the over-all yield was about the same as in the foregoing experiments and there was a great saving of time.

Anal. Calcd. for $C_{15}H_{13}O_4N$: C, 66.41; H, 4.64; N, 5.16. Found: C, 66.39; H, 4.83; N, 5.15.

Lactam of 2-Amino-2′-biphenylacetic Acid (VII).—In a low pressure Parr apparatus methyl 2-nitro-2′-biphenylacetate in the presence of platinum was reacted with hydrogen at room temperature. The amount of hydrogen needed to reduce the nitro group to an amino group was used in the course of one hour. Approximately 75 ml. of absolute ethanol was used for 10.56 g. (0.039 mole) of the nitro compound. After the filtered reaction mixture had stood at room temperature for 15 hours, 4.15 g. of long white needles, m.p. 231–234°, had separated. Concentration of the filtrate yielded an additional 1.66 g. of white crystals, m.p. 230–233°, to make the total yield 72%. Attempts to diazotize and acetylate this product were unsuccessful. Three crystallizations of the white needles from ethanol gave material with m.p. 231–233°.

Anal. Calcd. for $C_{14}H_{11}ON$: C, 80.36; H, 5.30; N, 6.70. Found: C, 80.21; H, 5.21; N, 6.69.

Acknowledgment.—The authors wish to express their appreciation to Dr. H. B. Hass who suggested this problem and to the General Aniline and Film Corporation for its generous sponsorship of part of the work.

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Action of Alkali on Allyl Alcohol Chloroiodides. "β-Epichlorohydrin" (2-Chloroallyl Alcohol)

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In 1891 Bigot[2] reported that action of powdered sodium hydroxide on allyl alcohol chloroiodides in ether solution yielded, as distillable products, allyl alcohol (19%), epichlorohydrin (12%), "β-epichlorohydrin" (10%), epiiodohydrin (1.8%) and "β-epiiodohydrin" (1.2%). The only evidence given for identification of allyl alcohol (b.p. 96°), epichlorohydrin (b.p. 115–116°) and epiiodohydrin (b.p. 160–162°) was their boiling points. "β-Epichlorohydrin" (b.p. 132–134°) was shown by elemental analysis and vapor density to be an isomer of epichlorohydrin. The choice between the unknown 2-chlorotrimethylene oxide (3-chlorocycloöxabutane) structure and 2-chloroallyl alcohol was based on an extensive study of the chemical properties of "β-epichlorohydrin." Bigot was unaware that 2-chloroallyl alcohol had been prepared nine years before, in 1882, by Henry[3] and van Romburgh.[4] "β-Epiiodohydrin" (b.p. 172–174°) had the correct iodine analysis for an isomer of epiiodohydrin, but the only chemical property reported was inertness to concentrated potassium hydroxide solution at 100°. The 2-iodotrimethylene oxide (3-iodocycloöxabutane) structure was assigned to "β-epiiodohydrin" by analogy with "β-epichlorohydrin."

In 1944 Nilsson and Smith[5] repeated Bigot's procedure in order to determine the heat of combustion of "β-epichlorohydrin." Epichlorohydrin (11.5%) and "β-epichlorohydrin" (6.3%) were obtained, but the other fractions were not investigated. The identity of epichlorohydrin was proved by comparison of physical properties with authentic samples. The measured heat of combustion of "β-epichlorohydrin" was 404.0 ± 0.2 kcal. per mole at 19.3°, where "β-epichlorohydrin" is a liquid and hydrogen chloride is in aqueous solution.[5,6] The structure of "β-epichlorohydrin" proposed by Bigot[2] was accepted although the molar refractivity (21.76) did not agree well with that calculated for 2-chlorotrimethylene oxide (20.85).[7] Nilsson and Smith did not notice the remarkable similarity of the physical properties which they reported for "β-epichlorohydrin" to those of 2-chloroallyl alcohol (see Table I).

TABLE I

COMPARISON OF PHYSICAL PROPERTIES OF "β-EPICHLOROHYDRIN" AND 2-CHLOROALLYL ALCOHOL

	Cl, %	B.p., °C.	n_D	d_4	Molar refractivity
"β-Epichlorohydrin"[a]	38.24 (found)	133.0–133.8 (atm.)	$1.4588^{20°}$	$1.1618^{20°}$	21.76 (found)
2-Chloroallyl alcohol[b]	38.32 (calcd.)	135–135.5 (752 mm.)	$1.4573^{19°}$	$1.1601^{19°}$	21.99[c] (calcd.)

[a] Reference 5. [b] A. N. Nesmeyanov and K. K. Kochetkov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 76 (1949) [*C.A.*, **43**, 7412 (1949)]. [c] Reference 7.

Formation of a four-membered oxide ring is difficult. For example, the rate of propylene oxide formation from 1-chloro-2-propanol (propylene chlorohydrin) with base is 10,000 times faster than the rate of trimethylene oxide formation from the isomeric 3-chloro-1-propanol (trimethylene chlorohydrin).[8] The expected difficulty in closing a trimethylene oxide ring, and the existence of a plausible alternative involving elimination of hydrogen iodide from 2-chloro-3-iodo-1-propanol to give 2-chloroallyl alcohol, cast doubt upon the 2-chlorotrimethylene oxide structure for "β-epichlorohydrin." This, together with our belief that the reported reactions and physical properties of "β-epichlorohydrin" could better be interpreted as those of 2-chloroallyl alcohol caused us to reinvestigate the structure of "β-epichlorohydrin."

Since Bigot[2] did not state the amount of powdered sodium hydroxide used, the molar ratio of sodium hydroxide to allyl alcohol chloroiodides was varied from 1.15 to 3.19. Increasing the amount of alkali reduced the yield of distillable products and changed the nature of the higher boiling fractions. In contrast to the report of Bigot, allyl alcohol was obtained only in small amount. The presence of epichlorohydrin was confirmed. The fraction corresponding in physical properties to the "β-epichlorohydrin" of Bigot[2] and Nilsson and Smith[5] had an infrared spectrum identical with that

(1) From the M.S. Thesis of Bruce N. Bastian, University of Minnesota, 1954. On training assignment from the U. S. Air Force Institute of Technology.

(2) A. Bigot, *Ann. chim. et phys.*, [6] **22**, 433 (1891).

(3) L. Henry, *Compt. rend.*, **95**, 849 (1882).

(4) P. van Romburgh, *Rec. trav. chim.*, **1**, 233 (1882).

(5) T. Nilsson and L. Smith, *Svensk Kem. Tidskr.*, **56**, 156 (1944).

(6) L. Smith and E. Schjånberg, *ibid.*, **43**, 218, 221 (1931).

(7) Calculated from the atomic refractivities and the correction for a 4-membered ring given in S. M. McElvain, "The Characterization of Organic Compounds," revised ed., The Macmillan Co., New York, N. Y., 1953, p. 35. (Nilsson and Smith[5] used the calculated value of 20.36.)

(8) W. P. Evans, *Z. physik. Chem.*, **7**, 337 (1891).

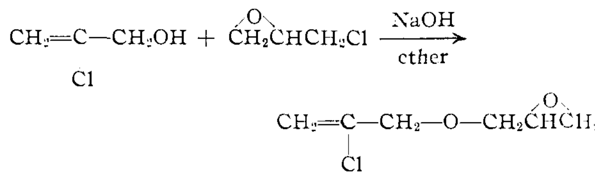
of 2-chloroallyl alcohol. Likewise, its *p*-nitrobenzoate and 3,5-dinitrobenzoate had infrared spectra identical with those of the corresponding derivatives from 2-chloroallyl alcohol, and there was no depression in mixed melting points. Consequently, the compound previously called "β-epichlorohydrin" has now been found to be 2-chloroallyl alcohol. The *p*-nitrobenzoate (m.p. 64.0°) and the 3,5-dinitrobenzoate (m.p. 82.3°) are easier to isolate than the phenylurethan (m.p. 44°),[9] the only derivative previously reported, and the *p*-nitrobenzoate was obtained in particularly high yield (90%). The nuclear magnetic resonance spectrum[10] of "β-epichlorohydrin" showed the following ratios of area under the two maxima: 1.45, 1.48, 1.55, average 1.49. The calculated value for three hydrogens in $-CH_2OH$ and two hydrogens in $CH_2=$ is 1.50.

Contrary to the previous reports,[2,5] 2-chloroallyl alcohol was obtained in higher yield than epichlorohydrin. This suggests that 2-chloro-3-iodo-1-propanol is the isomer formed in larger amount by addition of iodine monochlororide to allyl alcohol.[11] This is analogous to the addition of iodine monochloride to propylene, in which the isomers present were 69% 1-iodo-2-chloropropane and 31% 1-chloro-2-iodopropane,[12] and to 2-chloro-1,3-butadiene (chloroprene), where a 70% yield of 4-iodo-2,3-dichloro-1-butene was claimed.[13]

Bigot's report of epiiodohydrin as a minor product is supported by our infrared data. The relatively large yields of 2-chloroallyl alcohol compared to the maximum possible amounts of epiiodohydrin present suggest that in 2-chloro-3-iodo-1-propanol elimination of hydrogen iodide is dominant over epoxide formation involving loss of hydrogen chloride.

The higher boiling fractions from the less basic reaction contained large amounts of iodo compounds. These fractions had medium double bond and very strong hydroxyl bands in the infrared, but attempts to prepare crystalline alcohol derivatives were unsuccessful. Since Bigot assigned the structure of "β-epiiodohydrin" by analogy with "β-epichlorohydrin," the 2-iodotrimethylene oxide (3-iodocycloöxabutane) structure is in doubt.

In the more basic reaction the relatively large amounts of iodohydroxy compounds were absent. Instead, there was obtained in substantial amount a new component having an infrared spectrum identical with that of the compound for which the structure of 2-chloroallyl glycidyl ether is proposed. This was synthesized independently from 2-chloroallyl alcohol and epichlorohydrin with powdered sodium hydroxide under conditions analogous to those under which the two organic reagents were themselves formed.



Epiiodohydrin and 2-chloroallyl alcohol under similar conditions gave a mixture of products containing only small amounts of impure 2-chloroallyl glycidyl ether. Hence, it is concluded that in the basification of the allyl alcohol chloroiodides the major initial products, epichlorohydrin and 2-chloroallyl alcohol, can react with excess sodium hydroxide to form 2-chloroallyl glycidyl ether.

Experimental

All melting points were determined on a Kofler micro hot stage.

2-Chloroallyl *p*-Nitrobenzoate.—Redistilled Shell Development Co. 2-chloroallyl alcohol[14] and *p*-nitrobenzoyl chloride were subjected to the Schotten–Baumann reaction essentially by the method of Lipscomb and Baker.[15] Three recrystallizations of the product from light petroleum (b.p. 60–68°) gave 2-chloroallyl *p*-nitrobenzoate in 90% yield as white needles, m.p. 64.0°.

Anal. Calcd. for $C_{10}H_8NO_4Cl$ (241.63): C, 49.70; H, 3.34; N, 5.80. Found: C, 49.71, 50.00; H, 3.33, 3.52; N, 5.75, 5.80.

2-Chloroallyl 3,5-Dinitrobenzoate.—Redistilled Shell Development Co. 2-chloroallyl alcohol and 3,5-dinitrobenzoyl chloride gave by the method of Lipscomb and Baker[15] a 45% yield of crude product. Four recrystallizations from light petroleum (b.p. 60–68°) yielded 2-chloroallyl 3,5-dinitrobenzoate as white needles, m.p. 82.3°.

Anal. Calcd. for $C_{10}H_7N_2O_6Cl$ (286.63): C, 41.90; H, 2.46; N, 9.77. Found: C, 41.62, 41.73, 41.91; H, 2.82, 2.86, 3.03; N, 9.81, 9.75.

Epiiodohydrin.—A spectrally pure sample of epiiodohydrin was prepared in 29% yield by the method of Nef[16]; b.p. 44–46° (8 mm.), $n^{25.5}D$ 1.5465, ν_{C-O-C} 1257, 842 cm.$^{-1}$.

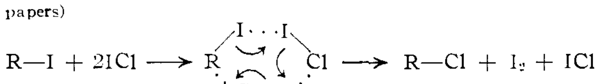
Anal. Calcd. for C_3H_5OI (183.99): C, 19.58; H, 2.74. Found: C, 19.66; H, 2.96.

Allyl Alcohol Chloroiodides.—Bigot's procedure[2] was followed as closely as his description permitted. The amount of crushed ice used as solvent was not specified. Bigot reported that the end of the reaction between iodine monochloride and allyl alcohol was recognized when the liquid developed a yellow tint. In our experience the reaction mixture developed a yellow tint after less than 1% of the stoichiometric amount of iodine monochloride had been added and, when addition was complete, the heavy oily product was black. Variation in the amount of ice and water used as solvent had little effect on the yield, but substitution of carbon tetrachloride reduced the yield to 53%. Distillation time was important since prolonged heating of the thermally unstable chloroiodides reduced the yield.

(9) G. Kremer, *Bull. soc. chim.*, [5] **15**, 166 (1948).

(10) Determined in these laboratories by Prof. John E. Wertz and Mr. Robert L. Batdorf.

(11) The fact that free iodine was evolved during distillation of the allyl alcohol chloroiodides is consistent with the possibility that allyl alcohol dichloride may also have been present. This could have been formed from the chloroiodides since it is known that iodine monochloride can replace chlorine for iodine in alkyl iodides (see R. M. Keefer and L. J. Andrews, THIS JOURNAL, **76**, 253 (1954), and earlier papers)



Since allyl alcohol dichloride, like 3-chloro-2-iodo-1-propanol, would yield epichlorohydrin upon basification, the amount of epichlorohydrin formed could exceed the amount of 3-chloro-2-iodo-1-propanol initially formed by the extent to which the other, more abundant, isomer, 2-chloro-3-iodo-1-propanol, has been converted to allyl alcohol dichloride. Consequently, the ratio of 2-chloroallyl alcohol to epichlorohydrin may represent only a lower limiting value for the ratio of 2-chloro-3-iodo-1-propanol to 3-chloro-2-iodo-1-propanol initially formed.

(12) C. K. Ingold and H. G. Smith, *J. Chem. Soc.*, 2742 (1931).

(13) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **13**, 155 (1943) [*C. A.*, **38**, 1466 (1944)].

(14) Also prepared by refluxing 2-chloroallyl chloride with aqueous potassium carbonate as described by Kremer,[9] except that a longer time than 12 hours was used. Refluxing for 65 hours gave 22% 2-chloroallyl alcohol and 51% unreacted 2-chloroallyl chloride.

(15) W. N. Lipscomb and R. H. Baker, THIS JOURNAL, **64**, 179 (1942).

(16) J. U. Nef, *Ann.*, **335**, 237 (1904).

Early in the distillation solid iodine tended to plug the distillation column or condenser. This difficulty is avoided in the procedure described, in which the yield (72%) compares favorably with Bigot's (58%).

Iodine monochloride (650 g., 4.00 moles) was added dropwise during 1.5 hours to a vigorously stirred mixture of allyl alcohol (240 g., 4.13 moles) and crushed ice (200 g.). Each addition of iodine monochloride produced a vigorous release of acidic, white fumes. The initial addition turned the solution yellow and further amounts caused the product to become red and finally black. Stirring was maintained for an additional 1.25 hours while the reaction flask was kept surrounded by ice. Then the dense black oil was separated and the aqueous layer extracted with ether (250 cc.) and the extracted oil combined with the original oily layer. The oily layer was placed in a simple distilling flask attached to a condenser connected in succession to receivers A and B. The distilling flask was warmed in an oil-bath and its contents vacuum distilled. A forerun containing water was followed by copious evolution of iodine. Steam was passed through the condenser and receiver A was heated in a water-bath until iodine was no longer evolved. Receiver B was cooled in an ice-bath at all times so that the aqueous forerun and iodine collected in it. Then cold water was passed through the condenser and receiver A was cooled in an ice-bath. The red, oily allyl alcohol chloroiodides (638 g., 2.89 moles, 72%) were collected in A at 69–95° (1.5 mm.). The total distillation time was 5.5 hours. There was a residue of 151 g.

Action of Sodium Hydroxide on Allyl Alcohol Chloroiodides.—Bigot's procedure[2] was followed as closely as his description permitted. He reported stopping the addition of powdered sodium hydroxide to the allyl alcohol chloroiodides when the ethereal solution became colorless. The amount of sodium hydroxide was not stated. In the present work the molar ratio of sodium hydroxide was varied from 1.15 (A) to 3.19 (B). In neither case did the yellow color of the solution completely disappear, and increasing the amount of alkali reduced the yield of distillable products.

A.—Allyl alcohol chloroiodides (1014 g., 4.60 moles) in anhydrous ether (1500 cc.) were warmed in a water-bath (45°) under reflux until the deep red ether solution began to boil. The water-bath was then removed and powdered (20 mesh) sodium hydroxide (212 g., 5.30 moles) was added in 1–2 g. portions, with vigorous stirring, during 4.75 hours. The vigorous exothermic reaction following each addition was allowed to subside before more sodium hydroxide was added. The mixture was allowed to remain at room temperature overnight without stirring, and then was stirred for an additional 5.5 hours. The inorganic solids were filtered off and dissolved in water (400 cc.). The ethereal filtrate was washed with water (200 cc.) and the aqueous solutions were combined and washed twice with ether (210 cc. each). The combined ether solutions were dried over anhydrous potassium carbonate. The ether was removed under reduced pressure and the resulting yellow oil vacuum-distilled through a 2 × 30 cm. column containing Cannon protruded packing to give 301 g. of distillable products. Further distillation gave epichlorohydrin (49.9 g., 0.54 mole, 12%) and 2-chloroallyl alcohol (67.2 g., 0.73 mole, 16%). Redistillation gave epichlorohydrin b.p. 116° (742 mm.), $n^{25.5}D$ 1.4350, ν_{C-O-C} 1271, 855, ν_{C-Cl} 724 cm.$^{-1}$, identical in infrared spectrum with that of redistilled Eastman Kodak material, and 2-chloroallyl alcohol, b.p. 133.5–133.6° (735 mm.), $n^{25}D$ 1.4565, ν_{OH} 3330, $\nu_{C=C}$ 1648, ν_{C-Cl} 716 cm.$^{-1}$, identical in infrared spectrum with that of redistilled Shell Development Co. material. None of the distillable products had infrared spectra containing all of the bands of redistilled Shell Development Co. 3-chloroallyl alcohol, b.p. 52–52.5° (12 mm.), $n^{25.5}D$ 1.4640, ν_{OH} 3350, $\nu_{C=C}$ 1631, ν_{C-Cl} 743 cm.$^{-1}$.

B.—Allyl alcohol chloroiodides (578 g., 2.62 moles) in anhydrous ether (500 cc.) were treated with powdered sodium hydroxide (334.5 g., 8.36 moles) as in A. Distillation through a 1.5 × 6 cm. column containing Cannon protruded packing gave 121 g. of distillable products. The first fraction (2.0 g.) corresponded in boiling point, 87–89 (743 mm.), to that of an azeotrope of allyl alcohol (72.3%) and water (27.7%), b.p. 88.89°.[17] The 3,5-dinitrobenzoate from this fraction showed no depression in mixed melting point (49°) with a sample prepared[15] from allyl alcohol.

Further distillation of the main fractions yielded epichlorohydrin (43.1 g., 0.466 mole, 18%) and 2-chloroallyl alcohol (46.0 g., 0.498 mole, 19%). Redistillation gave samples whose infrared spectra were identical with those of the authentic samples. The *p*-nitrobenzoate and 3,5-dinitrobenzoate of the 2-chloroallyl alcohol also had infrared spectra identical with those of authentic samples and there was no depression in mixed melting points with the authentic samples.

The higher boiling fractions contained substantial amounts of a new component (19.7 g., 0.133 mole, 10%). Redistillation gave a sample, b.p. 80–82° (9 mm.), $n^{25}D$ 1.4605, having an infrared spectrum identical with that of 2-chloroallyl glycidyl ether.

Synthesis of 2-Chloroallyl Glycidyl Ether (with David O. Halvorson).—2-Chloroallyl alcohol (40 g., 0.43 mole) and epichlorohydrin (40 g., 0.43 mole) in anhydrous ether (500 cc.) were treated with powdered sodium hydroxide (30 g., 0.75 mole) as in Reaction A. The addition of sodium hydroxide produced an exothermic reaction. After the mixture was refluxed for 16 hours the organic layer was separated, washed with water, dried over anhydrous potassium carbonate, and distilled through a 2 × 30 cm. column containing Cannon protruded packing to give 23 g. of distillable products. In addition to unreacted starting materials, there was obtained 2-chloroallyl glycidyl ether (10 g., 0.68 mole, 16%). Redistillation gave a sample, b.p. 37.5–38.0° (3 mm.), $n^{25.5}D$ 1.4591, $d^{25.5}_4$ 1.1468, MD calcd.[18] 36.11, found 35.43. The infrared spectrum was identical with that of the corresponding sample from reaction B, $\nu_{C=C}$ 1640, ν_{C-O-C} 1250, 857, ν_{C-O-C} 1097, ν_{C-Cl} 716 cm.$^{-1}$.

Anal. Calcd. for $C_6H_9O_2Cl$ (148.59): C, 48.50; H, 6.11. Found: C, 48.61; H, 6.38.

(17) Shell Chemical Corp., "Allyl Alcohol," Technical Publication SC:46-32, San Francisco, Calif., 1946, p. 2.

(18) See reference in note 7.

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Dehydration of β-Phenylethylcyclohexanol-3

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Perlman and Bogert in their study of the dehydration of β-phenylethyl-3-methylcyclohexanol-1[1] and β-phenylethylcyclohexanol-1[2] (I) showed that under the acid conditions of the dehydration with sulfuric acid, the olefins formed immediately cyclized to 2-methyloctahydrophenanthrene and octahydrophenanthrene, respectively. These experiments led to the view that β-phenylethyl-Δ^1-cyclohexene is the intermediate in the Bardhan–Sengupta synthesis[3,4] of octahydrophenanthrene through cyclodehydration of β-phenylethylcyclohexanol-2 (II). We believed that the intermediate formation of β-phenylethyl-Δ^2-cyclohexene in the above synthesis might also be a possibility and with that idea in view, we decided to prepare β-phenylethylcyclohexanol-3 and study the course of its dehydration.

In the first instance, 1-styryl-cyclohexan-3,5-dione, prepared according to the method of Vorländer and Groebel, was converted through the unsaturated chloroketone to β-phenylethylcyclohexanone-3. Reduction of this substance by sodium and moist ether afforded β-phenylethylcyclohexanol-3 (III) which, on treatment with phospho-

(1) M. T. Bogert and D. Perlman, THIS JOURNAL, **59**, 2534 (1937).
(2) M. T. Bogert, *Science*, **77**, 289 (1933).
(3) J. C. Bardhan and S. C. Sengupta, *J. Chem. Soc.*, **143**, 2520 (1932).
(4) J. C. Bardhan and S. C. Sengupta, *ibid.*, **143**, 2798 (1932).