

1.47 mmoles of $(CF_3PH)_2$ and 129.5 mg. of a liquid having 3.7 mm. vapor tension at 0° . The gas volume of this sample implied a mol. wt. value of 298; calcd. for the formula $H_2(CF_3P)_3$, 302. The yield, from a far-from-complete reaction, was 10%.

Proof and Properties of 1,2,3-Tris-(trifluoromethyl)-triphosphine.—A sample of the supposed triphosphine weighed as 85.7 mg. (0.284 mmole) was left in contact with an active nickel surface (formed by the decomposition of nickel carbonyl in the vacuum system) at 25° . The decomposition, signalled by a pressure increase, was essentially complete in 24 hr. After six days the products were separated by fractional condensation to give 0.28 mmole of CF_3-PH_2 (identified by its infrared spectrum) and a tetramer-pentamer mixture equivalent to 0.560 mmole of CF_3P units, as shown by conversion to CF_3PCl_2 . Thus the total CF_3P groups amounted to 0.840 mmole (calcd., 0.852) and the hydrogen 0.56 mg. atom (calcd., 0.568). Thus the formula of the triphosphine was not in doubt. Although unstable on the active nickel surface, this triphosphine showed no tendency toward decomposition in two months of storage in a clean Pyrex-glass tube. Its formation even at 140° also argues for its stability in the practical sense.

The room temperature hydrolysis of 0.246 mmole of $H_2(CF_3P)_3$ with 10% sodium hydroxide gave 0.236 mmole of HCF_3 .

The infrared spectrum of the triphosphine is represented in Table VII. The separation of the peaks due to the C-F vibrations (1145 and 1160 cm^{-1}) is typical for one CF_3 group on each phosphorus atom, and supports the open chain structure $H-P-P-P-H$.



TABLE VII

INFRARED SPECTRUM OF THE TRIPHOSPHINE

Frequency (cm^{-1})	2330	2260	1160	1145	870	850	745
Intensity	Med.	Weak	V. str.	V. str.	(Infl.)	Str.	Med.

In the ultraviolet the triphosphine shows an absorption peak at 2075 Å. (molar extinction coefficient ϵ 7,600) and a shoulder at 2240 Å. (ϵ 5,500). The shift toward the visible region, relative to the biphosphine $(CF_3PH)_2$ (maximum at 2040 Å.) is qualitatively in agreement with expectations, since more resonance structures can be written for the triphosphine. Since all of the resonance structures (except the classical Lewis picture) involve charge-separations, these make their major contribution to the excited state, lowering it relative to the ground state.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

A New Metal Carbonyl Synthesis¹

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RECEIVED JUNE 6, 1958

The reaction of benzophenone sodium with chromic chloride in tetrahydrofuran yielded an intermediate, which upon carbonylation at 200 atmospheres and 100° for 1 hr., gave chromium carbonyl in 59% yield. The use of manganese chloride in an analogous carbonylation after hydrolysis gave a 32% yield of manganese carbonyl. This new process appears to offer advantages in yield and ease of operation.

The preparation of the carbonyls of iron, cobalt and nickel has been effected in a variety of ways, including direct reaction of the metal with carbon monoxide. On the other hand, synthesis of chromium and manganese carbonyls has required more elegant methods. One such method involves treating a mixture of a Grignard reagent and a salt of the metal with carbon monoxide. This procedure has given yields of up to 67% of chromium carbonyl³ and also gave the first indication that a carbonyl of manganese could be prepared.⁴

More recently chromium carbonyl was prepared in substantial yields by Brimm, Lynch and Sesny.⁵ They carbonylated a mixture of chromic chloride, magnesium and iodine in ethyl ether to obtain a 57% yield. Natta, Ercoli, Calderazzo and Rabizzoni⁶ carbonylated a mixture of chromic acetylacetonate, magnesium and iodine in pyridine to obtain an 82% yield. Fischer and Hafner⁷ report an 83% yield from the carbonylation of a reaction mixture

prepared from chromic chloride, aluminum powder, aluminum chloride and benzene.

The first preparation of manganese carbonyl that yielded enough material for adequate characterization was the reaction of manganese iodide, copper and magnesium in ethyl ether with carbon monoxide.⁸ The yield was about 1%. Somewhat improved yields have been reported by a modified Grignard procedure.⁹

This paper describes the results of an investigation in these laboratories in which it was found that the action of carbon monoxide on chromium benzophenone ketyl in tetrahydrofuran yielded chromium carbonyl in 59% yield. Application of the reaction to manganese gave manganese carbonyl in 32% yield.

The preparation and the chemistry of the benzophenone ketyls of the alkali and alkaline earth elements has been studied by Bachmann¹⁰ and many of the anomalous results of previous literature have been elucidated. In contrast, the preparation and chemistry of ketyls of the metals of other groups has received little attention. This may have been due, in part, to the fact that preparing the ketyls directly from the ketone and the metal is in many cases difficult or even thermodynamically impossible. In the present investigation, the ketyls were

(1) Presented in part before the Division of Inorganic Chemistry at the 134th meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

(2) Koppers Company, Pittsburgh, Pennsylvania.

(3) B. B. Owen, J. English, H. G. Cassidy and C. V. Dundon, *THIS JOURNAL*, **69**, 1723 (1947).

(4) D. T. Hurd, G. W. Sentell, Jr., and F. J. Norton, *ibid.*, **71**, 1899 (1949).

(5) E. O. Brimm, M. A. Lynch and W. J. Sesny, U. S. Patent 2,803,525 (August 20, 1957).

(6) G. Natta, R. Ercoli, F. Calderazzo and A. Rabizzoni, *THIS JOURNAL*, **79**, 3611 (1957).

(7) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10B**, 665 (1955); German Patent 1,007,305 (May 2, 1957).

(8) E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, *THIS JOURNAL*, **76**, 3831 (1954); M. A. Lynch, Jr., U. S. Patent 2,825,631 (March 4, 1958).

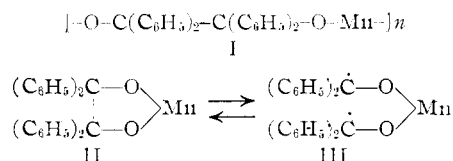
(9) V. Hnizda, U. S. Patent 2,822,247 (February 4, 1958).

(10) W. E. Bachmann, *THIS JOURNAL*, **55**, 1179 (1933).

formed indirectly by treating the sodium ketyl with the chloride of the metal.

The chemistry of manganese benzophenone ketyl is quite similar to that of the corresponding sodium ketyl. Thus, addition of a tetrahydrofuran solution of the ketyl to aqueous acetic acid solution gives benzpinacol in high yield, whereas the action of oxygen on the ketyl gives benzophenone. Also, the purple color of the ketyl apparently arises from partial dissociation into free radicals. This may be demonstrated by the incremental addition of reagents that are known to react with free radicals (such as O₂ or I₂). After each addition, the purple color discharges rapidly and then slowly reappears upon standing.

Some consideration should be given to the structure of the manganese ketyl. When manganese chloride is added to the blue sodium ketyl, a viscous yellow slurry is produced. Upon refluxing (65–70°), the viscosity decreases and the mixture acquires a purple color. When permitted to stand, the sodium chloride settles to the bottom, and the ketyl may be decanted in a clear purple solution. In media of low dielectric constant, the most simple explanation might be to attribute the viscosity of the yellow intermediate to a polymeric intermediate such as I. The purple solution may contain an equilibrium mixture of II and III.



The reaction of the sodium benzophenone ketyl with chromic chloride yields a viscous yellow slurry quite similar to the yellow intermediate in the manganese case. Heating at 65–70° produces no further change in appearance.

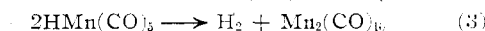
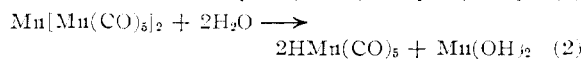
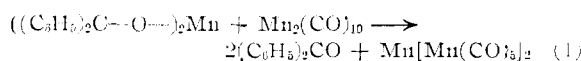
The essential function of the ketyl in the carbonyl synthesis is the reduction of the chromium or manganese from its initial valence state in the metal chloride to the zero valence of the carbonyl. It has been observed that manganese ketyl will break down to manganese metal at elevated temperatures in the absence of carbon monoxide. However, it is not known whether such reduction occurs prior to, or after, partial coordination with carbon monoxide or the ether solvent.

The solvent appears to play an important role in the synthesis. Although manganese ketyl may be formed in toluene and is soluble in that medium, carbonylation gives very low yields of manganese carbonyl. Similarly, iso-octane and ethyl ether give low yields. The best results are obtained with strongly coordinating ethers such as tetrahydrofuran, dioxane or 1,2-dimethoxyethane.

Although the carbonylation of chromium ketyl gives chromium carbonyl and benzophenone in good yield without appreciable side reactions, complications occur in the manganese case. The fundamental difficulty appears to be a reaction between manganese ketyl and manganese carbonyl. Such a reaction may be observed readily by adding manganese carbonyl to a solution of manganese ketyl. A small amount of carbonyl instantly discharges

the purple color; however, upon standing the color returns. This is analogous to the reaction of the ketyl with oxygen, in which the dissociated form reacts rapidly and, after consumption of the oxygen by the ketyl radical, further dissociation occurs to yield again a colored solution.

The infrared spectra of a reaction product of the ketyl with manganese carbonyl and of a ketyl carbonylation product are virtually identical. The typical three manganese carbonyl bands centered at 5 μ are absent, and a strong absorption occurs in the 5.2–5.4 μ region. Since sodium manganese pentacarbonyl also absorbs in the latter region, it would appear possible that a salt containing the manganese pentacarbonyl negative ion may be present in the product. A reaction such as that presented in equation 1 would account for the formation of such a product, and equations 2 and 3 would account for the ultimate formation of manganese carbonyl.



In reality, the chemistry appears to be somewhat more complex. Crude experiments indicate that more than one mole of ketyl can react with each mole of manganese carbonyl. Furthermore, the decomposition of manganese carbonyl hydride may be a more complex process than that indicated by equation 3.

Experimental

Chromium Carbonyl Synthesis.—To a solution of 127.5 g. (0.70 mole) of benzophenone in 1500 ml. of purified tetrahydrofuran¹¹ in a three-neck flask and protected by an inert atmosphere, 16.1 g. (0.70 mole) of sodium, as a 50% dispersion in white mineral oil, was added with stirring. The sodium dispersion was added from a polyethylene squeeze bottle at a rate such that gentle refluxing was maintained by the heat of reaction. After the reaction was completed, the reaction mixture was cooled to 40° and 37 g. (0.23 mole) of finely divided anhydrous chromic chloride was added rapidly with constant stirring. After a short induction period, reaction occurred, as evidenced by a five degree increase in the temperature of the reaction mixture and a color change from blue to yellow to yellow green. After the mixture had cooled to room temperature, it was charged to an autoclave without coming into contact with air. With stirring, the autoclave was pressured to 2500 p.s.i.g. with carbon monoxide. Over a period of 30 minutes, the temperature was increased to 100°. At about 70°, reaction was evidenced by a 75 p.s.i. decrease in recorded pressure, even though the temperature was increasing. To complete the reaction, the autoclave was held at 100° and 2800 p.s.i.g. pressure for 1 hr. After cooling, it was vented and discharged, using a small quantity of tetrahydrofuran for rinsing. Approximately 1500 ml. of tetrahydrofuran was distilled through a column packed with glass helices. The residue was mixed with water and steam distilled. The chromium carbonyl was filtered from the steam distillate, dried by azeotropic distillation with benzene and crystallized from the benzene. The yield was 30 g. (59%) of chromium carbonyl having a melting point of 151–152°.

Synthesis of Manganese Carbonyl.—To a solution of one mole of monosodiobenzophenone in 1000 ml. of tetrahydrofuran, 62.9 g. (0.50 mole) of finely divided anhydrous manganese chloride was added. The mixture had from blue to yellow, but after refluxing for 45 minutes it had a bluish-

(11) M. S. Kharasch and O. Reimuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954 p. 25.

TABLE I
 MANGANESE CARBONYL PREPARATIONS

Run	Solvent	Reaction temp., °C.	Time heating to reaction temp., hr.	Time at reaction temp., hr.	Pressure at room temp., p.s.i.g.	Pressure at reaction temp., p.s.i.g.	Yield, %
1	Tetrahydrofuran	65	0.75	4.0	2450	3000	10
2	Tetrahydrofuran	150	0.75	0.8	2050	3000	17
3	Tetrahydrofuran	200	1.6	1.0	1400	3000	32 ^a
4	Tetrahydrofuran	150	^b	1.0	..	3000	4
5	Tetrahydrofuran	150	1.0	0.7	6050	10000	22
6	Tetrahydrofuran	200	1.5	3.0	6000	10000	30
7	Toluene	150	1.0	0.5	2000	3000	ca. 1 ^c
8	Ethyl ether	150	1.0	1.0	2000	3000	ca. 1 ^c
9	Dioxane	150	1.0	0.75	2000	3000	25 ^c
10	Monoglyme ^d	150	1.0	1.0	2500	3600	12 ^c

^a Flame-photometric analysis of the reaction product prior to work up indicated a 42% yield of manganese carbonyl.

^b Heated at 150° for 1 hr. before pressuring with carbon monoxide. ^c Product not isolated—yield based on flame photometer analysis. ^d Dimethyl ether of ethylene glycol (H. C. Brown, E. I. Mead and B. C. Subba Rao, *THIS JOURNAL*, 77, 6209 (1955)).

purple color. The mixture was cooled and transferred to a two-liter autoclave in the absence of air. The autoclave was pressured to 6000 p.s.i.g. with carbon monoxide and, over a period of 90 minutes, was heated to 200°, at which time the pressure was 10,000 p.s.i.g. The autoclave was maintained at these conditions for 3 hr. After cooling, the carbon monoxide was vented, and the autoclave was discharged and washed with 500 ml. of ether to recover the last portions of the product. The combined product and ether wash were hydrolyzed and steam distilled until manganese carbonyl no longer distilled at a significant rate. The manganese carbonyl was extracted with benzene and dried by azeotropic distillation. The benzene was distilled until approximately 100 ml. of solution remained. Upon cooling, the manganese carbonyl crystallized and was collected by filtration. A yield of 29 g. (30%) of manganese carbonyl was collected, having a melting point of 151–152°.

Synthesis of Manganese Carbonyl—Effect of Variables.—A number of runs were made following the general procedure described above, in order to determine the effect of solvent and temperature on yield of manganese carbonyl. The data summarized in Table I show that "active ether" solvent, such as tetrahydrofuran and dioxane, are required to obtain maximum yield. The data also indicate that reaction temperatures above 150° probably are advantageous for obtaining maximum yield. In the pressure range of 3,000 to 10,000 p.s.i.g., the yield is not affected by pressure. In run number 4, where the manganese benzophenone ketyl was largely decomposed by heating in the absence of carbon monoxide for 1 hr. at 150°, only a 4% yield of manganese carbonyl was obtained on subsequent carbonylation.

Preparation of Manganese Benzophenone Ketyl Solution.—All of the following steps were carried out under an atmosphere of prepurified nitrogen. A dispersion of 23 g. (1.0 mole) of sodium in 200 ml. of toluene was prepared, using high-speed stirring. The mixture was permitted to cool and the sodium to settle, after which most of the supernatant toluene was removed by suction. Tetrahydrofuran (THF) then was added twice and removed by the same process, in order to free the sodium of the last of the toluene. The total volume finally was brought to 200 ml. by the addition of THF. The mixture was given an occasional swirl to keep the sodium suspended, and it then was added to a stirred solution of 1.0 mole (182 g.) of benzophenone in 1600 ml. of THF to yield the blue sodium ketyl. To this mixture was added 0.5 mole (63 g.) of powdered anhydrous manganese chloride. The color passed rapidly through a green stage and became yellow. The green phase is believed to be merely a blending of the blue of the sodium ketyl with the yellow of the subsequent intermediate. Upon refluxing for 30 minutes, the mixture passed through a brown color to become a deep purple. The brown color is believed to be a mixture of the yellow and the purple compounds. The yellow intermediate was a viscous mixture; whereas the purple product, upon standing several days, settled to yield a deposit of sodium chloride and a clear purple solution containing the manganese ketyl. This supernatant solution was the manganese ketyl solution referred to in the following experiments. Hydrolysis and analysis of a sample of the

manganese ketyl solution revealed it to contain 0.0145 g. of Mn per ml.

Reactions of Manganese Benzophenone Ketyl.—The following reactions were carried out to show the similarity of the reactions of the manganese ketyl to those of the sodium benzophenone ketyl reported by Bachmann.¹⁰

(a) **Hydrolysis.**—A 20-ml. portion of the manganese ketyl solution was added, with stirring, to 100 ml. of 10% aqueous acetic acid. The mixture was extracted with ether, and the ether extract was washed with 5% potassium bicarbonate solution and finally with water. Evaporation of the ether gave 1.8 g. of a white solid, m.p. 170–180°. Infrared analysis indicated that the solid consisted of about 14% benzophenone and 80% benzpinacol.

(b) **Oxidation.**—A 25-ml. portion of the manganese ketyl solution was stirred under nitrogen and small amounts of oxygen bubbled in intermittently. The purple color was immediately discharged by each addition of oxygen, but it reappeared upon standing several minutes without further oxygen addition. Complete oxidation of the ketyl finally resulted, and the mixture contained a black solid. The mixture was poured into 150 ml. of 10% acetic acid, and the product was worked up as in the above hydrolysis experiment. Evaporation of the ether yielded a solid which was sublimed to give 1.60 g. (64%) of crude benzophenone (m.p. 41–46°; mixed with authentic sample m.p. 42–49°).

Similar temporary decoloration of the manganese ketyl solution was obtained by the incremental addition of iodine, benzoyl peroxide and manganese carbonyl. Bachmann¹⁰ observed this effect with the sodium ketyl using iodine, and he has attributed it to rapid reaction of the iodine with the free radical form of the ketyl. The color is regained when the iodine is consumed and more of the metal benzpinacolate dissociates to the colored free radical.

(c) **Pyrolysis of the Ketyl Solution.**—A 20-ml. sample of the ketyl solution was sealed in a glass tube under nitrogen, and the tube was heated at 100° for 3 hr. without any evidence of reaction. However, when the tube was heated at 146° for 3 hr., decomposition did occur, as evidenced by the formation of a black precipitate and the solution's changing to a blood-red color. An additional 3 hr. heating at this temperature produced no further visible change.

The tube was opened, and the solvent was removed from a 5-ml. portion of the solution. The residue was sublimed to yield 0.25 g. of benzophenone, m.p. 45–47°. (This is a 50% yield, assuming the pyrolysis to give two molecules of benzophenone and one atom of manganese metal.) Another portion of the pyrolysis solution was hydrolyzed by addition of aqueous acetic acid and was shown to yield both benzophenone and benzpinacol. The black solid from the pyrolysis evolved a gas upon the addition of 1.0 *N* hydrochloric acid and is assumed to be manganese metal.

(d) **Reaction of Manganese Benzophenone Ketyl with Manganese Carbonyl.**—Preliminary experiments showed that adding manganese carbonyl to aliquots of the ketyl solution caused the solution to lose its characteristic color. This required somewhat less than 0.5 mole of manganese carbonyl per mole of ketyl. In more carefully controlled experiments, the following volumes of the THF-ketyl

solution (0.0144 g. Mn/ml.) and weights of manganese carbonyl were sealed in glass ampoules under nitrogen:

Sample	1	2	3	4
Vol. ketyl soln. (ml.)	9.85	8.0	9.90	7.56
Wt. $Mn_2(CO)_{10}$ (g.)	0.4212	0.2443	0.2358	0.1469
Molar ratio (ketyl:carbonyl)	2.38	3.34	4.29	5.27
Color after 2 days	Orange	Orange	Orange-red	Red

After standing for two days at room temperature, the tubes were opened and the infrared spectra of the solutions were obtained. The 5.0μ (manganese carbonyl) band was strongest in sample 1 and much weaker in the other three samples. Although the data are not subject to quantitative interpretation, it appears that somewhat in excess of 2.38 moles of manganese benzophenone ketyl will react with one mole of manganese carbonyl.

In order to study the products of the ketyl-carbonyl reaction, two hydrolysis experiments were carried out. In

the first experiment, a 20-ml. sample of the THF-ketyl solution was poured into 100 ml. of 10% acetic acid. The solution was extracted with ether, and the extract was washed with 5% potassium bicarbonate solution and with water. The ether was distilled, and the residue was analyzed by infrared spectroscopy. In the second experiment, 2.5 g. of manganese carbonyl was dissolved in 20 ml. of THF-ketyl solution, and the mixture was let stand for 30 minutes. The molar ratio of carbonyl to ketyl was 1.22. The solution was hydrolyzed, worked up and analyzed in the same manner as the control experiment with ketyl alone. The hydrolysis product from the control experiment contained 15% benzophenone and 79% benzpinacol, while the hydrolysis product from the reaction of manganese carbonyl with the ketyl solution contained 24% benzophenone, 23% benzpinacol and about 50% manganese carbonyl. These data show that benzophenone is produced by the reaction of the ketyl with manganese carbonyl.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

Free Energy Relations in Fluorocarbon-Hydrocarbon Systems

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RECEIVED JUNE 25, 1958

The mutual solubility curves have been determined for 14 fluorocarbon-hydrocarbon systems. The equations of Hildebrand fail to predict consolute temperatures of these systems although consolute compositions are satisfactorily predicted. Examples are given which show that the agreement between observed and calculated consolute temperature is not a good criterion for testing the applicability of the Scatchard-Hildebrand theory. The total vapor pressures of some fluorocarbon-hydrocarbon mixtures were measured in the two liquid phase region. It is shown that excess free energies of mixing in binary fluorocarbon-hydrocarbon systems can be estimated quite well from mutual solubility data through the use of Van Laar equations. An empirical correlation is also presented for the estimation of excess free energies of mixing or consolute temperatures in fluorocarbon-paraffin hydrocarbon systems from properties of the pure components. This correlation is based on a negative excess entropy of mixing at constant volume.

Experimental

Materials.—Most of the hydrocarbons used in this work were obtainable commercially in a reasonable degree of purity and were not further purified. The physical properties of these compounds are listed in Table I along with the reported literature values.

fluorocarbons have been reported in the literature; these values are also included in Table I.

Perfluorocyclic Oxide ($C_8F_{16}O$).—This material was the major constituent in "Fluorochemical O-75" manufactured by the Minnesota Mining and Manufacturing Company. It is believed that this fluorocarbon is a five- or six-membered

TABLE I
PHYSICAL PROPERTIES OF MATERIALS

Compound	Refractive index 25°		Density 25° (g./ml.)		B.p. 1 atm. (°C.)	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
<i>n</i> -Heptane	1.3852	1.38511 ²	0.6798	0.67951 ²	98.4	98.427 ²
Methylcyclohexane	1.4206	1.42058 ²	.76511	.76506 ²	100.9	100.934 ²
Toluene86232	.86230 ²	110.7	110.625 ²
Carbon tetrachloride	1.4567	1.4573 ³	1.5844	1.5845 ³
2-Butanone	1.3761	1.37643 ²	0.7995	0.79970 ²	79.6	79.59 ²
Perfluoroheptane (C_7F_{16})	1.2594	1.25818 ⁴	1.7258	1.71802 ⁴	82.1	82.5 ⁴
Perfluorocyclic oxide ($C_8F_{16}O$)	1.2770	1.7633	102.8
1-Hydroperfluoroheptane ($C_7F_{15}H$)	1.2700	1.2718 ⁵	1.7233	95.4	94-95 ⁶
Perfluorotributylamine [$(C_4F_9)_3N$]	1.2906	1.8772	177.6
Methyl perfluorooctanoate [$C_7F_{15}COOCH_3$]	1.2033	1.6967	160.8

Five fluorocarbon compounds were used in this work. The physical properties of these compounds are also listed in Table I. The physical properties of some of these

oxygen-containing ring with side chains. This material first was fractionated in a laboratory distillation column. The center cut from this fractionation was further purified by an azeotropic distillation with *n*-heptane.

The fluorocarbon then was separated from the *n*-heptane by cooling the azeotrope to Dry Ice Temperature where the liquid phases were found to have very low mutual solubility. The perfluorocyclic oxide now was freed from the small amount of remaining *n*-heptane by redistillation. This purified material exhibited only one peak when subjected to chromatographic analysis using a partitioning liquid found to be especially good at resolving fluorocarbon mixtures.⁶

(1) Department of Chemical Engineering, Kansas State College, Manhattan, Kansas.

(2) American Petroleum Institute Research Project 41, "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, Washington, D. C., 1950.

(3) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., New York, N. Y.

(4) G. D. Oliver, S. Blumkin and C. W. Cunningham, THIS JOURNAL, **73**, 5722 (1951).

(5) E. P. McLaughlin and R. L. Scott, *J. Phys. Chem.*, **60**, 674 (1956).

(6) T. M. Reed, III, *Anal. Chem.*, **30**, 221 (1958).