

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.,  $n_D^{20}$  1.4225.<sup>4</sup>

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), 2-butene (3,4-dimethylhexane), cyclopentene (bicyclopentyl), cyclohexene (bicyclohexyl), 2-methyl-2-butene (2,3,4,5-tetramethylhexane)<sup>5</sup> 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. Obshchei Khim. (J. Gen. Chem.)*, **18**, 1086 (1948), report b.p. 92.5–95° at 23 mm.,  $n_D^{20}$  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-dimethylhexane in the vapor phase chromatographic analysis.

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# A NOVEL SYNTHESIS OF CYCLOPROPENES

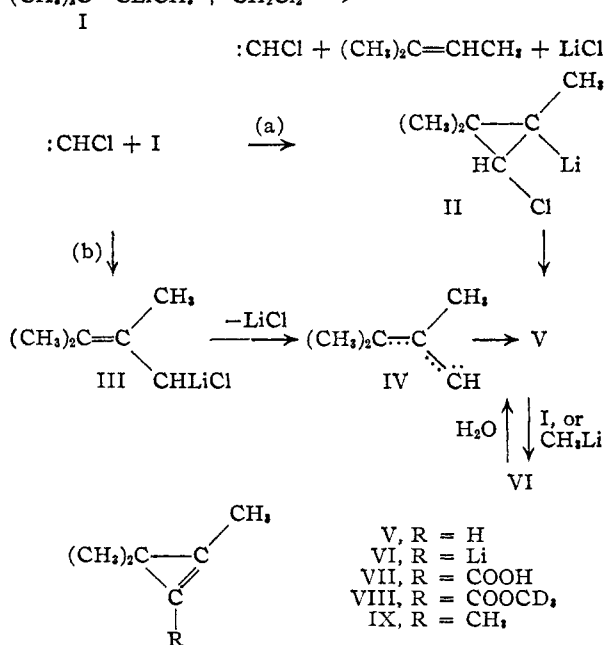
Sir:

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.);  $n_D^{20}$  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.);  $n_D^{20}$  1.4021; *anal.* found: C, 87.43; H, 12.32).

Structures of compounds V, VII and IX, which were obtained in 40 to 50% yield<sup>1</sup> 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  $\tau$  (1.1 c.p.s. separation, relative intensity 3), and a multiple (relative intensity 1) centered at 3.45  $\tau$ , the resonances of the *gem.* dimethyl, allylic methyl and olefinic protons, respectively. The infrared spectrum of the olefin is

in agreement with structure V ( $\text{H}-\text{C}=\text{C}$ , 3070  $\text{cm}^{-1}$ ;  $>\text{C}=\text{C}<$ , 1755  $\text{cm}^{-1}$ ). The structure of carboxylic acid VII is also confirmed by the observed spectral data (n.m.r.: sharp lines at 8.88,  $(\text{CH}_3)_2\text{C}=\text{C}(\text{LiCH}_3) + \text{CH}_2\text{Cl}_2 \rightarrow$



7.82 and – 2.28  $\tau$ , relative intensities 6:3:1; infrared:  $>\text{C}=\text{O}$ , 1690  $\text{cm}^{-1}$ ;  $>\text{C}=\text{C}<$  1822  $\text{cm}^{-1}$ ; ultraviolet:  $\lambda_{\text{max}}$  (hexane) 237  $\text{m}\mu$ ,  $\epsilon$  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  $\tau$ , relative intensities 2:1:1; infrared:  $>\text{C}=\text{O}$ , 1700  $\text{cm}^{-1}$ ;  $>\text{C}=\text{C}<$  1820  $\text{cm}^{-1}$ ; ultraviolet:  $\lambda_{\text{max}}$  (hexane) 226  $\text{m}\mu$ ,  $\epsilon$  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  $\tau$ ; infrared:  $>C=C<$  8165  $\text{cm}^{-1}$ ).<sup>2,3</sup>

As to the mechanism of the reaction, formation of chlorocarbene from methylene chloride and I is likely to be the first step.<sup>4</sup> 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  $\pi$ -electrons of the double bond, generating intermediate II which gives V via  $\beta$ -elimination. Or, the carbene may attack the incipient vinylcarbanion to form intermediate III, (path b), which generates vinylcarbene IV by  $\alpha$ -elimination.<sup>5</sup> 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 methylolithium in tetrahydrofuran at 0°.

This increased acidity of the olefinic proton in cyclopropenes has been predicted from theoretical considerations<sup>6,7</sup> which attribute a high degree of s-character to the C—H bond because of the large "ring strain." Deuterium exchange work on short-lived cyclopropene intermediates supports this concept.<sup>7</sup> Additional indication of the correctness of the theory is given by the increased acidity of VII ( $pK_a$  3.7) when compared with other  $\alpha,\beta$ -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  $\text{cm}^{-1}$ ) 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 alkylolithium 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).

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#### A NEW FLUORIDE OF OXYGEN— $O_4F_2$ <sup>1</sup>

Sir:

The preparation and properties of pure ozone fluoride, or  $O_3F_2$ , were described recently.<sup>2,3,4</sup> It has now been established that the elusive  $O_4F_2$ <sup>2,3</sup> 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

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 needle-like 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°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  $O_4F_2$  was established both by (a) synthesis and (b) analysis. In a synthetic case 355  $\text{cm}^3$  (at S.T.P.), of a  $2.05 \pm 0.03:1$   $O_2/F_2$  mixture reacted at 77°K. in a discharge vessel described previously.<sup>1,2</sup> The gases were admitted at a rate of 2.0  $\text{cm}^3/\text{min}$ . (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  $\text{cm}^3$  of gas, which was pumped off periodically in order to keep the gas phase composition constant. Even assuming these 15.4  $\text{cm}^3$  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  $\text{cm}^3$  (at S.T.P.) contained 66.3 mole %  $O_2$  and 33.7 mole %  $F_2$ , ratio  $O_2:F_2 = 1.95 \pm 0.03$ ; 55.6  $\text{cm}^3$  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  $O_2$  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  $O_2$  gas alone, under the pressure, temperature and discharge conditions, is converted into liquid or solid  $O_3$ . Furthermore, liquid  $O_3$  and liquid  $O_3F_2$  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  $O_2$  ( $\approx 25$  cc.), gave no visible trace of  $O_3$ . On analysis this particular sample, after liquid  $O_2$  extraction and pumping off all  $O_2$ , had the composition  $O_{4.00}F_{2.04}$ . 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  $O_2$ .

(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).