washed with 10 ml. of 50% ethanol. It weighed 4.0 g. and melted at 155–159°. After recrystallization from ethanol it melted at 162–165° and gave no depression on admixture and melting with authentic formaldehyde 2,4-dinitrophenylhydrazone.

N,N'-Di-t-butyl-1,3-diazine (V) *from N,N'-di-t-butyltrimethylenediamine.* To 3.44 g. of *N,N'*-di-*t*-butyltrimethylenediamine was added 1.6 g. of 37% aqueous formaldehyde and the mixture stirred for 16 hr. at room temperature. Water (5 ml.) was added and the mixture extracted with methylene chloride. The organic layer was dried over anhydrous magnesium sulfate and distilled to yield 2.8 g. of *N,N'*-di-*t*-butyl-1,3-diazine (V), b.p. 55–56° (0.2 mm.), n_D^{25} 1.4609. The infrared spectrum of this material was identical with that *N,N'*-di-*t*-butyl-1,3-diazine (V) prepared by lithium aluminum hydride reduction of *N,N'*-di-*t*-butyl-1,3-diazine-4-one (IIIa).

ROHM & HAAS COMPANY
5000 RICHMOND STREET
PHILADELPHIA 37, PA.

Reaction of Phenyl Isocyanate with Phenyl Glycidyl Ether

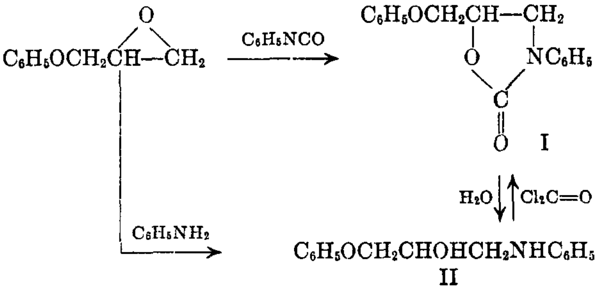
MILTON L. WEINER[1]

Received May 5, 1960

Under forcing conditions and in the presence of a catalytic quantity of benzyldimethylamine, phenyl glycidyl ether reacts with phenyl isocyanate to form the 1:1 cyclic adduct, 5-phenoxymethyl-3-phenyloxazolidin-2-one (I) in a 45% yield. The assignment of structure I to the product is based on the hydrolysis of the latter to an amino alcohol (II) which proved to be identical with that obtained by the reaction of phenyl glycidyl ether with aniline. The amino alcohol (II) has not previously been characterized nor is it firmly characterized in the present work; however, in view of the known greater susceptibility of terminal epoxides to nucleophilic attack at the primary rather than the secondary carbon atom,[2] it seems reasonable that II is 1-anilino-3-phenoxypropanol-2 rather than the isomeric 2-anilino-3-phenoxypropanol-1.

The hydrolysis of the oxazolidinone (I) was accompanied by the evolution of carbon dioxide in the amount required by structure I, and the resultant amino alcohol (II) could be converted back to I in a 49% yield by treatment with phosgene, thus further substantiating structure I.

When the duration of the reaction between the epoxide and the isocyanate was shortened from sixteen hours to one and one-half hours, the yield of I was markedly reduced and part of the isocyanate was recovered in the form of its trimer, triphenyl isocyanurate (III). None of the trimer III could be isolated after the more extended reaction time. A separate experiment established the fact that catalytic quantities of benzyldimethylamine and phenyl glycidyl ether, used in combination, caused a relatively rapid and almost quantitative trimerization of phenyl isocyanate to III. These results suggest that the actual course of the oxazolidinone-forming reaction involves a relatively rapid, reversible trimerization of phenyl isocyanate to III accompanied by a slower reaction between phenyl glycidyl ether and phenyl isocyanate. While the isocyanurate structure III is commonly held to be relatively stable and has not been previously reported as subject to dissociation, in the present work it has been found that III, when treated with a stoichiometric amount of phenyl glycidyl ether in the presence of benzyldimethylamine, forms the oxazolidinone I in yields corresponding to those obtained from phenyl glycidyl ether and phenyl isocyanate. Further evidence for the dissociation of III was furnished by the isolation of *n*-butylphenylurethan in a 73% yield from the reaction of III with *n*-butyl alcohol in the presence of the co-catalysts, benzyldimethylamine and phenyl glycidyl ether.



The reaction of phenyl isocyanate with one other epoxide has been briefly studied. Under reaction conditions that were similar to those used in the reaction with phenyl glycidyl ether, benzylethylene oxide provided a 12% yield of a compound that had the correct analysis for 5-benzyl-3-phenyloxazolidin-2-one (IV). In addition, a 36% yield of the trimer III was isolated along with a 50% recovery of unconsumed benzylethylene oxide. A more extended reaction time resulted in an increase in the yield of IV to 34%. Only 6% of unchanged epoxide was recovered and none of the trimer III could be isolated. The decreased degree of reactivity of benzylethylene oxide as compared to phenyl glycidyl ether in this reaction is consistent with the reported order of reactivity of substituted ethylene oxides to nucleophilic attack.[3]

EXPERIMENTAL[4]

5-Phenoxymethyl-3-phenyloxazolidin-2-one (I). A mixture of 11.9 g. (0.1 mole) of phenyl isocyanate, 15.0 g. (0.1 mole) of redistilled phenyl glycidyl ether, and 0.1 g. of benzyldimethylamine was heated in a sealed tube at 160° for 17 hr. The semicrystalline reaction mass was repeatedly recrystallized from benzene to yield 12.1 g. (45%) of 5-phen-

---

(1) Kordite Company, Macedon, N. Y.

(2) R. C. Elderfield, *Heterocyclic Compounds*, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 32.

(3) L. Shechter, J. Wynstra, and R. Kurkjy, *Ind. Eng. Chem.*, 49, 1107 (1957).

(4) All melting points are uncorrected.

oxymethyl-3-phenyloxazolidin-2-one (I), m.p. 134.5–136.5°, infrared band at 5.75μ.

Anal. Calcd. for $C_{16}H_{15}NO_3$: N, 5.20. Found: N, 5.38.

Hydrolysis of the oxazolidinone I. A mixture of 23.4 g. (0.087 mole) of the oxazolidinone I, 20 g. (0.3 mole) of potassium hydroxide, 90 ml. of water, and 200 ml. of methanol was heated in a pressure bottle at 107° for 16 hr. Methanol was removed by distillation and the aqueous distillation residue was extracted with two 100-ml. portions of a 1:1 mixture of toluene and methylene chloride. The organic extract was combined with 250 ml. of 5% hydrochloric acid and the resultant mixture was steam distilled until all solvents had been removed. The clear aqueous residue was made basic by the addition of concentrated aqueous sodium hydroxide solution, whereupon an oil separated. Upon standing, the separated oil solidified and was recrystallized from a toluene/ligroin mixture to provide 16 g. (67%) of amino alcohol II, m.p. 61–62.5°, undepressed on admixture with a sample of the product from the reaction of aniline with phenyl glycidyl ether, infrared band at 3.05μ, shoulder at 3.10–3.15μ.

Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.0; H, 7.0; N, 5.75. Found: C, 74.30; H, 7.24; N, 5.62.

The aqueous solution remaining after the extraction of the methanol-free reaction mixture was found to contain 0.0835 mole of carbonate ion (96%).

Amino alcohol II *from the reaction of aniline with phenyl glycidyl ether.* To 0.62 mole of redistilled aniline, held at 123–137°, was added 0.3 mole of redistilled phenyl glycidyl ether over a period of 90 min. Heating was continued for 15 min. longer after which the reaction mixture was distilled at 10 mm. to yield 0.33 mole of unchanged aniline. The pressure was then reduced and 56.2 g. of a viscous oil, b.p. 168–181° (0.05 mm.), was distilled. The oil was dissolved in a toluene/ligroin mixture and upon cooling, 53.8 g. (74%) of amino alcohol II crystallized, m.p. 61–63°.

Oxazolidinone I *from amino alcohol* II *and phosgene.* Phosgene was passed into a solution of 7.4 g. (0.03 mole) of amino alcohol II and 4.74 g. (0.06 mole) of dry pyridine in 100 ml. of methylene chloride until 0.030 mole had been absorbed. The temperature of the mixture was held at 25–30° during the addition. After standing for 24 hr., the solution was combined with 100 ml. of water and the methylene chloride was removed by distillation. The crude solid product (7 g.) was filtered, taken up in hot toluene, and clarified with Norite. Upon cooling, 4.0 g. (49%) of the oxazolidinone I crystallized, m.p. 133.5–135.5°, undepressed upon admixture with a sample of I that was prepared by the reaction of phenyl glycidyl ether with phenyl isocyanate.

Triphenyl isocyanurate (III). A mixture of 16.55 g. of phenyl isocyanate, 0.5 g. of phenyl glycidyl ether, and 0.1 g. of benzyldimethylamine was heated at 150° in a sealed tube for 2 hr. The solidified reaction mass was recrystallized from acetone to yield 15.4 g. (93%) of triphenyl isocyanurate (III), m.p. 275–277° (lit.[5] m.p. 280–281°), melting point undepressed on admixture with a sample of III prepared by the method of Hofmann,[6] infrared bands at 5.85 and 7.1μ.

Separate experiments established that none of the trimer III is formed when either phenyl glycidyl ether or benzyldimethylamine is omitted from the mixture of reactants.

Short time reaction of phenyl glycidyl ether with phenyl isocyanate. A mixture of 12.25 g. (0.103 mole) of phenyl isocyanate, 15.5 g. (0.103 mole) of redistilled phenyl glycidyl ether, and 0.1 g. of benzyldimethylamine was heated in a sealed tube at 165–170° for 90 min. The reaction mass, a semisolid sludge, was taken up in hot benzene and ligroin. Upon cooling, an impure solid (10.9 g.) separated which was resolved into two fractions by fractional crystallization. The first (5.6 g., 19%) proved to be the oxazolidinone I as evidenced by its melting point and mixed melting point with an authentic sample of I. The second product, similarly identified, proved to be the trimer III.

Oxazolidinone I *from the reaction of phenyl glycidyl ether with* III. The trimer III was prepared from the amine-epoxide catalyzed trimerization of phenyl isocyanate and melted at 276–278°. A mixture of 4.2 g. (0.0118 mole) of III, 5.4 g. (0.036 mole) of redistilled phenyl glycidyl ether, and 0.05 g. of benzyldimethylamine was heated in a sealed tube at 160° for 16 hr. The semisolid reaction mass was recrystallized from acetone to yield 3.73 g. (40%) of the oxazolidinone I, m.p. 135–137.5°, undepressed on admixture with an authentic sample of I.

n-Butylphenylurethan from the reaction of III *with n-butyl alcohol.* A mixture of 2.38 g. (0.0067 mole) of III, 1.48 g. (0.02 mole) of dry *n*-butyl alcohol, 0.03 g. of benzyldimethylamine, and 0.06 g. of phenyl glycidyl ether was heated in a sealed tube at 150° for 2 hr. The reaction mixture was taken up in hot ligroin and upon cooling, a 73% yield of impure *n*-butylphenylurethane crystallized, m.p. 54.5–58°. After repeated recrystallizations from ligroin, the melting point was raised to 59–61°, undepressed on admixture with an authentic sample prepared from the benzyldimethylamine-catalyzed reaction of *n*-butyl alcohol with phenyl isocyanate at room temperature.

Parallel experiments were carried out in which first the benzyldimethylamine and then the phenyl glycidyl ether were omitted. In either case, no urethan was formed.

5-Benzyl-3-phenyloxazolidin-2-one (IV). A mixture of 26.8 g. (0.2 mole) of redistilled benzylethylene oxide, 23.8 g. (0.2 mole) of phenyl isocyanate, and 0.2 g. of benzyldimethylamine was heated in a sealed tube at 170° for 20 hr. The reaction mixture was then heated at 110° (0.1 mm.) and 13.4 g. of distillate was collected. The latter was redistilled to provide 12 g. of unchanged benzylethylene oxide, b.p. 88–90° (8.5 mm.), $n_D^{24.5}$ 1.5194. The stripped reaction mass was taken up in hot benzene and 9.28 g. of insoluble solids were separated which yielded, after recrystallization from acetone, 8.65 g. (36.5%) of the trimer III, m.p. 277–279°, undepressed on admixture with authentic III. The benzene solution of the residual reaction produts was distilled *in vacuo* to leave a gum. The latter was recrystallized several times from a 1:1 mixture of benzene and ligroin to give 6.0 g. (12%) of 5-benzyl-3-phenyloxazolidin-2-one, m.p. 90.5–93°, infrared band at 5.76μ.

Anal. Calcd. for $C_{16}H_{15}NO_2$: N, 5.53. Found: N, 5.62.

In a second experiment, a mixture of 11.1 g. (0.093 mole) of phenyl isocyanate, 12.6 g. (0.094 mole) of redistilled benzylethylene oxide, and 0.1 g. of benzyldimethylamine was heated in a sealed tube at 160° for 69 hr. The reaction mixture was worked up as in the 20 hr. reaction to provide a 33.6% yield of the oxazolidinone IV, m.p. 90–93°. A recovery of 6% of unchanged benzylethylene oxide was realized. None of the trimer III could be isolated.

Acknowledgment. The author is indebted to D. L. Harms for the infrared spectral determinations.

Materials and Processes Laboratory
Large Steam Turbine-Generator Department
General Electric Company
Schenectady, N. Y.

Evidence for the Existence of Azidoximes

F. Eloy

Received June 30, 1960

It has been suggested[1] that linear systems containing azido-azomethine groups irreversibly isom-

---

(5) I. C. Kogon, Symposium on Isocyanate Polymers, 130th Meeting, American Chemical Society, Atlantic City, N. J., September 1956, p. 62.

(6) A. W. Hofmann, *Ber.*, 18, 764 (1886).