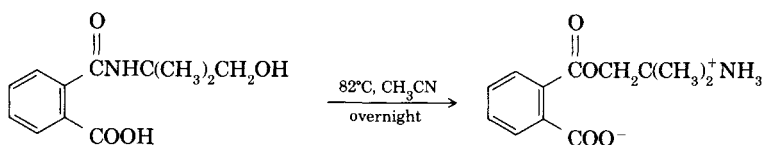
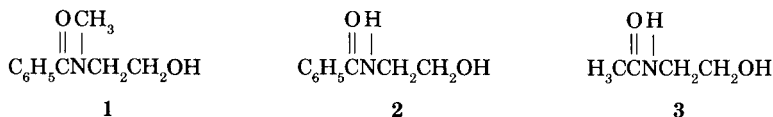


***N*-(2-Hydroxyalkyl) Amides as Internally Blocked Crosslinkers for Epoxy Resins**

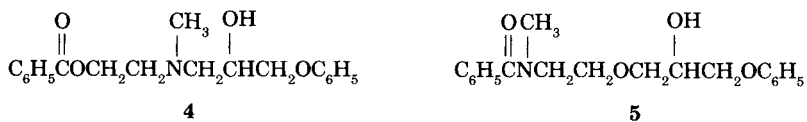
It is well known¹⁻⁴ that *N*-(2-hydroxyalkyl)amides exist in equilibrium with the isomeric 2-aminoalkyl esters. Equilibration occurs via an internal acyl shift rearrangement. At room temperature the population of amine/ester is almost nil, and the acyl shift is slow; but at elevated temperatures the rate of equilibration becomes appreciable, and it becomes possible to isolate the amine/ester by forming salts. An example was reported by Wicks and Chen⁵:



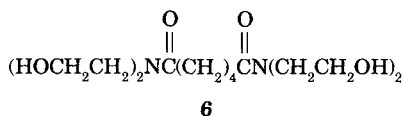
This study was designed to test the hypothesis the *N*-(2-hydroxyalkyl)amides will react with oxiranes at lower temperatures than ordinary hydroxy compounds because of preferential reaction with the amino ester formed by the acyl shift rearrangement. Amines react with oxiranes much more readily than alcohols.⁶ If so this type of reaction might be a basis for useful internally blocked crosslinkers for epoxy resins. *N*-(2-hydroxyalkyl)amides 1-3 were selected as model compounds for study:



The key experiments were to probe the minimum temperatures needed to induce 1-3 to react with phenyl glycidyl ether (PGE, a model compound for epoxy resins) and to determine structures of the products. For example, is the product of 1 with PGE ester-amine 4 or amide-ether 5?



Curing of an epoxy resin with tetra-2-hydroxyalkyl diamide 6 was briefly investigated:



EXPERIMENTAL

Preparation of *N*-(2-hydroxyalkyl)amides

***N*-(2-hydroxyethyl)benzamide, 2.** A solution of 70.2 g (0.5 mol) of benzoyl chloride in 300 mL of toluene was added for 6 h to a stirred flask containing 30.5 g (0.5 mol) 2-hydroxyethyl amine and 69.1 g (0.5 mol) K_2CO_3 , 250 mL of H_2O , and 250 mL of ether. The reaction mixture formed three layers. The middle layer was concentrated and dissolved in 150 mL of methanol. This solution was treated with Amberlite IR-120 and anhydrous $MgSO_4$, filtered, and concentrated. Recrystallization from petroleum ether/ethyl acetate yielded 51.0 g (62%) of **2**, mp 56–57°C; IR (Nujol) 3350 (OH), 1630 (C=O); NMR ($CDCl_3$) ppm: 3.5–3.7 (2xt, 4H, CH_2CH_2), 3.6 (s, 1H), 7.1 (b, 1H), 7.3–7.8 (m, 5H, C_6H_5).

Amides **1**, **3** and **6** were prepared as reported by Wicks and Chiang.⁷

Reaction of *N*-(2-hydroxyalkyl)amide **1** with Phenyl Glycidyl Ether (PGE)

A solution of 12.3 g (0.069 mol) of amide **1** and 10.4 g (0.069 mol) of PGE in 39.0 g of *m*-xylene was heated at reflux for 24 h. The xylene was evaporated, and a slight excess of aq HCl was added. The resulting precipitate was recrystallized from chloroform to yield 15.0 g (60%) of the hydrochloride salt of amino ester **4**, mp 84.5–85.5°C; NMR ($CHCl_3$), ppm: 3.1 (s, 3H, CH_3N), 3.3–4.8 (b, 9H, methylene, methine, NH and OH), 4.9 (t, 2H, $CH_2OC=O$), 6.8–8.2 (m, 10H, aromatic H). IR (Nujol): 3300–3500 (OH), 3100–3200 (NH), 1720 (C=O).

ANAL: Calcd. for $C_{19}H_{24}NO_4Cl$: C, 62.38%; H, 6.85%; N, 3.83%. Found: C, 60.12%; H, 6.85%; N, 3.56% (adsorbed H_2O suspected).

Treatment of the above salt with dilute NaOH gave ester-amine **4**, a pale amber liquid. NMR ($CDCl_3$), ppm: 2.3 (s, 3H, CH_3N), 2.6 (d, 2H, CH_2N), 2.8 (s, 2H, CH_2N), 3.3 (s, 1H, OH), 4.0 (m, 3H, $OCHCH_2O$), 4.4 (t, 2H, $CH_2OC=O$), 6.8–8.1 (m, 10H, aromatic H); IR (neat): 3300–3500 (OH), 1720 (C=O).

ANAL: Calcd. for $C_{19}H_{23}NO_4$: C, 69.30%; H, 6.99%; N, 4.26%. Found: C, 68.99%; H, 7.02%; N, 4.10%.

The methiodide salt of amine **4** was noncrystalline. NMR ($CDCl_3$), ppm: 3.5 (s, 6H, CH_3NCH_3), 3.8–5.0 (b, 10H, methylene, methine and OH), 6.8–8.1 (m, 10H, aromatic H); IR (neat): 3300–3500 (OH), 1720 (C=O).

Estimates of Minimum Reaction Temperatures

Solutions containing equimolar amounts of amides **1–3** and PGE were heated in NMR tubes at various temperatures, and NMR spectra were recorded. For example when **1** was heated with PGE in *o*-dichlorobenzene the NMR peaks of the starting materials disappeared within 24 h at 130°C. At 110°C little change occurred. The product spectrum indicated a high conversion to ester-amine **4**.

Amides **2** and **3** required temperatures of 150°C and 160°C, respectively, to achieve appreciable reaction rates, and NMR spectra of the products suggested mixtures. Infrared spectra showed a sharp reduction in the intensity of the amide bands at about 1610 cm^{-1} and appearance of ester bands at about 1720 cm^{-1} .

Epoxy Film Formation

An equimolar mixture of a bisphenol A type epoxy resin of intermediate molecular weight (Epon 1004, Shell) and *N,N,N',N'*-tetrakis-(2-hydroxyethyl)adipamide (**6**) was cast from solution on an aluminum panel and baked in a convection oven at 150°C for 16 h to give a light amber film which had excellent adhesion and flexibility (conical mandrel). Reverse impace resistance (falling weight test) exceeded 92 kg · cm (film thickness = 0.04 mm). Pencil hardness was 4H.

RESULTS AND DISCUSSION

All evidence favors ester-amine **4**, not amide-ether **5**, as the predominant product of the reaction of 2-hydroxyalkyl amide **1** with PGE at 130°C. The ability of the product to form salts reversibly with hydrochloric acid and irreversibly with methyl iodide demonstrates that it is an amine. Elemental analysis confirms that it is a 1:1 adduct. IR spectra of the amine and

its derivatives show strong ester bands at about 1720 cm^{-1} and no bands attributable to amides. NMR spectra of the amine and its derivatives are consistent with the structures assigned; peaks of amide **1** at 2.9 ppm ($\text{CH}_3\text{NC}=\text{O}$) and 3.7 ppm ($\text{CH}_2\text{NC}=\text{O}$) were replaced by peaks at 2.3 ppm and 4.4 ppm assignable to CH_3NR_2 and $-\text{CH}_2\text{OC}=\text{O}$, respectively.

The fact that reaction occurs at 130°C also indicates that the acyl shift occurs before reaction with the oxirane. Aliphatic alcohols usually require higher temperatures to react with oxiranes in the absence of catalyst. For example, the widely used advancement process of making epoxy resins⁸ would not work if secondary aliphatic alcohols reacted appreciably with glycidyl ethers at 177°C .

It appears that aromatic and aliphatic amides of primary *N*-(2-hydroxylalkyl) amines such as **2** and **3** undergo a similar reaction, although temperatures above 150°C are required, more darkening occurs and the reaction products appear to be complex mixtures.

Thus it appears that polyfunctional amides of secondary *N*-(2-hydroxyalkyl) amines might be useful crosslinkers for epoxy resins. They would be expected to react at useful rates in the vicinity of 150°C , a desirable curing range for such applications as powder coatings and potting. The potential utility of amides of primary 2-hydroxy amines appears questionable because the reactions are slower and more complex.

The film formation experiment offers further encouragement. While the effective functionality of bishydroxyamide **6** is uncertain, it is capable of curing a nominally difunctional epoxy resin to a hard, tough film.

A literature search uncovered no descriptions of use of acyl shift reactants as internally blocked epoxy crosslinkers. Two patents^{9,10} state that condensation products of *N,N*-dialkyl-alkanol amines with carboxylic acids can be used to cure epoxy resins, but there was no discussion of reactant structure or of reaction course and mechanism.

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