Synthesis of Diepoxide of Bis(2-cyclohexenylidene)pentaerythritol. A Trispiro Diepoxy Ketal

S. Yen Lee

Department of the Army, Harry Diamond Laboratories, Washington, D. C. 20433.

Received May 1, 1973

ABSTRACT: In an attempt to prepare a cycloaliphatic epoxy resin that can be cured with amines similarly to the curing of the conventional epoxy resin of glycidyl ether type, the diepoxide of bis(2-cyclohexenylidene)pentaerythritol, a trispiro diepoxy ketal, was synthesized in two steps starting from 2-cyclohexen-1-one and pentaerythritol. The trispiro epoxy was found to be inert to amines, and curing with acid anhydrides was also sluggish. The effect of steric hindrance and the electropositive effect of the alkyl substitution are considered.

Cycloaliphatic epoxy resins have been introduced lately to give improved electrical properties and superior resistance to light and weather. Some of them show a unique combination of high elongation and high heat distortion temperature.[1] Their superior light and weather resistance is attributed to their nonaromatic structure. Since they are usually made by peracid oxidation of olefins, no ionic impurities can be left in the polymer to degrade the dielectric properties of the cured resins. This constitutes an advantage over the conventional epoxy resin, diglycidyl ether of bisphenol A (DGEBA), which usually contains some residual sodium chloride as a by-product of the introduction of the epoxy group with epichlorohydrin in the presence of sodium hydroxide. However, cycloaliphatic epoxy resins made by peracid oxidation show a serious shortcoming in curing. They are most easily cured with acids or acid anhydrides, but react either very slowly or not at all with amines.[2] Since curing with acids or acid anhydrides usually requires elevated temperature, cycloaliphatic epoxy resins fail to have the desirable characteristics of being curable at or near room temperature.

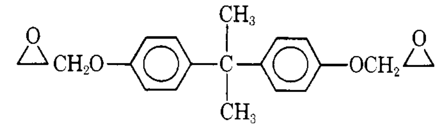
The high reactivity of glycidyl ether type epoxides (Chart I) to amines is attributed primarily to the inductive effect of the etheral oxygen and to the fact that this oxygen is able to form hydrogen bonding with amines, thereby holding the amine in a favorable position for reaction with the epoxy ring.[3]

In an attempt to attain similar reactivity in a cycloaliphatic system, a cycloaliphatic diepoxide was synthesized containing double etheral oxygen atoms in a complete spiro ketal structure at positions similar to the etheral oxygen in the glycidyl ether type epoxy resin. This paper reports its synthesis and the exploration of its curing properties.

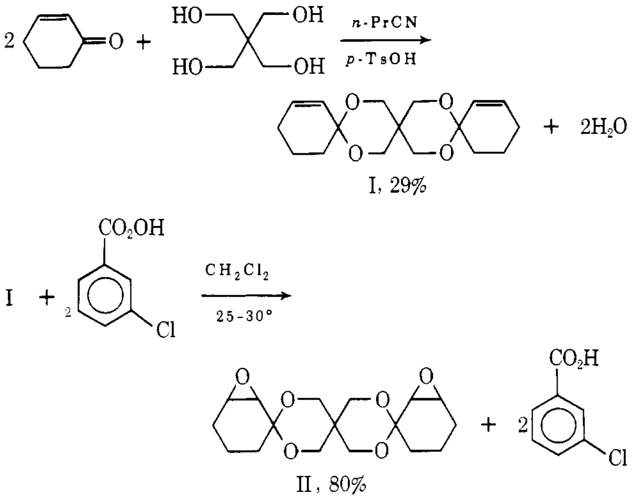
Results and Discussion

Diepoxide (II) of Bis(2-cyclohexenylidene)pentaerythritol (I). The diepoxide was synthesized in two steps as shown in Scheme I. Spirodiene I was prepared from 2-cyclohexen-1-one and pentaerythritol essentially according to a known procedure for ketal formation.[4] n-Butyronitrile was found to be more satisfactory than other solvents tried including isopropyl ether, n-butyl chloride, propiononitrile, and benzene. All of these solvents are known to form azeotropes with water and hence water can be distilled off as azeotropes and separated with a Dean-Stark trap. The crude product of the condensation reaction was a brown soft solid. By column chromatography, the desired spirodiene I was isolated in an overall yield of about 29%.

Chart I
Diglycidyl Ether of Bisphenol A (DGEBA)



Scheme I
Synthetic Steps



Since spiranes have their successive rings orthogonal to each other, spirodiene I is expected to exist as a mixture of geometrical enantiomers.[5] Its structure was established by elemental analysis, as well as ir and nmr spectroscopic evidence. The appearance of two oxymethylene singlets of equal intensity in the nmr spectrum (Figure 1) at 3.73 and 3.83 ppm reflects the fact that the two oxymethylene groups in each ring exist in different environments. It is considered less likely that the two singlets could arise from the different environments each geminal proton of the oxymethylene groups experiences. There is no sign in either of the 60-MHz or the 100-MHz spectrum which in-

---

(1) (a) H. Batzer, *Chem. Ind.* (*London*), 179-189 (Feb 1, 1971). (b) J. J. Madden, A. S. Burhans, C. F. Pitt, *Adhesives Age* **8**, 22-27 (1965). (c) J. J. Steven, Jr., in "Epoxy Resin Technology," P. F. Bruins, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 2.

(2) (a) Union Carbide Technical Bulletin F42953, Oct 1970. (b) CIBA Technical Bulletin for Araldite Cycloaliphatic Epoxy Resins.

(3) (a) H. Lee and K. Neville, "Handbook of Epoxy Resins," McGraw-Hill, New York, N. Y., 1967. (b) H. Lee, A. L. Cupples, and D. G. Stoner, *Advan. Chem. Ser.*, **92**, 173-207. (c) A. M. Partansky, *Prepr., Amer. Chem. Soc., Div. Org. Coatings Plastics Chem.*, **28**, 366 (1968).

(4) W. J. Bailey and A. A. Volpe, *Polym. Prepr., Amer. Chem. Soc. Div. Polym. Chem.*, **8**, 292 (1967).

(5) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 307-311. (b) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1966.

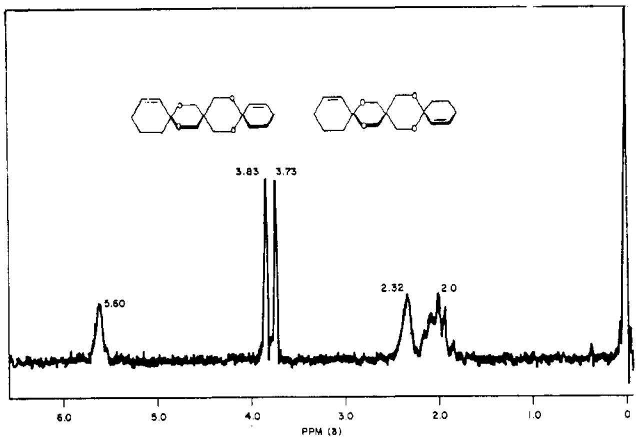


Figure 1. Nmr spectrum (60 MHz) of bis(2-cyclohexenylidene)pentaerythritol.

dicates any splitting expected from the spin-spin coupling of the geminal protons. Molecular models do appear to show that one oxymethylene group is apparently more affected by the double bond than the other oxymethylene in the same ring. Such difference in environments is eliminated in the saturated dicyclohexylidenepentaerythritol III as shown by one singlet at 3.68 ppm for the oxymethylene groups.[6,7] Spriane III was made by the hydrogenation of spirodiene I as well as by the condensation of cyclohexanone with pentaerythritol. Both methods gave identical products.

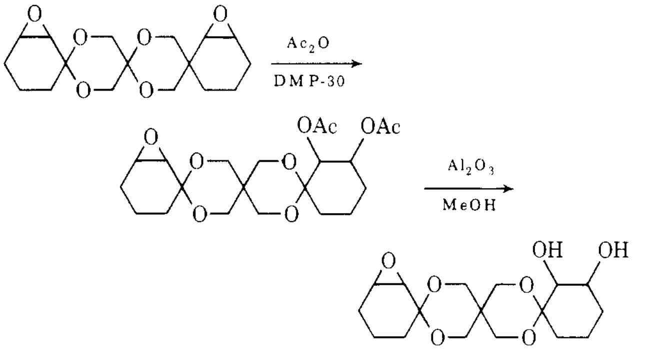
Spirodiene I was epoxidized readily with *m*-chloroperbenzoic acid which is known to be able to epoxidize double bonds with electronegative substituents.[1a,8] After the reaction, excess peracid was partially reduced with sodium sulfite, and all of the excess peracid and produced acid were then removed by washing with a 5% $NaHCO_3$ solution. The crude spiro diepoxide II was a white solid, mp 135.5-142.0°. Tlc showed the absence of starting material and the appearance of a new, rather lengthy spot, an indication of a mixture of isomeric products. No attempt was made to separate them. Nmr spectrum showed no olefinic protons (see Table I). The presence of four singlets for oxymethylene and three singlets for oxiranic protons revealed also the picture of a stereoisomeric mixture. Analysis of the oxirane absorptions in the ir spectrum is difficult due to the presence of multiple C-O-C bonds. The changes of C-O-C absorptions shown in the regions of 1000-1200 and 800-950 cm^{-1} after epoxidation appear to be expectable.

Curing Reactions of Spiro Diepoxide II. Both amines and acid anhydrides, common curatives for epoxy resins, were evaluated as curing agents for II. The diepoxide was mixed at room temperature with an excess amount of an amine, such as diethylaminopropylamine (DEAPA) or 2-ethyl-4-methylimidazole (EMI-24), and a catalyst such as tris(dimethylaminomethyl)phenol (DMP-30) or 1,3-propanediol. The mixture was then heated at 84-90° for 2-3 hr. No curing reaction was observed by periodical ir analysis during the mixing and the heating process. Negative reaction was also obtained from diethylenetriamine which is known to be one of the fastest amine curatives. The result was contrary to what was expected since the amines used are typical amine hardeners for the conventional glycidyl-type epoxy resins.

Acid anhydrides are known to be effective in general to cure cycloaliphatic epoxides. Hexahydrophthalic acid anhydride (HHPA) and Nadic methyl anhydride (NMA) were tried, but the latter, a liquid commercial curative, was preferred for the convenience of mixing. Benzyldimethylamine (BDMA) was used as catalyst. The anhydride and catalyst were mixed with II and subjected to a cure cycle normally adopted for anhydride curing, namely heating for 2 hr at 120° and for 7 hr at 160°. The reaction was followed by ir analysis. Positive reaction was shown by the intensity decrease of ester carbonyl absorption, as well as by the weakening of the oxirane absorptions at 900-940, 840, and 800 cm^{-1}. However, the reaction rate was much slower than that of the conventional DGEBA.

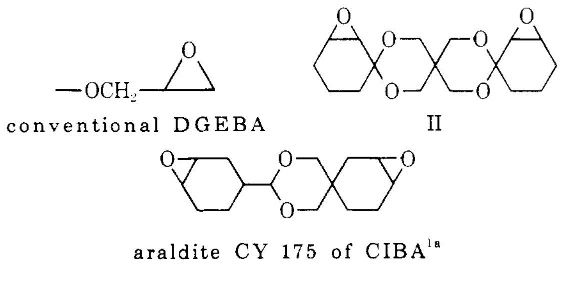
The sluggishness of II was further demonstrated by its reaction with acetic anhydride. No reaction took place when II was heated in acetic anhydride with BDMA added as catalyst. When DMP-30 was used as catalyst, ester formation was discernible by ir spectra. However, the acetylated II was hydrolyzed to alcohol when it was chromatographed over a column of alumina. All analyses of the end-products indicate a half-hydrolyzed diepoxide (see Scheme II).

Scheme II
Reaction with Acetic Anhydride



Reactivity of the Trispiro Ketal System. The ready epoxidation of spirodiene I seems to indicate that I reacted like a regular cyclohexene system,[9] irrespective of the neighboring electronegative etheral linkages. The electronegative linkages also failed to show any positive effect on the reactivity of the epoxide group of diepoxide II toward amine curing. In fact, the curing of II with acid anhydrides does not seem to be more rapid than the commercial cycloaliphatic epoxides. This is unexpected because the double etheral oxygen atoms in II are located by design at positions similar to that of the etheral oxygen in the glycidyl ether type epoxy. Apparently, the steric hindrance and the higher degree of electropositive alkyl substitution in II than in the conventional DGEBA system are predominant enough to counterbalance the electronegative effect of the double etheral oxygen (Chart II). Another dif-

Chart II
Epoxide Group in Epoxy Resins



---

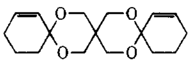
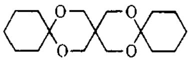
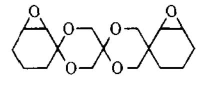
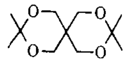
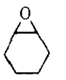
(6) J. Radell and R. E. Rondeau, *J. Chem. Eng. Data*, **16**, 104 (1971).

(7) The Sadtler Standard Spectra, NMR No. 6228, Sadtler Research Labs, Philadelphia, Pa.

(8) N. N. Schwartz and J. H. Blumbergs, *J. Org. Chem.*, **29**, 1976 (1964).

(9) R. G. Carlson, N. S. Behn, and C. Cowles, *J. Org. Chem.*, **36**, 3832 (1971).

Table I
Proton Chemical Shifts (60 MHz, ppm)

Compound	Oxymethylene	Allylic	Olefinic or Oxiranic	Methylene	Compound or Ref No.
	3.73 (s) 3.83 (s)	2.32 (s, broad)	5.60 (s, broad)	1.82-2.18 (m)	I
	3.68 (s)			1.40-1.68 (m)	III
 Isomers	3.82 (s) 3.75 (s) 3.65 (s) 3.58 (s)		3.22 (s) 3.18 (s) 3.11 (s)	1.74-2.29 (m)	II
	3.70 (s)				6
			2.94 (s)	*ca.* 1.82 (m) 0.91-1.60 (m)	7

ference in the spiro system which might be contributed to the lack of reactivity is that the etheral oxygen atoms and the epoxide groups are held in two rings connected through a spiro atom junction. It would be interesting to see the comparison of the transmission of inductive effect through a spiro atom junction with that through a bridgehead atom. The transmission through a bridgehead atom is known to be effective.[10]

Experimental Section

Melting points were taken in capillary tubes in an oil bath and are corrected. The ir spectra were determined in KBr pellets with a Perkin-Elmer 337 grating infrared spectrophotometer. The nmr spectra were taken with a Varian Model A-60 nmr spectrometer using tetramethylsilane as an internal standard. Hydroxyl peaks were identified, whenever necessary, by D_2O exchange. Elemental analyses were performed by the Galbraith Labs, Inc. Tlc was run on precoated plates (Mannagram No. 7926) with 250-μ thick silica gel film supplied by Mann Research Labs, New York. For elution chromatography, Fisher No. A-540 alumina (80-200 mesh) was treated with ethyl acetate to make it neutral. Tensile strength of adhesive material was tested according to ASTM D2059-69.

Materials. 2-Cyclohexen-1-one, a colorless liquid from Mobil Chemical, N. Y., was distilled and stored in a refrigerator. Pentaerythritol, from Eastman Kodak, was dried before use. *n*-Butyronitrile, practical grade, from Aldrich Chemical, was dried before use. *m*-Chloroperbenzoic acid, 85% pure, was obtained from Aldrich Chemical; a purity of 99% was obtained by washing the 85% material with a phosphate buffer of pH 7.5 and drying the residue at reduced pressure. A standard diglycidyl ether of bisphenol A, epoxy equiv wt 185-192, was obtained from Shell Chemical as Epon 828. 2-Ethyl-4-methylimidazole (EMI-24), from Roberts Chemicals, Nitro, W. Va., was industrial grade. Nadic methyl anhydride liquid (NMA), from Allied Chemical, was technical grade. Benzyldimethylamine (BDMA), from Maumee Chemical Co., was industrial grade. DMP-30 or tris(dimethylaminomethyl)phenol was obtained from Polysciences, Inc., Pa.

Bis(2-cyclohexenylidene)pentaerythritol (I). A mixture of 13.62 g of pentaerythritol (0.10 mol), 19.20 g of 2-cyclohexen-1-one (0.20 mol), 0.30 g of *p*-toluenesulfonic acid, and 350 ml of anhydrous *n*-butyronitrile in a 1-l. round-bottomed flask was heated under reflux for 53 hr with stirring under a nitrogen atmosphere. The water produced in the reaction was distilled as a water-nitrile azeotrope (bp 85°), condensed, and separated in a Dean-Stark distilling trap. All of the pentaerythritol was dissolved in 22 hr when 2.6 ml (72%) of the water was collected. The total water collected was 3.0 ml (83%). The cooled brown solution was washed successively with a 10% NaOH solution, water, and a saturated NaCl solution, and dried over anhydrous Na_2SO_4. Removal of the solvent by evaporation with a rotary evaporator under vacuum gave 27.6 g of residue—crystals mixed with brown soft solid. Isolation of the product from the residue was made by elution chromatography. Only the eluate fractions from benzene gave white solids (29% overall yield) which showed identical ir spectra without OH absorption. Recrystallization from ethyl ether-*n*-pentane afforded an analytical sample of I, mp 140-142°; ir 3015 (s) and 3050 (vw) (vinylic C-H), 1650 (w) and 1620 (vw) (C=C), 1100, 1200, 1136, and 1170 cm^{-1} (C-O-C); nmr ($CDCl_3$) δ 5.10 (broad singlet, 4, olefinic), 3.73 and 3.83 (two singlets, 8, oxymethylene), 2.32 (broad singlet, 4, allylic), 1.82-2.18 (multiplet, 8, methylene). *Anal.* Calcd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 69.79; H, 8.47.

Diepoxide of Bis(2-cyclohexenylidene)pentaerythritol (II). To a stirred solution of 0.292 g (1 mmol) of recrystallized spirodiene I in 30 ml of methylene chloride in a three-necked 100-ml flask was added dropwise in 35 min a solution of 0.380 g (2.2 mmol) of purified *m*-chloroperbenzoic acid in 20 ml of methylene chloride. The reaction mixture was maintained at 25° during the addition and then stirred at 30° for 2 hr.

The excess peracid was partially destroyed with a 10% Na_2SO_3 solution. The mixture was washed successively with a 5% $NaHCO_3$ solution, water, and a saturated NaCl solution, and dried over anhydrous Na_2SO_4. Removal of the solvent at room temperature by evaporation with a rotary evaporator afforded 0.40 g (80%) of diepoxide II, mp 136.5-143.0°. Tlc indicated no starting spirodiene I, but showed the appearance of a new and rather lengthy spot: ir 1100 (s), 1110 (shoulder), 1165 (s), 1150 (shoulder), and 800 cm^{-1} (s) (C-O-C), no vinylic C-H; nmr ($CDCl_3$) δ 3.82, 3.75, 3.65, 3.58 (4 singlets, 8, oxymethylene), 3.22, 3.18, 3.11 (3 singlets, 4, methine protons on the oxirane rings), 1.74-2.29 (multiplet, 12, methylene). *Anal.* Calcd for $C_{17}H_{24}O_6$: C, 62.94; H, 7.46. Found: C, 63.04; H, 7.22.

Dicyclohexylidenepentaerythritol (III) by Hydrogenation of Spirodiene I. To a 380-ml hydrogenation glass bottle containing 0.12 g of 10% Pd/C catalyst was added slowly a solution of 0.30 g of spirodiene I in 140 ml of methanol. Hydrogenation was run for 2 hr with a Parr hydrogenator under a hydrogen pressure of 22.5-25.0 psig. The catalyst was removed by filtration and the filtrate was evaporated to give 0.30 g (99%) of III, mp 109-115°. Ir showed no unsaturation. Recrystallization from methanol afforded microprisms: mp 116.5-118.5° (lit.[11] 135°); ir 1095 (s), 1115 (m), 1145 (m), and 1166 cm^{-1} (s) (C-O-C); nmr ($CDCl_3$) δ 3.68 (singlet, 8, oxymethylene), 1.40-1.68 (multiplet, 20, methylene). *Anal.* Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 69.12; H, 9.53.

Dicyclohexylidenepentaerythritol (III) by Ketalization of Cyclohexanone. A mixture of 19.6 g (0.20 mol) of cyclohexanone (99% pure), 13.62 g (0.10 mol) of pentaerythritol, 0.30 g of *p*-toluenesulfonic acid, and 250 ml of benzene (reagent grade) was heated under reflux for 7.5 hr with stirring under a nitrogen atmosphere. The water produced, 2.6 ml (72%), was collected and separated in a Dean-Start distilling trap. After the unreacted pentaerythritol was removed by filtration, the filtrate was washed suc-

---

(10) J. D. Roberts and W. T. Moreland, Jr., *J. Amer. Chem. Soc.*, **75**, 2167 (1953).

(11) V. M. Micovic *et al.*, *Tetrahedron*, **4**, 186 (1958).

cessively with a 5% NaOH solution, water, and a saturated NaCl solution, and dried over anhydrous $MgSO_4$. Evaporating the solvent left 24.32 g (82%) of white crystals, mp 133-136°. Mixture melting point with the sample made by hydrogenation of I showed no depression. Ir spectra of the two were also identical. Recrystallization from $MeOH-Et_2O$ gave prisms, mp 116–118°.

Curing of Diepoxide II with Amines. An excess amount of amine was mixed with diepoxide II. The curing reaction was followed by ir spectroscopy. With 3-diethylaminopropylamine (DEAPA), the cure cycle was 25°/1 hr + 90°/2 hr; with 2-ethyl-4-methylimidazole (EMI-24), the cycle was 25°/0.5 hr plus 84°/3 hr. No spectral change was observed in the cure cycle. Negative results were also obtained when DMP-30 or 1,3-propanediol was used as catalyst together with DEAPA.

Curing of Diepoxide II with an Acid Anhydride. Diepoxide II (0.0844 g), Nadic methyl anhydride (NMA), and benzyldimethylamine were mixed in a weight ratio of 100:100:16. A film of the liquid mixture was spread between two NaCl crystal plates and put through a cure cycle of 120°/2 hr plus 160°/7 hr. The ir spectra of the films were recorded periodically. The following spectral changes were observed. Anhydride carbonyl absorptions at 1775 and 1860 cm^{-1} decreased in intensity as the ester carbonyl absorption at 1730 cm^{-1} appeared and intensified, but the anhydride carbonyl peaks failed to disappear completely after the cure cycle; ester carbonyl absorption at 1730 cm^{-1} appeared after 120°/2 hr and intensified strongly in the later part of the cure cycle; carboxylate ion carbonyl absorption at 1575 cm^{-1} appeared as a very weak peak as soon as the compounds were mixed, and its intensity increased during the first 2 hr/120° but remained the same thereafter; oxirane absorptions at 900–940, 840, and 800 cm^{-1} were weakened as the curing went on. The solid film formed between the NaCl plates was clear, poor in strength, and insoluble in water or acetone. It melted at 256–281°.

A second run was made with the wt ratio of the components changed to 100:91:1. A little methylene chloride was first added to facilitate mixing and removed later by evacuation. Similar spectral changes were observed in the cure cycle. The absorption of carboxylate anion carbonyl appeared much weaker, obviously because much less amine catalyst was used this time. The curing reaction essentially stopped after 4 hr/160°, while a control sample made of a conventional epoxy resin Epon 828 completed its curing after 1 hr/160°. The degree of cure in the second run was lower according to melting point. It showed an adhesive strength of only 2400-psi tensile in comparison with 6400 psi from the control sample.

Reaction of Diepoxide II with Acetic Anhydride. Four-tenths of a gram of diepoxide II was dissolved in 25 ml of freshly distilled acetic anhydride and a few drops of benzyldimethylamine were added to the solution. The solution was heated at 80–120° for 2 hr and at 125° for 2 hr, and was then heated under reflux for 1 hr (*ca.* 155°). The yellowish solution was evaporated under vacuum with a rotary evaporator at a temperature not higher than 70° to give 0.35 g of a brownish residue. Ir indicated essentially the starting material, and no carbonyl absorption was discernable.

The residue was redissolved in 23 ml of acetic anhydride, and 0.20 ml of DMP-30 was added as catalyst. The mixture was stirred at 120° for 2 hr and heated under reflux for 1 hr (*ca.* 150°). After removing the excess anhydride under vacuum with a rotary evaporator, the residue was dissolved in methylene chloride. The solution was washed successively with 3% HCl solution, 3% NaOH solution, and water to remove all the acidic and basic ingredients. Evaporating the solvent left a brownish residue, 0.63 g of crystals mixed with oily substance. Ir showed a strong ester carbonyl peak at 1730 cm^{-1}, but no hydroxyl absorption. Recrystallization of the residue from $CHCl_3-Et_2O$ or $CHCl_3$-pentane was not successful.

Separation of the reaction residue was made by elution chromatography over a column of ethyl acetate treated alumina. The column was developed with benzene and eluted progressively with mixtures of benzene, ethyl ether, chloroform, and methanol. The major fraction was obtained with a 5% methanol solution in chloroform, giving 0.26 g (61.5%) of a white solid. Recrystallization from $CHCl_3-Et_2O$ afforded an analytical sample (IV) of the half-hydrolyzed diepoxide II: mp 191.5–192.5°; nmr (Me_2SO-d_6) δ 4.55 (multiplet, 2, hydroxyl), 3.69 (multiplet, 8, oxymethylene), *ca.* 3.10 (multiplet, 4, protons α to hydroxyl and protons on the oxirane rings), 1.0–2.3 (multiplet, 12, methylene). Ir showed a strong hydroxyl band at 3370 cm^{-1}, but no carbonyl absorption. The absorptions of C–O–C in the regions of 1000–1200 and 800–940 cm^{-1} remained similar to that of the starting diepoxide except that the oxirane peaks at 800 and 840 cm^{-1} were relatively weakened. *Anal.* Calcd for $C_{17}H_{26}O_7$: C, 59.63; H, 7.66. Found: C, 60.4; H, 7.89.

Acknowledgment. The author thanks Mrs. H. C. Sing of the Walter Reed Army Institute of Research for her assistance in the nmr experiments.

Synthesis of Diethynylbenzenes. II

James M. Watson

Cosden Oil and Chemical Company, Big Spring, Texas 79720. *Received May 17, 1973*

ABSTRACT: The synthesis of *m*-diethynylbenzene *via* radical chlorination of *m*-diethylbenzene in the presence of PCl_5 and visible light followed by dehydrochlorination using $NaNH_2$ in liquid NH_3 has been optimized with respect to the reaction variables involved. Data are presented which demonstrate the usefulness of the present route and comparisons to previously reported synthesis of diethynylbenzenes are drawn.

The continuing intense interest in diethynylbenzenes as precursors to high-performance thermally stable polymers is confirmed by the regular appearance of publications dealing with their preparation,[1-4] purification,[5,6] characterization,[7] and utilization.[8-12] The classical route to these compounds was first reported by Hay[13] and involves dehydrogenation of diethylbenzenes to the corresponding divinylbenzenes followed by bromination and subsequent dehydrobromination. The limitations of this route have been noted previously,[3] and several syntheses of diethynylbenzenes based in diacetylbenzenes have subsequently been reported.[1,3,4] Nevertheless, the "ideal" route to diethynylbenzenes would appear to be one entailing direct halogenation of diethylbenzenes followed by dehydrohalogenation. Though monochlorination of the side chains of diethylbenzene in yields of 36–60% has previously been reported,[14] the inherent lack of selectivity of radical chlorination has apparently discouraged attempts to prepare diethynylbenzenes by this means. Interestingly, a rather

---

(1) H. M. Relles, U. S. Patent 3,696,158 (1972).
(2) H. M. Relles, U. S. Patent 3,594,423 (1971).
(3) J. M. Watson, *Macromolecules*, **5**, 331 (1972).
(4) H. M. Relles, U. S. Patent 3,700,743 (1972).
(5) D. M. White, U. S. Patent 3,594,437 (1971).
(6) C. L. Daniels and J. M. Watson, U. S. Patent 3,720,727 (1973).
(7) D. M. White and G. C. Levy, *Macromolecules*, **5**, 526 (1972).
(8) J. K. Stille *et al.*, *J. Polym. Sci., Part B*, **4**, 791 (1966).
(9) J. K. Stille, Macromolecular Preprints, Vol. 2, XXIII International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971, p 929.
(10) A. S. Hay, U. S. Patent 3,300,456 (1967).
(11) A. S. Hay, U. S. Patent 3,594,175 (1971).
(12) C. L. Schilling, Jr., J. A. Reed, and J. K. Stille, *Macromolecules*, **2**, 85 (1969).
(13) A. S. Hay, *J. Org. Chem.*, **25**, 637 (1960).
(14) B. H. Kress, British Patent 627,509 (1949).