concentrated aqueous ammonia was heated slowly under reflux to about 250–300°. At this temperature the reaction reached a homogeneous melt. Anhydride, which sublimed into the condenser, was pushed back with a glass rod. After cooling, 95% alcohol was added and the solution filtered. Addition of water to the alcoholic solution precipitated a light tan solid, m. p. 145–150° (yield 0.3 g.). For purification it was dissolved in ethyl alcohol and water added to the hot solution until almost cloudy. Upon cooling prismatic needles separated. After recrystallizing three times from benzene and low boiling petroleum ether, the product formed colorless needles, m. p. 182–183°.

Anal. Calcd. for $C_{16}H_{21}O_2N$: N, 5.40. Found: N, 5.36.

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9-al (III).—A mixture of 17 g. of the dicyclohexene in 15 cc. of dry benzene and 6 g. of pure acrolein was heated under reflux for twenty-two hours at 50–60°. The benzene and the unreacted acrolein were removed and the residue fractionally distilled in vacuo. After distilling off all of the unreacted dicyclohexene (up to 126° (6.5 mm.)), the residue was dissolved in a small amount of ether and shaken with a 10% solution of sodium bisulfite. The solid which formed was filtered, washed with a little alcohol and decomposed with warm dilute aqueous sodium carbonate. The oil which separated was extracted with ether. The aldehyde was a colorless oil and was distilled in an atmosphere of nitrogen, b. p. 136–137° (4 mm.); yield, 4.2 g. (20%).

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.50; H, 10.65. Found: C, 82.87; H, 10.49.

The semicarbazone, purified from dilute alcohol, melted at 179–180°.

Anal. Calcd. for $C_{16}H_{26}ON_3$: N, 15.21. Found: N 14.99.

Summary

Addition of maleic anhydride and acrolein to di-$\Delta^{1,1}$-cyclohexene gives the hydrogenated phenanthrene derivatives, $\Delta^{4a,5a}$-dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride and $\Delta^{4a,5a}$-dodecahydrophenanthrene-9-al.

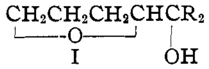
Urbana, Illinois Received October 10, 1935

[Contribution from the Baker Laboratory of Chemistry at Cornell University]

The Preparation and Reactions of Tertiary Tetrahydrofurylcarbinols

By A. L. Dounce, Ralph H. Wardlow[1] and Ralph Connor[2]

Two methods are available for the synthesis of tertiary tetrahydrofurylcarbinols (I): (1) the action of the appropriate Grignard reagent upon ethyl tetrahydrofuroate, obtained by the hydrogenation of ethyl furoate over nickel, or (2) the reaction of the Grignard reagent with ethyl furoate, followed by the hydrogenation over nickel of the furyldialkylcarbinols thus obtained. Both of these methods have been used for the preparation of tetrahydrofuryldiethylcarbinol (II) and tetrahydrofuryldi-*n*-butylcarbinol (III). The former method gave



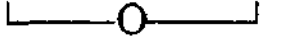
$CH_2CH_2CH_2CHCR_2(OH)$, ring closed through O

I

II, R = $-C_2H_5$
III, R = n-C_4H_9
IV, R = $-C_6H_5$

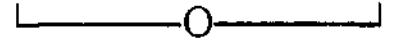
in over-all yields of 71% (II), 50% (III) and 77% (IV) and is to be preferred to the latter, which gave 52% (II) and 45% (III). Because of the well-known tendency[3] for hydrogenolysis of the carbon–oxygen bond in the α-position to aromatic nuclei, the latter method is not applicable to such compounds as IV.

Dehydration of these carbinols was readily accomplished by heating with magnesium sulfate until the theoretical amount of water had distilled. The product obtained by the dehydration of tetrahydrofuryldi-*n*-butylcarbinol (III) was a mixture of isomers which could not be separated by fractional distillation. With tetrahydrofuryldiphenylcarbinol (IV), however, the sole product isolated was 1,1-diphenyl-2,5-epoxy-1-pentene (V). The structure of the latter was established by the isolation of benzophenone and γ-butyrolactone from the hydrolysis of the ozonide; examination of the ozonolysis products failed to show any evidence of the formation of a dihydropyran during the dehydration.



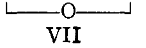
$CH_2CH_2CH_2C{=}C(C_6H_5)_2$

V



$CH_2CH_2CH_2CH{=}CH$

VI



$CH_2CH_2CH_2C{=}CH_2$

VII

The fact that no ring enlargement occurred under the conditions used in the dehydration of IV is in contrast to the results of Paul,[4] who obtained a dihydropyran (VI) by the catalytic dehydration of tetrahydrofurfuryl alcohol at 370–380°. Fur-

---

[1] A portion of this communication is abstracted from the thesis submitted by Ralph H. Wardlow in partial fulfilment of the requirements for the degree of Master of Science at Cornell University in June, 1933.

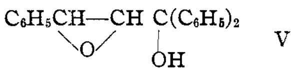
[2] Present address, Harrison Laboratory, University of Pennsylvania, Philadelphia, Pa.

[3] *Cf.* Covert, Connor and Adkins, This Journal, **54**, 1660 (1932).

[4] Paul, *Bull. soc. chim.*, [4] **53**, 417 (1933); *ibid.*, 1489 (1933); *Compt. rend.*, **196**, 1409 (1933); *Bull. soc. chim.*, [5] **2**, 311 (1935); *ibid.*, 745 (1935).

thermore, a comparison of the properties of V with the properties of 2,5-epoxy-1-pentene (VII), obtained by Paul by the action of alkaline reagents upon tetrahydrofurfuryl bromide, shows that they are markedly different. The former (V) was very stable; it was distilled without decomposition (b. p. 195° at 10 mm.), was stored for several months without decomposition or polymerization, and was recovered unchanged from contact with dilute sulfuric acid. The product (VII) isolated by Paul was a very unstable and reactive substance; it was hydrolyzed almost instantly by dilute acid, was attacked by oxygen of the air, and was not obtained in an analytically pure state. The conjugation of the olefinic double bond of V with the aromatic nuclei may be responsible for its greater stability.

The formation in excellent yields of tetrahydrofuryldiphenylcarbinol (IV) by the reaction of phenylmagnesium bromide with ethyl tetrahydrofuroate in ether solution indicated that cleavage of the tetrahydrofuran ring did not occur to any appreciable extent during the reaction. It therefore seemed of interest to test the stability of the ring under "forced" conditions. It was found, however, that when IV was refluxed for fifty-two hours in boiling xylene with three equivalents of phenylmagnesium bromide there were no indications of cleavage. Instead, an 87% yield of the dehydration product (VII) was obtained. That the dehydration product was formed after hydrolysis of the reaction mixture was indicated by the facts (a) that water appeared in the distillate *after* most of the xylene had been distilled (at atmospheric pressure), (b) that α,β-unsaturated ethers react with the Grignard reagent,[5] and (c) that in another experiment in which the time of refluxing was nine hours and in which the xylene was removed under diminished pressure, 76% of IV was recovered unchanged along with a small amount of impure dehydration product. The stability of V toward phenylmagnesium bromide is interesting in comparison with the reactivity of the α-oxido carbinol (VIII)



$C_6H_5CH{-}CH\,C(C_6H_5)_2$ (O bridging the two CH; OH on C) VIII

which suffers cleavage both of the oxide ring and the carbon chain.[6] The two carbon atoms between which cleavage occurs in VIII bear substituents similar to those on the corresponding carbon atoms in IV; the well-known difference in the stability of three-and five-membered rings undoubtedly is responsible for the difference in the reactions of these compounds.

Experimental

Ethyl Tetrahydrofuroate.—Ethyl furoate was hydrogenated[7] in the presence of the Raney catalyst[8] at 150°, using pressures of 100–130 atmospheres. With 15 g. of catalyst and 200 g. of ethyl furoate, hydrogenation was complete in four hours; average yield from five hydrogenations, 93.3%, b. p. 188–190° (740 mm.).

Furyldiethylcarbinol.[10]—An ethereal solution of 0.5 mole of ethylmagnesium bromide was prepared in the usual manner and a solution of 35 g. (0.25 mole) of ethyl furoate in anhydrous ether was added to the solution, the rate of addition being determined by the vigor of the reaction. The reaction mixture was refluxed on a water-bath for three hours, cooled, poured into a mixture of 200 g. of cracked ice with 200 ml. of a saturated aqueous solution of ammonium chloride, stirred vigorously, allowed to stand for three hours, the ethereal layer separated, and the aqueous layer extracted twice with ether. The combined ether extracts were then washed with 100 ml. of saturated ammonium chloride solution, dried with magnesium sulfate and distilled. There was obtained 28.5 g. (77%) of furyldiethylcarbinol, b. p. 92–95° (14 mm.). The distillation residue was tarry and was larger in quantity when heating during distillation was prolonged.

Furyldi-*n*-butylcarbinol.—The procedure was exactly like that described above for furyldiethylcarbinol. The yield was 40.9 g. (78%), b. p. 128–131° (14 mm.), $n^{25}{}_{D}$ 1.4703, $d^{25}{}_{25}$ 0.9251, MR'$_D$ found 63.30, MR'$_D$ calcd. 62.29.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 74.28; H, 10.47. Found: C, 74.47; H, 10.60.

Tetrahydrofuryldiphenylcarbinol (IV).—To a solution of phenylmagnesium bromide prepared from 8.2 g. (0.34 gram atom) of magnesium in 500 ml. of dry ether was added with stirring 24.5 g. (0.17 mole) of ethyl tetrahydrofuroate at such a rate as to maintain gentle refluxing. The reaction mixture was refluxed with stirring on the water-bath for one hour, cooled, and added to a mixture of 200 g. of cracked ice and 20 ml. of 1:1 sulfuric acid. The ether layer was washed with a cold 5% solution of sulfuric acid, dried with anhydrous magnesium sulfate, concentrated on the steam-bath and the solid residue recrystallized from petroleum ether (b. p. 60–70°). The product weighed 41 g. (83%), m. p. 79–80° (uncorr.).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.31; H, 7.08. Found: C, 80.38; H, 7.20.

---

[5] Hill and Tallman, unpublished results.

[6] Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 205 (1931); Bachman and Wiselogle, *ibid.*, **56**, 1559 (1934); Kohler and Bickel, *ibid.*, **57**, 1099 (1935).

[7] The bomb used for the hydrogenations had a capacity of 275 ml. and did not differ in any important respects from those previously described.[9] The authors are very grateful to Professor Homer Adkins of the University of Wisconsin for his advice and aid in planning the hydrogenation equipment.

[8] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[9] Adkins, *Ind. Eng. Chem., Anal. Ed.*, **4**, 342 (1932); THIS JOURNAL, **55**, 4272 (1933).

[10] Hale, McNally and Peter, *Am. Chem. J.*, **35**, 68 (1906).

Tetrahydrofuryldiethylcarbinol (II).—This preparation was carried out like that of IV, except that 1.0 mole of ethyl tetrahydrofuroate (with correspondingly larger amounts of the other materials) was used. The yield was 120 g. (76%), b. p. 200–203° (740 mm.). The product was a colorless liquid with an agreeable ethereal odor, d^{25}_{25} 0.9744, n^{25}D 1.4552, MR'D found 44.01, MR'D calcd. 44.75.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.35; H, 11.39. Found: C, 68.20; H, 11.41.

Hydrogenation of 18.0 g. of furyldiethylcarbinol in the presence of 5.0 g. of Raney nickel catalyst and 25 ml. of absolute ethanol at an initial hydrogen pressure of 115 atmospheres was complete in three hours at 150°. Some tarry material was formed but there was also obtained 12.0 g. (67%) of II, b. p. 203° (740 mm.).

Tetrahydrofuryldi-*n*-butylcarbinol (III).—This preparation was carried out like that of II. The yield was 114.5 g. (53.4%), b. p. 151–152° (24 mm.), 251–252° (740 mm.), d^{25}_{25} 0.9219, n^{25}D 1.4543, MR'D found 62.90, MR'D calcd. 63.18.

Anal. Calcd. for $C_{13}H_{26}O_2$: C, 72.89; H, 12.14. Found: C, 72.84; H, 12.20.

Hydrogenation of 11.8 g. of furyldi-*n*-butylcarbinol in the presence of 1.5 g. of Raney nickel catalyst and 25 ml. of absolute ethanol at an initial hydrogen pressure of 120 atmospheres was complete in one and one-half hours at 175°. A small amount of low-boiling material was formed, presumably hydrogenolysis products, along with 7.0 g. (58%) of III, b. p. 254° (740 mm.), n^{25}D 1.4545.

1,1-Diphenyl-2,5-epoxy-1-pentene (V).[11]—Tetrahydrofuryldiphenylcarbinol (IV) was dehydrated under a variety of conditions and the following procedure was found to be the most satisfactory. To 101.6 g. (0.4 mole) of IV was added 5.0 g. of anhydrous magnesium sulfate and the mixture heated in a 100-cc. round-bottomed flask until the theoretical amount of water had distilled through a Vigreux column 8 cm. long and 1.5 cm. in diameter. The dark residue which solidified on cooling was crystallized once from alcohol with decolorizing charcoal, once from alcohol alone and once from petroleum ether, b. p. 60–70°. After these recrystallizations the product was slightly yellow and melted at 107.5–108.5° (uncorr.). Further recrystallizations rendered it white but did not change the melting point. The yield was 52.6 g. (56%). The compound reduced alkaline potassium permanganate solution, decolorized a 5% solution of bromine in carbon tetrachloride and could be distilled without decomposition, b. p. 195° (10 mm.).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.44; H, 6.77. Found: C, 86.10; H, 6.87.

Ozonolysis of 1,1-Diphenyl-2,5-epoxy-1-pentene.—The ozonide prepared from 1.5 g. of V dissolved in 35 ml. of a 50–50 mixture of petroleum ether, b. p. 30° and b. p. 60–70° was hydrolyzed, after removal of the solvent under diminished pressure, by gentle boiling with 2 to 3 ml. of superoxol. The insoluble material was then extracted with ether and an insoluble compound,[12] m. p. 210–214° (dec.) removed by filtration. Distillation of the ether solution gave 0.5 g. (50%) of benzophenone, b. p. 156° (10 mm.), m. p. 46–48°, m. p. of oxime 139–140°. A sample of authentic benzophenone, m. p. 47–48.5°, boiled at 153–154° (10 mm.) in the same apparatus and the melting point of benzophenone oxime (140–141°) was not altered by mixture with the oxime of the ozonolysis product.

The ozonide prepared by passing ozone through a solution of 23.6 g. (0.1 mole) of V in 175 ml. of dry carbon tetrachloride was hydrolyzed with zinc and water, using hydroquinone and silver nitrate as catalysts by the recently described method.[13] The water-insoluble portion of the product was removed by extraction with ether, the zinc removed from the water layer by filtration, the ether distilled from the water-insoluble layer and the residue added to the aqueous filtrate to remove water-soluble materials. The water insoluble layer was separated and distilled. The sole product was benzophenone (b. p. 140–150° (10 mm.), m. p. 46.5–48.5°, m. p. of oxime, 141.5–142°) the identity of which was confirmed by its mixed melting point with an authentic sample of benzophenone and by the mixed melting point of its oxime with benzophenone oxime. The melting points of the mixtures were 46.5–48.5° and 141–142°, respectively. The aqueous layer from which the benzophenone had been separated was distilled through a small indented column until a sirupy residue remained. This residue contained zinc chloride (because of the incomplete removal of carbon tetrachloride before decomposition of the ozonide) and was extracted repeatedly with ether and the ether extracts dried and distilled. The ether extracts contained enough zinc chloride to cause considerable decomposition during distillation but there was obtained 0.5 g. of pure γ-butyrolactone, b. p. 95° (15 mm.).

γ-Butyrolactone.—Two hundred grams of ethyl succinate was heated at 250° with 18 g. of copper–chromium–barium oxide catalyst[14] (37KAF) for ten hours at a pressure of 90 to 130 atmospheres. Fractional distillation of the product through a very efficient fractionating column gave 10 g. (10%) of γ-butyrolactone, b. p. 92–94° (18–19 mm.).

Hydrazide of γ-Hydroxybutyric Acid.—The procedure was exactly like that previously used[15] with ε-caprolactone. The solid product obtained from the reaction of hydrazine hydrate with the γ-butyrolactone prepared from the hydrogenation of ethyl succinate gave, upon recrystallization from ethanol, a small amount of the dihydrazide of succinic acid,[16] m. p. 165–166° (uncorr.), and a much larger amount of the hydrazide of γ-hydroxybutyric acid, m. p. 89–90° (uncorr.).

Anal.[18] Calcd. for $C_4H_{10}O_2N_2$: N, 23.7. Found: N, 24.03, 24.05.

---

[11] The authors wish to express their gratitude to Professor J. R. Johnson for his interest and advice during this portion of the work.

[12] The same compound was formed from the ozonolysis of unsymmetrical diphenylethylene under these conditions.

[13] Whitmore and Church, This Journal, **54**, 3711 (1932); Church, Whitmore and McGrew, *ibid.*, **56**, 178 (1934).

[14] Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

[15] Van Natta, Hill and Carothers, *ibid.*, **56**, 456 (1934).

[16] This melting point was unchanged when the product was mixed with an authentic sample of the hydrazide of succinic acid.[17] This shows that γ-butyrolactone was not completely separated from ethyl succinate by the fractional distillation. This dihydrazide is quite insoluble in alcohol, while the hydrazide of the hydroxy acid is very soluble.

[17] Schöfer and Schwan, *J. prakt. Chem.*, **51**, 190 (1895).

[18] The micro-Dumas analyses were made by Dr. M. T. Bush.

The reaction of hydrazine hydrate with the ozonolysis product believed to be γ-butyrolactone gave a solid hydrazide, m. p. 90.5-92° (uncorr.). The mixture of this product with the hydrazide of the γ-butyrolactone prepared from ethyl succinate melted at 90.5-91.5° (uncorr.).

Dehydration of Tetrahydrofuryldi-*n*-butylcarbinol.—A mixture of 10 g. of the carbinol (III) with 0.5 g. of magnesium sulfate and 0.5 g. of potassium hydroxide was heated under a small Vigreux column. Water and an oil with an ethereal odor distilled and the residue in the flask became tarry. The experiment was repeated with similar results using lime in place of the magnesium sulfate. The combined dried products from both experiments distilled between 40 and 150° (740 mm.) with a uniform temperature rise.

Tetrahydrofuryldiphenylcarbinol with Phenylmagnesium Bromide.—To a solution of 0.6 mole of phenylmagnesium bromide in 400 ml. of ether was slowly added in small portions 48.5 g. (0.2 mole) of tetrahydrofuryldiphenylcarbinol (IV). To the reaction mixture was then added 500 ml. of dry xylene, the reflux condenser replaced by a short fractionating column with a condenser set downward for distillation and the mixture heated on an oil-bath until the vapors reached a temperature of 131°. The reflux condenser was then replaced and the xylene refluxed for fifty hours. After the reaction mixture was cooled it was poured into a mixture of cracked ice with 40 ml. of 1:1 sulfuric acid and the xylene layer separated and distilled at atmospheric pressure. Water appeared in the distillate near the end of the distillation. The residue (50 g.) solidified upon cooling and after recrystallization from petroleum ether (b. p. 60-70°) and from alcohol gave 41 g. (87%) of pure material, m. p. 107.5-108.5° (uncorr.). This melting point was unchanged when the material was mixed with a sample of V prepared by the dehydration of IV. In another experiment in which the time of refluxing was nine hours and in which the xylene was removed under reduced pressure, 76% of IV was recovered unchanged (m. p. 77-79°) along with 4 g. of an oil (b. p. 250°) which decolorized bromine in carbon tetrachloride and was apparently impure dehydration product.

Summary

Tetrahydrofuryldialkylcarbinols have been synthesized by the reaction of alkylmagnesium halides with ethyl tetrahydrofuroate and by the catalytic hydrogenation of furyldialkylcarbinols. Tetrahydrofuryldiphenylcarbinol was readily dehydrated to give 1,1-diphenyl-2,5-epoxy-1-pentene; in contrast to the dehydration of furfuryl alcohol, there was no indication of ring enlargement. The dehydration product was much more stable than 2,5-epoxy-1-pentene. Tetrahydrofuryldiphenylcarbinol was not cleaved by phenylmagnesium bromide under "forced" conditions.

ITHACA, NEW YORK RECEIVED OCTOBER 5, 1935

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF JOHNS HOPKINS UNIVERSITY]

The Preparation of Some of the Lower Alkyl Sulfonic Acids

BY D. L. VIVIAN AND E. EMMET REID

Much work has been done by earlier investigators on the preparation of alkyl sulfonic acids by various procedures, but very little effort has been made to isolate and characterize the anhydrous acids. Two exceptions occur in the work of Noller and Gordon[1] on the acids containing from nine to fourteen carbon atoms, and in that of Berthoud[2] on methyl sulfonic and ethyl sulfonic acids. The present paper gives data on the four straight-chain primary sulfonic acids containing from three to six carbon atoms.

The propyl, amyl and hexyl sulfonic acids were prepared from barium salts remaining from a previous investigation[3] by precipitating the barium with sulfuric acid. The butyl sulfonic acid was prepared by oxidation of *n*-butyl mercaptan[4] by dropping 48 g. of it into 180 cc. of concentrated nitric acid with mechanical stirring and evaporating on the steam-bath until the oxides of nitrogen were completely removed. The crude acid was diluted with ten volumes of water, neutralized with lead carbonate, filtered and the filtrate evaporated to dryness. The crude lead salt obtained in 72-96% yields was recrystallized from 80% alcohol and then decomposed in aqueous solution with hydrogen sulfide. After removing the lead sulfide the aqueous solution was concentrated on the steam-bath.

The pure anhydrous sulfonic acids were obtained from the concentrated aqueous solutions as colorless liquids after four or five distillations at 1 mm. Their hot vapors attack rubber but a coating of sodium silicate on the stoppers prevents this. The pure acids soon darken even in a vacuum.

The average purity of these acids as determined by two concordant titrations with methyl orange

---

[1] Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

[2] Berthoud, *Helv. Chim. Acta*, **12**, 859 (1929).

[3] Wagner and Reid, THIS JOURNAL, **53**, 3407 (1931).

[4] This acid was also prepared by converting butyl mercaptan into disulfide (b. p. 107-109° at 12 mm.) and oxidizing this with nitric acid, but the yield was not quite as good.