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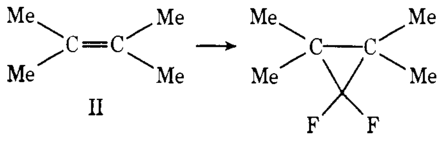
Bromodifluoromethylphosphonium Salts. A Convenient Source of Difluorocarbene[1]

Sir:

In recent years considerable attention has been focused on the generation of difluorocarbene for the synthesis of *gem*-difluorocyclopropanes and other difluoromethylene derivatives. A variety of difluorocarbene precursors have been examined,[2] but these precursors are either inefficient or difficult to obtain in large quantities. For example, difluorodiazirine,[3] Me_3SnCF_3,[4] and $PhHgCF_3$[5] require several steps to prepare and involve expensive and/or toxic materials. The most common precursor, CF_2ClCO_2Na, is hygroscopic and requires large excesses to ensure good yields of products.[6] This communication describes a simple, facile, and convenient one-step method of difluorocarbene generation from readily available commercial reagents.

When bromodifluoromethylphosphonium bromide (I)[7] was treated with sodium methoxide in the presence of tetramethylethylene (II), a 21% yield of the cyclopropane adduct (III) was obtained. Similarly, other olefins gave low yields of cyclopropanes under similar conditions. To the best of our knowledge, this reaction represents the first known example of carbene generation from a phosphonium salt. Presumably, attack by methoxide on the phosphonium salt to displace $[CF_2Br^-]$ or $:CF_2$ had occurred. The low yield of III is presumably due to competition between methoxide and II for the carbene.[8]

$[Ph_3\overset{+}{P}CF_2Br]Br^- + NaOMe +$



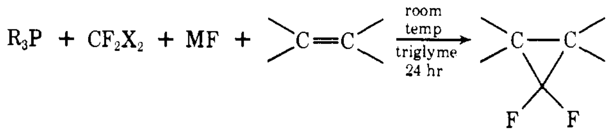
II

III

To circumvent the competition of the nucleophile for the carbene, a base was required which would form a strong bond to phosphorus and generate the carbene but would not compete for the carbene. The strength of the P–F bond[9] (117 kcal/mol) compared to the P–O bond[6] (120 kcal/mol) suggested that fluoride ion[10] would fulfill these requirements. Indeed, substitution of potassium fluoride or cesium fluoride in these reactions provided a smooth high-yield conversion of the phosphonium salt to the cyclopropane adduct.[11]

$$I + CsF + II \longrightarrow III + Ph_3PFBr + CsBr$$

Subsequent investigation of these reactions has shown that prior preparation of I is unnecessary and that the phosphonium salt could be prepared "*in situ*" from the appropriate phosphine and difluorodihalomethanes in the presence of the fluoride salt and olefin. A number of representative olefins were examined to determine the utility of this "*in situ*" scheme and are tabulated in Table I. All of the cyclopropane adducts were completely identified by comparison with authentic samples or with reported infrared and/or ^{19}F nmr spectra.



R = Ph or Me_2N; X = Br, Cl; M = K, Cs

Table I. Formation of 1,1-Difluorocyclopropanes

Olefin	R	M	*n*	% cyclopropane[a]
Tetramethylethylene	Ph	Cs	1	79
Tetramethylethylene	Ph	K	1	74
Tetramethylethylene	Me_2N	Cs	1	65
Trimethylethylene	Ph	Cs	1	75
Isobutylene	Ph	Cs	4	66
trans-2-Butene	Me_2N	Cs	4	12[b]
cis-2-Butene	Ph	Cs	4	6[b]
Cyclohexene	Me_2N	K	5	21[c]

[a] Glpc yield base on phosphine. [b] Cyclopropane adduct is the stereospecific product. [c] Reaction temperature is 85°.

As Table I indicates, all olefins except 1,2-disubstituted olefins gave excellent yields, and stereospecific addition occurred with *cis*- and *trans*-2-butenes. Similar stereospecificity and decreased reactivity of 1,2-substituted olefins were also observed by Mitsch in the reactions of difluorodiazirine. A competition reaction between isobutylene and *cis*-2-butene gave a reactivity ratio of 13.0. For a similar competition experiment with CF_2N_2, Mitsch[12] observed a reactivity ratio of 12.8. Consequently, the discriminating ability of our carbene species appears to be similar to that of Mitsch.

The following procedure is presented to provide operational detail for the generation of difluorocarbene.

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(1) (a) Abstracted in part from Ph.D. Thesis of D. G. N., University of Iowa, 1972. (b) Presented in part at the Seventh International Symposium on Fluorine Chemistry, Santa Cruz, Calif., July 1973.

(2) *Cf.* W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, pp 237–271.

(3) R. A. Mitsch, *J. Heterocycl. Chem.*, **1**, 59 (1964).

(4) (a) D. Seyferth, J. Y. -P. Mui, M. E. Gordon, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **87**, 681 (1965); (b) D. Seyferth, H. Dentouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, **32**, 2980 (1967).

(5) D. Seyferth, S. P. Hopper, and K. V. Darragh, *J. Amer. Chem. Soc.*, **91**, 6536 (1969); D. Seyferth and S. P. Hopper, *J. Org. Chem.*, **37**, 4070 (1972).

(6) L. H. Knox, E. Velarde, S. Berger, D. Cuadriello, P. W. Landis, and A. D. Cross, *J. Amer. Chem. Soc.*, **85**, 1851 (1963); C. Beard, N. H. Dyson, and J. H. Fried, *Tetrahedron Lett.*, 3281 (1966); C. Beard, I. T. Harrison, L. Kirkham, and J. H. Fried, *ibid.*, 3287 (1966).

(7) Complete characterization and other chemical properties of these phosphonium salts have been made and will be reported in detail in the complete paper.

(8) Unpublished results of H. S. Kesling from this laboratory.

(9) T. L. Cottrel, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958.

(10) In addition to forming a strong P–F bond, fluoride would also be expected to react reversibly with difluorocarbene.

(11) Other halide ion sources, such as NaCl or NaI, gave only trace amounts of cyclopropane products.

(12) R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 758 (1965).

When 0.25 mol of CF_2Br_2[13] (52.5 g, 22.8 ml) was added to a solution of 0.25 mol of Ph_3P (65.5 g) in 450 ml of dry triglyme, a heavy precipitate of $[Ph_3P^+CF_2Br]Br^-$ quickly formed. The solution was stirred for 30 min under dry nitrogen followed by addition of 0.25 mol of $Me_2C{=}CHMe$ (17.5 g, 26.25 ml) and 1.0 mol of anhydrous KF (58.1 g). The solution was stirred vigorously for 24 hr and then flash distilled at *ca.* 3 mm. Fractionation of the distillate yielded 20.0 g of product (bp = 69–70°) which was 99% pure by glpc analysis. The ^1H nmr showed a multiplet at δ 0.85–1.35 ppm and the ^{19}F nmr consisted of two signals, 139.8 ppm (d of m) and 151.9 ppm (d of broad singlets) (ϕ^*, $CFCl_3$) with a doublet splitting of 153.6 Hz. The mass spectrum was consistent with the assigned structure of the product, 1,1-difluorotrimethylcyclopropane. The isolated yield was 67%.

The use of these phosphonium salts compares favorably with other precursors of difluorocarbene. In most cases, however, the availability of reagents, ease of scaling up the reaction, mild conditions of the reaction, and the ease of isolation of the products make this mode of carbene generation the method of choice.

Related work in our laboratories indicates that other phosphonium salts may be useful carbene precursors.[8] Details of these experiments will be presented in due course.

Acknowledgment. We are indebted to Paul Vander Valk for the large scale trimethylethylene experiment.

(13) Fluorocarbon 12B2, available from E. I. duPont de Nemours.

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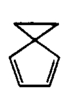
Synthesis and Characterization of Spiro[3.4]octa-5,7-diene

Sir:

The recent confirmation by photoelectron spectroscopy of direct interaction between the cyclopropane ring and the π-orbitals in spiro[2.4]hepta-4,6-diene (**1**)[1] has rekindled interest in the properties of spirocyclopentadiene derivatives. Within the homologous series of spirodienes **1**–**3**, spiro[3.4]octa-5,7-diene (**2**) has until now escaped synthesis and characterization despite a number of reported attempts.[2,3] This material by virtue of its structural rigidity and appropriate bisected geometry is an ideal candidate for probing the interactions between the cyclobutane ring and the diene moiety. We now report the preparation and characterization of **2** by a new synthetic route.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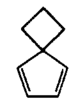
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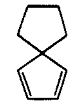
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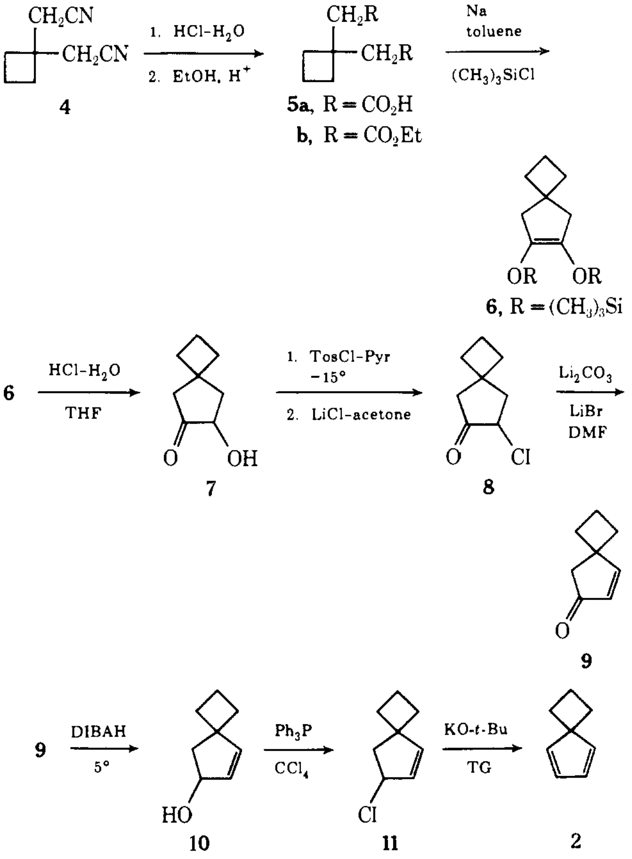
The starting material for the synthesis was 1,1-dicyanomethylcyclobutane prepared as described by Najer and coworkers.[4] The dinitrile **4** was hydrolyzed to the diacid **5a** with concentrated hydrochloric acid, which was then converted without further purification into the desired ester **5b**, using standard techniques: bp 91–96° (0.75 mm).[5] **5b** was cyclized *via* the Rühlmann[6] modification of the acyloin condensation to produce the disiloxene derivative **6** in 84% yield: bp 87–89° (1 mm); ^1H nmr (CCl_4) τ 7.73 (s, 4), 7.93–8.19 (m, 6), and 9.88 (s, 18); ir (neat) 2960, 2830, 1700, 1320, 1250, 1085, 910, 860, and 840 cm^{-1}; mass spectroscopic mol wt 284. The hydrolysis of **6** to produce the acyloin **7** (95%) was effected by a THF–1 *N* $HCl–H_2O$ mixture with limited heating (15 min, 60°) to minimize polymerization. The acyloin **7** was immediately converted into the tosylate derivative which was transformed without purification into the chloro ketone **8**, by treatment with anhydrous LiCl in dry acetone at reflux. **8** was purified by chromatography on silica gel by eluting with 9:1 hexane–benzene (81%): ^1H nmr (CCl_4) τ 6.09 (m, 1) and 7.37–8.28 (m, 10); ir (neat) 2950, 1755, 1425, 1390, 1175, 1155, 1120, 1080, 850, 700, and 685 cm^{-1}; mass spectroscopic mol wt 158. Dehydrohalogenation of **8** was accomplished by heating in dry DMF with Li_2CO_3–LiBr for 2–2.5 hr at 140° to produce **9** in 74% yield: bp 98–100° (20 mm); ^1H nmr (CCl_4) τ 2.5 (d, J = 5 Hz, 1), 4.18 (d, J = 5 Hz, 1), 7.65 (s, 2), and 7.70–8.21 (m, 6); ir (neat) 3030, 2930,



(1) R. Gleiter, E. Heilbronner, and A. de Meijere, *Helv. Chim. Acta*, **54**, 1029 (1971).

(2) We and others[3b] have been unable to reproduce the results of Chuirdoglu and Tursch[3a] who have claimed the synthesis of **2**. Additionally, our ir spectral data do not correspond to that reported by the above authors.

(3) (a) G. Chiurdoglu and B. Tursch, *Bull. Soc. Chim. Belg.*, **46**, 600 (1957); (b) C. F. Wilcox, Jr., and G. C. Whitney, *J. Org. Chem.*, **32**, 2933 (1967), and references cited therein.

(4) H. Najer, R. Guidicelli, and J. Sette, *Bull. Soc. Chim. Fr.*, 2572 (1964).

(5) Complete spectral data are available for all compounds described here upon request.

(6) (a) K. Rühlmann and S. Poredda, *J. Prakt. Chem.*, **12**, 18 (1960); (b) U. Schrapler and K. Rühlmann, *Chem. Ber.*, **97**, 1383 (1964).