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REACTIONS OF FLUORO OLEFINS

COMMUNICATION 13. CATALYTIC HYDROGENATION OF PERFLUORO OLEFINS

I. L. Krunyants, M. P. Krasuskaya, and E. I. Mysov

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

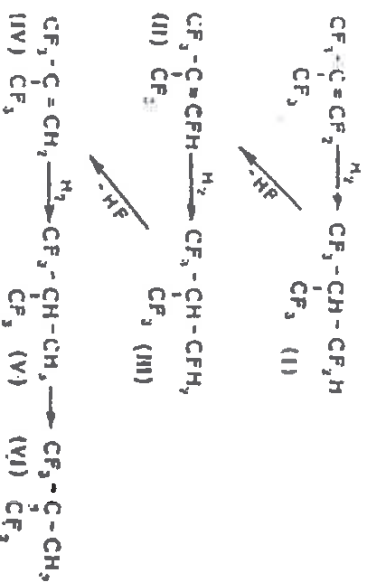
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Apart from its practical importance, the study of the catalytic hydrogenation of perfluoro olefins has a direct bearing on the theory of heterogeneous catalysis. As the rate of hydrogenation must be directly related to the state of the π -bond of the olefins and increase with reduction in its electron density, it may be supposed that the hydrogenation of perfluoro olefins, which have a strong affinity for nucleophiles, will proceed very readily and that in the series of perfluoro olefins the ease of hydrogenation will increase from perfluoroethylene to perfluoroisobutene; this view corresponds to the observations of Schuster [1] on the diminution in the rate of hydrogenation of the usual olefins as we pass from ethylene through propene to isobutene, and also to the results of Park's work [2] on the comparison of the heats of hydrogenation of vinyl chloride and chlorotrifluoroethylene. Our work on the hydrogenation of perfluoroethylene, perfluoropropene, and perfluoroisobutene showed that perfluoro olefins are hydrogenated smoothly with molecular hydrogen over palladium and nickel catalysts [3, 4]. Over a palladium catalyst (1% Pd/Al₂O₃) at room temperature products of the normal addition of hydrogen are formed almost exclusively in quantitative yield: 1,1,2,2-tetrafluoroethane, 1,1,1,2,3,3,3-hexafluoropropane, and 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane, respectively. Hydrogenation over a nickel catalyst (reduced nickel oxide) requires a higher temperature (60-100°) and leads to a mixture of hydrogenation products, consisting of the normal products and products of the replacement of fluorine by hydrogen, e.g., 1,1,2-trifluoroethane, in the hydrogenation of perfluoroethylene, and 1,1,1,3,3,3-hexafluoro-2-methylpropane, in the hydrogenation of perfluoroisobutene. In the hydrogenation of chlorotrifluoroethylene over 1% Pd/Al₂O₃ at room temperature replacement of chlorine by hydrogen occurred with the formation of trifluoroethylene and its subsequent hydrogenation. Under certain experimental conditions CF₂=CFH is the main reaction product and can be obtained in about 60% yield together with trifluoroethane.

The hydrogenation of perfluorobutadiene proceeded with the formation of 1,1,2,3,4,4-hexafluorobutane. The dehydrofluorination of fluoro hydrocarbons obtained by the hydrogenation of perfluoro olefins made it possible to prepare some previously unknown or difficultly accessible fluoro olefins. Thus, the product of the hydrogenation of perfluoroisobutene, 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane (I), readily eliminates hydrogen fluoride, even under the action of aqueous alkali, with formation of 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propene (II). The structure of the olefin obtained was proved by its oxidation to hexafluoroacetone, which simultaneously confirmed the structure of the original 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane, to which a different boiling point had previously been attributed [5]. Further hydrogenation of 1,3,3,3-tetrafluoro-2-(trifluoromethyl) propene gave 1,1,1,3,3,3-hexafluoro-2-(fluoromethyl) propene (III), the dehydrofluorination of which readily gave the previously difficultly accessible 3,3,3-trifluoro-2-(trifluoromethyl) propene (IV) [6].

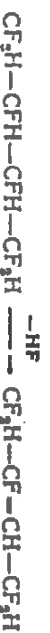
3,3,3-Trifluoro-2-(trifluoromethyl) propene (V) was hydrogenated over a palladium catalyst with formation of 1,1,1,3,3,3-hexafluoro-2-methylpropane (V); the latter, as indicated above, was obtained in considerable amount in the hydrogenation of perfluoroisobutene over a nickel catalyst at about 100°. The dehydrofluorination



of this fluoro hydrocarbon with the formation of 1,1,3,3,3-pentafluoro-2-methylpropene (VI) occurred when it was passed through a melt of 90% potassium hydroxide at 170°. The hydrogenation product from perfluoropropene, 1,1,1,2,3,3-hexafluoropropene (VII), was readily dehydrofluorinated with formation of 1,2,3,3,3-pentafluoropropene (VIII), which is isomeric with the known 1,1,3,3,3-pentafluoropropene (IX) [7]. The structure of the olefin obtained was proved by a comparison of the nuclear magnetic resonance spectra of these olefins and by their further transformations on hydrogenation and dehydrogenation. Thus, on the hydrogenation of 1,2,3,3,3-pentafluoropropene we obtained 1,1,1,2,3-pentafluoropropane (X), b. p. 20°, the nuclear magnetic spectrum of which differed greatly from that of 1,1,1,3,3-pentafluoropropane (XI), b. p. 12°, obtained by the hydrogenation of 1,1,3,3,3-pentafluoropropene. By the dehydrofluorination of these hydrogenation products we obtained, respectively, the olefins 2,3,3,3-tetrafluoropropene (XII), b. p. -28° [7], and 1,3,3,3-tetrafluoropropene (XIII), b. p. -16° [8, 9].



In the hydrogenation of 1,2,3,3,3-pentafluoropropene, together with the main reaction product 1,1,1,2,3,3-pentafluoropropane, we isolated 1,1,1,2-tetrafluoropropane $\text{CF}_3-\text{CFH}-\text{CH}_3$, b. p. -1°. The dehydrofluorination of the hydrogenation product from perfluorobutadiene, 1,1,2,3,4,4-hexafluorobutane, occurred with the elimination of one molecule of HF from the 2,3-positions:



The structure of the resulting olefin was proved by its oxidation to difluoroacetic acid.

The study of the catalytic hydrogenation of perfluoro olefins widens the possibilities for the synthesis of saturated and unsaturated fluoro hydrocarbons. The usual general method for the preparation of fluorine-containing compounds is the replacement of hydrogen atoms by halogen and further fluorination. Catalytic hydrogenation with subsequent dehydrofluorination leads to a process of stepwise replacement of fluorine atoms by hydrogen, and in this case the fluorine- and hydrogen containing olefins that cannot be obtained by the usual method become accessible. Moreover, this method makes it possible to prepare compounds in an individual, pure state, which is usually not attained by the halogenation method (see table). The work is being continued, particularly in relation to the kinetics of the hydrogenation of perfluoro olefins.

TABLE
Compounds Obtained by Catalytic Hydrogenation and Dehydrofluorination Reactions

No.	Formula	B.p. (°C)	No.	Formula	B.p. (°C)
1	CF ₃ H · CF ₃ H	-22, 5	12	CF ₃ -C · CFH	17
2	CF ₃ H-CF ₃ H ₂	3	13	CF ₃ · CH-CF ₃ H ₂	40
3	CF ₃ · CFH	-51	14	CF ₃ · C-CH ₃	13
4	CF ₃ -CFH-CF ₃ H	5	15	CF ₃ -CH-CH ₃	21
5	CF ₃ -CF · CFH	-20	16	CF ₃ -C=CF ₂	12
6	CF ₃ -CFH-CF ₃ H ₂	20	17	CH ₃	65
7	CF ₃ · CF · CH ₃	-28	18	CF ₃ H-CF ₃ H-CF ₃ H-CF ₃ H	56
8	CF ₃ · CFH-CH ₃	-1			
9	CF ₃ -CH ₂ -CF ₃ H	12			
10	CF ₃ -CH · CFH	-16			
11	CF ₃ -CH · CF ₃ H	33			

EXPERIMENTAL

Preparation of Palladium Catalyst. Calcined alumina (41 g) in the form of small pieces, 4-5 mm in diameter, was immersed in a solution of 0.87 g of palladium chloride in 100 ml of water and left for several hours. The solution was decanted, and a mixture of 5 ml of 38% formaldehyde solution, 10 ml of 2 N NaOH, and 75 ml of water was added to the residue. After several hours the resulting catalyst was washed with distilled water until alkali was completely removed, placed in the electrically heated reaction tube, and dried in a stream of air at 250-280°. We obtained 39 g of Pd/Al₂O₃ catalyst.

Preparation of Nickel Catalyst. Pieces of compressed nickel oxide, diameter 3-4 mm, were placed in a hydrogenation tube and heated in a stream of hydrogen at 300° until water ceased to be liberated. The resulting nickel catalyst was preserved in a hydrogen atmosphere.

Hydrogenation of Tetrafluoroethylene. 1. Through a glass tube containing nickel catalyst obtained by the reduction of 70 g of nickel oxide we passed 20 liters (STP) of a mixture containing 40% of C₂F₄ and 60% of H₂. The rate of passage was 4.6 liters/hr. At the start of the experiment the temperature rose as a result of the exothermic character of the reaction from 95° to 158°, and it then remained at this level. As a result of the reaction we obtained 28.5 g of condensate, which was collected in a trap at -60°, and distillation of this through a column gave 24.2 g (66%) of tetrafluoroethane, b. p. -22.5°, and 4.2 g of trifluoroethane, b. p. 2.5°. The total yield was 80% on the tetrafluoroethylene taken. The literature gives: CF₃HC₂F₃H has b. p. -23° [10], and CF₃HC₂F₃H₂ has b. p. 3° [11].

2. A mixture (35.2 liters at STP) of 40% of C₂F₄ and 60% of H₂ was passed through a glass tube containing 5.6 g of 1% Pd/Al₂O₃ at 5.25 liters/hr. The temperature rose from 19° to 90° and remained in the range 85-90°. In the experiment 63.5 g of substance was condensed, and from this we obtained 52.4 g of tetrafluoroethane by distillation. The condensate did not contain trifluoroethane. The yield of CF₃HC₂F₃H on the amount of tetrafluoroethylene taken was 97.3%.

Hydrogenation of Chlorotrifluoroethylene. A mixture (18.65 liters at STP) of 40% of chlorotrifluoroethylene (by volume) and 60% of H₂ was passed for three hours at room temperature through a tube containing 15 g of 1% Pd/Al₂O₃. The gaseous reaction products were passed through a vessel containing aqueous NaOH for the absorption of HCl and were condensed in a receiver cooled to -78°. As a result of the reaction we collected 27.2 g of condensate, from which, after distillation, we obtained 5 g of unchanged chlorotrifluoroethylene, 14 g of trifluoroethylene, b. p. -51°, and 6.7 g of trifluoroethane, b. p. 3°. The over-all yield of trifluoroethylene and

trifluoroethane was 75.5% on the amount of chlorotrifluoroethylene taken for reaction. The yield of $\text{CF}_2=\text{CF}$ was 51%; it was identified as its dibromide $\text{CF}_2\text{BrCFHBr}$, b. p. 76° and n_D^{20} 1.415 [12].

Hydrogenation of Perfluoropropene. A mixture (8 liters at STP) of 40% of perfluoropropene and 60% of H_2 was passed at 3 liters/hr over 15 g of 1% Pd/ Al_2O_3 . At the start of the experiment the temperature rose from 20° to 50°, and during the hydrogenation it kept at 50°. As a result of the reaction 50.4 g of substance was condensed in the receiver, which was cooled to -70°; from this distillation gave 48.4 g (96% on perfluoropropene taken) of 1,1,1,2,3,3-hexafluoropropane, b. p. 4-5°. Found %: C 23.33; H 1.28; F 74.53; mol. wt. 151 $\text{C}_3\text{H}_2\text{F}_6$. Calculated %: C 23.67; H 1.31; F 75.00; mol. wt. 152.

Hydrogenation of Perfluoroisobutene. 1. A mixture (8.7 liters at STP) of 40% of perfluoroisobutene (by volume) and 60% of H_2 was passed at 3 liters/hr over 15 g of 1% palladium on alumina. At the start of the experiment the temperature rose from 20° to 60°, and during the hydrogenation it kept at 55-60°. As a result of the reaction 65 g of substance was condensed in the receiver, which was cooled to -60°; from this distillation through a column gave 8 g of unchanged perfluoroisobutene and 57% (85% on the perfluoroisobutene taken) of 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane, b. p. 33-34° and d_4^{20} 1.558. Found %: C 23.88; H 1.06; F 74.76; mol. wt. 202.8. $\text{C}_4\text{H}_2\text{F}_8$. Calculated %: C 23.76; H 0.99; F 75.25; mol. wt. 202.

2. A mixture (37.2 liters at STP) of 20% of perfluoroisobutene and 80% of H_2 was passed at 100-130° through a glass tube containing nickel catalyst prepared by the reduction of 100 g of nickel oxide. The reaction products were passed through a wash bottle containing aqueous alkali and were condensed in a trap cooled to -60°. Distillation of 50 g of the mixture of hydrogenation products gave 12 g of unreacted perfluoroisobutene, 5.5 g (10%) of 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane, b. p. 33-34°, and 32.1 g (70% on the perfluoroisobutene that reacted) of 1,1,1,3,3,3-hexafluoro-2-methylpropane, b. p. 21°. Found %: C 28.46; H 2.35; mol. wt. 166. Calculated %: C 28.91; H 2.35; mol. wt. 166. $\text{C}_4\text{H}_4\text{F}_6$. According to the literature [13] 1,1,1,3,3,3-hexafluoro-2-methylpropane has b. p. 21°.

Dehydrofluorination of 2-(Difluoromethyl)-1,1,1,3,3,3-hexafluoropropane. 2-(Difluoromethyl)-1,1,1,3,3,3-hexafluoropropane (50 g) was added gradually to 30% aqueous KOH (40 ml), and the mixture was heated for 15-20 minutes at 40-50° under reflux; the reaction products were then distilled off into a trap cooled to -70°. We obtained 46 g of condensate, from which by distillation through a column we isolated 7 g of unchanged 2-(difluoromethyl)-1,1,1,3,3,3-hexafluoropropane and 35 g (76%) of 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene, b. p. 17-18°. Found %: C 25.96; H 0.64; F 73.17; mol. wt. 182.5. $\text{C}_3\text{H}_2\text{F}_7$. Calculated %: C 26.37; H 0.54; F 73.07; mol. wt. 182.

Oxidation of 1,3,3,3-Tetrafluoro-2-(trifluoromethyl)propene. 1,3,3,3-Tetrafluoro-2-(trifluoromethyl)propene (16 g) was gradually added to a stirred solution of 30 g of potassium permanganate in 130-150 ml of water warmed to 35-40°; the reaction mixture was heated further for 2-2.5 hours under reflux at 30-40°. Sulfur dioxide was passed through the cooled solution until colorless, and the precipitate was filtered off and washed with hot water; the filtrate was extracted with ether for 24 hours in a continuous-extraction apparatus. The ether extract was dried with anhydrous magnesium sulfate and distilled. After the removal of ether we obtained 8 g (50%) of hexafluoroacetone hydrate, b. p. 55° (80 mm) and n_D^{20} 1.332. The semicarbazone had m. p. 153°, undepressed by admixture of a sample of hexafluoroacetone semicarbazone prepared by the oxidation of perfluoroisobutene [14, 15].

Hydrogenation of 1,3,3,3-Tetrafluoro-2-(trifluoromethyl)propene. A mixture of 40 g of gaseous 1,3,3,3-tetrafluoro-2-(trifluoromethyl)propene and hydrogen (2:3 by volume) was passed over 1% Pd/ Al_2O_3 at room temperature. The hydrogenation gave 34 g (80%) of 1,1,1,3,3,3-hexafluoro-2-(fluoromethyl)propene, b. p. 39-40°. Found %: C 26.10; H 1.66; F 72.29. $\text{C}_4\text{H}_3\text{F}_7$. Calculated %: C 26.08; H 1.62; F 72.28.

Dehydrofluorination of 1,1,1,3,3,3-Hexafluoro-2-(fluoromethyl)propene. 1,1,1,3,3,3-Hexafluoro-2-(fluoromethyl)propene (34 g) was added to a suspension of 20 g of KOH powder in 20-25 ml of dibutyl ether; after the addition the reaction mixture was heated for 20-30 minutes at 40-50° under reflux. The reaction products were then distilled off into a trap cooled to -60°. After distillation we obtained 21.5 g (70%) of 3,3,3-trifluoro-2-(trifluoromethyl)propene, b. p. 13-14° [6]. Found %: C 29.46; H 1.30; F 69.90; mol. wt. 164. $\text{C}_3\text{H}_2\text{F}_6$. Calculated %: C 29.26; H 1.15; F 69.51; mol. wt. 164.

Dehydrofluorination of 1,1,1,3,3,3-Hexafluoro-2-methylpropane. 40-50 g of 90% KOH was placed in a *J*-tube and melted by heating it to 170-172° in a glycerol bath. Gaseous 1,1,1,3,3,3-hexafluoro-2-methylpropane (34 g) was passed slowly through the melt, and the reaction products were collected in a cooled trap and then again passed through the alkali melt 2-3 times. As a result of the reaction we obtained 20 g of substance, from which by distillation through a column we isolated 6 g of unchanged 1,1,1,3,3,3-hexafluoro-2-methylpropane and 13.2 g (54% on the 1,1,1,3,3,3-hexafluoro-2-methylpropane that reacted) of 1,1,3,3,3-pentafluoro-2-methylpropene, b. p. 12-13°. For 1,1,3,3,3-pentafluoro-2-methylpropene the literature [6, 13] gives b. p. 13.8°. Found %: C 32.07; H 2.04; F 65.96; mol. wt. 147. $C_4H_5F_5$. Calculated %: C 32.87; H 2.05; F 65.06; mol. wt. 146.

Dehydrofluorination of 1,1,1,2,3,3-Hexafluoropropane. 1,1,1,2,3,3-Hexafluoropropane (24 g) was passed slowly into a suspension of 18 g of KOH powder in 15 ml of dibutyl ether with stirring and cooling with ice water. Reaction occurred with evolution of heat, and the reaction products liberated were collected in a trap cooled to -70°. We obtained 17.3 g of substance, from which by distillation we isolated 3.5 g of unchanged 1,1,1,2,3,3-hexafluoropropane, b. p. 4-5°, and 12.8 g (80%) of 1,2,3,3,3-pentafluoropropene ($CF_3CF=CFH$), b. p. -20°. Found %: C 27.21; H 0.79; F 71.71; mol. wt. 132.5. $C_3H_2F_5$. Calculated %: C 27.27; H 0.75; F 71.96; mol. wt. 132.

Hydrogenation of 1,2,3,3,3-pentafluoropropene. A mixture of 23 g of gaseous 1,2,3,3,3-pentafluoropropene and hydrogen (2:3 by volume) was passed over 1% Pd/ Al_2O_3 at room temperature. The hydrogenation products were collected in a cooled trap and distilled through a column. We obtained 13.2 g (60%) of 1,1,1,2,3,3-pentafluoropropane, b. p. 20°. NMR (nuclear magnetic resonance spectrum): δ 7.15 (CF_3); 20.59 (CFH); 23.46 (CF_2H_2). Found %: C 26.88; H 2.59; F 70.22; mol. wt. 134.5. $C_3H_2F_5$. Calculated %: C 26.84; H 2.23; F 70.88; mol. wt. 134. We isolated also 6.6 g (about 30%) of 1,1,1,2-tetrafluoropropane, b. p. -1°. Found %: C 30.71; H 3.95; mol. wt. 115. $C_3H_4F_4$. Calculated %: C 31.03; H 3.44; mol. wt. 116.

Dehydrofluorination of 1,1,1,2,3,3-Pentafluoropropane. 1,1,1,2,3,3-Pentafluoropropane (20 g) was added with stirring to a suspension of 20 g of KOH in dibutyl ether. The reaction products were collected in a trap cooled to -78°, and were then passed again through the suspension of alkali. Distillation of the reaction products through a column gave 11.5 g (70%) of 2,3,3,3-tetrafluoropropene, b. p. -28° [7].

Hydrogenation of 1,1,3,3,3-Pentafluoropropene. A mixture of 20 g of gaseous 1,1,3,3,3-pentafluoropropene and hydrogen (2:3 by volume) was passed over 1% Pd/ Al_2O_3 at room temperature. Distillation of the reaction products gave 16 g (70% on the 1,1,3,3,3-pentafluoropropene taken) of 1,1,1,3,3-pentafluoropropane, b. p. 12°. NMR: δ 5.57 (CF_3); 10.72 (CF_2H) * Found %: C 27.03; H 2.05; F 70.43; mol. wt. 135. $C_3H_2F_5$. Calculated %: C 26.84; H 2.23; F 70.88; mol. wt. 134.

Dehydrofluorination of 1,1,1,3,3-Pentafluoropropane. 1,1,1,3,3-Pentafluoropropane (15 g) was passed twice through a suspension of 20 g of KOH powder in dibutyl ether. The condensed reaction product was distilled through a column and gave 9 g (70%) of 1,3,3,3-tetrafluoropropene, b. p. -16° [8, 9].

Hydrogenation of Perfluorobutadiene. A mixture (20 liters) of perfluorobutadiene and hydrogen (ratio 1:4 by volume) was passed over 15 g of 1% Pd/ Al_2O_3 at room temperature. The reaction gave 20 g (66%) of 1,1,2,3,4,4-hexafluorobutane [16], b. p. 63-65° and n_D^{20} 1.2985.

Dehydrofluorination of 1,1,2,3,4,4-Hexafluorobutane. 1,1,2,3,4,4-Hexafluorobutane (11 g) was refluxed for 1-1.5 hours in presence of KOH powder (25-30 g); the reaction products were then distilled off through a column. We obtained 8.5 g (85%) of 1,1,2,4,4-pentafluoro-2-butene, b. p. 56° and n_D^{20} 1.306. Found %: C 32.76; H 2.24; F 64.91. $C_4F_5H_3$. Calculated %: C 32.87; H 2.04; F 65.06.

* The spectra of nuclear magnetic resonance (NMR) of F^{19} were determined at the Radioelectronics Department of the Physics Faculty of the Moscow State University by Yu. S. Konstantinov. The resonance frequency of the supporting sample (CF_2Cl_2) was 18.25 MHz. The relative chemical displacement was calculated from the formula $\delta = \Delta f / f_{\text{support}} \cdot 10^5$, in which f is the resonance frequency.

Oxidation of 1,1,2,4,4-Pentafluoro-2-butene. With passage of carbon dioxide, 15 g of 1,1,2,4,4-pentafluoro-2-butene was added gradually to a solution of 50 g of potassium permanganate in 250 ml of water at room temperature; reaction occurred with evolution of heat; stirring was continued for 4-4.5 hours. The reaction mixture was then stirred further for 5-6 hours with passage of carbon dioxide and warming to 60-70°. Sulfur dioxide was passed through the cooled solution until colorless, and the precipitate was filtered off. The filtrate was placed in a continuous extractor and extracted with ether for 24 hours. The ether solution was dried and distilled; we isolated 7.6 g (40%) of difluoroacetic acid, b. p. 128-130°. The acid was identified as its aniline salt, m. p. 78°, undepressed by admixture of the aniline salt prepared from pure difluoroacetic acid.

Bromination of 1,1,2,4,4-Pentafluoro-2-butene. Bromine (3 ml) was added to a solution of 8 g of 1,1,2,4,4-pentafluoro-2-butene in 10 ml of glacial acetic acid, and the mixture was heated in a sealed tube in a boiling water bath. The reaction solution was washed with sodium bicarbonate solution and with water, and it was dried with anhydrous magnesium sulfate. Distillation gave 9.5 g (about 45%) of the dibromide, b. p. 146-148°. Found %: C 16.00; H 1.07; F 31.46. $C_4H_2F_8Br_2$. Calculated %: C 15.69; H 0.98; F 31.06.

SUMMARY

1. It is shown that perfluoro olefins may be catalytically hydrogenated. Perfluoroethylene, perfluoropropene, perfluoroisobutene, and other fluoro olefins were hydrogenated over nickel and palladium catalysts.
2. In hydrogenation over a nickel catalyst, in addition to the normal products of hydrogen addition, products resulting from the further replacement of fluorine by hydrogen are formed. Over a palladium catalyst products of normal hydrogenation are formed almost exclusively.
3. By the catalytic hydrogenation of perfluoro olefins with subsequent dehydrofluorination, various ethylene, propene, and isobutene derivatives containing different amounts of fluorine were synthesized.

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