tively unstable, showing signs of decomposition in several weeks when exposed to light, and in several months in the dark.

6-Tosyl-2,3,5-tribenzoyl-1,4-sorbitan.—To a solution of 10 g. (0.031 mole) of 6-tosyl-1,4-sorbitan in 100 cc. of pyridine, cooled in ice, was added 14.6 g. (0.10 mole) of benzoyl chloride. After standing twenty-four hours at room temperature, the reaction mixture was poured into water. The water layer was decanted from the sirupy product which precipitated. On stirring the sirup with 50 cc. of methanol, rapid crystallization occurred. After two recrystallizations from 10 parts of 95% ethanol, 18 g. (90% of theory) of colorless product was obtained in needles, melting at 106–107° (cor.),[10] and rotating $[\alpha]^{25}D$ +47.2° (*c*, 5.55 in chloroform), readily soluble in acetone, chloroform and benzene and insoluble in petroleum ether and water.

Anal. Calcd. for $C_{34}H_{30}O_{10}S$: C, 64.76; H, 4.80; S, 5.08. Found: C, 65.2, 64.5; H, 4.72, 4.76; S, 5.30.

6-Iodo-6-desoxy-2,3,5-tribenzoyl-1,4-sorbitan.—A solution of 19 g. (0.03 mole) of 6-tosyl-2,3,5-tribenzoyl-1,4-sorbitan and 9 g. (0.06 mole) of sodium iodide in 100 cc. of acetone was heated for one hour at 100° in a pressure flask. The precipitated sodium *p*-toluenesulfonate was filtered off, and the solvent removed from the filtrate. The residue solidified on addition of water, and was twice recrystallized from 600 cc. of 95% ethanol; yield, 15 g., 85%. The substance crystallized in plates melting at 151–153° (cor.) and rotating $[\alpha]^{25}D$ +5.1° (*c*, 2.92 in chloroform), insoluble in petroleum ether, ethyl ether and water and soluble in acetone, chloroform and benzene.

Anal. Calcd. for $C_{27}H_{23}O_7I$: C, 55.30; H, 3.95; I, 21.65. Found: C, 55.9, 55.2; H, 3.87, 3.87; I, 21.34.

Summary

1. A number of water soluble iodo-sugar derivatives have been prepared in order to study their utility as X-ray contrast agents in intravenous urography. These include 6-iodo-6-desoxy-D-galactose, 6-iodo-6-desoxy-α- and β-methyl-D-glucopyranosides, and 6-iodo-6-desoxy-1,4-sorbitan.
2. Several other new derivatives of 1,4-sorbitan have been synthesized.
3. β-Methyl-D-glucopyranoside has been prepared in 21% yield by treatment of glucose with methanolic hydrogen chloride, followed by isolation of the glucoside through its complex with potassium acetate.

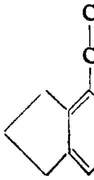
CHICAGO, ILLINOIS RECEIVED APRIL 12, 1948

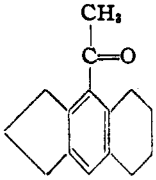
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Steric Effect of Methylene Groups. III

BY RICHARD T. ARNOLD AND PAUL N. CRAIG[1]

In an attempt to determine the relative steric influences of methylene groups in five- and six-membered rings, the following acetophenone derivatives have been prepared and examined.


(I)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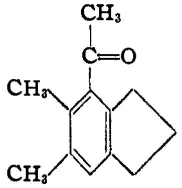
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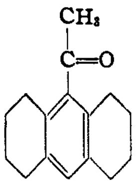
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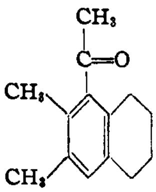
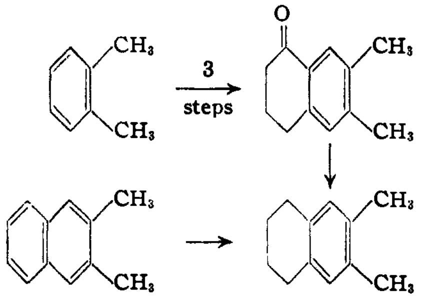

(V)

As reported earlier,[2] when treated with hypochlorite, acetohydrindacene (I) gives chloroform and 4-hydrindacenecarboxylic acid, whereas 9-acetoöctahydroanthracene (IV) gives a relatively stable trichloro ketone. The amount of methane evolved from methylmagnesium iodide (Zerewitinoff determination) decreases in the order IV > II > I. As a result of these observations and the values of carbonyl Raman frequencies, it was concluded that the steric hindrance around the carbonyl group decreases in the order IV > II > I.[2] Additional confirmatory evidence has now been obtained from observations on compounds III and V.

Of the above five ketones, only II is liquid; the others were readily purified by careful recrystallization. Tetrahydrobenz(f)indane, from which II is derived has now been prepared in a higher state of purity (m. p. 4°) and a sample of II obtained from this purer hydrocarbon has been reexamined.

6,7-Dimethyltetralin (VII) is obtained directly by catalytic reduction of 2,3-dimethylnaphthalene (m. p. 104°) in the presence of Raney nickel. The hydrocarbon so formed is essentially identical with that prepared from pure *o*-xylene.[3]



(VI) (VII)

It would appear that close approach to the cata-

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[1] Du Pont fellow, 1947. Present address: Smith, Kline and French Company, Philadelphia, Pa.

[2] Arnold and Rondestvedt, THIS JOURNAL, 68, 2176 (1946).

[3] Barnett and Sanders, *J. Chem. Soc.*, 434 (1933).

lyst of the benzenoid ring attached to the methyl groups in VI is sterically inhibited.[4]

Table I contains a summary of our observations of the action of methylmagnesium iodide on the ketones I–V.

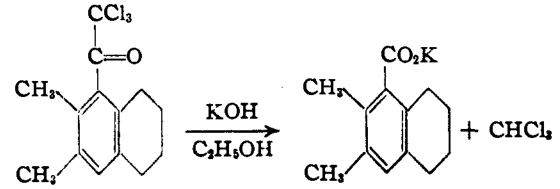
Table I

Compound	Action of CH_3MgI % Enolization[a]	% Addition
I	30	70
II	75[b]	25
III	93	9
IV	95	5
V	100	1.5

[a] The per cent. error is approximately ±2. [b] Reported earlier[2] as 62% on a less pure sample.

Ketones IV and V give well-defined trichloro derivatives when treated with sodium hypochlorite solutions. Compounds II and III gave complex mixtures of chlorinated ketones, chloroform and the corresponding aromatic acids.

By comparative studies it has been shown that alcoholic potassium hydroxide is much more effective than sodium hydroxide in bringing about the cleavage of hindered trichloromethyl ketones. Thus, 5-trichloroacetyl-6,7-dimethyltetralin is



relatively easily cleaved with alcoholic potassium hydroxide.

Experimental

6,7-Dimethyltetralin.—2,3-Dimethylnaphthalene (62.4 g.) was dissolved in ethanol (300 cc., 95%) and Raney nickel catalyst (4 g.) was added. Absorption of hydrogen (2 moles) was complete in one hour at 110° and a pressure of 1000 lb./sq. in. After removing the catalyst by filtration, the filtrate was fractionated directly to give 56.4 g. (89%) of 6,7-dimethyltetralin, b. p. 131–133 (20 mm.). Percolation through Alorco chromatographic alumina (80 mesh) gave a material having $n^{25}D$ 1.537.

Oxidation of 6,7-Dimethyltetralin.—A Carius tube was charged with 1.0 g. of the hydrocarbon (obtained from 2,3-dimethylnaphthalene) and nitric acid (15 cc. diluted 3 to 1 with water). This mixture was held at 165° for five hours. The solution was evaporated to dryness on a steam-bath; water (10 cc.) was added and the whole again evaporated to dryness. The residue was dissolved in ether and converted to its tetramethyl ester with diazomethane in the usual manner; m. p. 141–143°. When mixed with an authentic sample of the methyl ester of 1,2,4,5-benzenetetracarboxylic acid there was no depression of melting point.

5-Aceto-6,7-dimethyltetralin.—To 6,7-dimethyltetralin (22 g.) dissolved in carbon bisulfide (150 cc.) was added aluminum chloride (46 g.) at 0°. To this, acetic anhydride (17.3 g.) was added dropwise over a twenty-minute period. After one and three-quarters hours the reaction mixture was poured onto ice and hydrochloric acid. From the organic layer there was obtained the desired ketone; b. p. 150° (1 mm.); m. p. 50–52° (from 28–38° petroleum ether); yield 40%.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.28; H, 9.29.

5-Trichloroacetyl-6,7-dimethyltetralin.—One gram of the above ketone was treated with a solution of potassium hypochlorite prepared from commercial calcium hypochlorite (15 g. H.T.H. grade). After fifteen minutes the crude trichloro ketone was collected on a filter. Two recrystallizations from acetic acid and one from methanol gave a pure product; m. p. 57–58.5°.

Anal. Calcd. for $C_{14}H_{15}OCl_3$: C, 55.03; H, 4.95. Found: C, 55.10; H, 5.21.

6,7-Dimethyltetralin-5-carboxylic Acid.—The above described trichloro ketone (50 mg.) was heated under reflux for twenty minutes with ethanol (20 cc., 95%) and potassium hydroxide (4 pellets). After adding cold water (100 cc.), the solution was extracted with ether. Acidification of the aqueous phase gave the expected acid; m. p. 193–195°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.50; H, 8.13.

3,4-Dimethylphenyl-β-chloroethyl Ketone.—*o*-Xylene (53 g.) was added to a solution containing carbon bisulfide (600 cc.) and aluminum chloride (94 g.) at 0°. To this was added over a period of forty-five minutes, β-chloropropionyl chloride (69 g.) dissolved in carbon bisulfide (100 cc.). Stirring was continued for one hour at 0° and the solution was poured onto ice and hydrochloric acid. The organic layer was washed with dilute sodium hydroxide, dried with sodium sulfate and evaporated to dryness on a steam-bath. Dissolution of the residue in petroleum ether (b. p. 40–75°) gave a solution from which 82.5 g. (90%) of ketone was isolated at low temperature; m. p. 72–72.5°.

Anal. Calcd. for $C_{11}H_{13}OCl$: C, 67.18; H, 6.66. Found: C, 67.05; H, 6.53.

5,6-Dimethylhydrindanone-1.—The above described chloroketone (172 g.) was dissolved in sulfuric acid (1000 cc., sp. gr. 1.84), warmed on a steam-bath for three hours and then poured into 3.5 liters of ice and water. The brown product was recrystallized from petroleum ether (b. p. 60–68°) to give a yellowish-white product; m. p. 61–62°. This consisted of two isomers which were separated by one recrystallization from aqueous ethanol and two recrystallizations from petroleum ether. Only one pure ketone was isolated; m. p. 87–88°; yield 22 g.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.70; H, 7.54.

That this ketone had the assigned structure was established by its oxidation to 1,2,4,5-benzene tetracarboxylic acid.

The oxime of this ketone melted at 181–183°.

Anal. Calcd. for $C_{11}H_{13}ON$: C, 75.39; H, 7.49. Found: C, 75.10; H, 7.65.

5,6-Dimethylhydrindene.—A mixture of 5,6-dimethylhydrindanone-1 (17.0 g.), toluene (120 cc.), acetic acid (60 cc.), concentrated hydrochloric acid (200 cc.) and zinc (50 g. which had been amalgamated) was refluxed continuously for forty-three hours. Distillation of the toluene layer afforded 12 g. (77%) of the expected hydrocarbon, b. p. 115° (25 mm.), $n^{26.5}D$ 1.5314.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.14; H, 10.09.

4-Aceto-5,6-dimethylhydrindene.—The above hydrocarbon (8 g.) was acetylated at 0° in carbon bisulfide (200 cc.) with aluminum chloride (16 g.) and acetic anhydride (11.2 g.). The reaction was complete in thirty minutes. After distilling the crude ketone (b. p. 166–167° (25 mm.)) the material solidified. Recrystallization first from aqueous ethanol and then from petroleum ether gave a pure product; m. p. 43°; yield 42%.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.85; H, 8.73.

The oxime of this ketone was prepared from hydroxylamine in pyridine and absolute ethanol; m. p. 133–134°.

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[4] Linstead and co-workers, This Journal, 64, 1985 (1942).

Anal. Calcd. for $C_{13}H_{17}ON$: C, 76.81; H, 8.43. Found: C, 75.10; H, 8.65.

5,6-Dimethylhydrindene-4-carboxylic Acid.—The above ketone (35 mg.) was dissolved in methanol and treated with excess potassium hypochlorite at 60–65° for thirty minutes. At this time most of the methanol had evaporated. An ether extract of the solution upon evaporation deposited an oil containing much chlorine (Beilstein test). This oil was dissolved in methanol (15 cc.) to which potassium hydroxide (3 pellets) had been added and the solvent was evaporated on a steam-bath until the volume reached 3 cc. Addition of dilute hydrochloric acid precipitated the carboxylic acid; m. p. 169–170°.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.36; H, 7.72.

Tetrahydrobenz[f]indane.—To a mixture containing phosphoric acid (165 g., 85%) and phosphorus pentoxide (165 g.) was added γ-(5-hydrindenyl)-butyric acid (68.5). After being heated at 100–120° for five minutes with good stirring, the solution was poured into water (1000 cc.). The crude product was extracted with benzene and the benzene solution was washed with dilute alkali and dried. Removal of the benzene and distillation in a sausage flask gave a crude ketone which solidified on standing. Two recrystallizations from petroleum ether (b. p. 40–75°) followed by recrystallization from aqueous alcohol gave 28 g. of 6,7-cyclopentene-1-tetralone; m. p. 38–39°. Clemmensen reduction of this ketone gave pure tetrahydrobenz[f]indane; m. p. +4°. A sample prepared earlier in this Laboratory[5] melted at −3 to −5°.

Acetotetrahydrobenz(f)indane (V).—To tetrahydrobenz[f]indane (8 g., m. p. 4°) dissolved in carbon bisulfide (85 cc.) was added aluminum chloride (21 g.). Stirring was commenced and acetic anhydride (7.1 g.) was added over fifteen minutes. The entire reaction was carried out at 0° for one and three-quarters hours. After decomposition with ice and hydrochloric acid in the usual manner there was obtained a liquid ketone; wt. 6.8 g.; of b. p. 167–170° (1 mm.); $n^{25.5}_{D}$ 1.5610. This material could not be induced to crystallize.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.17; H, 8.44.

Summary

1. Further evidence is presented to prove that the steric effect of methylene groups in five membered rings (*i. e.*, hydrindene) is smaller than that in corresponding six-membered rings (*i. e.*, tetralin).

(5) R. Barnes, Ph.D. Thesis, University of Minnesota, 1943.

MINNEAPOLIS, MINNESOTA RECEIVED APRIL 30, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Tri-α-naphthylboron as a Highly Hindered Reference Acid; a Case of Polymorphism Ascribed to Hindered Rotation[1]

BY HERBERT C. BROWN[2] AND SEI SUJISHI[2,3]

Earlier results[4] have shown that the relative base strengths of ammonia and a given series of primary, secondary, and tertiary amines (NH_3, RNH_2, R_2NH, R_3N) are dependent upon the reference acid used to compare them. Thus the sequence in strength observed with trimethylboron as the reference acid is $NH_3 < CH_3NH_2 < (CH_3)_2NH > (CH_3)_3N$. This sequence is altered to $NH_3 < CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$, when tri-*t*-butylboron is used as the reference acid. This change in sequence has been ascribed to the increase in the steric requirements of the reference acid.[4b]

According to this interpretation, a reference acid of even greater steric requirements than tri-*t*-butylboron should cause the observed sequence to approach the theoretically possible limit, $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. It was of interest to test this conclusion.

The selection for this purpose of a triarylboron with large steric requirements was dictated by a number of considerations. Tri-*t*-butylboron is a very weak reference acid for the amines under discussion, considerably weaker than trimethylboron itself.[4a] This weakness has been attributed to the large steric requirements of the three tertiary butyl groups. Further increase in the bulk of the alkyl groups would be expected to decrease the stability of the addition compounds with the amines to the point where it would be relatively difficult experimentally to make comparisons. The available evidence strongly suggests that the replacement of alkyl groups by aryl groups markedly increases the acid strength of the boron compounds.

For a number of reasons, tri-α-naphthylboron[5] (hereafter TNB) appeared especially promising in attaining the theoretical limit sequence. It was therefore decided to prepare the addition compounds of ammonia and the three methylamines with TNB and to compare their relative stabilities by a careful study of each system. Since the addition compounds were found to be highly dissociated at temperatures at which neither TNB nor the addition compound were sensibly volatile, the problem reduced itself to measuring and comparing the pressures exerted by the only volatile component of the system—the gaseous base.

$$(\alpha\text{-}C_{10}H_7)_3B{:}NR_3\ (\text{solid}) \rightleftarrows (\alpha\text{-}C_{10}H_7)_3N\ (\text{solid}) + NR_3\ (\text{gas})$$

The observed pressures vary in the order $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$ (*vide post*), and support the conclusion that the theoretical

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(1) Studies in Stereochemistry. XII.

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(3) Ethyl Corporation Fellow at Wayne University, 1945–1947.

(4) (a) Brown, THIS JOURNAL, 67, 374 (1945); (b) 67, 378 (1945); (c) 67, 1452 (1945); (d) Brown and Pearsall, *ibid.*, 67, 1765 (1945).

(5) Krause and Nobbe, *Ber.*, 63, 934 (1930).