformamide or dimethylacetamide. Adjustment of the molar ratio of ethylene oxide to Ia permitted preparation of mixtures of mono- (Id), bis- (Ic), and tris(2-hydroxyethyl) isocyanurates (Ib) ranging from 99% tris at a ratio of 3.1, to 97% bis at 2.0, to 31.5% mono–68.5% bis at 1.0. The uncatalyzed reaction of Ia with propylene oxide in dimethylformamide gave quantitative yields of bis–tris mixtures containing 93–95% tris(2-hydroxypropyl) isocyanurate (Ig). Tris(2-hydroxyalkyl) isocyanurates are subject to decomposition to 2-oxazolidones (II) by bases generated during the reaction but this decomposition can be prevented by avoiding an excess of alkylene oxide. A mechanism for the decomposition is proposed. Ia reacted with styrene oxide to give a mixture of *N*-mono[2-(2-hydroxy-2-phenylethoxy)-2-phenylethyl]-*N'*,*N''*-bis(2-hydroxy-2-phenylethyl) isocyanurate (Ii), and *N*,*N'*-bis[2-(2-hydroxy-2-phenylethoxy)-2-phenylethyl]-*N''*-mono(2-hydroxy-2-phenylethyl) isocyanurate (Ij).

Epichlorohydrin is apparently the first epoxide described to react with cyanuric acid (Ia) to give an hydroxyalkyl isocyanurate believed to be substantially all tris(2-hydroxy-3-chloropropyl) isocyanurate.[1] The reaction was conducted at 100–120° in epichlorohydrin and dioxane in the presence of a variety of base catalysts. An earlier patent[2] discloses the general reaction of epoxides with Ia at 150–200° in the presence of base

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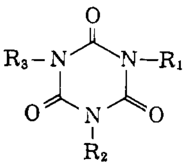
(1) H. G. Cooke, Jr., U.S. Patent 2,809,942 (1957).

(2) W. P. Ericks, U.S. Patent 2,381,121 (1945).

catalysts but without providing examples. Tris(2-hydroxyethyl) isocyanurate (Ib) has recently been reported to have been prepared from Ia and ethylene oxide both by a heterogeneous reaction in benzene at 110–130° and seven to eleven atmospheres catalyzed by dimethylaniline,[3] and in dimethylformamide solution at 135–140° and atmospheric pressure catalyzed by sodium hydroxide.[4] More recently a report[5] of inability to prepare Ib in isolable form from reaction of Ia with ethylene oxide in dimethylformamide has appeared.

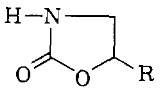
We have found that Ia reacts with ethylene oxide in dimethylformamide or dimethylacetamide solution at 100° and one atmosphere pressure gage in the absence of added catalyst to give tris-, bis-, or monobis-(2-hydroxyethyl) isocyanurate mixtures in close to quantitative yields by varying the ethylene oxide to Ia molar ratio. The reactions of several epoxides with Ia were investigated including ethylene, propylene, octylene, and styrene oxides. The following 2-hydroxyalkyl isocyanurates (I) were prepared:



I

Ia. R_1, R_2, R_3 = —H (cyanuric acid)
b. $R_1, R_2, R_3 = —CH_2CH_2OH$
c. $R_1, R_2 = —CH_2CH_2OH, R_3 = —H$
d. $R_1 = —CH_2CH_2OH, R_2, R_3 = —H$
e. $R_1, R_2, R_3 = —CH_2CH_2OC(O)CH_3$
f. $R_1, R_2 = —CH_2CH_2—OCH_2OH;\ R_3 = —CH_2CH_2OH$
g. $R_1, R_2, R_3 = —CH_2CH(OH)CH_3$
h. $R_1, R_2 = —CH_2CH(OH)CH_3;\ R_3 = —H$
i. $R_1, R_2 = —CH_2CH(OH)C_6H_5;\ R_3 = —CH_2CH(C_6H_5)OCH_2CH(OH)C_6H_5$
j. $R_1 = —CH_2CH(OH)C_6H_5;\ R_2, R_3 = —CH_2CH(C_6H_5)OCH_2CH(OH)C_6H_5$
k. $R_1, R_2 = —H;\ R_3 = —C(O)OH$ (postulated only)

Both Ib and Ig were transformed to 2-oxazolidones (II) on heating in alkaline dimethylformamide solution.



II

IIa. R = —H
b. $R = —CH_3$

2-Oxazolidone (IIa) has previously been reported to be formed from Ib by vacuum pyrolysis[4] and on heating in dimethylformamide solution at 150–155°.[5]

In the reaction of ethylene oxide with Ia at an ethylene oxide–Ia molar ratio of 3.1 and 100° under autogenous pressure up to 790 mm., reaction was complete in from 4.5 to 7.5 hours. At a dimethylformamide–ethylene oxide molar ratio of 6.3–6.9, runs 2–5, Table I, crude products, isolated by vacuum stripping, were mixtures of Ib and Ic containing from 94.9 to 99.3% Ib. Yields were 98% or better. A comparison of runs 6, 7, and 8 with runs 2–5 shows the effect of decreasing the dimethylformamide–ethylene oxide molar ratio from over 6 to 2.2 while maintaining the ethylene oxide–Ia ratio at 3.1. In runs 6 and 7 as the reaction proceeded, the pressure decreased to a minimum and then began to increase (see Table I). Alkaline vapor (dimethylamine) was present over the alkaline solutions (pH 9) at the end of the reactions. The products isolated by the standard technique contained 66.2 and 24.8% 2-oxazolidone (IIa). In run 8, the solution at the end was also alkaline (pH 9) but there was little or no alkaline vapor. 2-Oxazolidone formation was avoided by neutralizing the mixture to pH 7 with sulfuric acid before stripping. That dimethylformamide functions as a base catalyst is suggested by the results of run 9 in which the addition of 0.2 mole of sodium bisulfate per mole of Ia effectively prevented hydroxyethylation.

Reduction of the ethylene oxide–Ia ratio to 3.00, run 10, Table I, resulted in a quantitative yield of product containing 20.9% Ic and 79.1% Ib. Reduction of the ratio to 2.00 and 1.75, runs 11, 12, 13, 14, and 15, Table I, resulted in quantitative yields of products containing 97.0 to 100.0% Ic with the balance Id or Ib. In run 12, the addition of triethylamine amounting to 1 mole % of Ia did not change the product composition appreciably. Further reduction in the ethylene oxide–Ia ratio to 1.50 and 1.00 gave Ic–Id mixtures containing 82.7% Ic at a ratio of 1.50 and 68.5% Ic at 1.00. Table II summarizes the relations among ethylene oxide–Ia ratio, % of Ia reacting, and product composition. It is of interest that no Ia remained unchanged at ethylene oxide–Ia ratios of 2.00 or higher but that only 57% of Ia reacted at an ethylene oxide–Ia ratio of 1.00, and only 80% at 1.50 ratio.

An increase in the ethylene oxide–Ia ratio to 4.0, run 1, Table I, gave a quantitative yield of product containing 89.4% Ib and 10.6% 2-oxazolidone showing the effect of excess ethylene oxide on 2-oxazolidone formation.

Hydroxyethylation of Ia proceeded more slowly in dimethylacetamide than in dimethylformamide in the absence of added catalyst at 100° and at an ethylene oxide–Ia molar ratio of 3.1. Hydroxyethylations in dimethylpropionamide and di-*n*-butylacetamide required a base catalyst to attain reaction rates comparable to those obtained in dimethylformamide and dimethylacetamide in the absence of added catalyst. With 2 mole % triethylamine added as catalyst, 100.0 and 92.7% yields of Ic–Ib mixtures containing 96.9 and 92.5% Ib were obtained. See Table III for a comparison of these four *N,N*-dialkylamides as reaction media.

The formation of an alkaline gas (dimethylamine), an alkaline solution, and 2-oxazolidone during the hydroxyethylation of Ia in dimethylformamide at an ethylene oxide–Ia molar ratio of 3.1, which was especially pronounced at the lower dimethylformamide–ethylene oxide molar ratios, may be explained by the following interpretation: Ia and dimethylformamide react on heating to liberate dimethylamine suggesting that dimethylformamide can function as a base to liberate cyanurate ion ($Ia^{\ominus}$) from Ia which can then attack dimethylformamide to liberate dimethylamine and a formyl derivative of Ia (Ik) (steps 1 and 2).

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(3) G. B. Tal'kovskii, S. L. Lifina, A. A. Potashnik, and V. N. Chernetskii, U.S.S.R. Patent 118,042 (1959); *Chem. Abstr.*, **53**, 21673e (1959).

(4) T. C. Frazier, E. D. Little, and B. E. Lloyd, *J. Org. Chem.*, **25**, 1944 (1960).

(5) A. A. Savigh and H. Ulrich, *J. Chem. Soc.*, 3148 (1961).

TABLE I

HYDROXYETHYLATION OF CYANURIC ACID BY ETHYLENE OXIDE IN DIMETHYLFORMAMIDE[a]

Run no.	Molar ratios		Reaction time, hr.	Pressure range (mm.)		Final pH	Description	N, %	Product composition				Yield,[b] %
	Ethylene oxide/ cyanuric acid	Dimethylformamide/ ethylene oxide		Min.	Final				Id[c]	Ic[d]	Ib[e]	IIa[f]	
1	4.0	6.9	4.0	220	220	8–9	Solid	. .	0.0	0.0	89.4	10.6	102.8
2	3.1	6.7	4.5	0	0	7	Solid	. .	.0	5.1	94.9	0.0	99.2
3	3.1	6.9	6.2	0	0	7	Solid	16.2	.0	3.9	96.1	.0	99.9
4	3.1	6.9	5.0	13	13	7–8	Solid	. .	.0	5.0	95.0	.0	99.4
5	3.1	6.3	7.5	10	150	8–9	Solid	16.0	.0	0.7	99.3	.0	98.2
6	3.1	2.2	5.5	115	140	9	Solid–sirup	. .	.0	.0	33.8	66.2	99.3
7[g]	3.1	2.2	4.8	75	212	9	Solid–sirup	. .	.0	.0	75.2	24.8	101.7
8[h]	3.1	2.2	4.9	30	30	9	Solid	15.6	.0	3.6	96.4	0.0	104.8
9[i]	3.1	2.2	3.0	410	410	6–7	. . .	. .	. .	. . .	. .	. .	. . .
10	3.0	6.9	4.5	0	0	7	Solid–sirup	. .	.0	20.9	79.1	.0	99.9
11	2.0	6.9	3.0	0	0	7	Solid–sirup	19.5	3.0	97.0	0.0	.0	103.8
12[j]	2.0	6.9	5.0	0	0	7	Sirup	19.3	0.0	98.5	1.5	.0	99.0
13	2.0	3.5	1.8	0	0	7	Sirup	19.5	3.0	97.0	0.0	.0	103.3
14	2.0	3.3	3.5	0	0	7	Sirup	19.5	3.0	97.0	.0	.0	101.7
15	1.75	6.9	3.8	0	0	7	Sirup	19.3	0.0	100.0	.0	.0	102.6
16	1.50	6.9	2.0	0	0	7	Sirup	20.2	17.3	82.7	.0	.0	103.5
17	1.00	6.9	3.3	0	0	7	Sirup	20.9	31.5	68.5	.0	.0	105.3

[a] Hydroxyethylations of from 0.2 to 2.8 moles of Ia at 100° with no added catalyst under autogenous pressure. Maximum pressures ranged from 695 to 795 mm. [b] Based on indicated composition and Ia charged except in runs 15, 16, and 17 where yields are based on Ia consumed; run 15, 86.0%; 16, 80.2%; 17, 57.3% consumed. [c] Mono(2-hydroxyethyl) isocyanurate (Id) was assumed to be absent in runs 1–10 based on the high ethylene oxide–Ia ratios used and low acidities found; in runs 11–17, Id–Ic compositions are based on nitrogen contents. [d] Bis(2-hydroxyethyl) isocyanurate (Ic) was determined by alkalimetric titration in runs 1–10; in runs 11–17, Ic content is based on nitrogen content. [e] Tris(2-hydroxyethyl) isocyanurate (Ib) was determined by difference. [f] 2-Oxazolidone (IIa) was determined by infrared analysis. [g] The gas responsible for at least part of the final system pressure was demonstrated to be dimethylamine through the *p*-toluenesulfonyl derivative m.p. 79°. [h] Reaction mixture was neutralized to pH 7 before vacuum stripping. [i] Sodium bisulfate (20 mole % of Ia) was added to the reaction mixture before hydroxyethylation to scavenge any base formed. [j] Triethylamine (1 mole % of Ia) was added as a base catalyst.

TABLE II

EFFECT OF ETHYLENE OXIDE–CYANURIC ACID MOLAR RATIO ON PER CENT OF CYANURIC ACID REACTING AND PRODUCT COMPOSITION

Run no.	Ethylene oxide/Ia molar ratio	Cyanuric acid reacting, %	Product composition, %			
			Id[a]	Ic[b]	Ib[c]	IIa
14	1.00	57.3	31.5	68.5	0.0	0.0
13	1.50	80.2	17.3	82.7	.0	.0
12	1.75	86.0	0.0	100.0	.0	.0
11	2.00	100.0	3.0	97.0	.0	.0
10	3.00	100.0	0.0	20.9	79.1	.0
4	3.10	100.0	.0	0.7	99.3	.0
1	4.00	100 0	.0	0.0	89.4	10.6

[a] Mono (2-hydroxyethyl) isocyanurate (Id). [b] Bis (2-hydroxyethyl)isocyanurate (Ic). [c] Tris (2-hydroxyethyl) isocyanurate (Ib).

$$\mathrm{Ia} + \mathrm{HC(O)N(CH_3)_2} \rightleftharpoons \mathrm{Ia}^{\ominus} + \mathrm{HC(OH){=}}\overset{\oplus}{\mathrm{N}}\mathrm{(CH_3)_2} \qquad (1)$$

$$\mathrm{Ia}^{\ominus} + \mathrm{HC(O)N(CH_3)} \longrightarrow \mathrm{Ik} + {}^{\ominus}\!:\!\ddot{\mathrm{N}}\mathrm{(CH_3)_2} \qquad (2)$$

$$\mathrm{HC(OH){=}}\overset{\oplus}{\mathrm{N}}\mathrm{(CH_3)_2} \qquad \underbrace{\mathrm{HC(OH){=}}\overset{\oplus}{\mathrm{N}}\mathrm{(CH_3)_2}}_{\mathrm{HN(CH_3)_2} + \mathrm{HC(O)N(CH_3)_2}}$$

In the presence of ethylene oxide the cyanurate ion ($\mathrm{Ia}^{\ominus}$) reacts preferentially with ethylene oxide, which is shown in step 3.

$$\mathrm{Ia}^{\ominus} + \overline{\mathrm{CH_2CH_2O}} \longrightarrow \underbrace{\mathrm{Id}^{\ominus} + \mathrm{HC(OH){=}}\overset{+}{\mathrm{N}}\mathrm{(CH_3)_2}}_{\mathrm{Id} + \mathrm{HC(O)N(CH_3)_2}} \qquad (3)$$

$$\mathrm{HC(OH){=}}\overset{\oplus}{\mathrm{N}}\mathrm{(CH_3)_2}$$

When Ia has been converted to Ib, any excess ethylene oxide may react with dimethylformamide to give an inner quaternary ammonium hydroxide (III) (step 4).

TABLE III

HYDROXYETHYLATION OF CYANURIC ACID WITH ETHYLENE OXIDE. COMPARISON OF SEVERAL *N,N*-DIALKYLAMIDES AS REACTION MEDIA[a]

$\mathrm{R_1C(O)N(R_2)_2}$		Reaction time, hr.	Pressure range, mm.			Final, pH	M.p., °C.	N, %	Product composition[b]		Yield,[c] %
$\mathrm{R_1}$	$\mathrm{R_2}$		Max.	Min.	Final				Ic[d]	Ib[e]	
H—	$\mathrm{CH_3}$—	4.9	790	30	30	9	95–131	15.6	3.6	96.4	104.8
$\mathrm{CH_3}$—	$\mathrm{CH_3}$—	6.0	803	128	128	8	113–131	16.1	5.2	94.8	100.4
$\mathrm{CH_3CH_2}$—	$\mathrm{CH_3}$—	3.4	750	105	105	8	127–134	15.8	3.1	96.9	100.0
$\mathrm{CH_3}$—	$\mathrm{CH_3CH_2CH_2CH_2}$—	8.0	760	0	0	7	120–130	16.4	7.5	92.5	92.7[f]

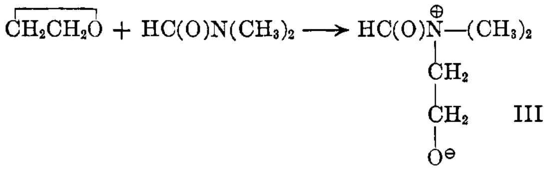
[a] Hydroxyethylations of 0.2-mole quantities of Ia at 100° under autogenous pressure. The reactant molar ratios were: ethylene oxide/Ia, 3.1; amide/ethylene oxide, 2.2. Hydroxyethylation proceeded readily in dimethylformamide and dimethylacetamide without added catalyst but a catalyst (triethylamine, triethylamine/Ia molar ratio 0.02) was required with both dimethylpropionamide and di-*n*-butylacetamide. [b] 2-Oxazolidone was absent in all cases. [c] Based on indicated composition and Ia charged. [d] Bis(2-hydroxyethyl) isocyanurate (Ic) as determined by alkalimetric titration. [e] Tris(2-hydroxyethyl) isocyanurate (Ib) obtained by difference. [f] A product recovery of 28.8% was obtained by collecting product insoluble in di-*n*-butylacetamide and vacuum stripping. This fraction contained 1.0% Ic, 99.0% Ib, m.p. 129.5 to 135.0.

TABLE IV

HYDROXYPROPYLATION OF CYANURIC ACID WITH PROPYLENE OXIDE IN DIMETHYLFORMAMIDE[a]

Run no.	Ia, moles	Reaction time, hr.	Pressure range, mm.			Description	OH, %[b]		N, %[b]		Composition, %			Yield,[f] %
			Max.	Min.	Final		Calcd.	Found	Calcd.	Found	Ih[c]	Ig[d]	IIb[e]	
1	0.201	8.5	800	205	290	Sirup	16.78	15.6	13.91	14.0	1.8	80.5	17.7	91.3[g]
2	.600	3.9	800	290	400	Glass	16.63	15.4	14.08	14.2	6.9	93.1	0.0	101.1
3	.600	3.9	775	200	280	Glass	16.63	15.6	14.08	14.2	6.9	93.1	.0	101.1

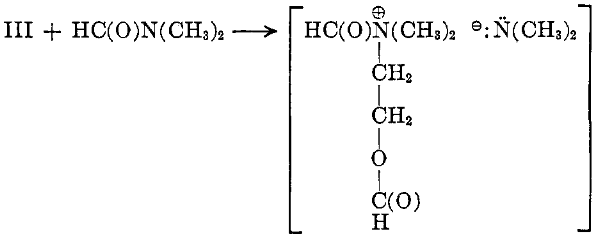
[a] Hydroxypropylations at 115–125° with no added catalyst under autogenous pressure. The reactant molar ratios were: propylene oxide/Ia, 3.1; dimethylformamide/propylene oxide, 2.2. The final reaction mixture pH values were all 8–9. [b] The calculated OH and N values are based on the indicated product compositions. [c] Bis(2-hydroxypropyl) isocyanurate (Ih) as determined by alkalimetric titration. [d] Tris(2-hydroxypropyl) isocyanurate (Ig) obtained by difference. [e] 5-Methyl-2-oxazolidone (IIb) as determined by chemical method. [f] Based on indicated composition and Ia charged. [g] Low recovery due to loss of some 5-methyl-2-oxazolidone during vacuum stripping. A sample of liquid distillate collected during the end of the stripping contained 95.8% 5-methyl-2-oxazolidone.



$$\overline{CH_2CH_2O} + HC(O)N(CH_3)_2 \longrightarrow HC(O)\overset{\oplus}{N}(CH_3)_2\text{—}CH_2\text{—}CH_2\text{—}O^{\ominus} \qquad (4)$$

III

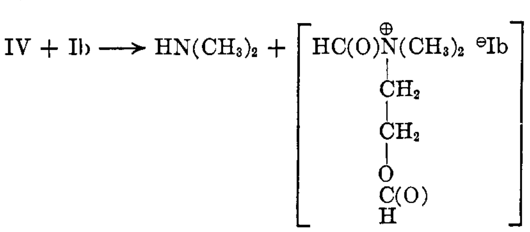
Step 4 does not proceed unless Ib is present presumably to supply protons required in step 6 and to increase solvent polarity. Dimethylformamide (2.02 moles) and ethylene oxide (0.196 mole) at a 10.3 molar ratio heated at 100° in the absence of Ib in a closed system for eight hours did not become alkaline to thymol blue. III is a strong base and should be capable of reacting with dimethylformamide, with the displacement of a dimethylamine anion, to form a quaternary ammonium salt (IV).



$$\text{III} + HC(O)N(CH_3)_2 \longrightarrow \left[HC(O)\overset{\oplus}{N}(CH_3)_2\text{—}CH_2\text{—}CH_2\text{—}O\text{—}C(O)H \quad {}^{\ominus}\!:\ddot{N}(CH_3)_2\right] \qquad (5)$$

IV

The salt IV should react readily with Ib to liberate dimethylamine and the quaternary salt V.



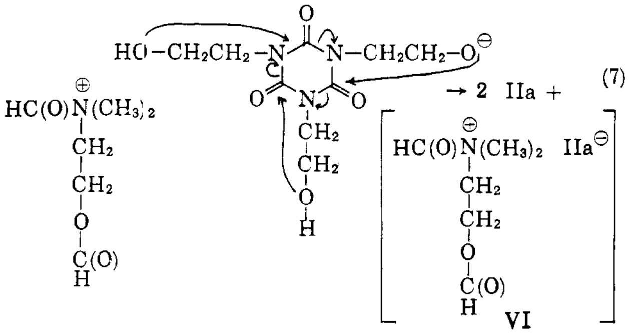
$$\text{IV} + \text{Ib} \longrightarrow HN(CH_3)_2 + \left[HC(O)\overset{\oplus}{N}(CH_3)_2\text{—}CH_2\text{—}CH_2\text{—}O\text{—}C(O)H \quad {}^{\ominus}\text{Ib}\right] \qquad (6)$$

V

It is presumed that V will readily decompose to 2-oxazolidone (IIa) and the quaternary salt VI *via* a concerted internal displacement.

The increase in pH of the reaction medium under the above defined conditions may be due to varying concentrations of III, IV, V, and VI (step 7).

Ib was readily acetylated to tris(2-acetoxyethyl) isocyanurate (Ie) a low melting solid by acetic anhydride in ethyl acetate with 72% perchloric acid as catalyst.[8] Methylolation of Ib with 37% formaldehyde gave *N*,*N*′-bis(2-hydroxymethoxyethyl)-*N*″-mono-(2-hydroxyethyl) isocyanurate (If) a viscous water-soluble sirup.



Propylene oxide reacted smoothly with Ia in dimethylformamide in the absence of added catalyst at 115–125° and at a propylene oxide – Ia ratio of 3.1 to give quantitative yields of mixtures of bis(2-hydroxypropyl) isocyanurate (Ih) and tris(2-hydroxypropyl) isocyanurate (Ig) containing 93.1% Ig. By stopping the reaction before the solution pH exceeded 8 and while the mixture still contained a few per cent of Ih partial degradation of Ig to 5-methyl-2-oxazolidone was effectively eliminated. See Table IV for a summary of the reactions of propylene oxide with Ia.

Ia failed to react with octylene oxide at an octylene oxide–Ia molar ratio of 15 in the presence of dimethylaniline (3 mole % based on Ia) during a 12.5-hr. period at 156°. Failure to react may have been due to the low 1,2-epoxide content (15%) of the octylene oxide used.

Reaction of Ia with styrene oxide (styrene oxide–Ia molar ratio 15) at 192° with dimethylaniline catalyst gave an 81% yield of a mixture containing 81% *N*-mono[2-(2-hydroxy-2-phenylethoxy)-2-phenylethyl]-*N*′,*N*″-bis(2-hydroxy-2-phenylethyl) isocyanurate (Ii) and 19% *N*,*N*′-bis[2-(2-hydroxy-2-phenylethoxy)-2-phenylethyl]-*N*″-mono(2-hydroxy-2-phenylethyl) isocyanurate (Ij), a light yellow low melting solid.

Experimental[6]

Materials.—Cyanuric acid (Ia) from FMC plant production was recrystallized from water and dried at 130° to give an anhydrous product of over 99.5% purity as determined by potentiometric titration with correction for ammelide as determined by an ultraviolet method. Ethylene oxide of 99.7% min. purity was used as received from Olin Matheson Chemical Corp. Propylene oxide, b.p. 34–35°, was obtained from Matheson Coleman and Bell Division. Octylene oxide, 85% 2,3- and 15% 1,2-epoxide, b.p. 156°, was from Chemicals and Plastics Division of FMC Corp. Styrene oxide, b.p. 74–76° (10 mm.), was from Matheson Coleman and Bell Division. 2-Oxazolidone, m.p. 89–90°, and 5-methyl-2-oxazolidone, b.p. 111–113°, (1 mm.),

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[6] Melting points reported are uncorrected.

n^{20}_D 1.4593, were prepared by the method of Bell, Jr., and Malkemus.[7]

Analytical.—All samples were analyzed for nitrogen by a Kjeldahl method. Carbon and hydrogen analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. 2-Oxazolidone was determined by an infrared method in dimethylformamide solution using the characteristic absorption bands at 10.45 and 10.90 μ. The presence of mono-, bis-, and tris(2-hydroxyethyl) isocyanurate did not interfere with the quantitative determination. 5-Methyl-2-oxazolidone was determined by a chemical method: A 0.2-g. sample is dissolved in 50 ml. of 0.1 N sodium hydroxide and titrated with 0.1 N silver nitrate to a faint turbid yellow end point. One gram of 5-methyl-2-oxazolidone = (ml. $AgNO_3$)(N_{AgNO_3}) (0.606) where 0.606 is the milliequivalent based on the stoichiometry: one Ag ≡ six 5-methyl-2-oxazolidone. Recoveries ranging from 95 to 105% were obtained on 5-methyl-2-oxazolidone, b.p. 111–113° (1 mm.).

Compositions containing largely Ib or 2-oxazolidone were analyzed for Ic by alkalimetric titration to the thymol blue end point. Reported compositions are based on nitrogen content, acidity, and 2-oxazolidone content. This analytical scheme does not always allow one to distinguish between products of ring hydroxyl and side chain hydroxyl hydroxyalkylations. It is least satisfactory for compositions containing large concentrations of Id and Ic. For this case, the concentrations were estimated from the nitrogen content. Infrared was found unsuitable for analyzing mixtures of Id, Ic, and Ib. The hydroxyl content of Ib and Ig was determined by the method of Fritz and Schenk.[8]

Tris(2-hydroxyethyl) Isocyanurate (Ib) (Run 5).—To 3928 ml. of dimethylformamide in a 5-l., one-necked, 24/40 S.T. joint, round-bottomed flask equipped with a magnetic stirrer, electric heating mantle, and 760-mm. mercury manometer was added 357.6 g. (2.77 moles) of Ia and 378.4 g. (8.59 moles) of ethylene oxide. The system was closed and heated to 100° with good agitation. The maximum pressure attained was 775 mm., the minimum 10 mm. and the final pressure after 7.5 hr. of reaction was 150 mm. The resulting reaction mixture was a clear liquid having a pH of 8–9. The crude product was isolated by vacuum stripping to constant weight at 100° and 2 mm. It was a white solid weighing 707.8 g. (yield 98%). The crude melted at 112–129° and contained 0.0% 2-oxazolidone and acidity equivalent to 0.7% Ic.

Anal. Calcd. for $C_9H_{15}N_3O_6$: N, 16.09; OH, 19.53. Found: N, 16.00; OH, 18.70.

Acetone extraction of the crude product at room temperature (2 ml./g.) gave a 91.1% recovery of product, m.p. 127.4–134.0°. Recrystallization of the acetone-extracted product from diethyl maleate (9 ml./g.) gave an 84.7% recovery of colorless crystals, m.p. 134.0–135.4° (lit.,[3,4] m.p. 134–136°). The over-all recovery of pure Ib based on Ia was 75.5%.

Anal. Calcd. for $C_9H_{15}N_3O_6$: C, 41.39; H, 5.79; N, 16.09; OH, 19.53. Found: C, 41.66; H, 5.88; N, 15.90; OH, 19.28.

An infrared scan of the recrystallized product showed it to contain hydroxyl groups and the isocyanurate ring. The sample was free of polyoxyethylene.

Tris(2-acetoxyethyl) Isocyanurate (Ie).—Ie was prepared by acetylating Ib with acetic anhydride in ethyl acetate with 72% perchloric acid as catalyst. The crude product isolated by vacuum stripping was a water-insoluble, petroleum ether-insoluble sirup readily soluble in glacial acetic acid, ethyl alcohol, chloroform, and acetone. On stirring the sirup vigorously with heptane at room temperature and vacuum drying a white granular solid, m.p. 59.5–62.0°, was obtained.

Anal. Calcd. for $C_{15}H_{21}N_3O_9$: C, 46.53; H, 5.47; N, 10.85. Found: C, 46.68; H, 5.56; N, 10.83.

***N*-Mono(2-hydroxyethyl)-*N'*,*N''*-bis(2-hydroxymethoxyethyl) Isocyanurate (If).**—A solution of Ib (7.83 g., 0.030 mole) in 7.33 g. (0.090 mole) of 37% formaldehyde was vacuum stripped at 100° and 2 mm. to give 9.59 g. of a clear, colorless, viscous water-soluble sirup (yield 99.5%).

Anal. Calcd. for $C_{11}H_{19}N_3O_8$: C, 41.11; H, 5.96; N, 13.08. Found: C, 40.82; H, 5.96; N, 13.23.

Bis(2-hydroxyethyl) Isocyanurate (Ic) (Run 14).—To 296 ml. of dimethylformamide (4.05 moles) in a reactor similar to that used for preparing Ib except of 1-l. capacity, was added 79.1 g. (0.61 mole) of Ia and 54.0 g. (1.23 moles) of ethylene oxide. The system was closed and heated to 100° with good agitation. The maximum pressure attained was 760 mm., the minimum 0 mm. The final pressure after 3.5 hr. was 0 mm. The resulting reaction mixture was a clear liquid having a pH of 7. Vacuum stripping to constant weight at 100° and 2 mm. gave 134.6 g. of a clear sirup containing 0.0% 2-oxazolidone.

Anal. Calcd. for Ic $C_7H_{11}N_3O_5$: N, 19.35; Id $C_5H_7N_3O_4$: N, 24.28. Found: N, 19.5.

The composition of the crude product estimated from the nitrogen content is 3.0% Id and 97.0% Ic. The yield based on the indicated composition and Ia charged is 101.7%.

Tris(2-hydroxypropyl) Isocyanurate (Ig).—Ia was hydroxypropylated in dimethylformamide solution at 115–125° in the absence of an added catalyst with the propylene oxide/Ia molar ratio at 3.1 and the dimethylformamide/propylene oxide molar ratio at 2.2. The procedure was similar to that used in the hydroxyethylations except that the propylene oxide was added in four portions and each portion allowed to react before adding the next so as to avoid exceeding 1-atm. pressure. About 4 hr. were required for reaction. The crude products were neutralized to a pH of 7 with 1 N sulfuric acid before stripping to minimize oxazolidone formation. The products were analyzed for hydroxyl, nitrogen, acidity, and 5-methyl-2-oxazolidone. See Table IV.

***N*-Mono[2-(2-hydroxy-2-phenylethoxy)-2-phenylethyl]-*N'*,*N''*-bis(2-hydroxy-2-phenylethyl) Isocyanurate (Ii)–*N*,*N'*-bis-2-(2-hydroxy-2-phenylethoxy)-2-phenylethyl-*N''*-mono(2-hydroxy-2-phenylethyl) Isocyanurate (Ij) Mixture.**—Ia (6.46 g., 0.050 mole), 94.5 ml. (0.750 mole) of styrene oxide and 0.2 ml. (0.0016 mole) of dimethylaniline were mixed and refluxed (192°) for 1 hr. The resulting solution was dissolved in methyl alcohol and extracted with heptane to remove excess styrene oxide and the sirup vacuum stripped at 95° to give 26.4 g. (yield 81%) of viscous sirup. Further purification was obtained by precipitating from carbon tetrachloride solution with heptane. A light yellow water-insoluble neutral solid was obtained m.p. 56–74°. The wide melting range suggests that the product is a mixture. The composition as estimated from elemental analysis is 81.2% Ii and 18.8% Ij.

Anal. Calcd. for $C_{36.5}H_{36.5}N_3O_{8.5}$: C, 67.08; H, 5.64; N, 6.44. Found: C, 66.57; H, 5.85; N, 6.40.

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[7] J. B. Bell, Jr., and J. D. Malkemus, U.S. Patent 2,755,286 (1956).

[8] J. S. Fritz and G. H. Schenk, *Anal. Chem.*, **31**, 1808 (1959).