

tinued. The temperature rose slowly at first, and then more rapidly, to 45°, at which point the solution was cooled in an alcohol-Dry Ice-bath. In spite of shaking in the Dry Ice-bath, the temperature rose rapidly to 98°, white fumes were evolved and the solution refluxed vigorously. During this time the color changed from yellow to green, brown and almost black. After a few minutes the temperature began to drop slowly. When the reaction appeared to have subsided completely, the solution was warmed at 80–85° for 3.5 hours. Distillation under reduced pressure removed a fore-run containing largely acetic acid, followed by a yellowish-orange solid, b.p. 90–105° (18 mm.), having a strong odor of dicyclopentadiene. Redistillation removed another fore-run and gave a waxy white solid (42.4 g., 0.276 mole, 27%), b.p. 105–110° (18 mm.). Recrystallization from ethanol-water gave a sample, m.p. 88–93°. Two sublimations at 1 mm. yielded white crystals of 5-nitro-5-methylbicyclo[2,2,1]-2-heptene, m.p. 104°, having an odor resembling dicyclopentadiene; ν_{NO_2} (cm⁻¹) 1537, 1387 or 1357 in Nujol, 1530, 1388 or 1357 in CHCl₃.

Anal. Calcd. for C₈H₁₁NO₂ (153.18): C, 62.72; H, 7.24; N, 9.14. Found: C, 62.57, 62.76; H, 7.34, 7.15; N, 9.02.

5-Nitro-5,6-dimethylbicyclo[2,2,1]-2-heptene (With Peter Pappas).—Freshly cracked cyclopentadiene (68.0 g., 1.03 moles) and 2-nitro-2-butene¹³ (32.7 g., 0.323 mole) were warmed for 5 hours on a steam-bath. During this time the temperature of the refluxing liquid rose slowly from 54 to 95° as the cyclopentadiene reacted or dimerized. Two vacuum distillations yielded crude product (22.2 g., 0.133 mole, 41%), b.p. 65° (2 mm.), which solidified in the receiver. Several sublimations yielded waxy white crystals of 5-nitro-5,6-dimethylbicyclo[2,2,1]-2-heptene, m.p. 84.5–86.5°, having an odor resembling dicyclopentadiene; ν_{NO_2} (cm⁻¹) 1531, 1388 or 1354 in Nujol, 1390 or 1355 in CS₂.

Anal. Calcd. for C₉H₁₃NO₂ (167.20): C, 64.65; H, 7.84; N, 8.38. Found: C, 64.75, 64.37, 64.38; H, 8.18, 8.03, 7.65; N, 8.41, 8.32, 8.42.

(13) H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

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The Reduction of Fluorine-containing Carbonyl Compounds with Heptafluoropropyllithium¹

BY E. T. MCBEE, C. W. ROBERTS AND SADIE G. CURTIS²
RECEIVED JUNE 24, 1955

The preparation and some reactions of perfluoropropyllithium recently were reported.³ The preparation of perfluoro-4-propyl-4-heptanol (I) from heptafluoropropyllithium and ethyl heptafluorobutyrate was claimed. An attempt to apply this reaction to the preparation of perfluoro-4-methyl-4-heptanol from the organolithium reagent and ethyl trifluoroacetate was unsuccessful; this led to a repetition of the earlier work. The exchange reaction between methyl lithium and heptafluoro-1-iodopropane went smoothly, and addition of ethyl heptafluorobutyrate to the perfluoroalkyllithium resulted in the isolation of a product having physical properties, derivatives, and an infrared spectrum identical with those reported for I.^{3,4} However, a comparison of the physical properties of the alcohol, and those of its 3,5-dinitrobenzoate, with those reported for 1,1,1,2,2,3,3,5,5,6,6,7,7,-

(1) From a thesis submitted by S. G. Curtis to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, January, 1955.

(2) National Science Foundation Fellow, 1952–1953.

(3) O. R. Pierce, E. T. McBee and G. F. Judd, *THIS JOURNAL*, **76**, 474 (1954).

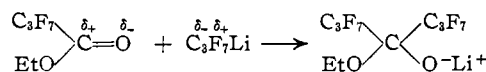
(4) G. F. Judd, Doctorate Thesis, Purdue University, 1953.

7-tetradecafluoro-4-heptanol⁵ (II) indicated that the product actually obtained was the secondary alcohol II. Lithium aluminum hydride reduction of tetradecafluoro-4-heptanone (III) gave an authentic sample of the secondary alcohol. The analytical data for three derivatives of the alcohol (see experimental) provide further evidence that this product is the secondary alcohol II. The infrared spectrum of this alcohol is in agreement with data previously reported for II.^{5,6}

Further attempts to prepare I from the reaction of heptafluoropropyllithium with the ester produced only II and III in varying yields depending on the conditions (Table I). By-products of the reaction were hexafluoropropene (from decomposition of the organolithium reagent), small amounts of perfluorohexane and tetradecafluoro-4-methyl-4-heptanol (IV), and large amounts of polymeric material. Attempts to prepare I by treating III with heptafluoropropyllithium were unsuccessful, resulting in the formation of hexafluoropropene and, in one instance, a 20% yield of IV. A large part of the ketone was recovered from the reactions.⁷

There are numerous examples in the literature of reduction of a carbonyl compound to the corresponding alcohol by a Grignard reagent.⁹ In the present work the reaction of heptafluoropropylmagnesium iodide with ethyl heptafluorobutyrate gave a small amount of the secondary alcohol II. Since there is no β -hydrogen on this Grignard reagent, the Whitmore mechanism does not apply, and it was concluded⁷ that the mechanism probably involves a hydride shift from the ether of solvation. No previous instance of reduction by an organolithium reagent of this type has been reported.

Table I indicates that the time of reaction has a marked effect on the products formed in the reaction of heptafluoropropyllithium with ethyl heptafluorobutyrate. A shorter time favors the formation of the ketone III, and a longer time results in reduction to the secondary alcohol II. The initial reaction is undoubtedly the addition of one molecule of the organolithium to the carbonyl group of the ester.¹⁰



(5) A. L. Henne and W. C. Francis, *THIS JOURNAL*, **75**, 991 (1953).

(6) R. N. Haszeldine, *J. Chem. Soc.*, 1757 (1953).

(7) R. N. Haszeldine, *ibid.*, 748 (1953), has reported the formation of I from the reaction of heptafluoropropylmagnesium iodide with ethyl heptafluorobutyrate. No properties were reported, however, and other workers⁸ have not been able to duplicate these results.

(8) A. L. Henne and W. C. Francis, *THIS JOURNAL*, **75**, 992 (1953).

(9) This is particularly common in reactions of Grignard reagents with fluorine-containing carbonyl compounds; see also E. T. McBee, O. R. Pierce and D. D. Meyer, *ibid.*, **77**, 83 (1955), for lead references.

(10) C. G. Swain and L. Kent, *ibid.*, **72**, 518 (1950), have proposed a mechanism for the reaction of alkyl lithium reagents with ketones, involving the slow, reversible formation of a complex between the lithium atom and the carbonyl oxygen followed by a rapid intramolecular rearrangement. However, it has been demonstrated that there is little, if any, complexing between fluorine-containing carbonyl compounds and magnesium bromide.⁹ Since magnesium bromide is undoubtedly a stronger complexing agent than an organolithium reagent, it is not likely that such a complex is formed in the present case. It is not necessary to assume the formation of a complex to explain addition to a fluorine-containing carbonyl compound. The inductive effect of the perfluoroalkyl group is sufficient to render the carbonyl carbon quite positive.

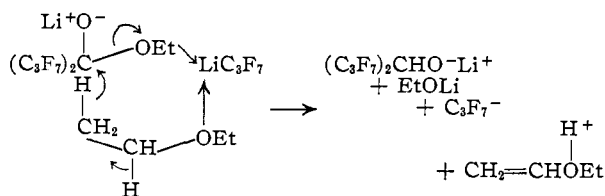
TABLE I
 REACTION OF HEPTAFLUOROPROPYLLITHIUM^a WITH ETHYL HEPTAFLUOROBUTYRATE

Expt.	Time, hr.	Addition		Time, hr.	Reaction Temp., °C.	Yield, %		C ₃ F ₆
		Temp., °C.	Temp., °C.			(C ₃ F ₇) ₂ CHOH	(C ₃ F ₇) ₂ CO	
1 ^b	2	-40 to -45		36	-35 to -50	26 ^e	0	12
2 ^c	2	-50 to -60		36	-40 to -50	28 ^f	0	17
3	2.5	-40 to -50		15	-65 to 20	0	33	30
4	2.5 ^d	-45 to -50 ^d		96	-70 to 20	0	0	36
	10 min.	-60						
5	45 min.	-60		36	-35 to -50	42 ^g	8.7	25

^a Final concentration about 1 mole C₃F₇Li/liter; experiment 5, 0.39 mole/liter. ^b Hydrolyzed in the manner described by Pierce,³ using a borate ester of diethylene glycol. Sulfuric acid hydrolysis was used in the other experiments. ^c Mole ratio of C₃F₇Li to ester 3:1; in the other experiments the ratio was 2:1. ^d The CH₃Li solution was added first (upper line), followed immediately by the ester (lower line). ^e Represents conversion of ester to alcohol; 12% of the ester was recovered. ^f No ester was recovered from this experiment, but there was evidence for the formation of heptafluorobutyric acid during hydrolysis. ^g A 3.7% yield of (C₃F₇)₂COHCH₃ was formed in this experiment.

The hemiketal salt formed is apparently stable; evidence for this is provided by the experimental results. The procedure used in working up the reaction mixture included removal of all volatile material before hydrolysis. No ketone was isolated on rectification of this material, even when there was an appreciable yield of III after hydrolysis of the residue. From this observation, and from the fact that the reaction of III with heptafluoropropyllithium did not result in reduction, it is concluded that the intermediate in the formation of II from the ester is not the free ketone, but the initial addition product of the ester and the organolithium.

Reduction must have occurred during the initial low temperature period, and an essential reactant must have been destroyed on warming to room temperature. The constituent known to be thermally unstable is heptafluoropropyllithium.³ It is concluded, therefore, that reduction involves a second molecule of the organolithium reagent and a hydrogen from the solvent.¹¹ A reasonable mechanism for the transfer of a hydride ion from ethyl ether to the hemiketal salt in the presence of heptafluoropropyllithium involves an intermediate similar to that proposed for reduction by heptafluoropropylmagnesium iodide.⁷



The heptafluoropropyl anion reacts with the proton to form heptafluoropropane, or it loses a fluoride

(11) The possible sources of hydrogen for reduction in the reaction mixture were methyl iodide (formed in the exchange reaction between methyl lithium and heptafluoro-1-iodopropane), the ethoxy group of the ester and the solvent. Any of these compounds could act as a source of hydrogen if a free radical mechanism were involved. However, it appears that there is no homolytic cleavage of heptafluoropropyllithium, since the decomposition of an ether solution of this reagent gave hexafluoropropene in 97% yield and no heptafluoropropane.³ The reduction must involve the replacement of ethoxide by a hydride ion. It is improbable that methyl iodide would act as a source of hydride ions. If the ethoxy group were to donate a hydride ion, ethylene oxide would be formed. Reaction of this product with the excess heptafluoropropyllithium would give 3,3,4,4,5,5,5-heptafluoro-1-pentanol after hydrolysis; there was no evidence for the formation of this compound.

ion to form hexafluoropropene.¹² This mechanism required the formation of ethyl vinyl ether. It was not possible to isolate this compound (b.p. 35.5°) from the ether solution, but a small sample of the recovered solvent gave a positive test for unsaturation with a 2% permanganate solution; addition of bromine led to the isolation of a small amount of α - β -dibromoethyl ether.

Experimental¹³

Materials.—Ethyl heptafluorobutyrate,¹⁴ b.p. 96.2°, n_D^{20} 1.3032, and heptafluoro-1-iodopropane,¹⁵ b.p. 40.5°, n_D^{20} 1.3270, were prepared by previously described procedures. An ether solution of methyl lithium was prepared by passing gaseous methyl bromide into ether containing lithium wire cut into 1.3 cm. lengths, until the lithium had disappeared.³ The yield based on the lithium was 97%.

Attempted Reaction of Heptafluoropropyllithium with Ethyl Trifluoroacetate.—The procedure described for the reaction of heptafluoropropyllithium with ethyl heptafluorobutyrate was used.³ Methyl lithium (0.5 mole) and ethyl trifluoroacetate (0.25 mole) were added simultaneously to heptafluoro-1-iodopropane (0.5 mole) in ether at -50 to -40°, and the mixture stirred at -50 to -40° for 36 hr. Rectification of the product gave ethanol as the only identifiable fraction. About 10 g. (14%) of hexafluoropropene was formed.

The reaction was repeated in dibutyl ether in an attempt to isolate any perfluoro-2-pentanone (b.p. 30.5°¹⁶) which might have formed. Neither the ketone nor the alcohol was isolated.

Reaction of Heptafluoropropyllithium with Ethyl Heptafluorobutyrate.—Table I summarizes the conditions used and products formed in this reaction. Experiment 5 will be described in detail.

A 3-l., 3-necked flask fitted with a thermometer well, a Trubore stirrer, and two 1-l. closed-circuit addition funnels was flamed and flushed with pure¹⁷ dry nitrogen and charged with anhydrous ether (1280 ml.) and heptafluoro-1-iodopropane (296 g., 1.0 mole). During the reaction, nitrogen was passed in one addition funnel and out the other, through a Dry Ice trap, drying tube and oil bubbler. The flask and contents were cooled to -70° in a Dry Ice-trichloroethylene-bath, and a solution of methyl lithium in ether (560 ml.

(12) The intermediate pictured need have only a transitory existence, since, once it formed, the formation of lithium ethoxide and the increased positive charge on the carbon atom, which would increase its attraction for the hydride ion, constitutes a sufficient driving force for the reaction.

(13) All temperatures are uncorrected. Analyses were determined by Mrs. C. S. T. Yeh, Microanalytical Laboratory, Purdue University. Infrared spectra were determined by H. Susi on a Perkin-Elmer model 21 spectrophotometer in sealed capillary cells.

(14) D. R. Husted and A. H. Ahlbrecht, *THIS JOURNAL*, **75**, 1605 (1953).

(15) M. Hauptschein and A. V. Grosse, *ibid.*, **73**, 2461 (1951).

(16) O. R. Pierce and M. Levine, *ibid.*, **75**, 1254 (1953).

(17) Purified by passing through Fieser solution,¹⁸ saturated lead acetate solution, concentrated sulfuric acid and Ascarite.

(18) L. F. Fieser, *THIS JOURNAL*, **46**, 2639 (1924).

of a 1.78 *M* solution, 1.0 mole) was placed in one addition funnel, and ethyl heptafluorobutyrate (121 g., 0.5 mole), diluted with ether to 560 ml., was placed in the other. A few milliliters of the methylolithium solution were run into the flask to initiate the reaction; the formation of heptafluoropropylolithium is instantaneous and exothermic. The remainder of the methylolithium solution was added simultaneously with the ester solution at -60° during 45 min. The resulting clear solution was about 0.39 *M* with respect to the organometallic. The reaction mixture was stirred between -50 and -35° for 36 hr.; the mixture and the bath were then allowed to warm to room temperature during 24 hr., and the solution was stirred at room temperature for an additional 24 hr. The clear solution was refluxed for 2 hr. to drive all gaseous products into the trap. The ether, methyl iodide and any remaining heptafluoro-1-iodopropane were removed by distillation up to 40° at atmospheric pressure, and finally at 25° (10–15 mm.).¹⁹ The nearly dry, powdery residue was suspended in anhydrous ether and hydrolyzed with 10% sulfuric acid (0.55 mole) at 20° . The layers were separated and washed; the ether solution was dried over anhydrous magnesium sulfate, and the ether was removed by distillation. The residue was treated with phosphorus pentoxide and distilled at 25° (7 mm.) into a Dry Ice trap. Rectification of the distillate through an 18 inch 14 mm. column packed with $1/8$ inch Pyrex helices gave ether containing 16 g. (8.7%) of tetradecafluoro-4-heptanone (III). The residue was rectified through the Podbielniak miniature Hyper-cal fractionation assembly with concentric tube packing to give 77 g. (42%) of 1,1,1,2,2,3,3,5,5,6,6,7,7,7-tetradecafluoro-4-heptanol (II), b.p. 114.3 – 117.5° , n_D^{20} 1.293–1.296, d_4^{20} 1.668,²⁰ and 7 g. (3.7%) of tetradecafluoro-4-methyl-4-heptanol (IV), b.p. 131° (see below). The infrared and ultraviolet²¹ spectra of II showed a slight contamination by a carbonyl compound, probably the ketone.

Anal. Calcd. for $C_7H_2F_{14}O$ (II): C, 22.83; H, 0.54. Calcd. for $C_{10}HF_{21}O$ (I): C, 22.40; H, 1. Found: C, 22.65; H, 0.13.

Heating II with concentrated nitric acid for 4 hr. gave no ketone III and 65% of the alcohol was recovered. Heating with a sulfuric acid–potassium dichromate mixture⁷ resulted in the recovery of 75% of the alcohol. The structure of the alcohol was finally confirmed by reduction of pure III with lithium aluminum hydride to give a product, b.p. 114.5° , n_D^{20} about 1.291, identical with that obtained above. The infrared spectrum of this product showed only slight contamination by the ketone, and it agreed with data previously given^{8,9} for the spectrum of this alcohol.²²

Distillation of the material collected in the Dry Ice trap during the reaction gave 38 g. (25%) of hexafluoropropene, from the decomposition of heptafluoropropylolithium, and 5 ml. of a dense, colorless liquid, b.p. 50 – 52° , n_D^{20} far below 1.3000, believed to be perfluorohexane (lit.²³ b.p. between 56 and 60°). A large amount of unidentified polymeric material was formed in the reaction.

Repetition of this reaction with a bromine–carbon tetrachloride trap in the system gave no ethylene dibromide. However, the solvent recovered from the initial reaction mixture by distillation decolorized a 2% permanganate solution. A portion of the ether distillate was treated at 0 to 5° with bromine; distillation gave an unstable liquid,

(19) Heating the reaction mixture to 70 – 75° to remove the volatile material resulted in the isolation, in yields as high as 9%, of the secondary alcohol before hydrolysis. No ketone was detected in the distillate.

(20) Henne and Francis⁸ reported II, b.p. 58° (87 mm.), n_D^{20} 1.2911, d_4^{20} 1.6735, from the reduction of III with lithium aluminum hydride. Haszeldine⁷ reported II, b.p. 70° (103 mm.), from the same reaction.

(21) The ultraviolet spectrum was run in a 1-cm. quartz cell at 25° by means of a Beckman model DU quartz spectrophotometer.

(22) Pierce and Levine¹⁹ have reported a 33% yield of II, b.p. 94 – 95° , from the reaction of heptafluoropropylmagnesium iodide with heptafluorobutyraldehyde. The alcohol was isolated as its 3,5-dinitrobenzoate, m.p. 106 – 107° . *Anal.* Calcd.: C, 29.9; H, 0.71. Found: C, 30.8; H, 0.98. The yield and boiling point are in close agreement with those reported by Henne and Francis⁸ for the hydrate of heptafluorobutyraldehyde isolated from the same reaction. The derivative is not the same as that obtained in the present work (m.p. 83.5 – 84°) or that obtained by Henne and Francis⁸ (m.p. 84.0 – 84.2°).

(23) R. L. Scott, *ibid.*, **70**, 4090 (1948).

b.p. 66° (15 mm.), n_D^{20} 1.5030, which appeared to be α,β -dibromoethyl ether.²⁴

Derivatives of 1,1,1,2,2,3,3,5,5,6,6,7,7,7-Tetradecafluoro-4-heptanol-*p*-Toluenesulfonate.—Treatment of II with *p*-toluenesulfonyl chloride in sodium hydroxide solution²⁵ or pyridine²⁶ followed by low-temperature recrystallization from pentane, gave the *p*-toluenesulfonate as white needles, m.p. 41 – 42° .

Anal. Calcd. for $C_{14}H_8F_{14}O_3S$ (from II): C, 32.19; H, 1.53. Calcd. for $C_{17}H_7F_{21}O_3S$ (from I): C, 29.59; H, 1.01. Found: C, 32.16; H, 1.82.

3,5-Dinitrobenzoate.—A mixture of II, 3,5-dinitrobenzoyl chloride and pyridine was heated for 15 minutes. The solid which formed on cooling was extracted several times with ether. The ether was filtered, washed with dilute hydrochloric acid, dilute sodium hydroxide and water, and evaporated on the steam-bath. Recrystallization from an ether–pentane mixture gave the 3,5-dinitrobenzoate as white needles, m.p. 83.5 – 84.0° .²⁷

Anal. Calcd. for $C_{14}H_4F_{14}N_2O_8$ (from II): C, 29.90; H, 0.71; N, 4.98. Calcd. for $C_{17}H_3F_{21}N_2O_8$ (from I): C, 27.97; H, 0.41. Found: C, 29.47; H, 0.79; N, 5.16.

This derivative could not be prepared if water was added directly to the reaction mixture. Hydrolysis took place, and the alcohol was recovered.

Phenylurethan.²⁸—Treatment of II with phenyl isocyanate, followed by recrystallization from carbon tetrachloride and then from hexane, gave the phenylurethan as white needles, m.p. 111.5 – 112° .²⁹

Anal. Calcd. for $C_{14}H_7F_{14}NO_2$ (from II): C, 34.51; H, 1.44; N, 2.88. Calcd. for $C_{17}H_6F_{21}NO_2$ (from I): C, 31.17; H, 0.92; N, 2.14. Found: C, 34.72; H, 1.84; N, 3.13.

Tetradecafluoro-4-heptanone.—A modification of the Grignard exchange reaction reported by Pierce³⁰ was used to prepare tetradecafluoro-4-heptanone (III).

A solution of phenylmagnesium bromide in ether (935 ml. of a 1.05 *M* solution, 1.0 mole) was added to a mixture of heptafluoro-1-iodopropane (296 g., 1.0 mole) in ether (1280 ml.) at -70° . The resulting suspension was stirred 0.5 hr., and ethyl heptafluorobutyrate (242 g., 1.0 mole) was added during 1 hr. at -70° . The mixture was allowed to warm to room temperature during 36 hr., refluxed for 2 hr. and was hydrolyzed with 10% sulfuric acid. After removal of most of the ether, the product was purified by distillation (2 mm.) from concentrated sulfuric acid at 25° . Rectification through an 18 inch 14 mm. column packed with $1/8$ inch Pyrex helices gave 225 g. (61.5%) of III, b.p. 75 – 76.5° , n_D^{20} far below 1.3000. Thirty-one grams (13%) of the ester was recovered, and 8 g. (5%) of hexafluoropropene was formed. A trace of II was also detected.

Reaction of Heptafluoropropylolithium with Tetradecafluoro-4-heptanone. Procedure A.—This reaction was carried out in a manner similar to the reaction of heptafluoropropylolithium with the ester. A solution of methylolithium in ether was added to a mixture of heptafluoro-1-iodopropane and ether at -65° . Tetradecafluoro-4-heptanone was then added at -65° . The reaction mixture and bath were allowed to warm to room temperature during 36 hr., and the reaction mixture was worked up as usual. Rectification gave only a small amount of unidentified high boiling material. A 40% yield of hexafluoropropene was formed, and 72% of the ketone was recovered.

Procedure B.—This procedure was the same as procedure A except that the methylolithium solution was added to a mixture of the ketone and iodide. A 20% yield of tetra-

(24) A. E. Favorskii and M. F. Shastakovskii, *J. Gen. Chem. (U.S.S.R.)*, **13**, 1 (1943), reported b.p. 62 – 65° (12 mm.), n_D^{20} 1.5044.

(25) A. T. Roos, H. Gilman and N. J. Beaber, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 145.

(26) C. S. Marvel and V. C. Sekera, *ibid.*, **20**, 50 (1940).

(27) Reference 5 reported, m.p. 84.0 – 84.2° . *Anal.*: C, 30.2; H, 0.9; N, 5.6. Reference 4 reported the 3,5-dinitrobenzoate of $(C_7F_7)_2COH$, m.p. 80° . *Anal.*: C, 30.08; H, 1.12; N, 4.51.

(28) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 136.

(29) Reference 4 reported the phenylurethan of $(C_7F_7)_2COH$, m.p. 111.5 – 112° . *Anal.*: C, 34.45; H, 2.14; N, 3.90.

(30) O. R. Pierce, A. F. Meiners and E. T. McBee, *THIS JOURNAL*, **75**, 2516 (1953).

decafluoro-4-methyl-4-heptanol (IV), b.p. 132–133°, n_D^{20} 1.3031, d_4^{25} 1.763, was obtained, along with a 67% yield of hexafluoropropene. The recovery of III was 36%. An infrared spectrum of IV agreed with the structure proposed.³¹

Procedure C.—Solid methylolithium was added to a mixture of the ketone and an excess of the iodide in the absence of ether. The exchange reaction proceeded normally to form heptafluoropropylolithium. Evidence for this was a 65–70% yield of hexafluoropropene. No other product was isolated, and 53% of the ketone was recovered.

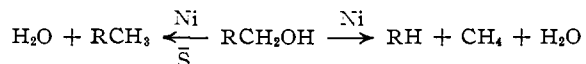
(31) Haszeldine⁷ has reported this alcohol from reactions of heptafluoropropylmagnesium iodide with acetyl chloride or ethyl acetate. No properties or other data were given.

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Specificity of Nickel Catalysts. Effect of Dimethyl Disulfide upon Hydrogenation of Olefinic Hydrocarbons

BY HERMAN PINES, JOSEPH MARECHAL¹ AND W. S. POSTL
RECEIVED JUNE 13, 1955

It was reported previously² that the presence of small amounts of sulfur-containing compounds can greatly influence the type of activity of a nickel catalyst. Thus in the absence of sulfur compounds primary alcohols are dehydroxymethylated at 250° and under 100 atmospheres of initial hydrogen pressure, while reductive elimination of the hydroxyl group takes place under similar conditions in the presence of dimethyl disulfide, thiophene, etc.



Evidence was given to show that the latter reaction proceeds *via* an ionic mechanism. It was suggested that a nickel catalyst possesses inherent acid properties and that sulfur compounds through their ability to poison the active contact sites of the nickel catalyst may accentuate the acid properties of the catalyst.

This study has been extended to olefinic hydrocarbons and has revealed that the presence of small amounts of sulfur compounds may also influence the hydrogenation of compounds such as 3,3-dimethylbutene or cyclohexene. These reactions were made in a flow type system at 300°, under 10 atmospheres of pressure using a ratio of hydrogen to hydrocarbons equal to 4:1 and nickel-kieselguhr as catalyst.

3,3-Dimethyl-1-butene.—In the absence of sulfur compounds this olefin yielded on hydrogenation hexanes composed of 93% 2,2- and 7% 2,3-dimethylbutane. When the hydrogenation was carried out, however, in the presence of a catalyst which was used previously for hydrogenation of compounds containing small amounts of thiophene, the extent of hydroisomerization of 3,3-dimethylbutene was greatly increased, and the product of the reaction contained 51% of 2,3-dimethylbutane. The hydroisomerization became the major reac-

tion when 1% by weight of dimethyl disulfide was added to the 3,3-dimethylbutene. The hydrocarbons recovered consisted of 25% 2,2- and 75% 2,3-dimethylbutane (Table I).

TABLE I

EFFECT OF DIMETHYL DISULFIDE UPON THE HYDROGENATION OF 3,3-DIMETHYLBUTENE

The hydrogenation was carried out in a flow type apparatus at 300°, 10 atmospheres of pressure and using a hydrogen to 3,3-dimethylbutene ratio of 4:1.

Experiment	1	2	3
Catalyst	Ni-K ^a	Ni-K ^b	Ni-K ^c
Dimethyl disulfide, wt. %	0	0	1
Compn. of reacn. product, mole %			
2,2-Dimethylbutane	93	45	25
2,3-Dimethylbutane	7	51	75
3,3-Dimethylbutene		4	

^a Fresh nickel-kieselguhr catalyst was used. ^b The catalyst was previously used in experiments in which a sulfur containing additive was present. ^c Catalyst from experiment 2 was used.

Cyclohexene.—Hydroisomerization of cyclohexene over nickel-kieselguhr catalyst under 10 atmospheres of pressure practically did not occur when the hydrogenation was carried out in the absence of sulfur compounds.⁸ In the presence of 1% of dimethyl disulfide, however, 5% of cyclohexene was converted to methylcyclopentane. In the presence of larger amounts of disulfide 16% of methylcyclopentane was produced. The low yield of methylcyclopentane in the presence of 1% of dimethyl disulfide is probably due to the fact that fresh catalyst was used and that only partial deactivation of the catalyst occurred before a sample of the reacted product was withdrawn for analysis.

TABLE II

EFFECT OF DIMETHYL DISULFIDE UPON THE HYDROGENATION OF CYCLOHEXENE

The apparatus and experimental conditions were the same as described in Table I. The mole ratio of hydrogen to cyclohexene was 4:1. Nickel-kieselguhr was used as a catalyst.

Experiment	1	2	3
Dimethyl disulfide, wt. %	0	1	5
Compn. of reacn. prod., mole %			
Methylcyclopentane	1	5	15
Cyclohexane	99	95	81
Benzene			4

Discussion of Results.—It was found, as in the hydrogenolysis of alcohols,² that the presence of small amounts of sulfur-containing compounds can influence the type of activity of a nickel catalyst. In the presence of sulfur the nickel assumes acid characteristics, as shown by its hydroisomerization effect. The skeletal isomerization occurs most probably prior to hydrogenation, since the saturated hydrocarbons, such as cyclohexane or 2,2-dimethylbutane, under similar experimental conditions do not undergo isomerization. The probable mechanism of the hydroisomerization reaction is similar to that suggested for the reductive dehydroxylation of primary alcohols.²

(1) On leave of absence from Laboratoires de Recherches Purifines S. A. Bruxelles, Belgium, 1953–1954.

(2) H. Pines, M. Shamaingar and W. S. Postl, *THIS JOURNAL*, **77**, 5099 (1955).

(3) H. Pines, A. Rudin, G. M. Bó and V. N. Ipatieff, *ibid.*, **76**, 2740 (1954).