was cooled to 0° and 24.0 cc. of 5.0 M aqueous silver nitrate was added with stirring over ten minutes. After one hour at 0°, the product was extracted with pentane. Vapor phase chromatographic analysis indicated 66% *n*-dodecane, 5% 5-methylundecane and 20% of a mixture of 1-hexene and *n*-hexane.

The coupling reaction for more hindered olefins, such as 2-methyl-1-pentene and cyclohexene, gives better yields in methanol solution, presumably because of the greater difficulty of reaction of potassium hydroxide with the more hindered organoborane in the two phase aqueous system.

2-Methyl-1-pentene, 8.4 g., 0.100 mole, was hydroborated as above. After destruction of residual hydride with 20 cc. of methanol, 120 cc. of 2.0 M potassium hydroxide in methanol was added. This was followed by 24.0 cc. of 5.0 *M* aqueous silver nitrate added over ten minutes with stirring, maintaining the temperature at 20-30°. After one hour, 100 ml. of water was added and the product isolated by extraction with pentane. Vapor phase chromatographic analysis indicated the presence of 71% of a single dodecane and 16% of a mixture of 2-methyl-1-pentene and 2-methylpentane. Distillation yielded 5.24 g., (61%) of 4,7-dimethyldecane, b.p. 194-196° at 742 mm., n^{20} D 1.4225.⁴

Yields of terminal olefins, as described above, are in the range of 60-80%. Internal olefins form the coupled products with yields in the range of 35-50%.

The reaction has been applied to a large number of olefins and appears to be quite general (product in parentheses): 1-butene (*n*-octane), 1-octene (*n*hexadecane), isobutylene (2,5-dimethylhexane), 2butene (3,4-dimethylhexane), cyclopentene (bicyclopentyl), cyclohexene (bicyclohexyl), 2-methyl-2-butene (2,3,4,5-tetramethylhexane)⁵ and anethole (dimethyl ether of hexestrol).

The hydroboration reaction can tolerate many different functional groups. Consequently, this coupling reaction should find very wide applicability in synthetic chemistry.

The financial assistance of the Ethyl Corporation in this study is gratefully acknowledged.

(4) I. N. Nazarov and G. P. Verkholetova, Zhur. Obshchel Khim. (J. Gen. Chem.), 18, 1086 (1948), report b.p. 92.5-95° at 23 mm., n¹⁰D 1.4230.

(5) Vapor phase chromatographic examination (Ucon Polar column) revealed the presence in nearly equal amounts of the two diastereoisomers (meso and racemic) to be anticipated for this structure. Resolution was not achieved for 4,7-dimethyldecane and 3,4-dimethyl herane in the vapor phase chromatographic analysis.

RICHARD B. WETHERILL LABORATORY	
PURDUE UNIVERSITY	HERBERT C. BROWN
Lafayette, Indiana	Carl H. Snyder
Received January 10	, 1961

A NOVEL SYNTHESIS OF CYCLOPROPENES Sir:

We wish to report a reaction resulting in the formation of a cyclopropenyllithium compound conveniently convertible into cyclopropene derivatives which are otherwise difficult to prepare. When methylene chloride is added to a solution of 1,2-dimethylpropenyllithium (I) in tetrahydrofuran at -35° , the resulting solution contains 2,3,3-trimethylcyclopropenyllithium (VI) as evidenced by the transformations: hydrolysis of the reaction mixture yields 1,3,3-trimethylcyclopropene (V) (b.p. 45° (750 mm.); n^{20} D 1.3893; anal. found: C, 87.14; H, 12.43), carboxylation gives 2,3,3-trimethylcyclopropene-1-carboxylic acid (VII) (m.p. 48.5°; anal. found: C, 66.62; H, 8.04) and treatment with methyl iodide results in the formation of tetramethylcyclopropene (IX) (b.p. 67° (755 mm.); n^{20} D 1.4021; anal. found: C, 87.43; H, 12.32).

Structures of compounds V, VII and IX, which were obtained in 40 to 50% yield¹ are based on spectral and chemical evidence. Confirmation of the carbon skeleton was obtained by catalytic hydrogenation of V to 1,2,2-trimethylcyclopropane. The endocyclic position of the double bond follows from the n.m.r. spectrum of V, which exhibits narrowly spaced doublets at 9.08 (0.7 c.p.s. separation, relative intensity 6) and 8.10 τ (1.1 c.p.s. separation, relative intensity 3), and a multiple (relativeintensity 1) centered at 3.45 τ , the resonances of the gem. dimethyl, allylic methyl and olefinic protons, respectively. The infrared spectrum of the olefin is

in agreement with structure V (H $-\dot{C}$ =, 3070 cm.⁻¹; >C=C<, 1755 cm.⁻¹). The structure of carboxylic acid VII is also confirmed by the observed spectral data (n.m.r.: sharp lines at 8.88, (CH₂)₂C=CLiCH₂ + CH₂Cl₂ \longrightarrow





7.82 and -2.28τ , relative intensities 6:3:1; infrared: >C=O, 1690 cm.⁻¹; >C=C< 1822 cm.⁻¹; ultraviolet: λ_{max} (hexane) 237 m μ , ϵ 7000). On treatment with diazomethane in ether at -15° VII is converted into its methyl ester (VIII) (b.p. 57° (15 mm.); n.m.r.: sharp lines at 8.98, 7.93 and 6.42 τ , relative intensities 2:1:1; infrared: >C= O, 1700 cm.⁻¹; >C=C< 1820 cm.⁻¹; ultraviolet: λ_{max} (hexane 226 m μ , ϵ 7700). Finally the tetramethylcyclopropene (IX) shows the anticipated spectral properties (n.m.r. sharp lines of equal intensities at (1) Yields are based on three moles of I. 9.13 and 8.25 τ ; infrared: >C=C< 8165 cm.⁻¹).^{2,3}

As to the mechanism of the reaction, formation of chlorocarbene from methylene chloride and I is likely to be the first step.⁴ As a strongly nucleophilic reagent, I can be visualized to combine with the carbene by either of two ways: path (a) assumes electrophilic addition of the carbene to the π -electrons of the double bond, generating inter-mediate II which gives V via β -elimination. Or, the carbene may attack the incipient vinylcarbanion to form intermediate III, (path b), which generates vinylcarbene IV by α -elimination.⁵ Cyclization of the latter by rotation of the gem dimethyl group through 90° will lead to the cyclopropene V. The subsequent replacement of the olefinic proton in V by lithium occurs on reaction with strongly basic I. The resulting cyclopropenyllithium compound VI is also formed when V is allowed to react with methyllithium in tetrahydrofuran at 0°

This increased acidity of the olefinic proton in cyclopropenes has been predicted from theoretical considerations^{6,7} which attribute a high degree of s-character to the C—H bond because of the large "ring strain." Deuterium exchange work on shortlived cyclopropene intermediates supports this concept.⁷ Additional indication of the correctness of the theory is given by the increased acidity of VII $(pK_a 3.7)$ when compared with other α,β -unsaturated carboxylic acids.

The reaction is being extended at the present time to the introduction of other functional groups in the 1-position of cyclopropenes. A detailed investigation of the mechanism is also in progress.

(2) Other 1,2-dialkyl-substituted cyclopropenes are reported to exhibit C==C stretching vibration in the same region: P. K. Faure and J. C. Smith, J. Chem. Soc., 1818 (1956); W. v. E. Doering and T. Mole, Tetrahedron, 10, 65 (1960).

(3) It may be of interest to point out the unusually large shift in the C==C stretching frequency (110 cm.⁻¹) of the cyclopropene ring system caused by introduction of a second alkyl substituent on the double bond.

(4) G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 82, 5723 (1960). (5) For the equivalent mechanism of the reaction of chlorocarbene with alkyllithium compounds see: G. L. Closs, Abstracts of Papers of the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 9-P.

(6) A. D. Walsh, Trans. Faraday Soc., 45, 179 (1949).
(7) K. B. Wiberg, R. K. Barnes and J. Albin, J. Am. Chem. Soc., 79, 4994 (1957).

GEORGE HERBERT JONES LABORATORY

THE UNIVERSITY OF CHICAGO	G. L. CLOSS
CHICAGO 37, ILLINOIS	L. E. Closs
RECEIVED DECEMBER 13, 1960	

A NEW FLUORIDE OF OXYGEN-O4F21

Sir:

The preparation and properties of pure ozone fluoride, or O_3F_2 , were described recently.^{2,3,4} It has now been established that the elusive $O_4F_2^{2,3}$ also can be obtained. As in the case of O_2F_2 , and O_3F_2 , it is produced by an electrical discharge at low

(1) This research was financed at first, in part, by the Army Ballistic Missile Agency, Redstone Arsenal, Huntsville, Alabama, and at present by the Department of the Navy, Office of Naval Research. (2) A. D. Kirshenbaum and A. V. Grosse, J. Am. Chem. Soc., 81,

1277 (1959), see there for previous literature.

(3) A. D. Kirshenbaum, J. G. Aston and A. V. Grosse, Final Report, Contract No. DA-36-034-ORD-2250, Nov. 18, 1958.

(4) A. D. Kirshenbaum, A. V. Grosse and J. G. Aston, J. Am. Chem. Soc. 81, 6398 (1959).

temperatures and pressures by using a mixture of 2 moles O_2 to 1 mole F_2 , by cooling more effectively and to lower temperatures, i.e., 60-77°K. (instead of 90°K.), and using less power in the discharge (*i.e.*, 4.5-4.8 milliamp at 840-1280 volts as against 20-30 ma. at 2000-3000 v.).

At 77°K. O_4F_2 is a reddish brown solid, depositing on the glass walls of the discharge vessel between the electrodes. It differs in color from O_3F_2 , and sometimes forms clusters of long needlelike brown crystals.

 O_4F_2 has a vapor pressure of less than 1 mm. at 90°K. It is a liquid and stable, at least for a couple of hours, at 90°K., since no noticeable rise in pressure occurs. Between 90 and 110°K. it decomposes slowly into O_3F_2 and O_2 , and the latter at $110^{\circ}K$. to O_2 and O_2F_2 . Since O_2F_2 in turn forms $O_2 + F_2$ at about 200°K. the whole O_4F_2 is decomposed into O_2 and F_2 gas.

The composition of O₄F₂ was established both by (a) synthesis and (b) analysis. In a synthetic case 355 cm.³ (at S.T.P.), of a 2.05 \pm 0.03:1 O₂/F₂ mixture reacted at 77°K. in a discharge vessel described previously.^{1,2} The gases were admitted at a rate of 2.0 cm.³/min. (S.T.P.); the pressure was 5-15 mm. and the current 4.5 to 4.8 milliamp. at 840-1280 volts. All of the mixture was converted quantitatively to the solid reaction product, except for 15,4 cm.³ of gas, which was pumped off periodically in order to keep the gas phase composition constant. Even assuming these 15.4 cm.3 to be pure O_2 , the composition of the product should equal $O_{4.00}$ F_{2.06}.

Typical analyses of the gas produced from the solid product, using a Moissan mercury absorption buret for F_2 and an Orsat apparatus for O_2 , are: 96.9 cm.³ (at S.T.P.) contained 66.3 mole % O₂ and 33.7 mole % F₂, ratio O₂: F₂ = 1.95 ± 0.03 ; 55.6 cm.³ gas (at S.T.P.) gave 66.5 mole % O_2 and 33.4 mole % F_2 , ratio O_2 : $F_2 = 1.98 \pm 0.05\%$. Theoretical for O_4F_2 is 2.00.

The vapor pressures of O_3F_2 , O_2F_2 and O_2 differ widely and any O₂ present can be pumped off easily; thus the elementary composition O_4F_2 cannot be due to dissolved O_2 . The proof that it is *not* due to O_3 is more difficult. This proof is necessary, however, because O2 gas alone, under the pressure, temperature and discharge conditions, is converted into liquid or solid O3. Furthermore, liquid O3 and liquid O₃F₂ mix homogeneously in any proportion at 90°K., and the $O_3 + 3O_3F_2$ mixture, on cooling to 77°K., forms a brown mass very similar in appearance to O_4F_2 . Attempts to distinguish O_4F_2 from the $O_3 + O_3F_2$ mixtures by visible spectra could not be made because the molecular extinction coefficients for O_3F_2 and O_4F_2 were not known.

It occurred to us that a simple differentiation could be provided by the solubility behavior of the compounds in liquid O_2 . It was found that our samples (0.7–1.0 g.) of O_4F_2 , extracted at 77°K. by condensation of liquid O_2 ($\simeq 25$ cc.), gave no visible trace of O₃. On analysis this particular sample, after liquid O_2 extraction and pumping off all O_2 , had the composition $O_{4\cdot00}F_{2\cdot04}$. In contrast, the $O_3 + 3O_3F_2$ mixture prepared from pure O_3 and O_3F_2 , immediately gave a deep blue extract of O_3 in O_2 .