33. *Stereochemistry of the Acenaphthylene and Tetrahydroacenaphthylene Glycols. Part I.*

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Two acenaphthylene glycols are known, of which the lower-melting isomeride has now been proved to have the *trans*-structure by its resolution with the aid of *l*-menthoxyacetyl chloride. The optically active d-*acenaphthylene glycol* exhibited a

dextrorotation when dissolved in non-polar or weakly polar solvents, and a lævorotation in strongly polar media. In liquids of intermediate polarity the rotation approximated to zero.

Reduction of acenaphthenequinone with alcohol and sodium amalgam led to the isolation of trans-1 : 2 : 3 : 4-*tetrahydroacenaphthylene glycol*, which was also formed by the catalytic hydrogenation of *trans*-acenaphthylene glycol dissolved in alcohol at 50°, with platinum-black as catalyst. A corresponding cis-1 : 2 : 3 : 4-*tetrahydroacenaphthylene glycol* has been prepared by catalytic hydrogenation of *cis*-acenaphthylene glycol at 50°. When palladium dispersed on barium sulphate was employed as catalyst, the tendency was for acenaphthene to be formed by elimination of the hydroxyl groups.

A new and greatly improved method of preparing *cis*- and *trans*-acenaphthylene glycols has been found in the catalytic hydrogenation of acenaphthenequinone in cold alcoholic suspension in the presence of platinum-black.

By the interaction of bromine and acenaphthylene and hydrolysis of the resulting mixture of dibromides, Ewan and Cohen (J., 1889, **55**, 578) isolated two acenaphthylene glycols (I), m. p. 159° and 213°. Evidence indicating that the higher-melting form was the *cis*-isomeride was obtained by Criegee, Kraft, and Rank (*Annalen*, 1933, **507**, 194), who condensed it with acetone to give the *iso*propylidene derivative and supported their claim by showing that, like other *cis*-glycols, this form is rapidly oxidised by lead tetra-acetate.

These conclusions have now been verified by the optical resolution of the low-melting glycol, which must therefore be of the *trans*-structure. Resolution was accomplished by use of *l*-menthoxyacetyl chloride, a valuable reagent introduced by Read and Grubb (*J. Soc. Chem. Ind.*, 1932, **51**, 329T). The highly lævorotatory product obtained by fractionation of the mixed *l*-menthoxyacetic esters gave on hydrolysis the active d-trans-*acenaphthylene glycol*, m. p. 158—158·5°. The optical rotation of this compound varied in sign according to the electrochemical nature of the solvent in which it was dissolved (compare Rule and McLean, J., 1931, **674**), being dextrorotatory in non-polar media, practically inactive in moderately polar solvents, and lævorotatory in those of strongly polar character. Although the glycol molecules are presumably associated to some extent in benzene solution, even at the low concentrations employed, the effect of this upon the rotatory power is probably small in comparison with the optical change arising from the high degree of solvation of the glycol when dissolved in strongly polar solvents such as acetone or nitrobenzene. For this reason the benzene solutions may be considered the more normal and in the absence of other evidence the enantiomorph under examination is described as the *d*-form. Owing to the very low solubility of the glycol in the majority of organic liquids it was not found possible to make an extended examination of its optical properties; the dispersion in acetone solution, however, was found to be normal. As is not unexpected considering the polar nature of the glycol, the rotatory power in solution is so dominated by the polarity of the solvent that no visible relationship to the refractive index of the medium can be traced. The optical behaviour in solution thus resembles that of *l*-benzoin methyl ether (Rule and Crawford, J., 1937, 140) and is in complete contrast to that of the non-polar saturated hydrocarbon *d*-pinane (Rule and Chambers, J., 1937, 145), the rotatory power of which depends mainly upon the refractive properties of the solution.

Specific Rotatory Powers of trans-*Acenaphthylene Glycol in Solution* (l = 4; t = 20°).

Solvent.	*c.*	α (obs.).	$[\alpha]_{5461}$.	*μ*.	Solvent.	*c.*	α (obs.).	$[\alpha]_{5461}$.	*μ*.
Benzene	0·080	+0·21°	+66°	0	Methyl alcohol	0·378	±0°	0°	1·64
Chloroform	0·392	+0·81	+52	1·18	Acetone	0·400	−0·39	−25	2·76
Ethyl alcohol ...	0·372	±0	0	1·63	Nitrobenzene ...	0·324	−0·49 *	−76	3·98

* *l* = 2. The polarity of the solvent is indicated by the value of its dipole moment, *μ*.

Preparation of the acenaphthylene glycols by way of the corresponding bromides is a tedious process which only leads to small yields, chiefly on account of the difficulty in obtaining the starting material acenaphthylene. An alternative method of preparing

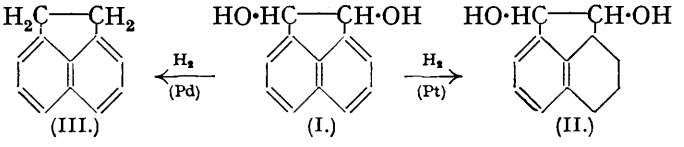
cis-acenaphthylene glycol due to Blount and Weissberger (**J., 1936, 336**), in which acenaphthenequinone is reduced with alcohol and sodium amalgam in an atmosphere of nitrogen, gave in our hands only a compound, m. p. 208·5—209°, later found to be a trans-*tetrahydroacenaphthylene glycol* (II); despite variations in time of reduction, temperature, and proportion of amalgam, none of the *cis*-acenaphthylene glycol could be obtained. The new tetrahydro-glycol gave a diacetate and did not react with bromine at the ordinary temperature. All four additional hydrogen atoms must therefore have entered the same ring in the acenaphthylene nucleus.

A tetrahydroacenaphthylene glycol of this type contains three asymmetric carbon atoms and should be capable of existing in eight stereoisomeric forms, comprising four racemic modifications. The form obtained by chemical reduction of the quinone could not be condensed with acetone, but even apart from the uncertainty which attaches to negative evidence, this is insufficient to characterise the compound as possessing a *trans*-configuration, since it has been concluded by Böeseken (*Rec. trav. chim.*, 1921, **40**, 566) that the formation of such condensation products occurs only when the hydroxyl groups are in the same plane as the carbon atoms to which they are linked and lie on the same side of them. Although these conditions are fulfilled in the case of *cis*-acenaphthylene glycol, they do not hold in that of its tetrahydro-derivative, as an inspection of the space model makes clear.

An unequivocal method of establishing the structure of the tetrahydro-glycol would be to prepare it from either the *cis*- or the *trans*-acenaphthylene glycol. Experiment showed that it could be obtained in excellent yield from the *trans*-glycol by catalytic hydrogenation, thus proving it to have a *trans*-arrangement of the hydroxyl groups. On the other hand, the hydrogenation of *cis*-acenaphthylene glycol under the same conditions led to the isolation of a cis-*tetrahydroacenaphthylene glycol*, m. p. 92·5—93·5°, in which all four hydrogen atoms had also entered the same ring in the nucleus. It is of interest that this *cis*-compound readily yields an *acetone* derivative even though one of the hydroxyl groups must be displaced in some degree from the plane occupied by the remaining hydroxyl group and the two carbon atoms of the acenaphthylene bridge.

Among the acenaphthylene glycols the higher-melting, less soluble isomeride (m. p. 213°) is the *cis*-form, whereas among the tetrahydroacenaphthylene glycols now isolated it is the *trans*-form (m. p. 209°). In view of the statement of Blount and Weissberger (*loc. cit.*) that they prepared *cis*-acenaphthylene glycol by reducing acenaphthenequinone with sodium amalgam, efforts were made during the present work to repeat this result by employing less vigorous conditions than those which had been found to lead to a tetrahydro-compound. In every case, however, *trans*-tetrahydroacenaphthylene glycol alone could be isolated in a state of purity. The two glycols in question have approximately the same melting points and are thus liable to be confused with one another, but each compound is also very much less soluble than its corresponding geometrical isomeride and it should therefore be possible to isolate either product at will by controlling the amount of hydrogen taken up.

Variation in the catalyst employed in the above hydrogenations led to an interesting difference in the product. Thus the use of palladium dispersed on barium sulphate caused reduction of the hydroxyl groups and formation of acenaphthene (III) in high yield. A small amount of acenaphthene was also obtained by the hydrogenation of the *cis*-glycol in the presence of platinum catalyst. The main reactions thus appear to proceed as indicated in the following scheme :



A greatly improved method of preparing *cis*- and *trans*-acenaphthylene glycols is the catalytic hydrogenation of acenaphthenequinone suspended in cold alcohol in the presence of platinum catalyst. The resulting mixture of glycols is readily separated by crystallis-

ation from water and the compounds may thus be prepared in a few hours and in good yields.

Experimental.

Acenaphthylene was prepared by passing the vapour of acenaphthene through a red-hot silica tube in an atmosphere of carbon dioxide (Dziewonski and Rapalski, *Ber.*, 1912, **45**, 2491), the maximum yield (47%) being obtained when the tube was packed with porous tile. Separation from unchanged acenaphthene was effected by recrystallisation of the mixed picrates.

Acenaphthylene dibromides (Blumenthal, *Ber.*, 1874, **7**, 1093) were prepared by slow addition of bromine to an ethereal solution of the hydrocarbon at − 10°. As both the *cis*- and the *trans*-glycol were desired, the mixture of dibromides obtained by evaporation of the ether and hydrogen bromide was hydrolysed directly by boiling for 1 hour with water (Graebe and Jequier, *Annalen*, 1896, **290**, 205). The less soluble *cis*-acenaphthylene glycol was deposited on cooling, and after recrystallisation (charcoal) was obtained in long silky needles, m. p. 212—213° (Graebe and Jequier and Ewan and Cohen record m. p. 204°; Criegee, Kraft, and Rank found 209—210°). The *trans*-glycol remained on evaporation of the mother-liquors from the *cis*-compound, the crude product melting at about 145°. In purifying this isomeride various methods were applied, including oxidation of the small content (about 18%) of *cis*-glycol present by use of lead tetra-acetate, as recommended by Criegee, Kraft, and Rank. The most convenient procedure was found in treating the crude *trans*-glycol, suspended in dry acetone, with 1% of hydrogen chloride and some anhydrous sodium sulphate. After 24 hours at room temperature any undissolved *trans*-glycol was brought into solution by further addition of acetone, and dry ammonia passed in to neutralise hydrogen chloride. The filtered solution was evaporated, and the acetone derivative of the *cis*-glycol boiled out with light petroleum, in which *trans*-acenaphthylene glycol is very sparingly soluble. Crystallisation of the latter from water gave the pure glycol, m. p. 159·5°. In a typical preparation 8 g. of acenaphthylene gave 1·7 g. of *cis*-glycol, m. p. 207—208°, and 0·88 g. of *trans*-glycol, m. p. 157°, the total yield of 2·58 g. representing 26% of the theoretical. In the literature no yields are recorded for these preparations.

Resolution of trans-*Acenaphthylene Glycol.*—The racemic glycol (2 g.) in pyridine (20 c.c.) was esterified with *l*-menthoxyacetyl chloride (7 g.). The resulting sticky solid was recrystallised four times from light petroleum, giving colourless needles (1·03 g.) of d-trans-*acenaphthylene glycol di-l-menthoxyacetate*, m. p. 114—115°; $[\alpha]_{5461}^{20°}$ − 327·3° in benzene (c = 0·414), the rotatory power being unaltered by continued recrystallisation (Found: C, 74·6; H, 8·7. $C_{36}H_{50}O_6$ requires C, 74·7; H, 8·7%).

The diester on hydrolysis with hot aqueous alcoholic sodium hydroxide gave a quantitative yield of d-trans-*acenaphthylene glycol*, which separated from water in colourless needles, m. p. 158—158·5° (depressed to 149—152° by the inactive glycol). Rotatory powers are given on p. 189 (Found: C, 77·4; H, 5·45. $C_{12}H_{10}O_2$ requires C, 77·2; H, 5·6%). An attempt to isolate the remaining optical isomeride from the mother-liquors obtained from the above ester was unsuccessful.

In a similar manner *cis*-acenaphthylene glycol was treated with *l*-menthoxyacetyl chloride and pyridine. The crude product, after being crystallised four times from light petroleum, afforded cis-*acenaphthylene glycol di-l-menthoxyacetate*, m. p. 40—42°, $[\alpha]_{5461}^{20°}$ − 114·8° in benzene (c = 0·418), these values being unchanged by further crystallisation (Found: C, 74·8; H, 8·9%). On hydrolysis with alcoholic potassium hydroxide the ester gave a quantitative yield of inactive *cis*-glycol (checked by mixed m. p.).

Reduction of Acenaphthenequinone with (2½%) *Sodium Amalgam.*—Reduction was effected in alcoholic solution with stirring at 50° and in an atmosphere of nitrogen as described by Blount and Weissberger (*loc. cit.*). At first a considerable deposition of dark blue solid occurred, later the tint changed to blue green and most of the solid passed into solution. After treatment with acetic acid and removal of mercury, the addition of water precipitated a yellow solid containing unchanged quinone (checked by mixed m. p.). The filtrate on evaporation gave a solid, m. p. 202—203° (38% of the theoretical yield) which on recrystallisation did not give the expected colourless needles of *cis*-acenaphthylene glycol, but plates, m. p. 208·5—209°, later proved to consist of trans-1 : 2 : 3 : 4-*tetrahydroacenaphthylene glycol* (the mixed m. p. with *cis*-acenaphthylene glycol, m. p. 212°, was strongly depressed) (Found: C, 75·5; H, 7·3. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

This compound, when heated with acetic anhydride, was converted quantitatively into

trans-*tetrahydroacenaphthylene glycol diacetate*, which crystallised in colourless plates, m. p. 139—140°, from aqueous alcohol (Found: C, 70·1; H, 6·5; *M*, by Rast method, 249. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·6%; *M*, 274). The glycol gave no condensation product with acetone, nor did it decolourise bromine in warm chloroform solution.

The above preparation was also carried out at 65—70°, an additional 33% of sodium amalgam being used; the time of reduction was varied in different preparations from 12 to 33 hours. The highest yield of pure tetrahydro-glycol was 32%, obtained by stirring the reactants for 24 hours at 65—70° and using 400 g. of amalgam to 5·5 g. of quinone.

By treatment with *l*-menthoxyacetyl chloride and pyridine the above glycol was converted into trans-*tetrahydroacenaphthylene glycol di*-l-*menthoxyacetate*, which crystallised from aqueous alcohol in colourless needles, m. p. 71—72°, $[\alpha]_{5461}^{20°}$ — 96° in benzene (c = 0·520) (Found: C, 73·9; H, 9·1. $C_{36}H_{54}O_6$ requires C, 74·2; H, 9·3%). The rotatory power of the ester was unchanged on repeated crystallisation, and on hydrolysis the original glycol was regenerated (confirmed by mixed m. p.), which was inactive in non-polar as well as in polar solvents.

Catalytic Hydrogenation of trans-*Acenaphthylene Glycol.*—Hydrogenation was carried out at 3 atms. and 50°, the glycol (1·86 g.) being dissolved in alcohol (50 c.c.), in the presence of 0·1 g. of platinum catalyst (prepared according to Adams, Voorhees, and Shriner, *Organic Syntheses*, 1928, **8**, 92). A few drops of concentrated hydrochloric acid and of aqueous ferric chloride were added as accelerators. After absorption of the required amount of gas the filtered liquid was diluted with water, affording crystalline plates of *trans*-tetrahydroacenaphthylene glycol, m. p. 208° alone or admixed with the product obtained by chemical reduction of acenaphthenequinone. A further quantity was recovered from the aqueous alcoholic mother-liquors, the total yield being 75% of the theoretical.

Catalytic Hydrogenation of cis-*Acenaphthylene Glycol.*—The same quantities and conditions as given above for the *trans*-compound being used, a solid (1·78 g.) was obtained, part of which was insoluble in water and consisted of acenaphthene, m. p. 92° (confirmed by mixed m. p.). The water-soluble fraction on purification proved to be cis-1 : 2 : 3 : 4-*tetrahydroacenaphthylene glycol* (0·5 g.), which separated from light petroleum in needles, m. p. 92·5—93·5° (Found: C, 75·4; H, 7·0. $C_{12}H_{14}O_2$ requires C, 75·7; H, 7·3%). In warm chloroform solution the compound did not decolourise bromine.

When the glycol (0·66 g.) was kept for 12 hours in dry acetone with addition of a little concentrated sulphuric acid, it afforded the iso*propylidene* derivative (0·7 g., m. p. 49—50°), which crystallised from light petroleum in needles, m. p. 51—52° (Found: C, 78·5; H, 7·7. $C_{15}H_{18}O_2$ requires C, 78·3; H, 7·8%).

Treatment with acetic anhydride converted the glycol quantitatively into cis-1 : 2 : 3 : 4-*tetrahydroacenaphthylene glycol diacetate*, which crystallised from light petroleum in needles, m. p. 121—121·5° (Found: C, 70·0; H, 6·3. $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·6%).

When hydrogenation was carried out at 50° with *cis*-acenaphthylene glycol (1·9 g.), alcohol (50 c.c.), and a palladium catalyst (0·5 g., prepared by reducing 1·7 g. of palladium chloride with formalin in a suspension of 20 g. of freshly precipitated barium sulphate), the only product isolated was acenaphthene (1·5 g.).

Catalytic Hydrogenation of Acenaphthenequinone.—The quinone (19 g.), suspended in cold alcohol (200 c.c.), was hydrogenated with vigorous shaking in the presence of platinum catalyst (1 g.) for about 12 hours. After the required amount of hydrogen had been absorbed, the precipitated solid was filtered off and recrystallised from alcohol, affording colourless needles of *cis*-acenaphthylene glycol (7 g.), m. p. 207—208°. The filtrate from the reaction mixture was evaporated to dryness, and the yellowish-brown residue crystallised from water (charcoal), giving the *trans*-acenaphthylene glycol (4·5 g.), m. p. 157°. Both products were identified by mixed melting points.

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