

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

ARKEMA FRANCE,

Petitioner,

v.

HONEYWELL INTERNATIONAL, INC.,

Patent Owner.

IPR No. IPR2015-00916

U.S. Patent No. 8,710,282

DECLARATION OF BRIAN DURRANCE

DECLARATION OF BRIAN DURRANCE

Dear Sir or Mam:

I, Brian Durrance, being over the age of eighteen, hereby declare the following based on my personal knowledge:

1. I was employed in the circulation department of University of Michigan Library System ("the University Library") from approximately 1985 until at least 1989. During this time I worked at the Medical School Library, the Dentistry Library, and the Graduate Library. During this time my responsibilities and duties included: managing journal collections; working with technical processing, bindery, and circulation departments; and intaking, organizing and cataloging journals. During this time I also received on-the-job training in library science and particularly the University Library procedures.
2. Through my employment with the University Library, I became aware of the University Library's hard copy cataloging system, call number system, and procedure for receiving and entering materials into the catalog. At least since the 1960's, the University Library has maintained a subscription to chemical abstracts, which is a database for chemical journals and which is organized, among other things, by subject matter. Through the University Library's subscription to chemical abstracts, members of the general public have access to database for chemical journals.
3. Through my employment with the University Library, I also became familiar with the file and record maintenance procedures at the University Library, including procedures relating to cataloguing, processing, and maintenance of books and references received by the University Library.

4. I am currently employed by AIC Services, a document search and delivery company, as the general manager; I have held this title since at least 2000. In my role as General Manager, I frequently go to libraries, including the University Library, to obtain reference materials.
5. Through my employment with the AIC, I kept current my knowledge and understanding of the University Library's hard copy cataloging system. I also became familiar with the University Library's electronic cataloging system, including electronic searching options, call number system, and procedure for receiving and entering materials into the catalog. The electronic searching options for the University Library include subject matter searches. The electronic cataloging system was introduced into the University Library in the late 1980's and matured into the dominant cataloging system for the University Library by the early 2000's.
6. I have been asked to review the University Library's records with respect to the following reference carried by the University Library and having Call No. QD1 .A323: *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science (Izvestiya Akademii Nauk SSSR), A Publication of the Academy of Sciences of the USSR, Volume 1960, Issue 8 (August 1960)* ("the August 1960 Bulletin"). The August 1960 Bulletin included, among other things, the article *Reactions of Fluoro Olefins, Catalytic Hydrogenation of Perfluoro Olefins*, I.L. Knunyants, et al. ("Knunyants"). Knunyants and excerpts of the August 1960 Bulletin, including the cover page and the table of contents of the August 1960 Bulletin, are attached hereto as Exhibit 1. My review of the University Library records indicates the following:
7. The August 1960 Bulletin states on its face that it was published in August, 1960.

8. The August 1960 Bulletin is bound with the remaining monthly issues from the 1960 Volume of *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science* (collectively “the 1960 Issues of the Bulletin”). The University Library received the 1960 Issues of the Bulletin, including the August 1960 Bulletin and Knunyants, at least by December, 1961, as indicated by the date stamp “DEC 1961” on the inside the 1960 Issues of the Bulletin. A copy of the date stamp is attached hereto as Exhibit 2.
9. Exhibit 1 is a true and accurate copy of the cover page of the Bulletin, the Contents of the Bulletin, and the complete Knunyants article (pages 1312-1317).
10. In my opinion, Exhibit 1 was maintained in the University Library’s ordinary course of business and made available to the public since at least December of 1961.
11. General library cataloging and shelving practices from the timeframe including 1961 dictate that references such as the Knunyants article that are deposited in the University Library would have been indexed by subject matter, cataloged, and shelved. The index and catalog information and Knunyants article itself would have been accessible and available to the public at least by 1961. Accordingly, such documents were made available to the public, and persons interested and those having ordinary skill in the subject matter or art, exercising reasonable diligence, would have been able to locate them.
12. The Bulletin currently remains available to the public, and persons interested and those having ordinary skill in the subject matter or art, exercising reasonable diligence, would have been able to locate the Bulletin. I have personally located Exhibit 1, which includes excerpts of the Bulletin and the entire Knunyants article.

13. I declare under penalty of perjury of the laws of the United States that all statements
made herein are true and correct.

3/26/15
Date

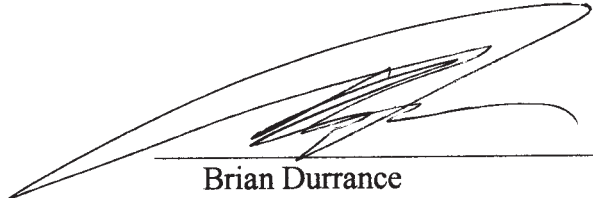

Brian Durrance

EXHIBIT 1

Number 8
August, 1960

BULLETIN OF THE ACADEMY OF SCIENCES

OF THE USSR

Division of Chemical Science

(IZVESTIYA AKADEMII NAUK SSSR)

(Otdelenie Khimicheskikh Nauk)

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:

No. 1

Jan.-Feb. 1952

	<i>U. S. and Canada</i>	<i>Foreign</i>
<i>Annual subscription</i>	\$80.00	\$85.00
<i>Annual subscription for libraries of nonprofit academic institutions</i>	30.00	35.00
<i>Single issue</i>	10.00	10.00

Copyright © 1961
CONSULTANTS BUREAU ENTERPRISES, INC.
227 West 17th Street, New York, N. Y.

Page 0000007

Editorial Board
(IZVESTIYA AKADEMII NAUK SSSR,
OTDELENIE KHIMICHESKIKH NAUK)

A. A. Akhrem (Secretary), I. I. Chernyaev, M. M. Dubinin
(Editor-in-Chief), A. F. Kapustinskii (Acting Editor),
V. N. Kondrat'ev, A. N. Nesmeyanov,
K. T. Poroshin

*Note: The sale of photostatic copies of any
portion of this copyright translation is expressly
prohibited by the copyright owners.*

Printed in the United States of America

CONTENTS

	PAGE	RUSS. PAGE
Synthesis and Study of the Properties of Lithium Peroxide Diperoxhydrate. S. Z. Makarov and T. A. Dobrynina	1229	1321
New Data on the Effect of Radioactive Radiation on Solids and External Radiation on Some Heterogeneous Chemical Processes. Vikt. I. Spitsyn	1233	1325
Determination of the Energy of the Bond of the Reacting Atoms of Organic Molecules with the Surface of MnO Catalyst. A. A. Tolstopyatova, A. A. Balandin, and V. Kh. Mayushenko	1240	1333
Change in Catalytic Activity of Nickel Stearate During the Oxidation of Ethylbenzene. R. F. Vasil'ev, Z. G. Kozlova, L. G. Chuchukina, V. Ya. Shlyapintokh, and N. M. Émanué1'	1244	1337
Macroscopic Stages in the Oxidation of Propane in the Presence of Chlorine. K. E. Kruglyakova and N. M. Émanué1'	1249	1342
Measurement of Ignition Lags at High Temperatures. S. M. Kogarko and A. A. Borisov	1255	1348
Theory of Chain-Thermal Flame Propagation. Communication 3. Effect of Transfer Coefficients on the Flame Propagation Rate. L. A. Lovachev	1261	1354
Potentials of Pt and Au Electrodes in HNO ₃ and NaNO ₃ Solutions Under the Action of Ionizing Radiation. N. A. Bakh and V. D. Bityukov	1265	1258
Steric Hindrance and the Conformation of Molecules. Communication 3. Molecular and Crystal Structure of 2,6-Dichloro-4-Nitrodimethylaniline. Yu. T. Struchkov and T. L. Khotsyanova	1275	1369
Covalent Radii of Carbon and the Conjugation Problem. B. M. Mikhailov	1284	1379
Action of Nucleophilic Reagents on Compounds of the Type [Cl(CH ₂) _n CCl =] ₂ . R. Kh. Freidlina and T. A. Kost	1291	1387
Action of Sulfur, Selenium, and Sulfur Chlorides on Trialkylaluminums. L. I. Zakharkin and V. V. Gavrilenko	1294	1391
2-Cyclopenten-1-ylphosphonic Esters and Some of Their Derivatives. B. A. Arbuzov and E. N. Dianova (Ukhvatova)	1301	1399
Tautomerism and Geometric Isomerism of Nitrogen-Containing Derivatives of Carbonyl Compounds. Communication 2. Polarographic Study of the Transformations of Phenylhydrazones of Some Aldehydes and Aliphatic-Aromatic Ketones in Methanol. Yu. P. Kitaev and A. E. Arbuzov	1306	1405
Reactions of Fluoro Olefins. Communication 13. Catalytic Hydrogenation of Perfluoro Olefins. I. L. Knunyants, M. P. Krasuskaya, and E. I. Mysov ...	1312	1412
Synthesis of Alkenylsilanes by the Addition of Dichloromethylsilane to Dienic and Acetylenic Compounds. V. F. Mironov and V. V. Nepomnina ...	1318	1419
Nitration of Aromatic Sila-Hydrocarbons in Which the Aromatic Ring Occupies Various Positions with Respect to the Silicon Atom. E. A. Chernyshev, M. E. Dolgaya, and A. D. Petrov	1323	1424

CONTENTS (continued)

	PAGE	RUSS. PAGE
Chemistry of 1,3-Cyclohexanedione: Communication 5. Chemical Properties of Enol Ethers of 1,3-Cyclohexanedione and Its Derivatives. S. I. Zav'yalov and G. V. Kondrat'eva	1328	1429
Possible Methods of Synthesizing Substances Allied to Vitamin A. L. A. Yanovskaya	1333	1435
Synthesis of Pyridine Bases from 1-Buten-3-Yne. Communication 3. Catalytic Synthesis of 6-t-Butyl- and 6-Aryl-2-Picolines. L. I. Vereshchagin and I. L. Kotlyarevskii	1338	1440
Synthesis and Properties of Di- and Tri- Phenylalkanes and Their Hydrogenation Products of Composition $C_{23}-C_{27}$. Communication 3. Selective Hydrogenation of Some Alkyl-triphenylmethanes. M. A. Chel'tsova and A. D. Petrov	1342	1445
Catalytic Synthesis of Nitriles. Communication 3. Preparation of Aromatic Nitriles. M. A. Popov and N. I. Shuikin	1349	1451
Catalytic Dehydrogenation of Branched C_6 Paraffins. N. I. Shuikin, E. A. Timofeeva, T. P. Dobrynina, Yu. N. Plotnikov, G. S. Petryaeva, and G. K. Gaivoronskaya	1353	1457
Effect of the Specific Surface of Platinized Aluminum Silicate on the Conversion of Nonane. Communication 2. Change of the Catalytic Activity of Platinized Aluminum Silicate on Treatment of the Carrier with Steam. Kh. M. Minachev, N. I. Shuikin, and M. A. Markov	1362	1466
Transformations of Hexane, Methylcyclopentane, and Cyclohexane in Presence of a Rhenium-Alumina Catalyst and of Hydrogen Under Pressure. Kh. M. Minachev, M. A. Ryashentseva, and B. A. Rudenko	1366	1471
Hydrogenation of Di-2-Cyclopenten-1-Ylacetylene Over Pd, Pt, and Ni Catalysts. A. F. Plate and V. I. Stanko	1375	1481
High-Temperature Dehydrogenation of Ethylbenzene. A. M. Brodskii, K. P. Lavrovskii, and E. D. Filatova	1383	1490
Catalytic Isomerization of Cyclopropane in Mixtures with Olefins. N. I. Ershov, V. R. Erokhina, and Ya. T. Eidus	1387	1495
Esters of Peptides Containing L-Proline and Glycine. V. A. Shibnev, T. D. Kozarenko, and K. T. Poroshin	1392	1500
BRIEF COMMUNICATIONS		
Preparation of Phenylboron Dibromide by Direct Synthesis. E. I. Frenkin, A. A. Prokhorova, Ya. M. Paushkin, and A. V. Topchiev	1398	1507
Dehydration of Tetrahydropyran Over $TiO_2-Al_2O_3$. N. I. Shuikin and V. V. An	1400	1508
Catalytic Synthesis of 2,4-Di-Tert-Amylphenol. E. A. Vikterova, N. I. Shuikin, and G. S. Korosteleva	1402	1510
Action of Nitric Acid on the β -Guaiacyl Ether of α -Veratrylglycerol. A. A. Chuksanova and N. N. Shorygina	1403	1511
Use of Wittig Reaction for Synthesizing α,β -Unsaturated and Polyenoic Acids. V. F. Kucherov, B. G. Kovalev, I. I. Nazarova, and L. A. Yanovskaya	1405	1512
Diene Synthesis with 1,4-Dithioethyl-1,3-Butadiene and Cyclopentadiene. M. F. Shostakovskii, A. V. Bogdanova, and G. I. Plotnikova	1408	1514
Some α -Amino Acids Containing Trifluoromethyl Groups. I. L. Knunyants and Yu. A. Cheburkov	1411	1516
Order of Addition of Diisobutylaluminum Hydride to Dimethylfulvene. L. I. Zakharkin, V. V. Gavrilenko, Z. N. Parnes, and D. N. Kursanov	1413	1518
Determination of Elements in Tungsten Sulfide Catalysts. V. A. Klimova, E. G. Bereznitskaya, and G. K. Mukhina	1416	1520

CONTENTS (continued)

	PAGE	RUSS. PAGE
LETTERS TO THE EDITOR		
N → O Benzoyl Migration of Diastereoisomeric 1,2-Diphenyl-1-Benzoylamino-3-Propanols B. I. Kurtev, N. M. Mollov, and A. S. Orakhovats	1418	1522
Catalytic Hydrogenation of Wood and Other Vegetable Materials. N. A. Vasyunina, A. A. Balandin, S. V. Chepigo, and G. S. Barysheva	1419	1522
Structure of Double Diazonium Salts. L. A. Kazitsyna, O. A. Reutov, and Z. F. Buchkovskii	1420	1523
Method of Synthesizing Mercaptals and Dimercaptals of Various Aldehydes from the Cor- responding Acetals. M. F. Shostakovskii, A. V. Bogdanova, and G. I. Plotnikova	1421	1524

REACTIONS OF FLUORO OLEFINS

COMMUNICATION 13. CATALYTIC HYDROGENATION OF PERFLUORO OLEFINS

I. L. Knunyants, 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*,

No. 8, pp. 1412-1418, August, 1960

Original article submitted March 3, 1959

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/ Al_2O_3) 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-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/ Al_2O_3 at room temperature replacement of chlorine by hydrogen occurred with the formation of trifluoroethylene and its subsequent hydrogenation. Under certain experimental conditions $\text{CF}_2=\text{CFH}$ 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)propane (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 (IV) 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

TABLE

Compounds Obtained by Catalytic Hydrogenation and Dehydrofluorination Reactions

No.	Formula	B.p. (°C)	No.	Formula	B.p. (°C)
1	$\text{CF}_3\text{H}-\text{CF}_2\text{H}$	-22, 5	12	$\text{CF}_3-\text{C}(\text{CF}_3)=\text{CFH}$	17
2	$\text{CF}_2\text{H}-\text{CFH}_2$	3	13	$\text{CF}_3-\text{CH}=\text{CFH}_2$	40
3	CF_2-CFH	-51	14	$\text{CF}_3-\text{C}(\text{CF}_3)=\text{CH}_2$	13
4	$\text{CF}_3-\text{CFH}-\text{CF}_2\text{H}$	5	15	$\text{CF}_3-\text{CH}=\text{CH}_2$	21
5	$\text{CF}_3-\text{CF}=\text{CFH}$	-20	16	$\text{CF}_3-\text{C}(\text{CF}_3)=\text{CF}_2$	12
6	$\text{CF}_3-\text{CFH}-\text{CFH}_2$	20	17	$\text{CF}_2\text{H}-\text{CFH}-\text{CFH}-\text{CF}_2\text{H}$	65
7	$\text{CF}_3-\text{CF}-\text{CH}_2$	-28	18	$\text{CF}_2\text{H}-\text{CF}=\text{CH}-\text{CF}_2\text{H}$	56
8	$\text{CF}_3-\text{CFH}-\text{CH}_3$	-1			
9	$\text{CF}_3-\text{CH}_2-\text{CF}_2\text{H}$	12			
10	$\text{CF}_3-\text{CH}=\text{CFH}$	-16			
11	$\text{CF}_3-\text{CH}-\text{CF}_2\text{H}$ CF_3	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: CF₂HCF₂H has b. p. -23° [10], and CF₂HCFH₂ 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 62.4 g of tetrafluoroethane by distillation. The condensate did not contain trifluoroethane. The yield of CF₂HCF₂H 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 $\text{CF}_2=\text{CFH}$ 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 (18 liters at STP) of 40% of perfluoropropene and 60% of H_2 was passed at 3 liters/hr over 15 g of 1% $\text{Pd}/\text{Al}_2\text{O}_3$. 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. $4-5^\circ$. 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 (18.7 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 $55-60^\circ$. 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. $33-34^\circ$ 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 $100-130^\circ$ 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. $33-34^\circ$, 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 $40-50^\circ$ 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. $17-18^\circ$. Found %: C 25.96; H 0.64; F 73.17; mol. wt. 182.5. C_4HF_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 $35-40^\circ$; the reaction mixture was heated further for 2-2.5 hours under reflux at $30-40^\circ$. 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% $\text{Pd}/\text{Al}_2\text{O}_3$ at room temperature. The hydrogenation gave 34 g (80%) of 1,1,1,3,3,3-hexafluoro-2-(fluoromethyl)propane, b. p. $39-40^\circ$. 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)propane. 1,1,1,3,3,3-Hexafluoro-2-(fluoromethyl)propane (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 $40-50^\circ$ 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. $13-14^\circ$ [6]. Found %: C 29.46; H 1.30; F 69.90; mol. wt. 164. $\text{C}_4\text{H}_2\text{F}_6$. 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 U-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. $C_4H_3F_5$. 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 (60%) 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_3HF_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-pentachloropropane, b. p. 20°. NMR (nuclear magnetic resonance spectrum): δ 7.15 (CF_3); 20.59 (CFH); 23.46 (CFH_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-tetrachloropropane, 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-Pentafluoropropane. 1,1,1,2,3-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. $C_3H_3F_5$. 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 Radiotechnics 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. $C_4H_3F_5Br_2$. 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.

LITERATURE CITED

1. C. Schuster, Z. Elektrochem. **38**, 614 (1932).
2. J. R. Lacher, A. Klanpour, F. Oettig, and J. D. Park, Trans. Faraday Soc. **52**, 1500 (1956).
3. I. L. Knunyants and E. I. Mysov, Authors' Certificate 110,936, February 11, 1957.
4. I. L. Knunyants, E. I. Mysov, and M. P. Krasuskaya, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 906 (1958).
5. R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 3005 (1955).
6. R. N. Haszeldine, J. Chem. Soc., 3565 (1953).
7. A. L. Henne and T. P. Waalkes, J. Am. Chem. Soc. **68**, 496 (1946).
8. R. N. Haszeldine, J. Chem. Soc., 3490 (1952).
9. R. N. Haszeldine and B. R. Steele, J. Chem. Soc., 1199 (1953).
10. A. L. Henne and M. W. Renoll, J. Am. Chem. Soc. **58**, 887 (1936).
11. D. S. Young, N. Fukuhara, and L. A. Bigelow, J. Am. Chem. Soc. **62**, 1171 (1940).
12. I. L. Knunyants, E. Ya. Pervova, and V. V. Tyuleneva, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 843 (1956).
13. A. L. Henne and J. W. Shepard, J. Am. Chem. Soc. **72**, 3577 (1950).
14. N. Fukuhara and L. A. Bigelow, J. Am. Chem. Soc. **63**, 788 (1941).
15. A. T. Morse, P. B. Ayscough, and L. C. Leitch, Canad. J. Chem. **33**, 453 (1955).
16. R. N. Haszeldine and J. E. Osborne, J. Chem. Soc., 3880 (1955).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

EXHIBIT 2

THE UNIVERSITY
OF MICHIGAN
DEC 1961
CHEMISTRY
LIBRARY

Number 12
December, 1960

ИЗВЕСТИЯ
АКАДЕМИИ НАУК СССР
ОТДЕЛЕНИЕ
ХИМИЧЕСКИХ НАУК

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science

(IZVESTIYA AKADEMII NAUK SSSR)

(OTDELENIE KHIMICHESKIKH NAUK)

IN ENGLISH TRANSLATION

$\left(\frac{c}{b}\right)$

CONSULTANTS BUREAU

THE UNIVERSITY,
OF MICHIGAN

DEC 1961

CHEMISTRY
LIBRARY

Number 12

December, 1960

OF THE