Registry No.—**2a**, 31910-69-7; **2b**, 41262-87-7; **3b**, 41262-88-8; **4a**, 41262-89-9; **4b**, 41262-90-2; **5a**, 41262-91-3; **5b**, 41262-92-4; **6**, 41262-93-5; 1-benzoyl-2-*p*-toluenesulfonylhydrazine, 3064-19-5; *p*-toluenesulfonyl chloride, 98-59-9; benzhydrazide, 613-94-5; triethylamine, 121-44-8; sodium benzoate, 532-32-1; 1-(2,4,6-trimethylbenzoyl)-2-(*p*-toluenesulfonyl)hydrazine, 41262-95-7; sodium 2,4,6-trimethylbenzoate, 32642-28-7; 5-phenyltetrazole, 18039-42-4; 3,6-diphenyl-*s*-tetrazine, 6830-78-0; *sym*-dibenzoylhydrazine, 787-84-8.

Reactions of Hydroxide Tetrakis(2-hydroxyethyl)ammonium

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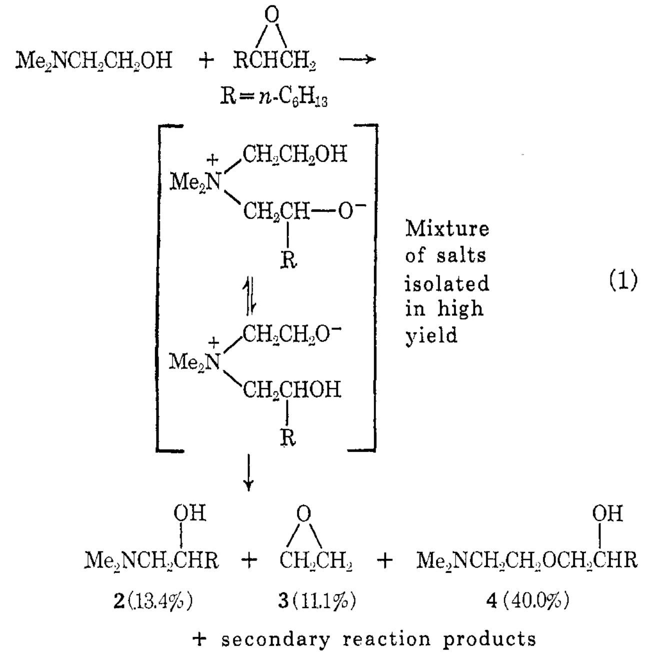
Usually quaternary ammonium hydroxides are considered synthetically useful for olefin formation *via* the Hofmann elimination.[1] However, quaternary ammonium hydroxides bearing one β-hydroxy-substituted side chain thermally decompose to give epoxides, in most cases in high yield to the exclusion of the desired olefin.[1] A paucity of information is available for the chemical reactions and the thermal decomposition of quaternary ammonium hydroxides with more than one β-hydroxy-substituted side chain. Tobler has reported the thermal decomposition of the mixture of quaternary ammonium alkoxides formed by the reaction of 2-(*N*,*N*-dimethylamino)ethanol with 1,2-epoxyoctane.[2] The thermal decomposition of this mixture of quaternary ammonium salts, each species bearing two β-hydroxy-substituted side chains, yields products postulated as occurring *via* intramolecular rearrangements as shown in eq 1.[2] Acetaldehyde formation by a Hofmann-type reaction was not observed.



In contrast to the reactions of alkyl-substituted quaternary ammonium salts containing one or two 2-hydroxyalkyl groups, tetrakis(2-hydroxyethyl)ammonium hydroxide, an easily prepared, stable, white, crystalline compound, behaves somewhat differently. Ethylene oxide and acetaldehyde, expected decomposition products, were not detected in significant quantities under any conditions. Instead the decomposition of **1** was found to take place largely by intermolecular SN2 processes as outlined below.

Thermal decomposition of neat tetrakis(2-hydroxyethyl)ammonium hydroxide (**1**) under nitrogen or high vacuum gives 2,2′,2″-nitrilotriethanol (**5**), 2-(2-hydroxyethoxy)ethyldi(2-hydroxyethyl)amine (**6**), 2-[(2-hydroxyethoxy)ethoxy]ethyldi(2-hydroxyethyl)amine (**7a**), or di[2-(2-hydroxyethoxy)ethyl]-2-hydroxyethylamine (**7b**), and higher homologs (X, Y) as illustrated by eq 2.[3]

$$\underset{\mathbf{1}}{(HOCH_2CH_2)_4\overset{+}{N}\ O\overset{-}{H}} \longrightarrow \underset{\mathbf{5}\ (29.1\%)}{N(CH_2CH_2OH)_3} +$$

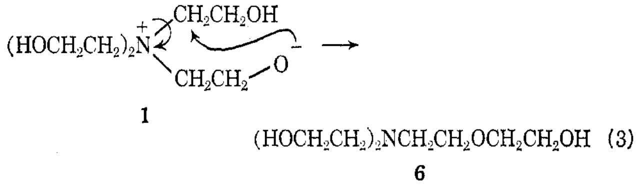
$$\underset{\mathbf{6}\ (36.5\%)}{(HOCH_2CH_2)_2NCH_2CH_2OCH_2CH_2OH} +$$

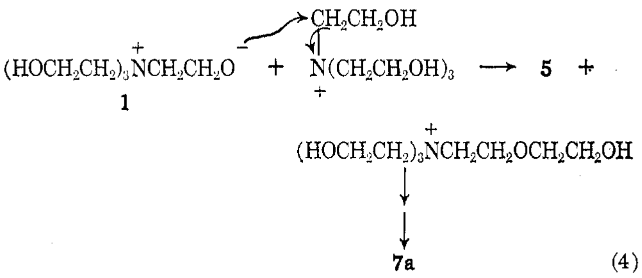
$$\underset{\mathbf{7a}\ (21.0\%)}{HOCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2CH_2OH)_2}$$

$$\text{and/or}$$

$$\underset{\mathbf{7b}}{(HOCH_2CH_2OCH_2CH_2)_2NCH_2CH_2OH} + \underset{10\%^4}{X} + \underset{3\%^4}{Y} \quad (2)$$

Formation of **6** could occur *via* an intramolecular pathway (eq 3). However, the isolation of the higher ethoxylated products, **7a** and **7b**, provides evidence for the decomposition proceeding at least partially by an intermolecular route (eq 4). In fact, recent work by Eschenmoser, *et al.*,[5] and earlier work by House and Pitt[6] have shown that, although an endocyclic SN2 displacement reaction is more appealing, the reaction actually proceeds by an intermolecular pathway in many cases. Similar examples of intermolecular attack by various nucleophiles on quaternary am-





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[1] A. C. Cope and E. R. Trumbull in "Organic Reactions," Vol. 11, Wiley, New York, N. Y., 1960, Chapter 5.

[2] E. Tobler, *Helv. Chim. Acta*, **52**, 408 (1969).

[3] For simplification **5** will be referred to as NTE and **6**, **7a** and **7b** as the NTE-1-mol and NTE-2-mol ethoxylates, respectively, in the remainder of the text.

[4] Identification of X, Y unknown; yields based on area per cent by vpc.

[5] L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 2059 (1970).

[6] H. O. House, and C. G. Pitt, *J. Org. Chem.*, **31**, 1062 (1966).

TABLE I

DECOMPOSITION OF TETRAKIS(2-HYDROXYETHYL)AMMONIUM HYDROXIDE. PRODUCT MOLE RATIO

		Mole ratio of products based on NTE = 1				
			NTE ethoxylates			
Solvent	Solvent:1 ratio	NTE	1-Mol	2-Mol	3-Mol	Other
None (vacuum 100 mm)		1	0.87	0.37	0.12	
None (vacuum 0.44–0.08 mm)		1	0.75	0.28	0.08	
Water	211:1	1	0.73	0.24	0.05	
2-Ethoxyethanol	54:1	1	0.32	0.04		0.27[a]
2,2′,2′′-Nitrilotriethanol (NTE)	7:1	1	2.57	0.21		
2,2′,2′′-Nitrilotriethanol	30:1	1	1.01	0.03		
2,2′-Iminodiethanol	39:1	1[b]				
2-Aminoethanol	9:1	1				1.06[c]
Ethylene glycol	20:1	1	0.06			0.52[d]

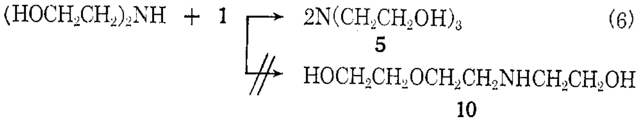
[a] 2-(2-Ethoxyethoxy)ethanol. [b] Only product. [c] 2,2′-Iminodiethanol. [d] Diethylene glycol.

monium salts having various β substituents other than hydroxyl groups have been reported.[7]

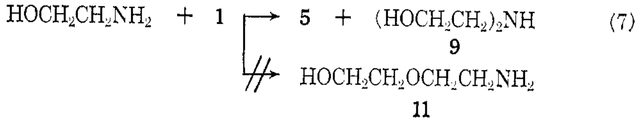
To distinguish between the extent of intermolecular *vs.* intramolecular SN2 reactions, the thermal decomposition of **1** was carried out in various solvents: water, 2-ethoxyethanol, ethylene glycol, 2-aminoethanol, 2,2′-iminodiethanol, and 2,2′,2′′-nitrilotriethanol at 100° (Table I).

Evidence for the intermolecular decomposition of **1** was provided by the isolation of 2-(2-ethoxyethoxy)-ethanol (**8**) when 2-ethoxyethanol was used as the solvent (eq 5). Some of the NTE-1-mol and -2-mol ethoxylates were also formed. The reactions of 2,2′-iminodiethanol (**9**) and 2-aminoethanol with **1** supplied conclusive evidence for the intermolecular nature of this reaction. The respective ethoxylation products **5** and **9** were isolated (eq 6 and 7). None of the ethoxylates of **5** were detected by vpc. Products corresponding to attack by the hydroxyl groups of 2,2′-iminodiethanol or 2-aminoethanol to produce the O-ethoxylation products **10** and **11** were not observed. Thus **1** acts as a discriminatory ethoxylation reagent for primary and secondary amines in the presence of hydroxyl groups.

$$EtOCH_2CH_2OH + \mathbf{1} \longrightarrow \underset{\mathbf{8}}{EtOCH_2CH_2OCH_2CH_2OH} + \mathbf{5} + \mathbf{6} + \mathbf{7a,b} \quad (5)$$

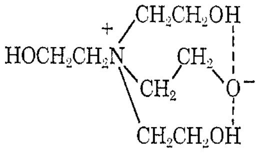


$$(HOCH_2CH_2)_2NH + \mathbf{1} \longrightarrow \underset{\mathbf{5}}{2N(CH_2CH_2OH)_3} \quad (6)$$
$$\not\longrightarrow \underset{\mathbf{10}}{HOCH_2CH_2OCH_2CH_2NHCH_2CH_2OH}$$

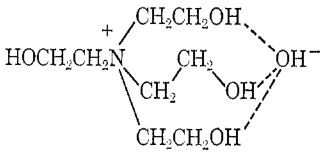


$$HOCH_2CH_2NH_2 + \mathbf{1} \longrightarrow \mathbf{5} + \underset{\mathbf{9}}{(HOCH_2CH_2)_2NH} \quad (7)$$
$$\not\longrightarrow \underset{\mathbf{11}}{HOCH_2CH_2OCH_2CH_2NH_2}$$

The ratio of **5** to the NTE ethoxylates formed on decomposition of **1** in water was essentially identical with the ratio of products obtained by decomposing **1** in the absence of solvent. Ethylene glycol, the expected intermolecular SN2 product, was not detected. A possible explanation for the apparent inertness of water as a reactant with **1** can be attributed to the relative acidity of water in comparison to the hydroxyl groups of the quaternary salt or of **5**. In any given solvent the hydrogen bonding shown in structures **1a** and **1b** postulated for the quaternary salt might stabilize the anion to such an extent that as a consequence the effectve basicity of the anion would be significantly reduced. If this is the case, water apparently is not a strong enough acid and the equilibrium represented by eq 8 (R = H) lies far to the left. Decomposition of **1** in water would then take place preferentially between two molecules of **1** as shown previously in eq 4. In an alcohol solvent, water is a weak acid in comparison to various alcohols such as 2-ethoxyethanol, ethylene glycol, or 2,2′-2′′-nitrilotriethanol.[8] With the more acidic alcohols, such as those mentioned, the equilibrium shown by eq 8 should shift to the right, producing a nucleophile capable of decomposing **1**. In agreement with this suggestion, the most acidic alcohols, ethylene glycol and **5**, are ethoxylated to diethylene glycol and **6**, respectively, almost to the total exclusion of the higher NTE-ethoxylates. Less acidic than ethylene glycol or 2,2′,2′′-nitrilotriethanol, but more acidic than water, 2-ethoxyethanol did not compete as effectively and the NTE-ethoxylates are produced in addition to **8**, the desired ethoxylation product.



1a



1b

$$\mathbf{1a} + ROH \rightleftharpoons \mathbf{1b} + RO^- \quad (8)$$

The stability of **1** is attributed to the internal hydrogen bonding possible from the β-hydroxyethyl side chains present. As one replaces these β-hydroxyethyl groups with alkyl substituents, the stability of the corresponding quaternary ammonium salt would be expected to decrease, as has already been observed. Further, the chemical reactivity of such a series of

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[7] (a) C. Bled-Charreton and A. Gaudemer, *C. R. Acad. Sci., Ser. C*, **272**, 1241 (1971); (b) E. Kitatsuji, N. Masuda, E. Yoshii, and T. Iida, *Yakugaku Zasshi*, **91**, 732 (1971); *Chem. Abstr.*, **75** 117837t (1971); (c) S. H. Pine, B. A. Catto, and F. G. Yamagishi, *J. Org. Chem.*, **35**, 3663 (1970); (d) M. Mori, *Kagaku No Ryoiki*, **25**, 872 (1971); *Chem. Abstr.*, **75**, 140376a (1971); (e) E. C. F. Ko and K. T. Leffek, *Can. J. Chem.*, **49**, 129 (1971); **50**, 1297 (1972); (f) S. Bogdal, *Rocz. Chem.*, **44**, 121 (1970); *Chem. Abstr.*, **73**, 44672g (1970); (g) N. D. V. Wilson and J. A. Joule, *Tetrahedron*, **24**, 5493 (1968); (h) J. E. Gordon and P. Varughese, *J. Chem. Soc., Chem. Commun.*, 1160 (1971); (i) C. L. Bumgardner and H. Iwerks, *ibid.*, 431 (1968); (j) G. Costa, A. Puxeddu, and E. Reisenhofer, *Tetrahedron Lett.*, 2167 (1972).

[8] J. Hine and M. Hine, *J. Amer. Chem. Soc.*, **74**, 5266 (1952).

quaternary ammonium salts should change. These possibilities are under active investigation and will be reported later.

Experimental Section[9]

Preparation of Tetrakis(2-hydroxyethyl)ammonium Hydroxide (1).—A solution of tetrakis(2-hydroxyethyl)ammonium chloride (68.8 g, 0.3 mol) in water (22 ml) and methanol (200 ml) was kept under nitrogen with stirring (magnetic). Silver oxide freshly prepared from silver nitrate (102 g, 0.6 mol) was added as rapidly as possible (**5**). After stirring for 2 hr the thick slurry was filtered under nitrogen. The filter cake was washed once with methanol (50 ml). Solvent was removed under reduced pressure at room temperature. Ethanol (200 ml) was added to the thick syrup and the solvent was again removed under reduced pressure. The white, crystalline mass was dissolved in ethanol, placed under nitrogen, and cooled. The product was filtered and dried under reduced pressure (37.0 g, mp 150–155°). *Note:* On occasion the solution of product will assume a purple coloration, probably indicative of the decomposition of a soluble silver complex. A gentle treatment with activated charcoal will remove all coloration.

A lower melting species may be obtained by dissolving 1 in the minimum amount of water, then adding ethanol (ten times the amount of water used to dissolve 1). On cooling, large, white crystals are obtained, mp 120–125°.

Elemental analyses indicate that the structure of the higher melting quaternary salt is $C_8H_{19}O_4N$ and that of the lower melting form is $C_8H_{21}O_5N$. *Anal.* [high-melting form (**1a**)]. Calcd for $C_8H_{19}O_4N$: C, 49.72; H, 9.91; N, 7.25. Found: C, 49.52, 49.50; H, 9.92, 10.01; N, 7.05, 7.10. *Anal.* [low-melting form (**1b**)]. Calcd for $C_8H_{21}O_5N$: C, 45.48; H, 10.02; N, 6.63. Found: C, 45.51, 45.33; H, 10.10, 10.22; N, 6.57, 6.49.

Procedure 1. Thermal Decomposition of 1 without Solvent.—Tetrakis(2-hydroxyethyl)ammonium hydroxide (10.0 g, 99% pure, mp 144–150°) was placed in a 100-ml kettle equipped with a nitrogen inlet, thermowell, and gas outlet and heated to 184° for 4 hr. Vpc analysis of a small amount of the residue derivatized with Regisil [12 ft × 0.125 in. Al, 5% polyphenyl ether (five ring, OS-138) on Chromosorb G, 100–200° and hold, 10°/min; detector, 290°; injector, 270° He]. Three yeaks were collected and identified as the trimethylsilyl derivatives.

A.—2,2′,2″-Nitrilotriethanol (5) had nmr ($CDCl_3$) δ 0.09 (s, 27, $CH_3Si<$), 2.67 (t, 6, $-CH_2N<$), 3.57 (t, 6, $-CH_2O-$). *Anal.* Calcd for $C_{15}H_{39}NO_3Si_3$: C, 49.26; H, 10.74; N, 3.82. Found: C, 49.34; H, 10.48; N, 3.81.

B.—*N*-[2-(Hydroxyethoxy)ethyl]-*N*,*N*-di(2-hydroxyethyl)amine (**6**) had nmr ($CDCl_3$) δ 0.08 (s, 27, $CH_3Si<$), 2.74 (q, 6, $-CH_2N<$), 3.60 (mm, 10, CH_2O). *Anal.* Calcd for $C_{17}H_{43}NO_4Si_3$: C, 49.82; H, 10.58; N, 3.42. Found: C, 49.99; H, 10.87; N, 3.34.

C.—*N*,*N*-Di[(2-Hydroxyethoxy)ethyl]-*N*-(2-hydroxyethyl)amine (**7a,b**) had nmr ($CDCl_3$) δ 0.09 (s, 27, $CH_3Si<$), 2.74 (q, 6, $-CH_2N<$), 3.60 (mm, 14, $-CH_2O-$). *Anal.* Calcd for $C_{19}H_{47}NO_5Si_3$: C, 50.28; H, 10.43; N, 3.08. Found: C, 50.06; H, 10.76; N, 3.12.

Procedure 2. Decomposition of 1 in Solvent.—The quaternary ammonium hydroxide was dissolved in the minimum amount of water, diluted with the solvent, and heated to 100° until a pH of 10 was obtained. The reaction mixture was analyzed by distillation in conjunction with vpc.

Acknowledgments.—The author is indebted to Mr. C. B. Strow, Jr., Mr. W. H. Joyce, and Mr. J. T. Hildebrand for analytical data and interpretation and to Mr. R. L. Bailey for technical assistance.

Registry No.—**1a,** 41120-05-2; **1b,** 631-41-4; **5** trimethylsilyl derivative, 20836-42-4; **6** trimethylsilyl derivative, 41120-08-5; **7a** trimethylsilyl derivative, 41120-09-6; **7b** trimethylsilyl derivative, 41120-10-9; tetrakis(2-hydroxyethyl)ammonium chloride, 13269-66-4.

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[9] Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected. The nmr spectra were recorded on a Varian HA-100 nmr spectrometer. Elemental analyses were determined on a Perkin-Elmer 240 elemental analyzer.

The Preparation of 1,3,4-Thiadiazoline-2,5-dione and Its Use as a Dienophilic Reagent

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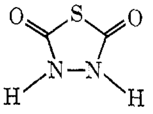
Received May 25, 1973

Over the past 10 years triazolinediones have been used as dienophiles with increasing frequency.[1,2] The use of these reagents suffers from the disadvantage that the resulting urazoles are very difficult to convert to hydrazines. Typically, prolonged treatment with potassium hydroxide in refluxing water–ethylene glycol[3] or lithium aluminum hydride in refluxing tetrahydrofuran[4] is necessary to effect hydrolysis. A need for a highly reactive dienophile that can be easily cleaved to a 1,2-disubstituted hydrazine led us to study the oxidation of 1,3,4-thiadiazolidine-2,5-dione (I).[5] It was found that I could be oxidized to the desired azo reagent II with lead tetraacetate in 2:1 tetrahydrofuran–dimethylformamide containing *ca.* 1% acetic acid (as stabilizer) at −78° giving a dark brown colored solution. When this solution was warmed to −20°, it became light yellow, indicating the decomposition of II. However, when the oxidation was run in the presence of an excess of a 1,3-diene, good yields of Diels–Alder products III could be isolated. The results are shown in Table I. Lower yields are obtained with the less reactive dienes owing mainly to concurrent decomposition of II.

Table I

Registry no.	Diene	Yield, % (adduct)
542-92-7	Cyclopentadiene	96 (IIIa)
592-57-4	Cyclohexadiene	92 (IIIb)
78-79-5	Isoprene	35 (IIIc)
2004-70-8	*trans*-Piperylene	55 (IIId)
513-81-5	2,3-Dimethylbutadiene	49 (IIIe)



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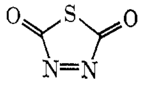
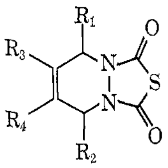


II



IIIa, $R_1 + R_2 = CH_2$; $R_3 = R_4 = H$
b, $R_1 + R_2 = CH_2CH_2$; $R_3 = R_4 = H$
c, $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$
d, $R_1 = R_3 = R_4 = H$; $R_2 = CH_3$
e, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$

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[1] B. T. Gillis and J. D. Hagarty, *J. Org. Chem.*, **32**, 330 (1967).

[2] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

[3] L. A. Paquette, *J. Amer. Chem. Soc.*, **92**, 5765 (1970).

[4] D. H. R. Barton, T. Shioiri, and D. A. Widdowson, *Chem. Commun.*, 939 (1970).

[5] K. Rufenact, *Helv. Chim. Acta*, **51**, 518 (1968).