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.

ROCHESTER, N. Y. RECEIVED JULY 23, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

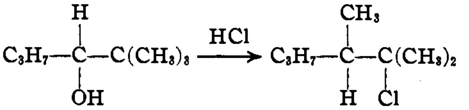
Racemization Accompanying Molecular Rearrangements

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).

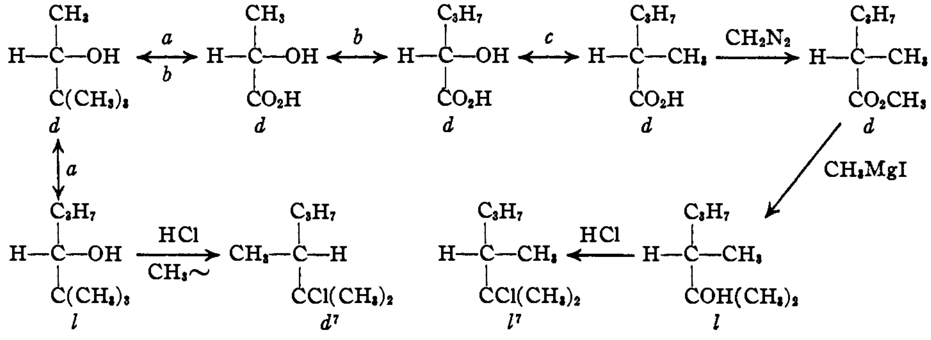


$$C_3H_7-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-C(CH_3)_3 \xrightarrow{HCl} C_3H_7-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-\underset{\displaystyle Cl}{C}(CH_3)_2$$

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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[1] Present address: Department of Chemistry, Yale University. New Haven, Connecticut.

[2] Present address: c/o Technical and Research Department of Imperial Oil, Ltd., Sarnia, Ontario.

[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).

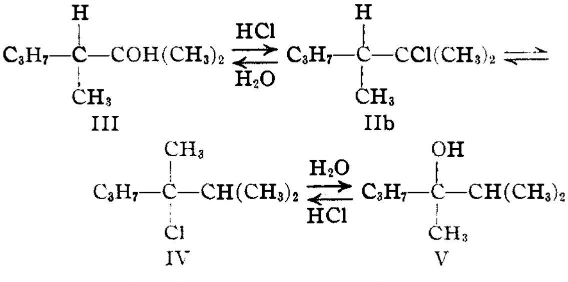
[10] Marker, THIS JOURNAL, 58, 976 (1936).

concentrated hydrochloric acid in the same way that carbinol I was treated, there resulted a completely inactive chloride. Examination showed that the chloride was a mixture of two inactive tertiary chlorides, the expected II, and 2,3-dimethyl-3-chlorohexane (IV). Hydrolysis of this mixture yielded inactive products, 2,3-dimethylhexanol-2 (III) and 2,3-dimethylhexanol-3 (V). The physical constants below in Table I indicate that the carbinol mixture is approximately a 1:1 mixture. Presumably the composition of the chloride mixture is about the same; furthermore *dl*-2,3-dimethylhexanol-3 appears to yield the same chloride mixture. It is therefore clear that the action of aqueous hydrochloric acid on tertiary carbinols of the general formula $R_1R_2CHCOHR_2R_3$ leads invariably to a mixture of tertiary chlorides.[11]

TABLE I

	B. p. (29 mm.), °C.	$n^{25}D$	M. p., °C., of phenylurethan	$n^{20}D$ of chloride
levo-2,3-Dimethylhexanol-2	75	1.4288	...	1.4352
dl-2,3-Dimethylhexanol-2	75	1.4290	74	1.4351
dl-2,3-Dimethylhexanol-3	72.5	1.4301	90.5	1.4353
Carbinol from chloride	71.5–73	1.4294	52–62.5	..
1:1 mixture of carbinols	...	1.4295	56–63	..

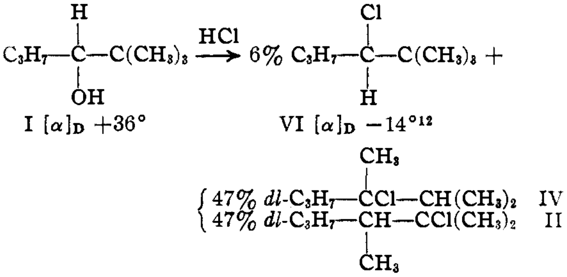
An explanation for this complete racemization is as follows: the active carbinol III undoubtedly forms the active halide IIb, but a reversible and surprisingly mobile rearrangement then occurs between IIb and IV. Every time IIb is transformed into IV, and *vice versa*, partial racemization takes place. Furthermore, additional racemization can result from a common ion effect on IV. Hence, given sufficient time (one day is enough), no active halide, neither IIb nor IV, can survive.



$$\underset{\text{III}}{C_3H_7-\overset{H}{\underset{CH_3}{C}}-COH(CH_3)_2} \underset{H_2O}{\overset{HCl}{\rightleftarrows}} \underset{\text{IIb}}{C_3H_7-\overset{H}{\underset{CH_3}{C}}-CCl(CH_3)_2} \rightleftarrows$$

$$\underset{\text{IV}}{C_3H_7-\overset{CH_3}{\underset{Cl}{C}}-CH(CH_3)_2} \underset{HCl}{\overset{H_2O}{\rightleftarrows}} \underset{\text{V}}{C_3H_7-\overset{OH}{\underset{CH_3}{C}}-CH(CH_3)_2}$$

The result of the formation of these two inactive tertiary chlorides from III now shows that the activity of the chloride mixture obtained originally from I could not be due to the rearranged optically active tertiary chloride IIa, because this would have become completely racemized. Instead the observed activity can only be due to the unrearranged secondary chloride, 2,2-dimethyl-3-chlorohexane (VI). The correct reaction of I with concentrated hydrochloric acid should therefore be formulated as follows



$$\underset{\text{I } [\alpha]_D\ +36°}{C_3H_7-\overset{H}{\underset{OH}{C}}-C(CH_3)_3} \xrightarrow{HCl} 6\%\ \underset{\text{VI } [\alpha]_D\ -14°^{12}}{C_3H_7-\overset{Cl}{\underset{H}{C}}-C(CH_3)_3} +$$

$$\begin{cases} 47\%\ dl\text{-}C_3H_7-\overset{CH_3}{CCl}-CH(CH_3)_2 & \text{IV} \\ 47\%\ dl\text{-}C_3H_7-\underset{CH_3}{CH}-CCl(CH_3)_2 & \text{II} \end{cases}$$

Further work with I and III, using reagents such as thionyl chloride, less likely to cause racemization of the reaction products, will be continued after the war.

Experimental Part

***dextro*-Methyl-α-Methylvalerate.**—Inactive α-methylvaleric acid was prepared according to the directions of Levene and Bass.[13] Resolution through the quinine salt proved so troublesome that the cinchonidine salt was used. This readily separated from 66% acetone, but even after repeated recrystallization yielded, on acidification, only partially resolved material, b. p. 84.5° (9 mm.), $(\alpha)^{25}D$ +7.1°. The ester was made using diazomethane, b. p. 77° (98.5 mm.), $n^{25}D$ 1.4004, $d^{25}{}_4$ 0.875, $(\alpha)^{25}D$ +9.1°.

***levo*-2,3-Dimethylhexanol-2 (III).**—The above dextro ester was added to an excess of methylmagnesium iodide at 0°, the reaction mixture was kept overnight at room temperature, and then decomposed with ammonium chloride. The carbinol boiled at 75° (29 mm.), $n^{25}D$ 1.4288, $d^{25}{}_4$ 0.831, $(\alpha)^{25}D$ −17.7°. The inactive carbinol was prepared by the action of the magnesium derivative of carefully purified 2-bromopentane ($n^{20}D$ 1.4414) on acetone in the usual way, b. p. 75° (29 mm.), $n^{25}D$ 1.4290.

Racemic 2,3-Dimethylhexanol-3 (V).—This carbinol was prepared by the method of Whitmore and Evers,[14] b. p. 72.5° (29 mm.), $n^{22}D$ 1.4301.

Preparation of the Racemic Isomeric Phenylurethans.—One ml. of each of the above racemic dimethylhexanols was treated at 0° with one ml. of phenyl isocyanate. After eight days at room temperature, the solidified reaction products were recrystallized from petroleum ether. The phenylurethan from the hexanol-2 melted at 74°, that from the hexanol-3, at 90.5°. *Anal.* Calcd. for $C_{13}H_{23}NO$: N, 5.62. Found: N, 6.27 and 5.86.

Preparation of the Tertiary Chlorides

A. From *levo*-2,3-Dimethylhexanol-2 (III).—The active carbinol (24 ml.) was added to 180 ml. of concentrated hydrochloric acid, saturated with hydrogen chloride at −10°, and the mixture was shaken for one day at room temperature. The resulting halide was well washed with concentrated hydrochloric acid, with ice water, with 3% sodium bicarbonate (0°), and dried with anhydrous potassium carbonate at 10°. The chloride was optically inactive, b. p. 43.5–44° (12 mm.), $n^{20}D$ 1.4352, $n^{25}D$ 1.4330. *Anal.* Calcd. for $C_8H_{17}Cl$: Cl, 23.86. Found: Cl, 23.64.

B. From the Racemic Isomeric Hexanols.—The chlorides were prepared by shaking the carbinols at room temperature six hours with a large excess of concentrated hydrochloric acid, and were isolated in a manner similar to that described above. The dried but undistilled

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(11) Closely related is the formation of approximately equal amounts of 1,8- and 1,4-cineol in the dehydration of 1,8-terpin, reported by Mosher (from the abstract of papers presented at Detroit, Michigan. April 14. 1943, page 28M).

(12) Rotation calculated.

(13) Levene and Bass, *J. Biol. Chem.*, **70**, 211 (1926).

(14) Whitmore and Evers, THIS JOURNAL, **55**, 812 (1933).

chloride from dimethylhexanol-2 had n^{20}_{D} 1.4351, n^{25}_{D} 1.4330, and that from dimethylhexanol-3 had n^{20}_{D} 1.4353,[15] n^{25}_{D} 1.4333.

Hydrolysis of the Chloride from *levo*-2,3-Dimethylhexanol-2.—Ten grams of the chloride was shaken with 3 liters of distilled water for six hours, the carbinols were extracted with purified petroleum ether, the combined extracts were washed with 3% sodium bicarbonate, with water, and dried with anhydrous potassium carbonate. After removal of the solvent, the carbinols were found to be free of chlorine and olefins, b. p. 71.5–73° (29 mm.), n^{25}_{D} 1.4294. The phenylurethan of this material melted at 52–52.5°, and when mixed with a 1:1 mixture of the two pure isomeric phenylurethans (m. p. 56–63°) melted at 53–63°

Summary

1. Treatment of *levo*-2,3-dimethylhexanol-2 with concentrated hydrochloric acid yields a mixture of 2,3-dimethyl-2-chloro- and 2,3-dimethyl-3-chlorohexane, both of which have been completely racemized.

2. Hydrolysis of the above chloride mixture yields a 1:1 mixture of racemic 2,3-dimethylhexanol-2 and 2,3-dimethylhexanol-3.

3. Both isomeric dimethylhexanols yield the same chloride mixture with concentrated hydrochloric acid.

4. The optical activity of the chloride mixture from *dextro*-2,2-dimethylhexanol-3 is due to the formation of the unrearranged secondary chloride, and not to any rearranged tertiary chloride.

NEW HAVEN, CONNECTICUT RECEIVED JULY 27, 1943

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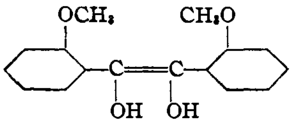
[15] Whitmore and Evers, *loc. cit.*, reported n^{20}_{D} 1.4350.

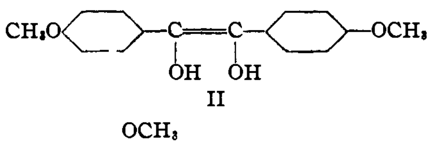
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

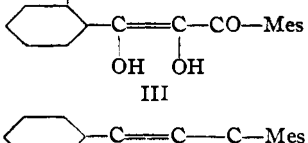
The Preparation and Properties of Mesityl-*p*-methoxybenzylglyoxal

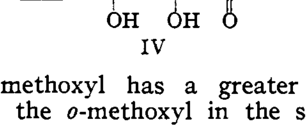
BY R. PERCY BARNES AND HAROLD DELANEY[1]

In recent publications[2] we pointed out the effect of methoxyl toward stabilizing enediols. We showed that when the 2,2'- and 4,4'-dimethoxydiphenylacetylene glycol diacetates were completely hydrolyzed, the intermediate 2,2'-dimethoxydiphenylacetylene glycol (I) ketonized to the benzoin, while the 4,4'-intermediate (II) was autoxidized to the corresponding benzil. We also showed that α-*o*-methoxyphenyl-β-mesitoylacetylene glycol (III) was more stable than the unsubstituted α-phenyl-β-mesitoylacetylene glycol (IV).

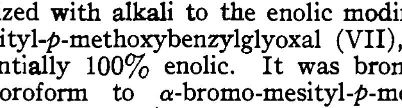

I


II


III


IV

Since *p*-methoxyl has a greater stabilizing effect than the *o*-methoxyl in the symmetrical molecules (I) and (II), we set out to make α-*p*-methoxyphenyl-β-mesitoylacetylene glycol (XI) in order to compare the methoxyl effects in (III) and (XI).


XI

We condensed acetylmesitylene with anisaldehyde, producing *p*-methoxybenzalacetomesitylene (V). This substance was oxidized with alkaline hydrogen peroxide to α-*p*-methoxyphenyl-β-mesitoyl ethylene oxide (IV). The oxide was in turn isomerized with alkali to the enolic modification of mesityl-*p*-methoxybenzylglyoxal (VII), which is essentially 100% enolic. It was brominated in chloroform to α-bromo-mesityl-*p*-methoxybenzylglyoxal (VIII), which is a deep orange-colored oil. The bromo compound was acetylated by means of freshly fused potassium acetate in glacial acetic acid to the monoacetate (IX). The acetate is approximately 80% enolic. The acetate (IX) was recovered unchanged after treatment with acetyl chloride. However, when the acetate (IX) was refluxed with freshly fused potassium acetate and acetic anhydride, it was converted into the diacetate (X). Both the monoacetate (IX) and the diacetate (X) upon hydrolysis obviously go by way of autoxidation of the ene-diol (XI) to mesityl-*p*-methoxyphenyltriketone (XII), for when the deep red solution of the monoacetate in cold concd. sulfuric acid is poured over finely crushed ice, a colorless solid is formed immediately. Portions of this solid in alcohol give the characteristic bluish-green color with alcoholic ferric chloride, and also decolorize indophenol. These positive tests indicate the actual formation and existence of the ene-diol.

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[1] In partial fulfillment of the requirements for the Master's degree.

[2] R. P. Barnes and Wendell M. Lucas, THIS JOURNAL, 64, 2258, 2260 (1942).