Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.68; H, 6.60.

The 2,5-dimethyl compound (III, 2,5-dimethyl) was prepared in a similar way and is listed in Table III together with its melting point and analytical data.

9-(2,4-Dimethylphenyl)anthracene (III, *2,4-dimethyl*). A mixture of 5 g. of the corresponding ketone (II, 2,4-dimethyl), 15 ml. of 48% hydrobromic acid, and 30 ml. of glacial acetic acid was sealed in a Caruis tube and heated for 48 hr. at 170°. The mixture was worked-up in a manner similar to that described above for the 2,3-dimethyl compound (III, 2,3-dimethyl) and gave 0.6 g. (13%) of white needle-like crystals, m.p. 102–104°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.66; H, 6.50. The remaining hydrocarbons were prepared in a similar way and are listed in Table III together with their respective melting points and analytical data.

TABLE III

NEW HYDROCARBONS[a]

Methyl groups at	Yield, %	M.P.	Carbon Found	Hydrogen Found
2,3	20	179–180	93.68	6.60
2,4	18	102–104	93.66	6.50
2,5	12	118–119	93.50	6.71
3,4	58	139–140	93.46	6.50
3,5	74	159–160	93.60	6.46

[a] Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43.

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BLACKSBURG, VA.

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., PLASTICS DIVISION]

Chloromethylation of β-Chloroethylbenzene and the Preparation of p-Vinylbenzyl Alcohol[1]

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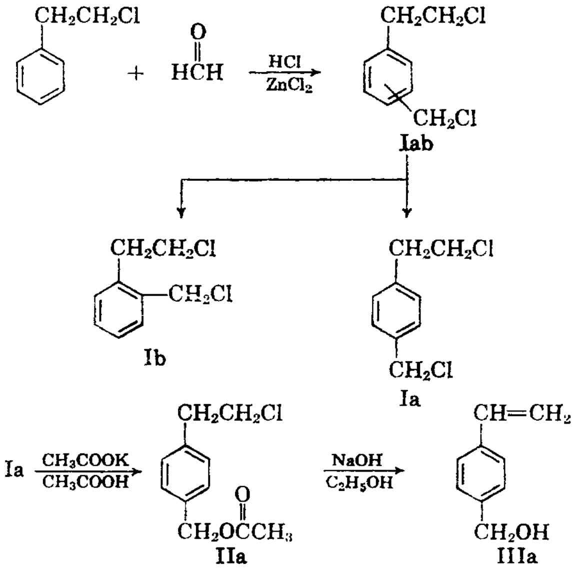
Chloromethylation of β-chloroethylbenzene gave a mixture of β-chloroethylbenzyl chlorides having an isomer distribution of 74 ± 3% *para* and 26 ± 3% *ortho*. No serious attempt was made to detect the *meta* isomer, although it could have been present only in small amount. Crystallization of this mixture gave the pure *para* isomer and fractional distillation afforded a sample of the *ortho* isomer. Higher boiling products obtained were identified as bis(chloromethyl)-β-chloroethylbenzene and bis(β-chloroethyl)diphenylmethane. The *ortho* and *para* isomers were converted to *ortho-* and *para-β*-chloroethylbenzyl acetate. Alcoholic base converted *p*-(β-chloroethyl)benzyl acetate to *p*-vinylbenzyl alcohol while similar treatment converted the *ortho* isomer to isochroman. The formation of isochroman is explained on the basis of a rapid saponification of the benzyl acetate portion of the molecule followed by nucleophilic displacement of the chlorine atom.

The preparation of vinylbenzyl alcohol first reported by Emerson *et al.*[3] utilized a series of steps starting with the chloromethylation of ethyl benzene. This work reports the synthesis of *p*-vinylbenzyl alcohol and the attempted synthesis of the *ortho* isomer.

The route used involved (a) the chloromethylation of β-chloroethylbenzene to yield a mixture of the *ortho* and *para* isomers of β-chloroethylbenzyl chloride, (Iab), which were separated into their pure components, (Ia and Ib); (b) conversion of the *p*-(β-chloroethyl)benzyl chloride (Ia) to *p*-(β-chloroethyl)benzyl acetate (IIa); and (c) the simultaneous hydrolysis and dehydrohalogenation of (IIa) to *p*-vinylbenzyl alcohol (III).



Chloromethylation. The chloromethylation of β-chloroethylbenzene proceeded smoothly to yield a mixture of *ortho* and *para* (β-chloroethyl)benzyl chloride. There was no apparent participation of the β-chlorine in alkylations under the conditions employed. Yields of 85% were obtained under optimum conditions. This reaction was reported previously by Kulka and Van Stryk,[4] but they did not report the separation of the two isomers. We have

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[1] Presented at the meeting of the Connecticut Valley Section of the American Chemical Society, November 19, 1960.

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[3] W. S. Emerson, J. W. Heyd, V. E. Lucas, W. I. Lyness, G. R. Owens, and R. W. Shortridge, *J. Am. Chem. Soc.*, 69, 1905 (1947).

[4] M. Kulka and F. G. Van Stryk, *Can. J. Chem.*, 33, 1130 (1955).

found that the *para* isomer is a crystalline material melting at 32.5–33.5° and can be isolated from the mixture of *ortho* and *para* isomers by crystallization from hexane. The *ortho* isomer can be isolated by fractional distillation of the liquors obtained from crystallization of the *para* isomer. The presence of a small amount of the meta isomer is probable in view of the study made by Brown and Nelson,[5] however, we did not attempt to isolate the small amount of this material that would result.

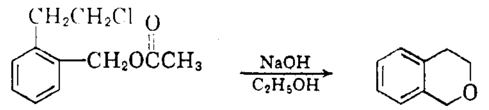
There are important differences in the infrared adsorption bands in the 760–840 cm.$^{-1}$ and 1490–1515 cm.$^{-1}$ regions for the *ortho* and *para* (β-chloroethyl)benzyl chlorides. It was found that the *para* isomer absorbs at 1515 cm.$^{-1}$ and the *ortho* isomer at 1493 cm.$^{-1}$ *Para* and *ortho* xylenes exhibit absorption bands at essentially the same location. The composition of mixtures of *ortho* and *para* (β-chloroethyl)benzyl chlorides were determined by measuring the intensities of these two bands as compared to pure samples of the two isomers. By this method it was determined that the product contained 74 ± 3% *para* isomer and 26 ± 3% *ortho* isomer. We have not been able to use gas phase chromatography in this case because these materials decompose in the chromatograph column. The high yield of *para* product is in line with the finding of Brown and Nelson.[5]

We were also able to isolate two high boiling products from the chloromethylation. One of these materials yields the correct analysis for bis(chloromethyl)-β-chloroethylbenzene. Several attempts have been made to determine the isomer distribution of this material without success.

The higher boiling product yields the correct analysis for a mixture of isomers of bis(β-chloroethyl)diphenylmethane. From this mixture a small amount of crystalline material melting at 45° was isolated. The infrared spectrum of the crystalline fraction shows a band at 1515 cm.$^{-1}$ The elemental analysis plus the adsorption band at this location strongly indicates that this crystalline product is the *p,p'*-(β-chloroethyl)diphenylmethane.

Vinylbenzyl alcohol. Replacement of the benzyl chlorine atom with an acetate group can be effected readily with potassium acetate in acetic acid without affecting the β-chlorine atom. This was done with both the *ortho* and *para* isomer. In the case of the *para* isomer, *p*-(β-chloroethyl)benzyl acetate was obtained in 90.5% yield. This material is converted to *p*-vinylbenzyl alcohol in 82% yield by refluxing alcoholic sodium hydroxide. The pure *para* isomer is a crystalline solid melting at 24°.

By contrast, the major product from the reaction of *o*-(β-chloroethyl)benzyl acetate with alcoholic base is isochroman.



Isochroman was first obtained by von Braun[6] by treatment of *o*-(β-bromoethyl)benzyl bromide with a calcium carbonate slurry. In our case isochroman probably arises from the rapid saponification of the benzyl acetate portion of the molecule followed by nucleophilic displacement of the β-chlorine atom. This displacement is no doubt facilitated by a favorable alignment and the formation of a strain-free 6-membered ring. Based on the infrared spectrum, the material left in the distillation flask appeared to be an impure vinylbenzyl alcohol. This material, however, may be mostly the *para* isomer resulting from a small amount of this isomer as an impurity in the *o*-(β-chloroethyl)benzyl alcohol.

EXPERIMENTAL

Chloromethylation of β-chloroethylbenzene. The chloromethylation of β-chloroethylbenzene as described by Kulka and Van Stryk was modified as follows: β-Chloroethylbenzene (2500 g., 18 moles, Eastman) was dissolved in 1 l. of carbon disulfide in a 5-l. three-neck round-bottom flask equipped with a stirrer, gas inlet tube having a glass frit below the liquid surface and a reflux condenser. Anhydrous zinc chloride (450 g.) and paraformaldehyde (540 g., 16.4 moles, commercial grade) were added to the flask in three separate portions during the course of reaction. Hydrogen chloride was bubbled into the reaction mixture with rapid stirring at a rate sufficient to maintain the temperature at gentle reflux without external heating. Total reaction time was about 16 hr.; the reaction being considered completed when hydrogen chloride adsorption ceased. The reaction mixture contained two liquid phases. The heavier phase was soluble in water and contained very little of the desired product. It was separated from the organic layer and discarded. The organic layer was washed with water, dilute sodium carbonate, and again with water. After drying with anhydrous magnesium sulfate, the carbon disulfide was distilled from the product and the unreacted β-chloroethylbenzene was recovered by distillation at a pressure of about 20 mm.

The product, a mixture of *ortho* and *para* (β-chloroethyl)benzyl chloride[7] was then obtained by distillation using an eight inch Vigreux column, b.p. 100–105° (0.3 mm.). A number of runs have been carried out in this manner giving conversions to the mixed isomers of 60 ± 5% and yields of 85 ± 3% based on recovered β-chloroethylbenzene.

In a typical run, there remained after distillation of the product about 250 g. of a brown, viscous residue. From this was distilled 143 g. of colorless liquid (cut A) boiling over a range of 120–133° (0.3–0.7 mm.) and 54 g. (cut B) of a viscous liquid boiling at 190–195° (0.7–1.0 mm.). An analytical sample of cut A, which was thought to be bis(chromethyl)-β-chloroethyl benzene, was prepared by redistillation, b.p. 125° (0.3 mm.).

Anal. Calcd. for $C_{10}H_{11}Cl_3$: C, 50.56; H, 4.67; Cl, 44.78. Found: C, 51.07, 51.08; H, 4.31, 4.56; Cl, 44.72, 44.84.

Cut B which was thought to be the mixed isomers of bis(β-chloroethyl)diphenylmethane was cooled in a refrigerator overnight to yield 6 g. of needle-like crystals, m.p. 45°, after recrystallization from benzene-hexane mixture.

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(5) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

(6) J. von Braun and F. Zobel, *Ber.*, **56B**, 2142 (1923).

(7) *Caution!* β-Chloroethylbenzyl chloride is a severe skin irritant and contact with skin or clothing should be avoided.

Anal. Calcd. for $C_{17}H_{18}Cl_2$: C, 69.64; H, 6.20; Cl, 24.18. Found: C, 69.69, 69.89; H, 6.20, 6.34; Cl, 24.18, 24.29.

Separation of ortho and para (β-chloroethyl)benzyl chlorides. The mixed *ortho* and *para* (β-chloroethyl)benzyl chlorides (1931 g., 10.2 moles) were dissolved in 800-ml. of commercial *n*-hexane and the solution chilled overnight in an ice box. The liquid remaining was decanted from the matt of well defined needle-like crystals. These crystals were recrystallized twice from 500-ml. portions of *n*-hexane and distilled through a 15 plate Oldershaw bubble cap column. A number of small fractions were obtained totaling 329.5 g., b.p. 175° (35 mm.) which were predominately the *para* isomer with decreasing amounts of *ortho* isomer as judged by the progressive decrease of the absorption band at 1493 cm.$^{-1}$ in the infrared. When the *ortho* band at 1493 cm.$^{-1}$ had completely disappeared the remaining material was more rapidly distilled at 145° (15 mm.). This fraction which was essentially pure *para* isomer weighed 900 g. and crystallized on cooling to room temperature, m.p. 32.5–33.5°.

The hexane solutions remaining from the crystallization experiment were combined and the hexane was evaporated on a steam bath. The remaining mixture of *ortho* and *para* (β-chloroethyl)benzyl chlorides was distilled through a 15 plate Oldershaw bubble cap column at 30 mm. The first fraction, 316.5 g., b.p. 170°, was shown to contain 79% *ortho* and 21% *para* isomer by infrared analysis. The middle fractions, 311 g., contained 42% *para* isomer and the final fraction, 157.5 g., which crystallized at room temperature, was essentially pure *para* isomer.

The high *ortho* fraction, 316.5 g., was redistilled using a Todd column to yield 157.8 g. of the *ortho* isomer, b.p. 132–133° (1 mm.), n_D^{25} 1.5570, which was shown by infrared analysis to contain only a trace of the *para* isomer. The remaining fractions totaling 135.7 grams were mixtures of the two isomers.

p-(β-Chloroethyl)benzyl acetate. Glacial acetic acid (1000 ml.), *p*-(β-chloroethyl)benzyl chloride (850 g., 4.46 moles), and potassium acetate (490 g., 5.0 moles) were heated to 110–120° for 16 hr. The potassium chloride which formed weighed 312 g., (4.18 moles), after washing with acetic acid and drying. The reaction mixture was added to about 2000 ml. of water, extracted with benzene, washed with water, and dried with anhydrous magnesium sulfate. The benzene was evaporated and the product distilled through a 24-inch column (burl saddle) under reduced pressure. A forerun of 27 g., b.p. 140° (5.5 mm.), was obtained, which was essentially unchanged *p*-(β-chloroethyl)benzyl chloride as shown by infrared analysis. The *p*-(β-chloroethyl)benzyl acetate, 866 g., b.p. 154–155° at 5.5 mm. was obtained in 90.5% conversion.

Anal. Calcd. for $C_{11}H_{13}O_2Cl$: C, 62.12; H, 6.16; Cl, 16.73. Found: C, 62.09, 62.24; H, 6.34, 6.06; Cl, 17.00, 17.00.

Higher boiling materials, 26 g., b.p. 155–170° at 5.0 mm. were also obtained.

p-Vinylbenzyl alcohol. p-(β-Chloroethyl)benzyl acetate (637.5 g., 3.0 moles) was added slowly to a warm solution of 1500 ml. of ethanol, containing about 0.2 g. hydroquinone and 200 g. of sodium hydroxide first dissolved in 200 ml. of water. The rate of addition was adjusted to maintain the reaction at gentle reflux. This addition required about 3 hr. and at the end of this time the reaction mixture was refluxed an additional hour by external heating. The reaction mixture was added to about 3 l. of water, extracted with benzene, washed with water, and dried with anhydrous magnesium sulfate. The benzene solution was inhibited with about 0.5 g. of hydroquinone, the benzene evaporated and the product distilled using an 8-inch Vigreux column. A small forerun of 3–5 g., b.p. 56–62° (0.8 mm.) was obtained which was shown to be isochroman by comparison of its infrared spectrum with an authentic sample prepared by the method of Rieche and Schmitz.[8] This isochroman must arise from a small amount of the *ortho* compound present as an impurity in the *p*-(β-chloroethyl)benzyl acetate. *p*-Vinylbenzyl alcohol, 330 g., b.p. 72° (0.8 mm.), m.p. 24°, was obtained in 82% conversion. The phenyl urethane melted at 95–96° after recrystallization from carbon tetrachloride.

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.83; H, 5.94; N, 5.54. Found: C, 73.75; H, 5.98; N, 5.59.

Preparation of o-(β-chloroethyl)benzyl acetate. A solution of 125 g. of *o*-(β-chloroethyl)benzyl chloride, 80 g. potassium acetate, and 340 ml. of glacial acetic acid was refluxed for 14 hr. The cooled solution was diluted with 1.5 l. of water, and the organic layer was separated. The aqueous layer was extracted with four 100-ml. portions of ether, which were combined with the organic layer and washed with aqueous sodium bicarbonate and water until the washings were neutral to litmus. After drying overnight with magnesium sulfate, the dessicant was filtered and the ether removed by distillation. Vacuum distillation of the remaining material through a 12-inch Vigreux column gave 117 g. (82.4%) *o*-(β-chloroethyl)benzyl acetate, b.p. 96–97 (0.1 mm.), n_D^{25} 1.5229.

Anal. Calcd. for $C_{11}H_{13}O_2Cl$: C, 62.25; H, 6.13; Cl, 16.71. Found: C, 61.95; H, 6.19; Cl, 16.89.

Twenty-one grams of *o*-(β-chloroethyl)benzyl acetate was added drop-wise to a refluxing solution of 20 g. of potassium hydroxide in 100 ml. of 95% ethanol. Heating was continued for 2 hr. after the addition was completed. After cooling to room temperature, the reaction mixture was diluted with 300 ml. of water and extracted with four 75-ml. portions of ether. The combined extracts were dried overnight, filtered and the ether removed by distillation.

Vacuum distillation in a Metroware Vigreux column gave 9.4 g. (70%) of isochroman b.p. 52° (0.65 mm.), n_D^{25} 1.5425, lit.,[7] n_D^{20} 1.5450. The spectrum of this product was identical with that of an authentic sample of isochroman prepared by the method of Rieche and Schmitz.[7] The residue in the distillation flask, 2.5 g., gave an infrared spectrum indicating that some vinyl benzyl alcohol was present. The material polymerized over a weekend.

Acknowledgment. The authors are indebted to Peter Shapras for the infrared data used in this work.

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[8] A. Rieche and E. Schmitz, *Ber.*, 89, 1259 (1956).