alkali. Dilution with 400 cc. of water followed by acidification with dilute hydrochloric acid yielded 8.5 g. of acidic material, m. p. 146–152°. Reprecipitation from sodium bicarbonate solution and three recrystallizations from water gave 3.3 g. of pale yellow prisms of 2-methoxy-5-nitrobenzoic acid (XIV), m. p. 159.5–160.5°[19]; neutral equivalent: calcd. 197.1. Found: 196.9, 197.6.

2-Benzyloxy-5-nitrobenzoic Acid (XI).—Ethyl 2-benzyloxy-5-nitrobenzoate (XIII) (40 g.) in a mixture of 75 cc. of Claisen alkali and 300 cc. of methanol stood at room temperature for one day. The solution was then diluted to 1 liter with water and acidified with dilute hydrochloric acid. The product which precipitated was collected and recrystallized twice from methanol, yielding 30.0 g. (83%) of 2-benzyloxy-5-nitrobenzoic acid (XI), m. p. 166–166.5°. The product crystallizes from methanol as long colorless needles, which, when separated from the mother liquor, disintegrate into smaller dull white crystals.

Anal. Calcd. for $C_{14}H_{11}O_5N$: C, 61.54; H, 4.06; neut. equiv., 273.1. Found: C, 61.41; H, 4.09; neut. equiv., 275.3.

Rearrangement of 2-Benzyloxy-5-nitrobenzoic Acid (XI).—2-Benzyloxy-5-nitrobenzoic acid (2.11 g.) was heated for seven minutes at 175° (refluxing hydrocarbon bath). The reaction mixture was taken up in 25 cc. of ether and extracted with three 10-cc. portions of 5% sodium bicarbonate solution. Acidification of the extract with dilute hydrochloric acid gave 0.40 g. of 5-nitrosalicylic acid (X), m. p. 225–229°, which represents 28% cleavage of XI to the parent acid.

The ether was evaporated and the residue heated on the steam-bath for three hours with 25 cc. of 10% aqueous sodium hydroxide. The solution was diluted with 50 cc. of water and extracted with ether. The ether layer was discarded, the aqueous layer acidified with dilute hydrochloric acid, the precipitated acid was taken up in ether and the ether solution extracted with three 10-cc. portions of 5% sodium bicarbonate solution. Acidification gave 0.88 g. of fine white needles, m. p. 228–231°. A mixed m. p. with 5-nitrosalicylic acid (Eastman Kodak Co.) was 232–234°. This amount of acid represents a 63% rearrangement of 2-benzyloxy-5-nitrobenzoic acid (XI) to benzyl 5-nitrosalicylate (XII).

Isolation of Benzyl 5-Nitrosalicylate (XII).—In a similar experiment, the reaction product was taken up in benzene and after removal of the 5-nitrosalicylic acid (X) by sodium bicarbonate extraction, the benzyl 5-nitrosalicylate (XII) was precipitated from the benzene solution as its sodium derivative by shaking with an excess of 10% sodium hydroxide. The product was a bright yellow powder. Refluxing for two hours with 1% hydrochloric acid gave a brown oil which solidified on cooling. Two recrystallizations from ethanol (Nuchar) gave white needles of m. p. 83.5–85.5°.

Anal. Calcd. for $C_{14}H_{11}O_5N$: C, 61.54; H, 4.06. Found: C, 61.81; H, 4.18.

This substance gave no depression on mixed m. p. with a sample prepared from sodium 5-nitrosalicylate and benzyl chloride by the method already described. It was not possible to get the synthetic material analytically pure.

Summary

1. 2-Benzyloxy-3,5-dichlorobenzoic acid, heated for forty minutes at 153°, yielded 20% of 3,5-dichlorosalicylic acid, 65% of benzyl 3,5-dichlorosalicylate and 10% of carbon dioxide. The same result was obtained in dimethylaniline solution, and in a quartz tube. A slow rearrangement was also observed in refluxing acetic acid solution.

2. 2-Benzyloxybenzoic acid, after three hours at 185–190°, gave 35% of salicylic acid, 35% of benzyl salicylate and smaller amounts of benzyl 5-benzylsalicylate.

3. 2-Benzyloxy-5-nitrobenzoic acid, after nine minutes at 175°, gave 63% of benzyl 5-nitrosalicylate, 28% of 5-nitrosalicylic acid and a few per cent. of carbon dioxide.

4. The rearrangement is not base catalyzed. The benzyl ethers do not resemble the corresponding allyl ethers in behavior on heating.

Rochester, N. Y. Received July 23, 1943

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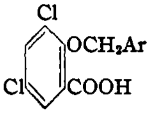
(19) Pohlmann, *Rec. trav. chim.*, **55**, 737 (1936), reports the m. p. to be 161°.

[Contribution from the Department of Chemistry of the University of Rochester]

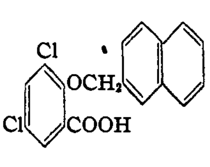
The Effect of Heat on the β-Naphthylmethyl and the 9-Phenanthrylmethyl Ether of 3,5-Dichlorosalicylic Acid

By D. S. Tarbell and V. P. Wystrach

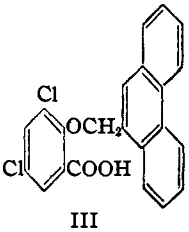
In the preceding article[1] it was shown that the benzyl ether of salicylic acids, such as I (Ar = C_6H_5), changes into the benzyl ester of the acid on heating, instead of rearranging with the loss of carbon dioxide as the analogous allyl ethers do. The present paper reports a study of 2-(β-naphthylmethoxy)-3,5-dichlorobenzoic acid (II) and the corresponding 9-phenanthrylmethyl ether (III).



I



II



III

The considerations leading to a study of these compounds are as follows. The contrast in behavior between an allyl ether (I, Ar = —CH=CH_2) and a benzyl ether (I, Ar = C_6H_5) must be due to the lack of an aliphatic double bond in the benzene nucleus. It is well-known, from both experimental and theoretical grounds,[2] that the 1,2-bond in naphthalene behaves more like an aliphatic double bond than like a bond in

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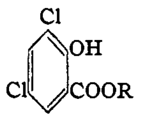
(1) Tarbell and Wystrach, This Journal, **65**, 2146 (1943).

(2) Fieser and Lothrop, *ibid.*, **57**, 1459 (1935); Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 142.

the benzene ring, and that the 1-position is far more reactive than the 2-position. This should make a β-naphthylmethyl ether resemble an allyl ether more closely than a benzyl ether does. Actually, we have found that II gives the corresponding ester on heating, and hence still behaves like a benzyl ether.[2a]

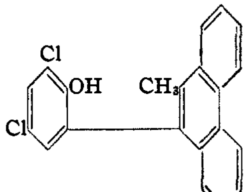
The 9,10-bond in phenanthrene has still more double bond character than the 1,2-bond in naphthalene, as shown, for instance, by the formation of a dibromo addition product.[3] In agreement with this, we have found that the 9-phenanthrylmethyl ether III differs in its behavior on heating from the benzyl and β-naphthylmethyl ethers, and resembles the allyl ethers.

The β-naphthylmethyl ether II, when heated for thirty-two minutes at 148°, gave 10% of carbon dioxide, 10% of dichlorosalicylic acid (IV) and 67% of β-naphthylmethyl 3,5-dichlorosalicylate (V), which was not isolated from the reaction mixture. Its presence was demonstrated, however, by saponification to the expected products. The β-naphthylmethyl ether II like the benzyl ether I (Ar = C_6H_5), rearranges also on heating in glacial acetic acid, giving the ester V.

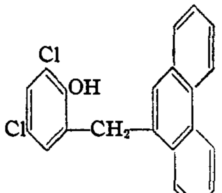


IV, R = H
V, R = $-CH_2C_{10}H_7(\beta)$

The 9-phenanthrylmethyl ether III, when heated at 229°, yielded 75% of the theoretical amount of carbon dioxide, 30% of dichlorosalicylic acid (IV) and 41% of a rearrangement product of the composition corresponding to VI or VII. The phenanthrylmethyl ether III was not affected by recrystallization from acetic acid.

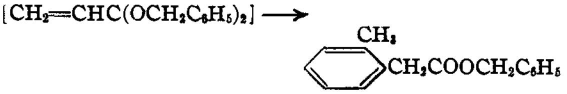


VI

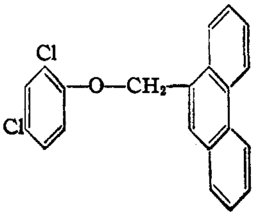


VII

The rearrangement product formed an acetate, which melted much higher than the original compound (137° *vs.* 208°), but the acetate on hydrolysis reformed the phenol, indicating that no anomalous change had taken place during the acetylation. Of the possible structures VI and VII, VI is preferred, in absence of synthetic evidence (which we hope to be able to present eventually), because in the rearrangement of the analogous crotyl ether,[4] inversion takes place with attachment of the γ-carbon atom. Inversion of III would lead to VI. It is interesting to note that ketene dibenzylacetal rearranges to benzyl *o*-tolylacetate,[5] as soon as formed, corresponding to inversion on rearrangement



It seemed possible that in the rearrangement of the 9-phenanthrylmethyl ether III, the first step was a decarboxylation of the acid, forming the ether VIII, which then rearranged. This possibility was ruled out by preparing VIII, and studying its behavior on heating; none of the product formed from III was obtained, and 2,4-dichlorophenol was the only product isolated from the reaction.



VIII

Preliminary attempts to synthesize VII by carbon alkylation of 2,4-dichlorophenol with 9-chloromethylphenanthrene were unsuccessful. Preparation of the corresponding ketone by Friedel–Crafts acylation of 2,4-dichlorophenol with 9-phenanthroyl chloride was also unsuccessful, the ester, 2,4-dichlorophenyl 9-phenanthroate, being obtained.

Di-(9-phenanthryl)-ethane was obtained almost exclusively when 9-chloromethylphenanthrene was treated with magnesium, in an attempt to make 9-methylphenanthrene[6] for some comparisons of absorption spectra.

Experimental[7]

2-(β-Naphthylmethoxy)-3,5-dichlorobenzoic Acid (II).—β-Chloromethylnaphthalene[8] (6.7 g.), 6.7 g. of methyl 3,5-dichlorosalicylate, 1.25 g. of sodium hydroxide in 5 cc. of water and 25 cc. of methyl ethyl ketone were refluxed with stirring for nine hours. The solvent was removed, water was added and the product taken up in 75 cc. of benzene. After extraction with Claisen alkali, the benzene solution was evaporated and the residue saponified by heating on the steam-bath with 15 cc. of Claisen alkali. Upon dilution with 100 cc. of water, a dark oil formed which dissolved when a total of 250 cc. of water had been added. Acidification produced 4.0 g. of a white solid, m. p. 135–138° dec., which, when combined with 6.2 g. of similar material from another run and recrystallized from 200 cc. of chloroform, yielded 8.6 g. of white micro needles of II, m. p. 143.5–144° dec. The yield was 50%, based on the total amount of β-chloromethylnaphthalene used. The compound is unchanged by refluxing in 20% potassium

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(2a) Behagell and Freiensehner, *Ber.*, **68**, 341 (1935), found that β-naphthylmethyl phenyl ether resembled benzyl phenyl ether in its behavior on pyrolysis.

(3) Fittig and Ostermayer, *ibid.*, **5**, 933 (1872); Price, This Journal, **58**, 1834 (1936); *cf.* Pauling, ref. 2.

(4) Tarbell and Wilson, This Journal, **64**, 607 (1942).

(5) McElvain, Anthes and Shapiro, *ibid.*, **64**, 2525 (1942).

(6) *Cf.* Grummitt and Buck, *ibid.*, **65**, 295 (1943).

(7) All m. p.'s corrected; analyses by Robert Bauman.

(8) Prepared in poor yield by the method of Wahl, Goedkoop and Heberlein, *Bull. soc. chim.*, [5] **6**, 533 (1939) (*C. A.*, **33**, 5841 (1939)).

hydroxide for three and one-half hours. The dec. point depends on the rate of heating; the analytical sample had m. p. 142–142.5° dec. after two recrystallizations from chloroform.

Anal. Calcd. for $C_{18}H_{12}O_3Cl_2$: C, 62.26; H, 3.49. Found: C, 61.82; H, 3.42.

The Pyrolysis of 2-(β-Naphthylmethoxy)-3,5-dichlorobenzoic Acid (II).—By gasometric analysis this ether was found to liberate 9.5% of the theoretical amount of carbon dioxide at a temperature just above its m. p. A 1.73-g. sample was heated at 147–148° (refluxing methyl amyl ketone) for thirty-two minutes. The reaction product was taken up in 100 cc. of ether and extracted with 35 cc. of 10% sodium bicarbonate solution. Acidification of the extract gave 0.18 g. of crude 3,5-dichlorosalicylic acid (IV), m. p. 215–221°, representing about 10% cleavage. The ether was evaporated and the residue saponified on the steam-bath for ten minutes with 20 cc. of Claisen alkali. After cooling, the solution was extracted with ether to remove the unsaponifiable matter, and was then acidified yielding 0.69 g. of 3,5-dichlorosalicylic acid, m. p. 223–225°. This amount of 3,5-dichlorosalicylic acid represents a 67% rearrangement of 2-(β-naphthylmethoxy)-3,5-dichlorobenzoic acid (II) to β-naphthylmethyl 3,5-dichlorosalicylate (V). The alcohol fragment was identified in the following manner. The ether extract from the saponification was evaporated and the residue subjected to a steam distillation. About 0.15 g. of fine white plates was recovered from the distillate. One recrystallization from ligroin (b. p. 60–70°) gave shiny colorless plates, m. p. 79–79.5°, which were shown to be β-naphthylcarbinol by a mixed m. p. with an authentic sample whose preparation is described later. The naphthylmethyl ester was not isolated as such from the pyrolysis.

β-Naphthylcarbinol.—β-Naphthylmethyl acetate[9] (0.25 g., m. p. 55–57°) was refluxed for two hours with 10 cc. of 10 *N* methanolic potassium hydroxide, after standing twelve hours at room temperature. Dilution with 50 cc. of water gave a good yield of fine white plates, m. p. 78.5–79.5°.[10]

β-Naphthylmethyl 3,5-Dichlorosalicylate (V).—This product was obtained when the isomeric ether (II) was recrystallized from glacial acetic acid, m. p. without dec., 138.5–139°. It was unchanged by an hour's heating at 157°, and when saponified with 10% sodium hydroxide, yielded β-naphthylcarbinol and 3,5-dichlorosalicylic acid, both being identified by mixed m. p.'s with authentic samples.

Anal. Calcd. for $C_{18}H_{12}O_3Cl_2$: C, 62.26; H, 3.49. Found: C, 62.19; H, 3.64.

9-Chloromethylphenanthrene.—The method of Cook[11] was modified as follows. A rapid stream of hydrogen chloride gas was bubbled through a mixture of 200 g. of phenanthrene (Eastman Technical), 175 cc. of 40% formaldehyde and 900 cc. of concentrated hydrochloric acid vigorously stirred in a 2-liter three-neck flask heated on the steam-bath at 94° for eight hours. The reaction product was taken up in 1200 cc. of diethyl ether and an insoluble green precipitate was removed by filtration. The ether solution was dried, the solvent removed and the residue distilled; after a forerun of unreacted phenanthrene, 88.8 g. of a yellow oil, b. p. 180–197° (1 mm.), was obtained. When refractionated, it yielded 76.0 g. of product, b. p. 186–188° (1 mm.), which solidified to a rather gummy solid. Trituration with petroleum ether (60–70°) yielded 48.0 g. (21%) of white crystalline 9-chloromethylphenanthrene, m. p. 97–99.5°. A sample of material prepared in this manner (20.1 g.), when recrystallized from a mixture of 50 cc. of benzene and 200 cc. of petroleum ether (60–70°), yielded 12.7 g. of white cottony needles, m. p. 101.5–102°, with an additional 2.9 g. of product being recovered from the mother liquors. The picrate was obtained as slender orange needles, m. p. 101.5–102°.[12]

Methyl 2-(9-Phenanthrylmethoxy)-3,5-dichlorobenzoate.—Potassium carbonate (13.8 g. in 35 cc. of water) was added dropwise to a stirred and refluxing mixture of 22.1 g. of methyl 3,5-dichlorosalicylate, 27.2 g. of 9-chloromethylphenanthrene and 15.0 g. of sodium iodide in 200 cc. of methyl ethyl ketone. After refluxing for twenty-two hours, the mixture was cooled and the crude ether-ester precipitated out. This crude product, after washing with water and alcohol, weighed 34.9 g., m. p. 156–160°. Recrystallization from 1:1 benzene and petroleum ether (90–100°) gave 23.0 g. (56%) of the pure ether-ester, m. p. 162.5–163.5°. Glacial acetic acid was later found to be a better solvent for the purification of this compound.

Anal. Calcd. for $C_{23}H_{16}O_3Cl_2$: C, 67.16; H, 3.92. Found: C, 67.57; H, 3.84.

2-(9-Phenanthrylmethoxy)-3,5-dichlorobenzoic Acid (III).—The preparation of this acid by alkaline hydrolysis of the corresponding methyl ester was not entirely satisfactory, but it was used because of its simplicity. Many combinations of solvents, potassium hydroxide concentrations and reaction times were studied and found to give only 15 to 60% yields of the desired ether-acid. Best results were obtained by using small samples (0.5–1.0 g.) of ester.

In a typical experiment 0.5 g. of methyl 2-(9-phenanthrylmethoxy)-3,5-dichlorobenzoate was refluxed for ten minutes (until solution was effected, the potassium salt being soluble in the hot methanolic potassium hydroxide solution) with 15 cc. of Claisen alkali and 15 cc. of methanol. Dilution with water gave a cloudy precipitation, which disappeared, however, after 140 cc. of water had been added. Acidification to congo red with dilute hydrochloric acid gave 0.47 g. of very impure material, m. p. 151–163°. Recrystallization from 5 cc. of glacial acetic acid gave 0.27 g. (57%) of the pure ether–acid as slender, colorless needles, m. p. 173–173.5°. A small sample recrystallized twice more from glacial acetic acid melted at 174.5–175°.

Anal. Calcd. for $C_{22}H_{14}O_3Cl_2$: C, 66.51; H, 3.55. Found: C, 66.36; H, 3.52.

A similar experiment using 6.0 g. of the ester resulted in 2.2 g. (38%) of the desired ether-acid. The material used in the pyrolyses was obtained from several 1-g. runs, m. p. 173.5–174.5°.

An alternative procedure employing a two-phase system of 1,4-dioxane and Claisen alkali was also found to give fair yields of the ether-acid with 0.5–1.0 g. samples of the ester but gave poor yields when larger amounts were used. In one run 1.0 g. of the ester was refluxed for three and three-quarters hours with a mixture of 3 cc. of Claisen alkali and 25 cc. of 1,4-dioxane. After working up the product a 0.57 g. (59%) yield of the ether-acid was obtained, m. p. 173.5–174.5°. However, a 10-g. run by this procedure resulted in a 15% yield. The other products resulting from this alkaline hydrolysis were not investigated.

Pyrolysis of 2-(9-Phenanthrylmethoxy)-3,5-dichlorobenzoic Acid (III).—Preliminary experiments showed that this ether released 75–78% of the theoretical amount of carbon dioxide, when heated for seventeen to twenty minutes at 229–231°.

A 2.13-g. sample was heated for twenty minutes at 229° (refluxing quinoline). Carbon dioxide evolution was quite rapid at first, then gradually decreased; after twenty minutes it had practically stopped. The resulting product was a dark glass which was easily soluble in 75 cc. of warm benzene. Extraction with 35 cc. of 5% sodium bicarbonate gave, upon subsequent acidification, 0.33 g. (29.8%) of 3,5-dichlorosalicylic acid (IV), m. p. 218–222°, identified by a mixed m. p.

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[9] Dam, Glavind and Karrer, *Helv. Chim. Acta*, **23**, 224 (1940). We are indebted to Mr. David K. Fukushima for the sample of β-naphthylmethyl acetate.

[10] Campbell, Anderson and Gilmore, *J. Chem. Soc.*, 819 (1940), report a m. p. of 80°.

[11] Cook, Dansi, Hewett, Iball, Mayneord and Roe, *ibid.*, 1323 (1935).

[12] Cook, *et al.*, (ref. 11) report 101–101.5° as m. p. for 9-chloromethylphenanthrene, and 99.5–100.5° for the picrate.

The benzene solution was then extracted with a total of 130 cc. of Claisen alkali. Each 10 cc. of the Claisen alkali extract was run into 30 cc. of 3 *N* hydrochloric acid. This procedure resulted in 0.86 g. of buff-colored flaky material, m. p. 129–134°. The material was recrystallized (animal charcoal) by allowing a dilute ethanol solution to evaporate slowly from it, giving 0.77 g. of small white needles, m. p. 135.5–137°. A small sample recrystallized twice more from dilute ethanol melted at 136.5–137.5°.

Anal. Calcd. for $C_{21}H_{14}OCl_2$: C, 71.40; H, 3.99. Found: C, 71.43; H, 4.04.

The analysis corresponds to that of a phenol formed by rearrangement of the phenanthrylmethyl group to the *ortho* position with loss of carbon dioxide, the rearrangement product being isolated in 41% yield.

Evaporation of the benzene solution gave 0.72 g. of a dark glass[13] from which no pure crystalline products could be isolated. No other decarboxylation product could be found to account for the total loss of carbon dioxide.

Acetyl Derivative of the Isolated Phenol.—About 80 mg. of the recrystallized phenol was refluxed for seven hours with 2 cc. of pure acetic anhydride. Upon cooling a good yield of white micro needles was obtained, m. p. 206–208°. Two recrystallizations from glacial acetic acid gave white micro needles, m. p. 208–208.5°. The phenol was regenerated by hydrolyzing the acetyl derivative with methanolic potassium hydroxide.

Anal. Calcd. for $C_{23}H_{16}O_2Cl_2$: C, 69.90; H, 4.06. Found: C, 69.78; H, 4.24.

Attempts to Prepare 2-(9-Phenanthrylmethyl)-4,6-dichlorophenol (VII).—The direct condensation of 9-chloromethylphenanthrene and 2,4-dichlorophenol in the presence of anhydrous aluminum chloride in carbon disulfide gave only high molecular weight products which were insoluble even in hot benzene.

An attempt was made to condense 9-phenanthroyl chloride[14] with 2,4-dichlorophenol in the presence of anhydrous aluminum chloride. However, in a reaction using one equivalent of 9-phenanthroyl chloride, two equivalents of 2,4-dichlorophenol and two equivalents of anhydrous aluminum chloride at the reflux temperature of carbon disulfide for nineteen hours, the main product was the isomeric 2,4-dichlorophenyl 9-phenanthroate, m. p. 181–182° (14%). A sample recrystallized twice from a 1 : 3 benzene-petroleum ether (b. p. 60–70°) mixture gave small colorless needles of m. p. 183–184°.

Anal. Calcd. for $C_{21}H_{12}O_2Cl_2$: C, 68.67; H, 3.29. Found: C, 68.38; H, 3.40.

A 20-mg. sample of the product from this reaction was refluxed for one and one-half hours with 10 cc. of about 12% methanolic potassium hydroxide. Dilution with 20 cc. of water and acidification gave a good yield of a gray powder, m. p. 253–256°. A mixed m. p. with an authentic sample of 9-phenanthroic acid (m. p. 254–255°)[14] was 254–256°. This hydrolysis to 9-phenanthroic acid indicates that the condensation product is the ester rather than the desired ketone.

A second product obtained in this reaction, in small yield, had the correct composition for ethyl 9-phenanthroate. It was isolated as colorless needles from ethanol (Nuchar), m. p. 114.5–115°, and was probably formed by an ester-interchange between 2,4-dichlorophenyl 9-phenanthroate and ethanol during isolation. This compound also gave 9-phenanthroic acid, m. p. 250–257°, on hydrolysis with methanolic potassium hydroxide.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.35; H, 5.71. Found: C, 81.48; H, 5.51.

9-Phenanthrylmethyl 2,4-Dichlorophenyl Ether (VIII).—A mixture of 5.0 g. of 9-chloromethylphenanthrene, 5.9 g. of 2,4-dichlorophenol (Eastman Kodak Co.), 3.5 g. of potassium carbonate and 3.3 g. of sodium iodide was refluxed with 35 cc. of methyl ethyl ketone and 10 cc. of water for seventeen hours. The solvent was distilled off and the product taken up in ether. The ether solution was extracted with 5% sodium hydroxide, after which the desired product precipitated out of the ether. Filtration and washing with ether gave 5.6 g. (60%) of short colorless needles, m. p. 122–124°. Recrystallization from a mixture of 20 cc. of benzene and 35 cc. of petroleum ether (b. p. 60–70°) gave a pure product of m. p. 125–125.5°.

Anal. Calcd. for $C_{21}H_{14}OCl_2$: C, 71.40; H, 3.99. Found: C, 71.13; H, 3.87.

Pyrolysis of 9-Phenanthrylmethyl 2,4-Dichlorophenyl Ether (VIII).—No extensive decomposition of this compound was observed at temperatures up to 240°. A satisfactory temperature was found to be 279–280°.

A 1.00-g. sample of the ether was heated for nine minutes at 279–280° (refluxing α-bromonaphthalene). A colorless liquid which distilled out of the reaction and refluxed down the sides of the reaction vessel was identified as 2,4-dichlorophenol, m. p. 42.5–43.5°; a mixed m. p. with a sample of 2,4-dichlorophenol (Eastman Kodak Co.) was 43.5–44°. This boiling out of the 2,4-dichlorophenol subsided after about seven or eight minutes as the reaction product became darker and more resinous.

The reaction product was treated with 25 cc. of benzene in which it dissolved completely with the formation of a dark green-brown fluorescent solution. The benzene solution was extracted with a total of 40 cc. of 10% sodium hydroxide solution. Acidification and extraction with ether gave 0.17 g. (37%) of 2,4-dichlorophenol. Further extraction of the benzene solution with Claisen alkali (60 cc.) gave only a very small amount of a tan solid from which nothing could be isolated. Evaporation of the benzene solution gave an intractable, glassy brown solid mass.

Di-(9-phenanthryl)-ethane.—Magnesium turnings (0.58 g.) were covered with 5 cc. of dry ether, and 5.65 g. of 9-phenanthrylmethyl chloride dissolved in a mixture of 30 cc. of dry ether and 35 cc. of benzene was added slowly along with a few drops of methyl iodide. After all of the chloride had been added, the mixture was refluxed on the steam-bath one hour to dissolve the magnesium completely. A white insoluble solid precipitated out in increasing amount as the reaction progressed. The Grignard was hydrolyzed by ammonium chloride solution, and 1.41 g., m. p. 251–253°, of the diphenanthrylethane collected by filtration. Two recrystallizations from nitrobenzene, followed by washing with ethanol, gave colorless prisms, m. p. 252.5–254.5°.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 93.81; H, 5.88.

Distillation of the benzene solution from the hydrolysis of the Grignard resulted in 0.19 g. of colorless solid, m. p. 78–84°, which may have been impure 9-methylphenanthrene.[15] From the residue in the distilling flask, 1.40 g. of additional diphenanthrylethane was obtained, giving a total yield of recrystallized material of 59%.

The reduction of 9-chloromethylphenanthrene to 9-methylphenanthrene using zinc and gaseous hydrogen chloride in ethanol[16] was also unsuccessful.

Summary

1. 2-(β-Naphthylmethoxy)-3,5-dichlorobenzoic acid at 148° for thirty-two minutes yields 10% of carbon dioxide, 10% of 3,5-dichlorosalicylic acid and 67% of β-naphthylmethyl 3,5-dichlorosalicylate. This compound is also produced when the ether is recrystallized from acetic acid.

2. In agreement with the high degree of double-bond character of the 9,10-bond in

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[13] This glassy material was soluble both in cold benzene and nitrobenzene, showing that di-(9-phenanthryl)-ethane was not present.

[14] Mosettig and van de Kamp, This Journal, **55**, 2995 (1933). *Cf.* Mosettig and van de Kamp, *ibid.*, **54**, 3328 (1932), for the preparation of 9-phenanthroic acid.

[15] Bradsher and Tess report the m. p. of 9-methylphenanthrene as 91–92.5°, This Journal, **61**, 2184 (1939).

[16] Anderson and Short, *J. Chem. Soc.*, 485 (1933).

phenanthrene, 2-(9-phenanthrylmethoxy)-3,5-dichlorobenzoic acid behaves like an allyl ether; at 229° for twenty minutes, it gives 75% of carbon dioxide, 30% of 3,5-dichlorosalicylic acid and 41% of 9-methyl-10-(2-hydroxy-3,5-dichlorophenyl)-phenanthrene (or isomer). 9-Phenanthrylmethyl 2,4-dichlorophenyl ether when pyrolyzed at 280° yielded 2,4-dichlorophenol as the only isolable product.

3. An improved procedure for the preparation of 9-chloromethylphenanthrene is given. Di-(9-phenanthryl)-ethane has been prepared and characterized.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF McGILL UNIVERSITY]

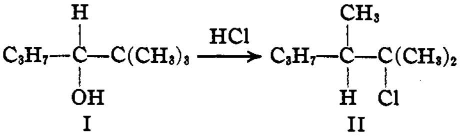
Racemization Accompanying Molecular Rearrangements

BY PHILIP G. STEVENS[1] AND SIDNEY H. J. GREENWOOD[2]

In 1934 Wallis and Bowman[3] found that *levo*-2-methyl-2-phenyl-butanol-1 reacted with thionyl chloride to form a *dextro*-rotatory tertiary chloride, the result of a molecular rearrangement with retention of the optical activity. Five years later Bernstein and Whitmore[4] showed that the semipinacolyl deamination of certain hydroxyamines likewise produced optically active products, and established from a consideration of the optical configurations that the rearrangement proceeded via a Walden inversion. This inversion was in harmony with that of the pinacolyl rearrangement of various cyclic glycols, investigated by Bartlett and co-workers.[5]

This paper deals with an attempt to determine the steric course of the retro-pinacoline rearrangement. An open chain alcohol was used so as to avoid the complications of cyclic systems, so often used in these studies, but from which, because of their special spatial restrictions, generalizations should not be made.

When *dextro*-2,2-dimethylhexanol-3(I), is treated with concentrated hydrochloric acid for three days, there results a *levo*-rotatory chloride[6] which is 94.2% tertiary. From the typical behavior of pinacolyl alcohols, and from the work of Wallis and Bowman, one would expect this *levo*-chloride to be 2,3-dimethyl-2-chlorohexane (II).

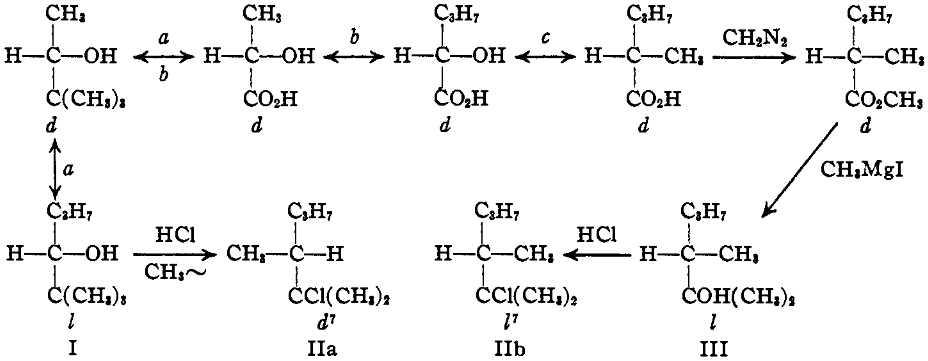


$$\mathrm{C_3H_7{-}\overset{H}{\underset{OH}{C}}{-}C(CH_3)_3 \xrightarrow{HCl} C_3H_7{-}\overset{CH_3}{\underset{H}{C}}{-}\underset{Cl}{C}(CH_3)_2}$$

I II

If this inference be correct and if the configuration of II with respect to I were established, then the steric course of the rearrangement could be determined.

The determination of this relationship seemed at first to be simple, because the tertiary carbinol III, corresponding to II, could be configurationally related to *dextro*-α-methyl-valeric acid, and this acid in turn to I as the following chart of reactions shows. It is clear that, if the rearrangement of *levo* I to IIa involves a shift of a methyl group by an inversion mechanism, the chloride IIb from III would be the enantiomer of IIa. Configurational relationships were established thus



[a] By Freudenberg's Displacement Rule.[6,8] [b] By direct chemical evidence.[9] [c] By Marker's rule.[10]

Unfortunately, the attempt to prepare IIb from III was unsuccessful because of a most unexpected racemization. When III was treated with

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[3] Wallis and Bowman, THIS JOURNAL, **56**, 491 (1934); *J. Org. Chem.*, **1**, 383 (1936).

[4] Bernstein and Whitmore, THIS JOURNAL, **61**, 1324 (1939).

[5] Bartlett and Pockel, *ibid.*, **59**, 820 (1937); Bartlett and Bavley, **60**, 2416 (1938); Bartlett and Brown, **62**, 2927 (1940); compare Meerwein, *Ann.*, **542**, 123 (1939).

[6] Originally reported erroneously as *dextro*, Stevens, Higbee and Armstrong, THIS JOURNAL, **60**, 2658 (1938).

[7] Rotations presumed.

[8] Stevens, THIS JOURNAL, **55**, 4237 (1933).

[9] Levene and Haller, *J. Biol. Chem.*, **79**, 475 (1928).

[10] Marker, THIS JOURNAL, **58**, 976 (1936).