The spectra reported in Table I were obtained with a 0.15 mm. cell width. The wave lengths are in "μ." The intensities (figures in parentheses) are expressed in units of 10% absorption. The letter "S" represents solvent absorption.

TABLE I

I	II	III	IV
2.90(1)	~2.90(1)	2.93(3)	2.95(2)
3.2–3.4 S	3.2–3.4 S	3.2–3.4 S	3.38(1)
6.04(9)	6.06(10)	6.07(10)	6.08(6)
6.25(3)	6.24(3)	6.21(4)	6.20(3)
6.67(5)	6.31(2)	6.58(8)	6.32(2)
6.85(3)	6.66(8)	7.02(6)	6.56(5)
7.24(7)	~7.0(8)	7.22(8)	6.78(1)
7.38(3)	7.25(9)	7.38(4)	6.90(1)
7.65(1)	7.38(4)	7.57(5)	7.02(2)
7.75(1)	7.63(5)	7.71(6)	7.25(4)
8.0–8.4 S	7.9(2)	8.0–8.4 S	7.37(3)
8.76(4)	8.0–8.4 S	8.54(4)	7.56(3)
9.02(1)	8.45(1)	8.75(8)	7.67(2)
9.27(4)	8.77(3)	9.01(1)	7.98(4)
9.57(2)	8.88(2)	9.26(3)	8.54(3)
9.98(2)	9.08(2)	9.43(2)	8.97(2)
10.20(3)	9.26(4)	9.63(4)	9.12(2)
>11.5 S	9.56(1)	10.23(2)	9.35(1)
	9.74(2)	>11.5 S	9.59(1)
	9.91(2)		9.70(1)
	10.17(3)		9.93(2)
	>11.5 S		10.81(1)
			11.40(1)
			>12 S

Summary

Spectroscopic and chemical data are presented which furnish strong evidence that the hydrolysis product of a 1,3-dialkylbenzimidazolium salt has an amide structure, N-acyl-N,N′-dialkyl-*o*-phenylenediamine instead of a 1,2,3-trialkyl-2,3-dihydro-2-benzimidazolol structure as previously supposed.

The product derived by subsequent acylation has been established as a diamide, N,N′-diacyl-N,N′-dialkyl-*o*-phenylenediamine rather than the previously supposed 1,2,3-trialkyl-2,3-dihydro-2-benzimidazolol ester.

In view of this disagreement, a critique of prior literature has been presented.

Finally it has been shown that the benzimidazolium hydroxides are stable in aqueous or alcohol solution in the absence of excess soluble base.

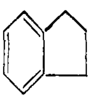
EMERYVILLE, CALIFORNIA RECEIVED AUGUST 23, 1948

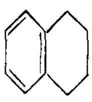
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

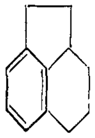
Tetrahydroacenaphthene and the Mills–Nixon Effect

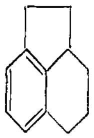
BY WILLIAM S JOHNSON AND HOWARD J. GLENN[1]

The original postulate of Mills and Nixon[2]—that the double bonds of the hydrindene and tetralin molecules are stabilized in the forms I and II due to steric effects exerted on the benzenoid nucleus by the fused alicyclic rings—although not literally acceptable in view of current concepts, nevertheless leads to the suggestion that molecules containing these ring structures might be expected to exhibit behavior attributable to steric inhibition of resonance in which the forms I and II contribute more than the alternate (Kekulé) canonical forms to the electronic state of the molecule. Since all attempts thus far to detect any marked degree of such resonance inhibition have failed, it occurred to us that such an effect might be more recognizable with a molecule such as tetrahydroacenaphthene (IIIa or b) in which the tetralin molecule is superimposed on the hydrindene structure in such a way that the postulated straining effect of the exocyclic rings is reinforced.[3] Thus if this strain were sufficient to render the structure IIIb enough higher in energy than IIIa, it might be expected that tetrahydroacenaphthene and its derivatives would behave chemically more like IIIa than a hybrid of IIIa and IIIb. With a view to studying this hypothesis, we have prepared tetrahydroacenaphthene and certain derivatives, and have made preliminary observation of some of their properties.


I


II


IIIa


IIIb

Tetrahydroacenaphthene was readily secured in 95% yield by hydrogenation of acenaphthene over Raney nickel catalyst. The difficulty in stopping the reduction at the tetrahydro stage, which has been the experience of previous workers,[4] was eliminated by limiting the amount of hydrogen available in the bomb to the calculated quantity. The reduction was thus simply carried out by shaking until all of the hydrogen was absorbed.[5] The in-

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[1] Wisconsin Alumni Research Foundation research assistant, 1946–1947; du Pont predoctorate fellow 1947–1948. Present address: Abbott Laboratories, North Chicago, Illinois.

[2] Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

[3] This hypothesis involves the assumption—justified only on the basis of examination of crude molecular models—that the mutual fusion of the five-six-membered alicyclic rings of tetrahydroacenaphthene does not in some way counteract the steric influence which these rings independently exert upon the benzenoid nucleus.

[4] (a) v. Braun and Kirschbaum, *Ber.*, **55**, 1680 (1922); (b) Goswami, *Compt. rend.*, **179**, 1269 (1924); (c) Orlow and Belopolski, *Ber.*, **62**, 1226 (1929); (d) Ipatiev, *Ber.*, **42**, 2092 (1909).

[5] We are indebted to Dr. Homer Adkins for suggesting this procedure.

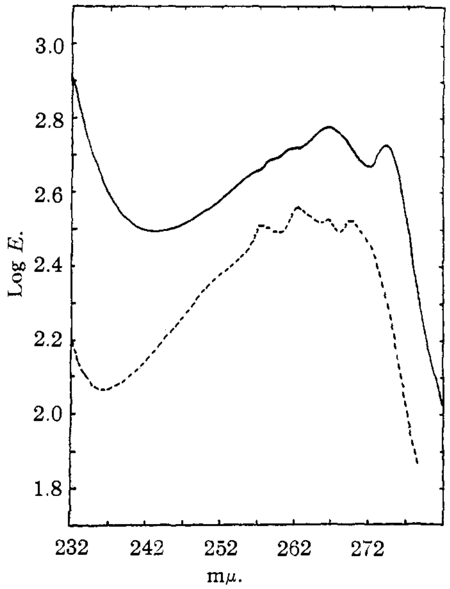
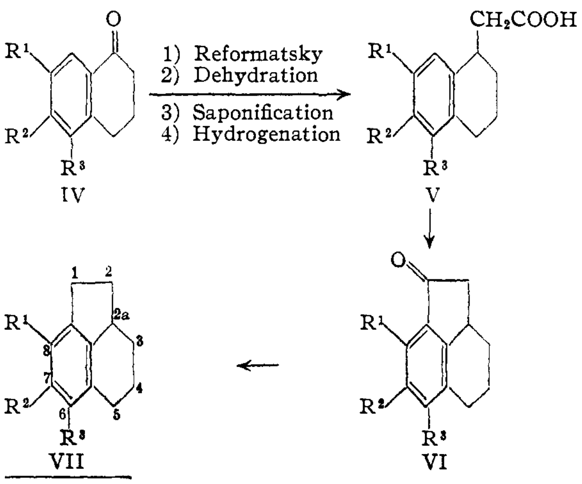


Fig. 1.—Solid line: 2a,3,4,5-tetrahydroacenaphthene; dotted line: 1,2,3-trimethylbenzene.[7]

dex of refraction ($n^{25}D$ 1.5573) of the product was in fair agreement with that of material prepared by synthesis from 1-tetralone according to the scheme represented in the flow sheet (formulas IV → VII, $R^1 = R^2 = R^3 = H$), but did not agree with that (nD 1.5777) reported for a substance, supposedly tetrahydroacenaphthene prepared by sodium and alcohol reduction of acenaphthene.[6] The MD found for our material was 50.54, while the calculated value is 49.63. The chemical behavior of the hydrocarbon is like that of simple polyalkylbenzenes,[4a] and the ultraviolet absorption spectrum (Fig. 1) resembles that reported[7] for 1,2,3-trimethylbenzene, the former exhibiting a slight bathochromic shift and increase of log E. Tetrahydroacenaphthene did not react with maleic anhydride in refluxing xylene.



Although the hypothesis of "bond fixation" as tested by coupling experiments with hydroxy derivatives of hydrindene and tetralin has been largely abandoned,[8,9] it is suggested[8,9] that there may be a "qualitative" effect in hydrindene from the fact that in strongly alkaline solutions the 5-hydroxy-6-methyl derivative undergoes coupling with diazonium salts somewhat less effectively than 2,4-dimethylphenol or other 5-hydroxyhydrindene derivatives having the 6-position available. If this difference in reactivity is due to steric inhibition of resonance, it might be expected, granting certain assumptions,[3] that similar and possibly more pronounced behavior would be observed with the appropriately substituted hydroxytetrahydroacenaphthene. Accordingly VII ($R^1 = OH$, $R^2 = R^3 = H$) and VII ($R^1 = H$, $R^2 = OH$, $R^3 = CH_3$) might be expected to undergo coupling less effectively than VII ($R^2 = OH$, $R^1 = R^3 = H$) or than β-naphthol. These tricyclic phenols were, therefore, synthesized from the corresponding 1-tetralones, IV, by the scheme outlined in the accompanying flow sheet and the coupling behavior studied. In those cases where $R^2 = OCH_3$ the cyclization step V → VI was effected by the inverse Friedel–Crafts method.[10] The phenol, m. p. 98–99°, obtained by v. Braun and Kirschbaum[4a] by alkaline fusion of the sulfonic acid from direct sulfonation of tetrahydroacenaphthene and presumed to be the 7-hydroxy derivative, was shown to be a mixture.

The coupling experiments were carried out with p-nitrobenzenediazonium chloride at controlled alkalinity by approximately the same method employed by Lothrop.[8] The results which are summarized in Table I indicate that all of the hydroxytetrahydroacenaphthenes have comparably highly reactive coupling centers. They appear to be somewhat more effective couplers than β-naphthol at pH 11–13 and somewhat less in 0.4 N sodium hydroxide solution. It is striking that under the latter conditions where the test for relative reactivity was expected to be most critical by analogy to the behavior in the hydrindene series,[8]

TABLE I

COUPLING EXPERIMENTS WITH p-NITROBENZENEDIAZONIUM CHLORIDE

Compound	% Yield of crude product at pH 8-10	at pH 11-13	in 0.4 N NaOH	in 1.0 N NaOH
β-Naphthol	100	61	17	0
VII ($R^1 = OH$, $R^2 = R^3 = H$)	98	94	0	0
VII ($R^2 = OH$, $R^1 = R^3 = H$)	95	100	0	0
VII ($R^1 = H$, $R^2 = OH$, $R^3 = CH_3$)	87	100	7.4	0
VII ($R^1 = R^2 = H$)	0	...	..	..

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(6) Fleischer and Siefert, *Ann.*, **422**, 272 (1921).

(7) The curve shown in Fig. 1 was constructed from data given by Conrad-Billroth, *Z. physik. Chem.*, **B29**, 170 (1935).

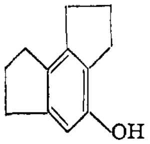
(8) Lothrop, THIS JOURNAL, **62**, 132 (1940).

(9) Fieser, Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, pp. 138–139.

(10) Johnson and Glenn, THIS JOURNAL, **71**, 1092 (1949).

the 6-methyl-7-hydroxy compound, VII (R^1 = H, R^2 = OH, R^3 = CH_3)—in which the position that would be expected to be most active is blocked by the methyl group—is *more* effective in coupling than the compound VII (R^2 = OH, R^1 = R^3 = H), lacking the 6-methyl substituent.

It may be concluded that experiments thus far have failed to reveal any marked steric inhibition of resonance in the tetrahydroacenaphthene system. It is hoped to investigate the coupling of the phenol VIII which would be of particular interest, because the benzene nucleus is under the influence of two five-membered rings acting independently, thus eliminating certain assumptions required in the present study.[3]



VIII

Experimental[11]

2a,3,4,5-Tetrahydroacenaphthene, VII (R^1 = R^2 = R^3 = H).—In a steel bomb (total void 270 ml.) was placed 30.8 g. (0.20 mole) of acenaphthene,[12] m. p. 94–94.5°, and enough ethanol to bring the total volume of suspension to 115 ml. at 23°. One-fourth teaspoon of Raney nickel catalyst[13] was added and hydrogen introduced to a pressure of 1010 p. s. i. (0.40 mole at 23°). The temperature was raised slowly as the bomb was shaken. At 100° the hydrogenation became rapid and slightly exothermic raising the temperature to 115°, and after fifteen minutes the hydrogenation appeared to be complete. The shaking was continued at 110° for an additional thirty minutes, and then the mixture was worked up in the usual way. The product was distilled through a 20-cm. modified Widmer column giving 29.84 g. (95% yield) of colorless hydrocarbon, b. p. 113.5–114° (10 mm.), n^{25}_{D} 1.5573. A sample of crude hydrogenation product was distilled through a 44-cm. Fenske column packed with glass helices and the refractive index was practically constant throughout, n^{25}_{D} 1.5570–1.5578; d^{25}_{4} 1.0082; M_{D} (found) 50.54, M_{D} (calcd.) 49.63.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.25; H, 8.79.

The absorption spectrum (Fig. 1) was determined in ethanol on a Beckman ultraviolet spectrophotometer: λ max. 266 mμ (log E 2.77), 274 (2.72).

Sulfonation of 2a,3,4,5-tetrahydroacenaphthene at 0° according to the method described by von Braun and Kirschbaum[4a] did not proceed satisfactorily, so the following modification was adopted.

A mixture of 16.80 g. of the hydrocarbon and 26.0 g. of 97% sulfuric acid was shaken vigorously for one hour with occasional cooling to maintain the temperature at about 23°. The dark red viscous solution was allowed to stand at room temperature overnight, then poured into 100 ml. of water. The solution was treated with Norit, washed once with ether to remove some unchanged hydrocarbon, neutralized with sodium carbonate and treated (at 65°) with about 50 ml. of saturated sodium chloride solution. On cooling 20.10 g. of crude sodium tetrahydroacenaphthenesulfonate crystallized. It was recrystallized from water before being employed in the alkaline fusion.

Alkaline Fusion of Sodium Tetrahydroacenaphthenesulfonate.—The procedure of von Braun and Kirschbaum,[4a] reported to give 10–15% yields, could not be repeated successfully. The following modification gave yields of phenol as high as 20%.

A mixture of 3.00 g. of dried sulfonate, 6.0 g. of potassium hydroxide and 4.0 g. of sodium hydroxide was placed in a steel bomb. The system was flushed with nitrogen, the bomb sealed, and heated with shaking for one and one-quarter hours as the temperature was raised to 335°. After an additional hour at this temperature, the bomb was cooled and the product worked up in the usual manner. The phenolic material after clarification with Norit was obtained as colorless crystals, m. p. 89.5–93.5° with previous softening; yield 0.40 g. Evaporative distillation at 110–120° (0.1 mm.) gave material (94% recovery) melting at 94.5–95.5°. A second evaporative distillation raised the m. p. to 96–97.2° with softening at 95°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.09. Found: C, 82.55; H, 7.97.

Recrystallization of this phenol from ethyl acetate–petroleum ether (60–68°) did not improve the melting point (*cf.* the behavior of 8-hydroxy-2a,3,4,5-tetrahydroacenaphthene described below). A mixture with 7-hydroxy-2a,3,4,5-tetrahydroacenaphthene, m. p. 96.8–97.6°, prepared as described below, melted at 76–94° with softening at 71°. A mixture with the 8-hydroxy compound, m. p. 99.6–102.6°, melted at 92.5–98.5° with softening at 89°.

The crude aryloxyacetic acid derivative prepared from 0.103 g. of the phenol, 0.40 ml. of 33% sodium hydroxide, 0.30 ml. of a 50% solution of chloroacetic acid in water and 1.5 ml. of water according to the usual procedure[14] amounted to 0.068 g. (50% yield) and melted with dec. at 183–184° and softening at 179°. Successive recrystallizations from ethyl acetate–petroleum ether (60–68°) gave material with the m. ps. 190.5–192°, 194.5–198.5°, 196–197.5°, the last crystallizate amounting to 7 mg.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.48; H, 6.74.

On admixture with the aryloxyacetic acid derivative of 8-hydroxy-2a,3,4,5-tetrahydroacenaphthene, m. p. 202–203°, the m. p. was 197–200°.

Synthesis of Tetrahydroacenaphthene Derivatives from Tetralones

The general scheme of synthesis is outlined in the flow sheet in the discussion part. For the Reformatsky reaction the procedure described by Bachmann, Cole and Wilds[15] with slight modifications proved most successful. The zinc was prepared from pure zinc foil which was cleaned with sandpaper, then cut into one-eighth inch squares and activated as described.[15] The proportion of solvent was decreased considerably, and mechanical stirring (mercury-sealed Hershberg wire stirrer) was employed throughout the heating period. No attempt was made to purify the hydroxy ester which was isolated in the crude form by evaporation of the ether–benzene solution and then dehydrated by refluxing for thirty minutes with 88–90% formic acid (about 2 ml. per gram of starting ketone). The acid was evaporated on the steam-bath in a current of air, and the brown oily residue saponified by refluxing for three and one-half hours with dilute methanolic potassium hydroxide (about 2–2.5 ml. each of methanol and 20% potassium hydroxide per gram of starting ketone). The methanol was removed on the steam-bath in a current of air, and the mixture diluted with two volumes of water. After cooling, the alkaline solution was washed with ether to remove unsaponified material, and after clarification with Norit, was acidified slowly in the cold with vigorous stirring. The unsaturated acid was thus obtained as a pale tan to colorless solid, melting over a wide range. This product was pure enough for low pressure hydrogenation in ethyl acetate solution over 5% palladium on charcoal,[16] which afforded the tetrahydronaphthylacetic acid V

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[11] Unless otherwise specified all melting points are corrected.

[12] Reilly Tar and Chemical Corp. commercial grade, once recrystallized from alcohol.

[13] Mozingo, *Org. Syn.*, **21**, 14 (1941).

[14] McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1946, p. 247.

[15] Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 824 (1940).

[16] Catalyst B, Mozingo, *Org. Syn.*, **26**, 77 (1946).

in good yield. The remaining steps of the synthesis are described below in connection with the individual cases.

2a,3,4,5-Tetrahydroacenaphthene, VII ($R^1 = R^2 = R^3 = H$).—When the procedure of Schroeter[17] was employed for the Reformatsky reaction and the product hydrogenated either directly or after dehydration with phosphorus pentoxide, a very impure acid was produced which was shown to consist of a mixture of the desired 1,2,3,4-tetrahydronaphthyl-1-acetic acid (about 43%) and 1-naphthylacetic acid (about 47%) evidently produced by disproportionation. The latter substance remained unchanged when the mixture was treated with hydrogen fluoride and was identified by conversion to the amide.

The disproportionation was not observed with the procedure described above. Thus from 15.0 g. of 1-tetralone, 30.0 g. of zinc,[18] 16 ml. of methyl bromoacetate, and 200 ml. of 1 to 1 ether–benzene there was obtained after dehydration and saponification, 14.2 g. (73% yield) of mixture of unsaturated acids, m. p. 86–96°. Hydrogenation of 13.0 g. of this material in 75 ml. of ethyl acetate at 2–3 atmospheres over a total of 5 g. of 5% palladium on charcoal,[16] afforded 12.1 g. (92% yield) of crude 1,2,3,4-tetrahydronaphthyl-1-acetic acid, V ($R^1 = R^2 = R^3 = H$) which was obtained as a viscous oil (reported m. p. 35–36°[19]). Cyclization of 11.0 g. with hydrogen fluoride[20] (six hours at room temperature) gave 7.40 g. (74% yield) of almost colorless crystalline 2a,3,4,5-tetrahydro-1-acenaphthenone, VI ($R^1 = R^2 = R^3 = H$), m. p. 100–101.5° (reported,[21] 102°). A solution of 7.00 g. of the ketone in 75 ml. of acetic acid containing 0.5 ml. of 60% perchloric acid[22] was hydrogenated over 2.0 g. of 5% palladium on charcoal catalyst,[16] at 2–3 atmospheres. In this case the hydrogenation did not go to completion and it was necessary to remove the catalyst, treat the partially reduced material with Raney nickel, and then to continue the reduction with fresh palladium catalyst. The mixture was filtered, made alkaline with excess potassium hydroxide solution and the hydrocarbon extracted. Distillation through a 20-cm. modified Widmer column gave 1.83 g. of colorless material, b. p. 125–126° (17 mm.), $n^{25}D$ 1.5566. The remainder of the product was retained as hold-up in the distillation apparatus.

8-Hydroxy-2a,3,4,5-tetrahydroacenaphthene, VI ($R^1 = OH$, $R^2 = R^3 = H$).—From 34.7 g. of 7-methoxy-1-tetralone,[10] m. p. 61–62°, 60 g. of zinc,[18] 28 ml. of methyl bromoacetate, and 400 ml. of 1 to 1 ether–benzene, there was obtained after dehydration and saponification, 41.8 g. (97% yield) of mixture of unsaturated acids, m. p. 122.5–138.5°. Hydrogenation of 10.9 g. of material, which was recrystallized once from alcohol, in 50 ml. of ethyl acetate at 2–3 atmospheres over 1.0 g. of 5% palladium on charcoal[16] was complete in about twenty minutes and afforded after trituration of the crude product with petroleum ether (40–60°) 10.02 g. of crystalline 7-methoxy-1,2,3,4-tetrahydronaphthyl-1-acetic acid, V ($R^1 = OCH_3$, $R^2 = R^3 = H$), m. p. 88.5–89.5° (reported,[23] 88–89°). An additional 0.36 g. of crude material, m. p. 77–85° was obtained from the petroleum ether solution.

A 10.00-g. sample of the above acid, m. p. 88.5–89.5°, was cyclized with hydrogen fluoride[20] (twenty hours at room temperature) to give 8.85 g. (96% yield) of crystalline **8-methoxy-2a,3,4,5-tetrahydro-1-acenaphthenone, VI ($R^1 = OCH_3$, $R^2 = R^3 = H$)**, m. p. 98–99.5°. This material seemed to be somewhat unstable showing a tendency to turn yellow during recrystallization. It was obtained as plates or needles from benzene–petroleum ether (60–68°), and after three recrystallizations melted at 95.8–98° with slight previous softening.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.30; H, 6.80.

A 10.10-g. sample of the above ketone was reduced by the Clemmensen method,[24] and 5.00 g. of the resulting 9.12 g. (97% yield) of oil,[25] was demethylated by refluxing with 50 ml. of 48% hydrobromic acid and 25 ml. of glacial acetic acid for four and one-half hours in an atmosphere of nitrogen. Since insoluble oil still remained after this treatment 50 ml. of acetic acid was added and refluxing continued for eight and one-half hours. The mixture was concentrated to about one-third its volume, diluted with water, and extracted with ether. The ether solution was washed with 5% sodium bicarbonate, and the phenol was then extracted with 5% potassium hydroxide followed by Claisen alkali.[26] The alkaline extracts were combined and acidified liberating 3.11 g. of tan crystalline phenol, m. p. 96–98.5°. An additional 0.50 g. of material of the same m. p. was obtained from the filtrate by extraction, thus making the total yield 78%. Evaporative distillation at 145–150° (0.1 mm.) gave in 88% recovery colorless crystals, m. p. 102–103° with slight previous softening. This material proved to be quite sensitive and on boiling in 60–68° petroleum ether the solution became turbid as a small amount of insoluble material gradually precipitated. After two recrystallizations from this solvent (each time turbidity necessitated filtration), the product melted at 101.5–102.5° to a cloudy liquid which did not clear up completely until about 180°. The high-melting contaminant could be removed by evaporative distillation. After a second evaporative distillation the product was obtained as pale yellow needles, m. p. 99.5–102.5°. The lower m. p. than that observed with the crude sample may have been due to polymorphism.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.09. Found: C, 82.52; H, 8.00.

The **aryloxyacetic acid derivative** was prepared from 0.121 g. of 8-hydroxy-2a,3,4,5-tetrahydroacenaphthene, 0.40 ml. of 33% sodium hydroxide, 0.30 ml. of 50% chloroacetic acid in water, and 0.5 ml. of water according to the usual procedure.[14] The crude derivative amounted to 0.068 g. (42% yield), m. p. 202–203° with darkening and softening at 200°. Recrystallization from ethyl acetate gave colorless needles, m. p. 202–203° (turning red).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.22; H, 6.61.

7-Hydroxy-2a,3,4,5-tetrahydroacenaphthene, VII (R^2 OH, $R^1 = R^3 = H$).—From 10.0 g. of 6-methoxy-1-tetralone,[27] m. p. 76–77.5°, 20 g. of zinc,[18] (10 ml.) of methyl bromoacetate, and 150 ml. of 1 to 1 ether–benzene, there was obtained after dehydration and saponification 9.50 g. (77% yield) of mixture of unsaturated acids, melting at about 64°, resolidifying at about 90° and remelting at 100–111°. Hydrogenation of 8.30 g. of this product in 75 ml. of ethyl acetate at 2–3 atmospheres over a total of 3 g. of 5% palladium on charcoal,[16] was complete after about three hours, and afforded 8.00 g. (95% yield) of crude 6-methoxy-1,2,3,4-tetrahydronaphthyl-1-acetic acid, V ($R^2 = OCH_3$, $R^1 = R^3 = H$), m. p. 76–80°. Recrystallization from benzene–petroleum ether (60–68°) raised the m. p. to 79–81.5°. In other runs material of better quality, m. p. 81–83.5°, was obtained although in lower (83%) yield. Recrystallization gave an 88% recovery of material m. p. 82.5–84° (reported, 84°[28] and

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[17] Schroeter, *Ber.*, **58B**, 713 (1925).

[18] This represents the total amount of zinc which was added in six portions (see ref. 15). The unchanged zinc was recovered and used again, after reactivation. This material was found to be more reactive than the fresh metal.

[19] von Braun, Gruber and Kirschbaum, *Ber.*, **55B**, 3664 (1922).

[20] See the procedure in "Organic Reactions," Vol. II, 1944, p. 158.

[21] von Braun and Reutter, *Ber.*, **59B**, 1922 (1926).

[22] Kindler and Dachi-yin-Kwok, *Ann.*, **554**, 9 (1943); Rosenmund and Karg, *Ber.*, **75**, 1850 (1942); Baker and Jenkins, THIS JOURNAL, **68**, 2102 (1946).

[23] Plimmer, Hill and Short, *J. Chem. Soc.*, 694 (1938).

[24] Martin in Adams, "Organic Reactions," Vol. I, 1942, p. 163.

[25] This product did not give a test with 2,4-dinitrophenylhydrazine reagent.

[26] Claisen, *Ann.*, **418**, 96 (1919); 35 g. of potassium hydroxide in 25 g. of water diluted to 100 ml. with methanol.

[27] Prepared by the procedure of Stork, THIS JOURNAL, **69**, 576 (1947).

[28] Schwenk and Papa, *ibid.*, **67**, 1432 (1945).

87°[29]). The cyclization of this acid to 7-methoxy-2a,3,4,5-tetrahydro-1-acenaphthenone, VI (R^2 = OCH_3, R^1 = R^3 = H) is described elsewhere.[10] A 1.015 g. sample of the ketone was reduced by the Clemmensen method[24] and 0.711 g. of the resulting 0.732 g. (77% yield) of oil,[25] was demethylated by refluxing with 10 ml. of 48% hydrobromic acid and 15 ml. of acetic acid for four hours in an atmosphere of nitrogen. The product was worked up essentially as described above for the 8-methoxy isomer except that the crude phenol being oily was separated by extraction. The total yield of crude semi-solid material was 0.620 g. (94%). Evaporative distillation at 100–110° (0.1 mm.) gave in about 65% recovery colorless crystalline phenol, m. p. 89–95°. The pure material was obtained by crystallization from petroleum ether (60–68°) followed by evaporative distillation. It was obtained as colorless needles, m. p. 96–97.6°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.09. Found: C, 82.68; H, 7.96.

6-Methyl-7-hydroxy-2a,3,4,5-tetrahydroacenaphthene, VII (R^1 = H, R^2 = OH, R^3 = CH_3).—5-Methyl-6-methoxytetralone-1, IV (R^1 = H, R^2 = OCH_3, R^3 = CH_3), was prepared according to the method of Martin and Robinson.[30] By slight modifications in the oxidation step it was possible to improve the yield of ketone as follows. A solution of 11.4 g. of chromic oxide in 70 ml. of acetic acid and 10 ml. of water was added slowly over a period of one and one-half hours to a stirred solution of 11.4 g. of 5-methyl-6-methoxytetralin, m. p. 49–50°, in 115 ml. of acetic acid, the internal temperature being maintained at 10–15°. After the addition was complete the mixture was stirred for one and one-half hours in the cold (ice-bath) and two hours at room temperature. After eighteen hours at room temperature (without stirring) 25 ml. of methanol was added, the mixture stirred for thirty minutes and then concentrated under reduced pressure. The gummy residue was treated with 200 ml. of water and extracted with ether. The ether solution was washed with 5% sodium carbonate solution, saturated salt solution, clarified with Norit, and dried over anhydrous potassium carbonate. Evaporation of the ether gave 10.28 g. (83% yield) of yellow ketone, m. p. 106.5–109.5°. Martin and Robinson[30] report an average yield of 70% of light yellow ketone, m. p. 103–105°. Our material after two recrystallizations from methanol melted at 109.5–111° (reported m. p.,[30] 112–113°).

From 4.23 g. of the above ketone, 10 g. of zinc,[18] 8 ml. of methyl bromoacetate and 80 ml. of 1 to 1 ether–benzene there was obtained after dehydration and saponification 3.84 g. (74% yield) of mixture of unsaturated acids, m. p. 146–154° (dec.). Hydrogenation of 3.00 g. of this product in 25 ml. of ethyl acetate at atmospheric pressure over a total of 1.5 g. of 5% palladium on charcoal,[16] was complete after about fifteen hours, and afforded 2.77 g. (91% yield) of **5-methyl-6-methoxy-1,2,3,4-tetrahydronaphthyl-1-acetic acid, V,** R^1 = H, R^2 = OCH_3, R^3 = CH_3, m. p. 154–156°. Recrystallization from ethyl acetate–petroleum ether (60–68°) gave a total of 2.38 g. of colorless blades, m. p. 158.5–159°. Further recrystallizations raised the m. p. to 159.2–159.8°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.95; H, 7.47.

The cyclization of the above acid to 6-methyl-7-methoxy-2a,3,4,5-tetrahydro-1-acenaphthenone, VI (R^1 = H, R^2 = OCH_3, R^3 = CH_3), is described elsewhere.[10] A 0.173-g. sample of this ketone, m. p. 123–125.5°, in 15 ml. of acetic acid containing 0.2 ml. of 60% perchloric acid[22] was hydrogenated at atmospheric pressure over 0.150 g. of 30% palladium on charcoal.[31] The uptake of hydrogen ceased after one and three-quarters hours, the calculated amount being absorbed. The mixture was filtered, diluted with water, neutralized with solid sodium bicarbonate and extracted with ether. The ether solution was washed with water, then with saturated salt solution and dried over anhydrous potassium carbonate. Evaporation of the ether left 0.162 g. of a colorless oil which crystallized on drying, m. p. 35–40.5°. Two recrystallizations from petroleum ether (40–60°) solution cooled in a Dry Ice–acetone bath gave colorless plates of **6-methyl-7-methoxy-2a,3,4,5-tetrahydroacenaphthene, VII** (R^1 = H, R^2 = OCH_3, R^3 = CH_3), m. p. 42–44°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.94; H, 8.74.

In another experiment it was noted that the perchloric acid was unnecessary for complete hydrogenolysis, but the rate of reaction was decreased, nine hours being required to reduce 0.458 g. of ketone. The yield was 0.430 g., m. p. 39.5–42.5°. A 0.430-g. sample of this material was demethylated by refluxing with 5 ml. of 48% hydrobromic acid and 10 ml. of acetic acid for ten hours in an atmosphere of nitrogen. The product was worked up essentially as described above for the 8-methoxy homolog to give 0.344 g. (86% yield) of crude tan crystalline phenol, m. p. 103–107.5°. Evaporative distillation at 130–140° (0.5 mm.) gave a 95% recovery of colorless needles, m. p. 106.5–108°. Recrystallization from ethyl acetate–petroleum ether (60–68°) gave colorless prisms, m. p. 109–110.4°.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.98; H, 8.35.

Coupling Experiments

Five grams of *p*-nitroaniline hydrochloride, prepared by treating the amine in dioxane solution with anhydrous hydrogen chloride, was diazotized by the procedure of Hantzsch and Jochem[32] with the following modifications. *n*-Butyl nitrite was used instead of amyl nitrite. Attempts to use the dried diazonium salt for preparing a standard solution did not appear promising since water-insoluble material was produced. A satisfactory procedure consisted in separating the diazonium salt by filtration, washing well with anhydrous ether to remove acetic acid and dissolving the ether-moist product in water at 0°. The solution was diluted to 250 ml. and standardized by titration of an aliquot with alkali using phenolphthalein as an indicator. The solution then was shown to contain 0.106 millimole of *p*-nitrobenzenediazonium chloride per ml. of solution.

The coupling procedure was as follows: The phenol (0.201–0.202 millimole) was dissolved in 10 ml. of buffered (or alkaline) solution and 5 ml. of purified[33] dioxane, and the solution cooled to 0° in an ice-bath. To this was added 3.00 ml. of the standardized diazonium salt solution (also at 0°) and the mixture was kept at 0° for twenty minutes. The mixture was then warmed on the steam-bath for twenty minutes and the dark red precipitate separated by filtration, washed with water, digested for five to ten minutes with warm 5% potassium carbonate solution (steam-bath), separated by filtration, washed with the carbonate solution and finally with water. The dyes were dried to constant weight in a vacuum desiccator and the melting points determined on a micro hot stage.

The melting point of the crude coupling products from β-naphthol varied from 251–254° to 253–255° (reported m. p.,[34] 250–251°).

The crude coupling product obtained from 8-hydroxy-2a,3,4,5-tetrahydroacenaphthene at *p*H 8–10 had the m. p. 211–216° and at *p*H 11–13, 213–217°. A sample purified by recrystallization from dioxane was obtained as red-brown needles, m. p. 219.5–220.5°.

Anal. Calcd. for $C_{18}H_{17}O_3N_3$: C, 66.86; H, 5.30. Found: C, 66.91; H, 5.04.

The crude coupling product obtained from 7-hydroxy-2a,3,4,5-tetrahydroacenaphthene at *p*H 8–10 had the m. p. 168–172° and at *p*H 11–13, m. p. 172–175°. A

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[29] Burnop, Elliott and Linstead, *J. Chem. Soc.*, 727 (1940).

[30] Martin and Robinson, *ibid.*, 491 (1943).

[31] Linstead and Thomas, *ibid.*, 1127 (1940).

[32] Hantzsch and Jochem, *Ber.*, **34**, 3337 (1901).

[33] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 2nd ed., 1941, p. 368.

[34] Charrier and Ferreri, *Gazz. chim. ital.*, **44**, 165 (1914).

sample purified by recrystallization from dioxane–petroleum ether (b. p. 60–68°), was obtained as red-brown needles, m. p. 181.5–183°.

Anal. Calcd. for $C_{18}H_{17}O_3N_3$: C, 66.86; H, 5.30. Found: C, 66.73; H, 5.10.

The crude coupling product from 6-methyl-7-hydroxy-2a,3,4,5-tetrahydroacenaphthene obtained at *p*H 8–10 had the m. p. 202–210°; at *p*H 11–13, m. p. 192–197°; in 0.4 *N* sodium hydroxide, m. p. 200–206°. A sample purified by recrystallization from dioxane was obtained as red-brown needles, m. p. 207–209°.

Anal. Calcd. for $C_{19}H_{19}O_3N_3$: C, 67.64; H, 5.68. Found: C, 67.68; H, 5.35.

Summary

2a,3,4,5-Tetrahydroacenaphthene has been prepared both by selective hydrogenation of acenaphthene and by synthesis from 1-tetralone. The properties of the hydrocarbon resemble those of simple polyalkylbenzenes.

7-Hydroxy-, 8-hydroxy-, and 6-methyl-7-hydroxy-2a,3,4,5-tetrahydroacenaphthene were prepared by synthesis from the appropriately substituted tetralones, and their coupling behavior with *p*-nitrobenzenediazonium chloride was observed at various concentrations of alkali. All of the phenols were comparably effective couplers, and it may be concluded that experiments thus far have failed to reveal any marked steric inhibition of resonance in the tetrahydroacenaphthene ring system.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Intramolecular Acylation. II.[1] The Inverse Friedel–Crafts Method

BY WILLIAM S. JOHNSON AND HOWARD J. GLENN[2]

Of the numerous methods available for effecting ring closure of β-arylpropionic or γ-arylbutyric acid derivatives to cyclic ketones, the intramolecular Friedel–Crafts reaction of the acid chloride with aluminum chloride promises to be particularly useful for acids like β-*p*-methoxyphenylpropionic acid, which are resistant to cyclization due to unfavorable reactivity of the aromatic nucleus.[1] Excellent yields have not been generally realized by this method, probably because a large proportion of the cylizations reported in the literature have been conducted under unfavorable conditions. In the present work we are describing a cyclization technique which combines the best features suggested by previous experience.[3] This procedure, which has been tested with nine acids of varying susceptibility to cyclization, apparently differs from others previously reported only in minor respects, some of which nevertheless, have proved to be critical factors and merit emphasis. (1) It has been found important to use acids of good quality, since small amounts of impurities may result in a very impure product. (2) For preparation of the acid chloride, phosphorus pentachloride instead of thionyl chloride was employed because of occasional complications which have been reported to attend the use of the latter.[4] The phosphorus oxychloride produced was always carefully removed, because its presence has been shown to interfere with the cyclization giving lower yields.[5,1] (3) The Friedel–Crafts step was carried out in the inverse manner, *i.e.*, the acid chloride (in benzene solution) was added to a stirred suspension of aluminum chloride in benzene. This technique has the advantage over the conventional method of (*a*) facilitating temperature control through regulation of the rate of addition of the acid chloride and (*b*) maintaining a high concentration of catalyst, a condition that has been shown in *inter*molecular acylation to minimize self-condensation of the resulting ketone,[6] which is a side-reaction that also competes with certain *intra*molecular acylations.[7] The yields for fifteen cases that were found in the literature in which the inverse Friedel–Crafts cyclization was employed apparently without particular regard to other critical factors, were nevertheless generally well above average,[3] thus suggesting a real advantage in this method. (4) Since heating has been shown to have undesirable effects,[7] the temperature of the reaction mixture was never permitted to rise above 25° during the cyclization step. Even with acids that are unusually resistant to cyclization, this treatment afforded excellent yields of ketones. Thus with β-*p*-methoxyphenylpropionic acid, I (R^1 = OCH_3, R^2 = H), which is notoriously resistant to cyclization,[1,8] 6-methoxy-1-hydrindone, II (R^1 = OCH_3, R^2 = H), of fair purity was obtained in practically quantitative yield on a 3-g. scale.

The ring closure of α,γ-diphenylbutyric acid, III (R^1 = H, R^2 = C_6H_5), afforded an interesting test since Newman[9] had studied this cyclization

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(1) See Johnson and Shelberg, THIS JOURNAL, **67**, 1853 (1945), for the first communication of this series.

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(3) Johnson in Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1944, Chapter 4.

(4) See ref. 3, p. 137.

(5) Newman, THIS JOURNAL, **62**, 870 (1940).

(6) Calloway and Green, *ibid.*, **59**, 809 (1937).

(7) See ref. 3, p. 130.

(8) Heinzelmann, Kolloff and Hunter, THIS JOURNAL, **70**, 1386 (1948).

(9) See Procedure III, ref. 3, p. 145.