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

The Hyperconjugative Effect of Methylene Groups in 5-Indanylphenylchloromethane and 5,6,7,8-Tetrahydro-2-naphthylphenylchloromethane

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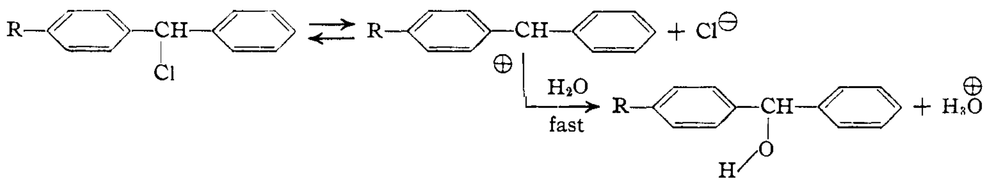
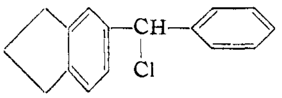
Kinetic studies dealing with the hydrolysis of benzhydryl chlorides[2] have shown the rate determining step of this reaction to be "unimolecular," and it is now generally agreed that this rate controlling step essentially involves an ionization of the halide.

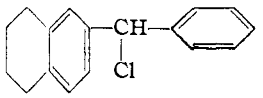


It is also known[2] that para alkyl groups increase the rate of hydrolysis of benzhydryl chlorides in the order $(CH_3)_3C- < (CH_3)_2CH- < CH_3CH_2- < CH_3-$. Since these rate differences can reasonably be attributed[2] to hyperconjugation (*i. e.*, no bond resonance) which stabilizes preferentially the transition state, such kinetic studies offer a sensitive measure of hyperconjugative effects in related substituents.

In a series of papers from this Laboratory[3] it has been reported that measurable differences exist in the steric effect of methylene groups in five- and six-membered rings. In order to determine whether or not certain well known differences in the aromatic rings of indane and tetralin can be attributed in part to inequalities in the hyperconjugative effects of the methylene groups in these two hydrocarbons, we have measured the rates of hydrolysis of 5-indanylphenylchloromethane (I) and 5,6,7,8-tetrahydro-2-naphthylphenylchloromethane (II).



I



II

Kinetic constants for these first-order reactions at 0° and 25°, the activation energies (E) and the non-exponential rate factors (B) were found to be identical within the limits of experimental error (Table I). It is therefore concluded that no appreciable difference in the degree to which hyperconjugation contributes to these systems (I and II) exists.

In order to relate the hyperconjugative effect of the *p*-methylene group in fused five- and six-membered rings to that of the alkyl substituents previously studied,[2] the rate constants for the hydrolysis of benzhydryl chloride and *p*-methylbenzhydryl chloride were determined under the same conditions. These values checked those previously reported[2] very satisfactorily (Table I). The hyperconjugative effect of the *p*-methylene group in fused five- and six-membered rings is approximately equal to that of the *p*-ethyl group.

TABLE I

Substituted benzhydryl chloride	$k_{25°}$ × 10^3 (sec.$^{-1}$)[a]	$k_{0°}$ × 10^5 (sec.$^{-1}$)	*E* act. (kcal.)	*B* × 10^{-11} (sec.$^{-1}$)
Compound I	1.306	6.34	19.6	2.96
Compound II	1.300	6.30	19.6	3.00
Benzhydryl chloride	0.0723	0.284	20.9	1.65
	0.0728[b]	0.282[b]	21.0[b]	1.91[b]
p-Methyl chloride	1.559	8.32	18.9	1.28
	1.560[b]	8.35[b]	18.9[b]	1.23[b]
p-Ethyl chloride	1.260[b]	6.26[b]	19.4[b]	2.19[b]

[a] The solvent for all of these determinations was prepared by diluting four volumes of acetone with one volume of water. [b] These values were determined by Hughes, Ingold and Taher, ref. 2.

Since it has recently been indicated that the hyperconjugation of methylene groups is subject to steric effects,[4] the hydrolysis of 3,4-pentamethylenediphenylchloromethane is now being studied.

Preparation of Compounds

In order to be certain of the structure of the compounds, 5-indanyl phenyl ketone was first prepared by the Friedel–Crafts reaction of 5-indancarbonyl chloride with benzene. The required 5-indancarboxylic acid was prepared either from 5-aminoindan via the nitrile,[5] or from the mixture of 4- and 5-indanyl methyl ketones[6] by means of the intermediate 5-indanacylpyridinium iodide.[7] This pyridinium salt was hydrolyzed to the acid with aqueous sodium hydroxide. In contrast, the haloform reaction on the mixture of 4- and 5-indanyl methyl ketones using bromine and alkali gave a mixture of acids which was very difficult to separate.[6] The 5-aminoindan was most conveniently prepared by the catalytic reduction of 5-

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[1] Abstracted from a thesis by Kotaro Murai, presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the Ph.D. degree, October, 1949.

[2] Hughes, Ingold and Taher, *J. Chem. Soc.*, 949 (1940).

[3] Arnold and Richter, THIS JOURNAL, **70**, 3505 (1948).

[4] Baddeley, Chadwick and Rawlinson, *Nature*, **164**, 833 (1949).

[5] Lindner, Schmitt and Zaunbauer, *Monats.*, **72**, 216 (1939).

[6] Borsche and Pommer, *Ber.*, **54**, 102 (1921).

[7] L. C. King, THIS JOURNAL, **66**, 894 (1944).

nitroindan[8] using a Raney nickel catalyst in ethanol. After seed crystals were available, pure 5-indanyl phenyl ketone could be readily prepared by the direct benzoylation of indan using the Friedel–Crafts reaction.[6]

5,6,7,8-Tetrahydro-2-naphthyl phenyl ketone was also prepared by two different routes; first, by the condensation of 5,6,7,8-tetrahydro-2-naphthoyl chloride with benzene using aluminum chloride. The required 5,6,7,8-tetrahydro-2-naphthoic acid was obtained from the impure 5,6,7,8-tetrahydro-2-naphthyl methyl ketone[9] by means of the preparation, crystallization and hydrolysis of 5,6,7,8-tetrahydro-2-naphthacylpyridinium iodide.[7] Most of the desired ketone was obtained by the second procedure, the direct benzoylation of tetralin.[9,10]

Both 5-indanyl phenyl ketone and 5,6,7,8-tetrahydro-2-naphthyl phenyl ketone were reduced to their respective carbinols by means of either a Raney nickel or a copper chromium oxide catalyst in ether solution. The former catalyst was preferred because the temperature required for reduction was lower. The carbinols were converted to the respective substituted benzhydryl chlorides (I and II) by treatment with hydrogen chloride in benzene solution.[11] All of the chlorides were stored under nitrogen in sealed ampules and were redistilled immediately prior to the kinetic determination.

Experimental[12]

5-Indanacylpyridinium Iodide.—A mixture of 16.0 g. (0.1 mole) of 4-and 5-indanyl methyl ketone, 25.4 g. (0.20 mole) of iodine and 50 ml. of pyridine was heated for one hour on the steam-bath. After being cooled overnight in the refrigerator, the solution was filtered. The solid product was washed twice with 100 ml. of ether and then with 100 ml. of water. The product was crystallized from 65% alcohol to give 13.0 g. (35.8%) of 5-indanacylpyridinium iodide, m. p. 203–205°.

Anal. Calcd. for $C_{16}H_{16}INO$: C, 52.62; H, 4.43. Found: C, 52.56; H, 4.73.

5-Indancarboxylic Acid.—A mixture of 25.5 g. (0.079 mole) of 5-indanacylpyridinium iodide, 20.0 g. (0.50 mole) of sodium hydroxide and 400 ml. of water was heated for two hours on the steam-bath. The solution was neutralized with six normal hydrochloric acid and digested for thirty minutes on the steam-bath. After being cooled, the product was separated by filtration. The precipitate was dissolved in 10% sodium carbonate solution, and the solution was boiled with carbon (Norit) for five minutes, then filtered through Hi-Flo. After being neutralized with 6 *N* hydrochloric acid, the mixture was digested on the steam-bath for 30 minutes, cooled, and filtered. In this way, 8.5 g. (75%) of 5-indancarboxylic acid, m. p. 182–183°, was obtained. The reported melting point[5] is 183–184°.

5-Indanyl Phenyl Ketone.—A mixture of 9.0 g. (0.046 mole) of 5-indancarbonyl chloride[13] (prepared from the acid with thionyl chloride), 6.5 g. (0.049 mole) of aluminum chloride and 80 ml. of anhydrous benzene was heated under reflux for two hours. The mixture was poured into a slurry of equal parts of ice and 12 *N* hydrochloric acid. The organic layer was separated, washed with five per cent. sodium carbonate solution, dried over anhydrous calcium chloride, and the solvent was removed. Distillation of the residue yielded 9.0 g. (89%) of 5-indanyl phenyl ketone, b. p. 195–203° (13 mm.) By crystallization from absolute ethanol at −40°, a solid product was obtained, m. p. 35–36°. The compound is reported as an oil, b. p. 203–204° (8 mm.),[14] and as a solid[6] with a melting point of over 40°.

5-Indanyl phenyl ketone, m. p. 35–36°, was also prepared by the direct benzoylation of indan and was crystallized from absolute alcohol at −40°. The oximes obtained from the above ketones both melted at 148–149° and showed no depression of melting point when mixed. The reported melting points of 5-indanyl phenyl ketoxime are 149–152°[14] and 153–154°.[6]

5,6,7,8-Tetrahydro-2-naphthacylpyridinium Iodide.—A mixture of 90 g. (0.516 mole) of 5,6,7,8-tetrahydro-2-(and 1)-naphthyl methyl ketone, 132 g. (0.516 mole) of iodine and 260 ml. of pyridine was warmed on the steam-bath for one hour. The mixture was allowed to stand overnight in the refrigerator and then was filtered. The product was washed twice with 100 ml. of ether and then with 100 ml. of water. After crystallization from 65% alcohol, the yellow product, m. p. 213–214°, weighed 79.0 g. (40.5%).

Anal. Calcd. for $C_{17}H_{18}INO$: C, 53.84; H, 4.78. Found: C, 54.11; H, 5.08.

5,6,7,8-Tetrahydro-2-naphthoic Acid.—A suspension of 79.0 g. (0.208 mole) of 5,6,7,8-tetrahydro-2-naphthacylpyridinium iodide and 80 g. (2 moles) of sodium hydroxide in 500 ml. of water was heated on the steam-bath for two hours. The acid was isolated as described above. After being crystallized from 65% alcohol, the white product, m. p. 153–154°, weighed 25.2 g. (69%). The acid is reported[13] to melt at 152–153°.

5,6,7,8-Tetrahydro-2-naphthyl Phenyl Ketone.—A mixture of 25.0 g. of 5,6,7,8-tetrahydro-2-naphthoyl chloride[13] (prepared from the acid with thionyl chloride), 21.9 g. of aluminum chloride and 75 ml. of anhydrous benzene was heated under reflux for three hours. The product was isolated as described above. Distillation yielded 20.0 g. (60%) of the desired ketone, b. p. 237° (19 mm.). A small sample of the ketone was crystallized from absolute ethanol at −40° and melted at 41–42°. 5,6,7,8-Tetrahydro-2-naphthyl phenyl ketone, m. p. 41–42°, was also prepared by the direct benzoylation of tetralin,[9,10] followed by crystallization from absolute ethanol at −20°. The ketone is reported to have a boiling point of 222–223° (12 mm.)[9] and a melting point of 40.4–41.2°.[10]

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.59; H, 6.73.

Both samples of the ketone formed oximes which melted at 141–142° and which showed no melting point depression when mixed. The reported[9] melting point of 5,6,7,8-tetrahydro-2-naphthyl phenyl ketoxime is 142°.

5,6,7,8-Tetrahydro-2-naphthylphenylcarbinol.—A solution of 110 g. (0.416 mole) of 5,6,7,8-tetrahydro-2-naphthyl phenyl ketone in 250 ml. of ether was reduced at 125° and 1400–1700 pounds per square inch of hydrogen using a Raney nickel catalyst. To insure complete reduction of the ketone, the reduction was continued until slightly more than one mole of hydrogen was absorbed. Three distillations of the product yielded two separate fractions. Fraction I, b. p. 163–165° (2 mm.), n^{25}_{D} 1.5818 weighed 12 g. Fraction II, b. p. 168.5–170° (2 mm.), n^{25}_{D} 1.5910, weighed 44.0 g. (44.5%). Fraction II was the desired carbinol.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.78; H, 7.60. Found: C, 86.01; H, 7.31.

Fraction I was 5,6,7,8-tetrahydro-2-naphthylphenylmethane.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.83; H, 8.16. Found: C, 91.63; H, 8.14.

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(8) Arnold and Zaugg, This Journal, **63**, 1317 (1941).

(9) Scharwin, *Ber.*, **35**, 2511 (1902).

(10) Orchin, Woolfolk and Reggel, This Journal, **71**, 1126 (1949).

(11) Böeseken, *Rec. trav. chim.*, **22**, 301 (1903).

(12) Microanalyses by William Cummings and Ralph Kelly.

(13) v. Braun, Kirschbaum and Schuhmann, *Ber.*, **53**, 1155 (1920).

(14) Fieser and Hershberg, This Journal, **62**, 49 (1940).

5-Indanylphenylcarbinol was obtained from the reduction of 5-indanyl phenyl ketone in ethanol by the procedure described above. By fractional distillation 46.0 g. (45.2%) of the desired carbinol, b. p. 168–172° (5 mm.), $n^{25}\mathrm{D}$ 1.5790, was obtained.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.66; H, 7.19. Found: C, 85.77; H, 7.04.

5-Indanylphenylchloromethane (I).—A solution of 2.0 g. of 5-indanylphenylcarbinol in 50 ml. of anhydrous benzene was cooled to 0°. Anhydrous calcium chloride (10 g.) was introduced and dry hydrogen chloride was bubbled through the mixture for twelve hours. The calcium chloride was replaced with 10 g. of fresh material, and the stream of gas was continued for another twelve hours. The solution was filtered and the benzene removed. Distillation under nitrogen yielded 1.10 g. (50.6%) of the desired chloride, I, b. p. 149–152° (1 mm.), $n^{25}\mathrm{D}$ 1.5920.

Anal. Calcd. for $C_{16}H_{15}Cl$: C, 79.16; H, 6.23; Cl, 14.61. Found: C, 78.92; H, 6.14; Cl, 14.59.

5,6,7,8-Tetrahydro-2-naphthylphenylchloromethane (II) was prepared from the carbinol by the method described above except that the total time of reaction was reduced from 24 to 12 hours. From 2.00 g. of carbinol, 1.13 g. (60%) of the desired chloride, II, b. p. 161–163° (1.5 mm.), $n^{25}\mathrm{D}$ 1.5961.

Anal. Calcd. for $C_{17}H_{17}Cl$: C, 79.52; H, 6.67; Cl, 13.81. Found: C, 79.78; H, 6.46; Cl, 13.76.

Benzhydryl chloride, b. p. 162° (13 mm.), was prepared from benzhydrol by the use of thionyl chloride.

***p*-Methylbenzhydryl chloride**, b. p. 167.5–168° (5 mm.), was also prepared from the corresponding alcohol by the use of thionyl chloride.

Kinetic Determinations.—The experiments were performed at 0.0 and 25.0° (±0.05°) using the same methods and conditions as previously described.[2] All kinetic determinations were run in duplicate and they checked each other to within 2%. Several kinetic runs were also checked by titration of the chloride ion with silver nitrate using potassium chromate as the indicator.

Summary

1. 5-Indanylphenylchloromethane and 5,6,7,8-tetrahydro-2-naphthylphenylchloromethane were prepared and their rates of hydrolysis in "80%" acetone were measured. The kinetic constants for the first-order hydrolysis at 0° and 25°, the activation energy (*E*), and the non-exponential rate factor (*B*) were found to be identical within experimental error.

2. The hyperconjugative effect of the *p*-methylene group in fused five- and six-membered rings is approximately equal to that of the *p*-ethyl group.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 2, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Addition of Acetic Acid to Perfluoro-2-butyne

BY ALBERT L. HENNE, JOHN V. SCHMITZ[1] AND WILLIAM G. FINNEGAN

Addition of symmetrical reagents to a double or a triple bond flanked by CF_3 groups is sluggish but slowly proceeds to completion; for instance, the chlorination and the hydrogenation of $CF_3CH{=}CH_2$, $CF_3CH{=}CHCF_3$ and $CF_3C{\equiv}CCF_3$ have been performed under experimental conditions favoring free radical addition.[2] Polar addition of unsymmetrical reagents has been found difficult, yet hydrogen chloride and hydrogen bromide have been added to $CF_3CH{=}CH_2$ in the presence of a Lewis acid,[2a] and alcohols and amines have been added to $CF_3C{\equiv}CCF_3$ in the presence of a base.[3] In contrast, we have not been able to add acetic acid to either $CF_3CH{=}CH_2$ or $CF_3CH{=}CHCF_3$ in the presence of a weak base,[4] and it has recently been stated that "trifluoromethyl olefins, CF_3-$CH{=}CHR$ were not attacked by nucleophilic reagents such as sodium methoxide, primary amines, sodium malonic ester, etc., under the conditions used."[5]

We are now reporting the addition, in basic medium, of one or of two molecules of acetic acid across the triple bond of $CF_3C{\equiv}CCF_3$ to yield an enol acetate $CF_3CH{=}C(CF_3)OAc$, (I) or a diacetate $CF_3CH_2C(CF_3)(OAc)_2$, (II), from either of which the ketone $CF_3CH_2COCF_3$ (III) has been prepared.

The reagents used were acetic acid, acetic anhydride and sodium acetate, in varied combinations. The reaction products were the monoacetate I, the diacetate II, trifluoroacetone CF_3-$COCH_3$ (IV), and acetyl fluoride. With equal molar quantities of acid, anhydride and salt, a vigorous reaction took place at 55–60°, which yielded 40% of monoacetate I, and 34% of trifluoroacetone, with small amounts of diacetate II and acetyl fluoride; at a higher temperature more diacetate II was formed at the expense of monoacetate I. In the absence of sodium acetate, no reaction took place up to 70°, the highest temperature tested. In the absence of anhydride, a mixture of acid and salt reacted exothermically with the alkyne at 90–95° to give much acetyl fluoride, small amounts of the diacetate II, and practically no monoacetate I. In the absence of acid, a mixture of anhydride and salt reacted slowly with the alkyne at about 65° over several hours to give an extensively decomposed product from which only acetyl fluoride could be collected.

Of the reaction products, the more useful is the monoacetate I, because it can be very efficiently (90% and up) converted into $CF_3COCH_2CF_3$ by mere refluxing with an excess of butanol treated with a few drops of sulfuric acid; the diacetate II

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[1] American Chemical Society Predoctoral Fellow.

[2] (a) Henne and Kaye, THIS JOURNAL, **72**, 3369 (1950); (b) Henne and Finnegan, *ibid.*, **71**, 298 (1949).

[3] W. T. Miller, private communication.

[4] Henne and Pelley, unpublished.

[5] Campbell and Knobloch, Abstracts of Papers, 116th meeting, Am. Chem. Soc., 6M, Atlantic City, September, 1949.