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.), $n^{25}D$ 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.), $n^{25}D$ 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.), $n^{25}D$ 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.

is convertible also but is inconvenient to prepare and its alcoholysis is not clean-cut. The hexafluorobutanone III formed a semicarbazone in the normal way, but did not give a 2,4-dinitrophenylhydrazone by any of the conventional procedures; it did not show unsaturation by the permanganate test, did not react with bromine in diffuse light, nor with chlorine under illumination, did not give the ferric chloride test for enols, nor form a chelate with cupric acetate; it was insoluble in concentrated sulfuric acid, but dissolved slowly in water; it dissolved readily in methanol with evolution of heat; it decomposed vigorously with loss of hydrogen fluoride when potassium hydroxide or sodium hydride was added to its ether solution. Its resistance to halogenation by a free radical attack is in line with our observations on $CF_3CH_2CH_3$, $CF_3CH_2CH_2CH_3$ and $CF_3CH_2CF_3$[6]; its halogenation under polar conditions is discussed in our next paper.[7]

The formation of acetyl fluoride is regarded as devoid of significance, because any mixture containing the elements of acetic acid and hydrogen fluoride will form a certain amount of this derivative. The formation of trifluoroacetone is the most important side-reaction, and it could even be developed into a practical preparation; we regard its formation as the result of the solvolysis of one of the CF_3 groups to create an acid function (or its equivalent), followed by a decarboxylation.

The formulation of the new compounds, I, II, and III was done as follows. The monoacetate I with a correct analysis, can only have the proposed formula. The diacetate II could be the proposed asymmetrical compound $CF_3CH_2C(CF_3)(OAc)_2$, in agreement with the general observations on addition of acetic acid to an enol acetate,[8] or else the symmetrical diacetate $CF_3CH(OAc)CH(OAc)CF_3$; the latter has however been prepared[9] by oxidation of $CF_3CH{=}CHCF_3$ to a diol and esterification to a diacetate m. p. 39.1 to 39.5°; since II melts at 97.8°, it should be given the alternate, asymmetrical formulation. For the ketone III, only the proposed formula is consistent with the analysis, the presence of one ketone function, and the knowledge that fluorine does not wander from CF_3 groups.

Experimental

Working conditions for maximum amounts of valuable products, trifluoroacetone and the enol monoacetate, were worked out by W. C. Francis and M. E. Tuvell. It is to be remembered that the monoacetate is easily transformed into hexafluorobutanone, while the diacetate is not and is practically a complete loss.

Addition of Acetic Acid.—Glacial acetic acid (60.0 g. or 1.0 mole), anhydrous sodium acetate (16.4 g. or 0.20 mole) and acetic anhydride (102.0 g. or 1.0 mole) were placed in a 500 ml. steel vessel and cooled to −78°; by condensation, perfluoro-2-butyne (81.0 g. or 0.50 mole) was added to this mixture. The vessel was closed and allowed to warm up to room temperature. It was then rocked on a mechanical shaker, the electrical jacket of which was adjusted for 60°. As soon as the reaction mixture reached the temperature of the jacket, a vigorous reaction occurred which, in a few minutes, brought the pressure from 170 p. s. i. to 300 p. s. i., and raised the temperature temporarily to 100°. In 30 minutes, an equilibrated condition was restored, at 60° and 70 p. s. i.

The gaseous products were tapped and directed to a Dry-Ice trap backed by a weighed tube of Ascarite and a gas buret which collected 0.022 mole of carbon dioxide and 0.12 mole of non-condensable gases. The trap held 1.8 g. (2.2% recovery) of $CF_3C{\equiv}CCF_3$ and 1.0 g. of a mixture of acetyl fluoride and trifluoroacetone; the former was identified by formation of acetanilide and testing for fluorine ions, while the latter was recognized by means of its 2,4-dinitrophenylhydrazone.

The liquid products were diluted to two liters with water, to precipitate a lower organic layer which was decanted, dried over sodium sulfate and distilled. This gave 40.8 g. (40% yield) of $CF_3CH{=}C(CF_3)OAc$ b. p. 94.0–94.2° at 748 mm., n^{25}_{D} 1.3183, d^{25}_{4} 1.3840, AR_F 1.2, F% calcd. 51.3 fd., 50.2; this material gave qualitative tests for unsaturation and acetate groups.

The aqueous solution gave a strong positive test for the fluoride ion, the acidimetric titration of which was not practical in the buffered solution. By refluxing this aqueous solution overnight under a water-cooled condenser, wet trifluoroacetone was slowly distilled past the condenser and into a Dry-Ice trap. From the amount of 2,4-dinitrophenylhydrazone obtained from an aliquot, the quantity of trifluoroacetone was estimated at 34%.

To obtain a maximum amount of monoacetate at the expense of trifluoroacetone and the diacetate, equimolecular amounts of acetic acid and butyne were used without changing the quantities of anhydride and acetate, and the temperature was controlled so that it never exceeded 72°. A 55% yield of monoacetate resulted.

In an effort to favor the formation of the diacetate, the addition of acetic acid to the alkyne was repeated at 100° for three hours. A material (80 g.) b. p. 17–23° was obtained, which contained 64% of acetyl fluoride and at least 15% of trifluoroacetone. Dilution of the reaction mixture with water gave a tarry solid which weighed 6 g. after two recrystallizations from absolute alcohol. Two further recrystallizations from a benzene/petroleum ether mixture, and one from an alcohol/petroleum ether mixture finally gave white needles m. p. 97.0 to 97.8° of the diacetate $CF_3CH_2C(CF_3)(OAc)_2$, % F calcd. 40.5, fd. 39.7; the acetate test was positive, unsaturation test was negative. Synthesis of the diacetate is thus patently unsatisfactory.

Preparation of $CF_3COCH_2CF_3$.—$CF_3CH{=}C(CF_3)OAc$ (199 g. or 0.89 mole) was refluxed for twenty-four hours with *n*-butanol (222 g. or 3.0 mole) containing 30 drops of sulfuric acid. Fractional distillation yielded 154 g. (95%) of $CF_3COCH_2CF_3$ m. p. −56°; b. p. 54.2° at 747 mm. n^{20}_{D} 1.282, d^{20}_{4} 1.5589, AR_F 1.2, % F calcd. 63.4, fd. 63.2, semicarbazone m. p. 121.8–122.5° after recrystallization from methanol, % N calcd. 17.7, fd. 17.8. In addition, 8.7 g. of starting material was recovered as distillation residue, to bring up the balance of materials to 99.7%, and the net yield to 99.5%.

Summary

The addition of acetic acid across the triple bond of $CF_3C{\equiv}CCF_3$ can be performed in the presence of sodium acetate at 50–60°, and seems to be base catalyzed. The main reaction products are the monoacetate $CF_3CH{=}C(CF_3)OAc$ (40–55%) and a decomposition product, CF_3COCH_3 (34%). Higher temperatures cause decomposition and the

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[6] Henne and Whaley, THIS JOURNAL, **64**, 1157 (1942); Henne and Hinkamp, *ibid.*, **67**, 1197 (1945); Henne, Hinkamp and Zimmerschied, *ibid.*, **67**, 1906 (1945); Henne and Waalkes, *ibid.*, **68**, 496 (1946).

[7] Henne and Mentcher, *ibid.*, in preparation.

[8] Nieuwland and Vogt, "The Chemistry of Acetylene," Reinhold Publishing Corp., New York, N. Y., 1945, p. 129.

[9] W. G. Finnegan, Ph.D. dissertation, The Ohio State University, 1949.

formation of small amounts of diacetate $CF_3CH_2C(CF_3)(OAc)_2$. The monoacetate is transformed into $CF_3COCH_2CF_3$ in 99% yield by alcoholysis with butanol, while the diacetate does not undergo alcoholysis cleanly.

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[CONTRIBUTION NO. 200 FROM THE DEPARTMENT OF ORGANIC CHEMISTRY AND ENZYMOLOGY, FORDHAM UNIVERSITY]

Investigations on the Mechanism of Catalytic Hydrogenations. XV. Studies with Colloidal Iridium

BY W. P. DUNWORTH AND F. F. NORD

I. Introduction

Results on the application of synthetic polymers in obtaining highly effective colloidal platinum, palladium and rhodium catalysts, studies on their physical properties and on the mechanism of their action have been reported by this laboratory in the past.[1] In the present paper observations will be communicated which were made with the aid of a colloidal iridium catalyst supported by polyvinyl alcohol (PVA).

More than three decades ago the preparation of colloidal iridium utilizing sodium protalbinate and sodium lysalbinate as protective colloids was reported.[2] Aside from the contents of these papers only scanty information is available on colloidal iridium and no systematic kinetic study has been made on hydrogenations with such a catalyst attempting to apply more recent developments in theoretical chemistry.

II. Experimental

Preparation of the Iridium–PVA Catalyst.—To 40 cc. of distilled water was added 50 cc. of a 4% aqueous PVA solution. Then 10 cc. of a 0.5% (of iridium) solution of potassium iridium chloride and 1.1 cc. of a 20% (by weight) aqueous solution of sodium hydroxide is added with stirring to bring about a change of the color of the solution from deep red to straw yellow. The covered contents of the beaker are then placed on the steam-bath for fifteen minutes. Due to this heating, the straw-colored solution assumed an opaque brownish black color. The solution is then allowed to cool to room temperature, measured, and, if necessary, distilled water is added to bring the total volume to 100 cc. Hereafter the solution is shaken with hydrogen at atmospheric pressure for twenty minutes and is then immediately neutralized with 10% acetic acid. The catalyst is now ready for use. Twenty cc. of this preparation contain 10 mg. of iridium.

Hydrogenation of Organic Substances.—In these experiments a constant mole fraction (usually 0.01 mole) of the substrate was dissolved in 100 cc. of 76% ethanol and 1 cc. of 10% sodium hydroxide. Then 20 cc. of the catalyst preparation was added to the ethanol-substrate solution and the mixture was placed in a vessel where it was shaken with hydrogen at atmospheric pressure and room temperature.

III. Results and Discussion

The first compound used as a substrate for hydrogenation with our colloidal iridium catalyst was nitrobenzene.[3] Complete reduction of 1/100 of a mole was effected in twenty minutes. The rate of the hydrogenation was found to be minimum in acid solution and maximum in alkaline solution.

While the catalyst was found to be useful for the reduction of nitrobenzene, it was noticed that it was ineffective for the hydrogenation of benzoic acid, benzaldehyde, phenyl cyanide, styrene, or allyl alcohol when the operation was carried on for twice as long a period of time as was required to completely reduce the same mole fraction of nitrobenzene.

It was also observed that elemental sulfur, hydrogen sulfide, thiophene, and allyl thiourea rendered the catalyst ineffective for the reduction of nitrobenzene.

However, since evidence has been presented showing that the mechanism of hydrogenation using colloidal palladium differs from that using colloidal rhodium,[1i and 1j] it was decided to study the mechanism of hydrogenation using colloidal iridium. For these reductions meta and para substituted nitrobenzene derivatives were chosen. The results of these experiments are recorded in the following tables.

TABLE I

NITROBENZENE COMPOUNDS SUBSTITUTED IN THE *meta* POSITION

Substituent	Hydrogen uptake in 5 minutes, cc.
Cl	220
Br	210
OCH_3	160
H	160
CH_3	142
CHO	105
NH_2	102
CN	86
NO_2	80 (0.5 total)
COOH	19

TABLE II

NITROBENZENE COMPOUNDS SUBSTITUTED IN THE *para* POSITION

Substituent	Hydrogen uptake in 5 minutes, cc.
CHO	225
Cl	212
Br	205
CN	185
H	160
NO_2	105 (0.5 total)
OCH_3	56
COOH	55
CH_3	49
NH_2	38

The only relationship which we could discern between the rate of hydrogenation with colloidal iridium and a property which is inherent in the molecules, was that between the dipole moment of nitrobenzenes substituted in the meta position by

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[1] F. F. Nord and co-workers, THIS JOURNAL, (a) **63**, 2745 (1941); (b) **63**, 3268 (1941); (c) **64**, 2721 (1942); (d) **65**, 429 (1943); (e) **65**, 2121 (1943); (f) **66**, 2126 (1944); (g) *Proc. Natl. Acad. Sci.*, U. S., **29**, 246 (1943); (h) *Experientia*, **3**, 489 (1947); (i) *J. Colloid Sci.*, **3**, 363 (1948); (j) **3**, 377 (1948).

[2] C. Paal and co-workers, *Ber.*, **50**, 722 (1917), and previous papers in this series.

[3] F. F. Nord, *ibid.*, **52** 1705 (1919).