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.

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

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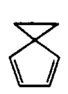
Synthesis and Characterization of Spiro[3.4]octa-5,7-diene

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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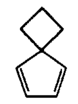

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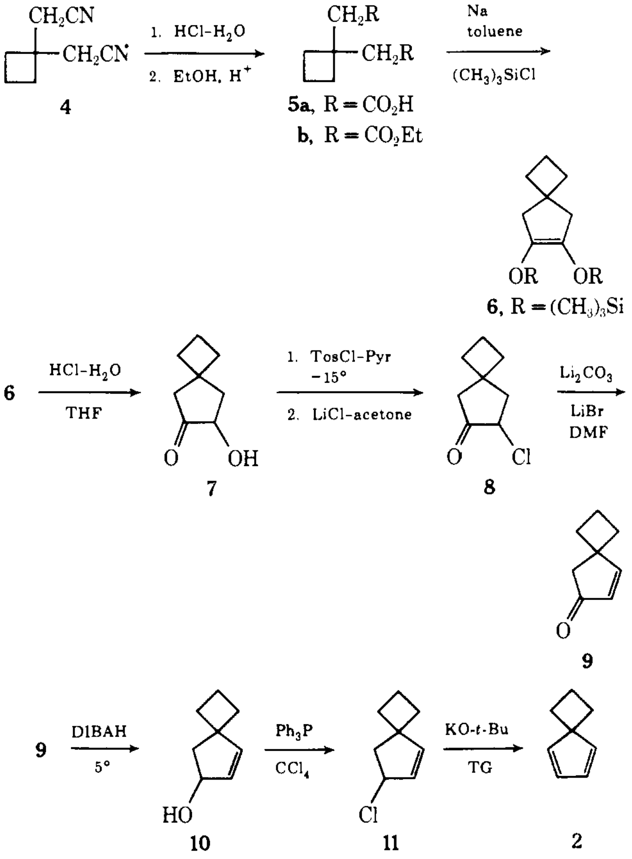

The starting material for the synthesis was 1,1-dicyanomethylcyclobutane prepared as described by Najer and coworkers.[4] The dinitrile **4** was hydrolyzed to the diacid **5a** with concentrated hydrochloric acid, which was then converted without further purification into the desired ester **5b**, using 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,

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(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.

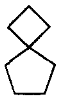
(3) (a) G. Chiurdoglu and B. Tursch, *Bull. Soc. Chim. Belg.*, **46**, 600 (1957); (b) C. F. Wilcox, Jr., and G. C. Whitney, *J. Org. Chem.*, **32**, 2933 (1967), and references cited therein.

(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).

2870, 2850, 1710, 1575, 1400, 1350, 1280, 1190, 1065, 1020, 830, 800, and 765 cm^{-1}; uv (EtOH) λ_{max} 315 (ϵ 51), 228.5 nm (ϵ 11,800); mass spectroscopic mol wt 122. The allylic alcohol **10** could be generated in high yield (90%) by reduction of **9** with diisobutylaluminum hydride at 0–5° in benzene:[7] ^{1}H nmr (CCl_4) τ 4.12 (d, d, J = 5.6, 1.0 Hz, 1), 4.47 (d, d, J = 5.6, 2.0 Hz, 1), 5.39 (m, 1), 6.33 (br s, 1), and 7.60–8.45 (m, 8); ir (neat) 3320, 3040, 2950, 2870, 2850, 1610, 1425, 1355, 1315, 1140, 1070, 1025, 790, and 750 cm^{-1}. The allylic chloride **11** could be prepared in an impure state by heating **10** with a 50% excess of triphenylphosphine in CCl_4[8] for *ca.* 1 hr. Nmr analysis of the crude reaction mixture indicated **11** was present as the major component (65–75%): ^{1}H (CCl_4) τ 4.02 (d, d, J = 5.0, 2.2 Hz), 5.23 (m), and 7.45–8.35 (m). Since the instability of **11** precluded further purification, the crude reaction mixture was utilized in subsequent transformations. The flask containing impure **11** dissolved in dry triglyme and a 100% excess of potassium *tert*-butoxide[9] was connected to a vacuum trap (77°K) and heated to 50° for 1 hr (125 mm). The remainder of the volatile material was removed by heating to 100° (0.07 mm) for 10 min. The volatile hydrocarbon was separated from *tert*-butyl alcohol, solvent, and some other less volatile material by preparative glpc: 6 ft × 0.25 in., SE-30 on 60–80 Chromosorb W, at 65°. The material collected in this manner (30% from **10**) was identified as **2** by its characteristic spectral data: ^{1}H nmr (CCl_4) τ 3.65 (m, 2), 3.95 (m, 2), and 7.67–8.07 (m, 6); ir (neat) 3100, 3080, 3060, 3040, 2970, 2940, 2870, 1630, 1510, 1445, 1370, 1330, 1080, 965, 910, 795, 765 (sh), 756, 728, and 715 (sh) cm^{-1}; mass spectroscopic mol wt 106.[10] Catalytic hydrogenation of **2** (PtO_2, hexane, 1 atm) resulted in the uptake of 2 mol of hydrogen to produce **12** which was prepared for comparison *via* an alternate and independent route by the Wolff-Kishner reduction of the known ketone **13**.[11] Predictably the diene **2** yielded a 1:1 adduct with maleic anhydride upon standing at room temperature overnight in benzene: mp 91°; ^{1}H nmr (CCl_4) τ 3.88 (t, J = 2 Hz, 2H), 6.58 (d, d, J = 3, 1.5 Hz, 2 H), 6.82 (m, 2 H), and 8.21 (m, 6 H); ir (KBr) 3060, 2980, 2940, 1855, 1775, 1325, 1300, 1220, 1130, 1080, 930, 910, and 660 cm^{-1}. Since orbital interaction is often manifested by an anomalous uv spectrum of the material in question relative to appropriate models, the ultraviolet spectra of **9** and **2** are discussed in some detail. The π–π* maximum of **9** occurs at 228.5 nm (ϵ 11,800) which is *ca.* 10-nm red shifted relative to 4,4-dimethylcyclopentenone (λ_{max} 218.5 nm (ϵ 12,100)[12] chosen as a model compound. The cause of this shift is difficult to determine due to the distortion caused by the small ring spirocyclic and a lack of more suitable model compounds. However, it should be noted that irradiation of **9** (ether, 0.05 *M*, 3000 Å)[13] leads to the loss of ethylene and production of the dienone **15** (45%).[14] This unusual fragmentation certainly suggests possible interaction between the four-membered ring and the enone moiety in the excited state. The ultraviolet spectrum of **2** shows a similar unusual red shift. In ethanol **2** exhibits a featureless maximum at 261 nm (ϵ 1950) with no other detectable maxima above 210 nm. In comparison with the model compounds **1** (λ_{max} 257 nm (ϵ 2200))[15] and **3** (λ_{max} 254 nm (ϵ 2200)),[15] the spectrum of **2** is significantly bathochromically shifted. While similar ambiguity exists in predicting the effect of geometric distortion, the possibility of direct σ–π interaction in **2** cannot be ruled out. The definitive answer concerning ground-state interactions in **9** and **2** must await analysis by photoelectron spectroscopy which is presently in progress. Investigation of the chemistry of **2** and related derivatives is proceeding.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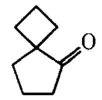
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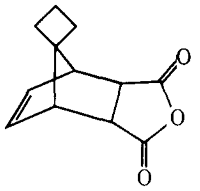
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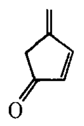
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[7] K. E. Wilson, R. T. Seidner, and S. Masamune, *Chem. Commun.*, 213 (1970).

[8] (a) I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind.* (*London*), 900 (1966); (b) J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).

[9] M. F. Semmelhack, J. S. Foos, and S. Katz, *J. Amer. Chem. Soc.*, **94**, 8637 (1972).

[10] A dimer is formed upon standing at room temperature in carbon tetrachloride: ^{1}H nmr (CCl_4) τ 4.46 (m, 3), 4.88 (d, d, J = 6, 2 Hz, 1), 6.78 (m, 1), 7.48 (m, 3), and 8.19 (m, 12); mass spectroscopic mol wt 212.

[11] R. Mayer, G. Wenschuh, and W. Topelmann, *Chem. Ber.*, **95**, 1616 (1958).

[12] R. D. Miller, unpublished results.

[13] The irradiation was conducted using a Rayonet Photochemical Reactor (RPR-100) with 3000-Å source lamps.

[14] Spectral data for **15**: ^{1}H nmr (CCl_4) τ 2.25 (d, J = 5.8 Hz, 1 H), 3.67 (d, d, d, J = 5.8, 1.8, 0.9 Hz, 1 H), 4.61 (br s, 1 H), 4.70 (br s, 1 H), and 7.1 (t, J = 1.4 Hz, 2 H); ir (neat) 3070 (w), 2980 (w), 2910 (w), 1710, 1635, 1545, 1280, 1175, 935, and 820 cm^{-1}; mass spectroscopic mol wt 94.

[15] C. F. Wilcox, Jr., and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 4258 (1961).

[16] IBM Postdoctoral Fellow, 1973–1974.

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Free Radical Reactions of Tetrafluorodiphosphine. The Preparation of 1,2-Bis(difluorophosphino)ethane

Sir:

Initial investigations of the free radical reactions of P_2F_4[1] have resulted in the preparation of the bidentate ligand, 1,2-bis(difluorophosphino)ethane. $F_2PCH_2CH_2PF_2$ results in greater than 50% yield from the photochemical reaction of P_2F_4 (1.9 m*M*) with C_2H_4 (1.01 m*M*) in the gas phase for a period of 6 hr. The photochemical cell consisted of a 200-ml quartz tube (45-mm o.d.) attached to a vacuum stopcock and a 10/30 joint to allow entry to the vacuum system. A Rayonet photochemical reactor (Southern N. E. Ultraviolet Co., Middleton, Conn.) containing reactor lamps RPR-3000A was used as the energy source. In the

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[1] Evidence has been presented for $\cdot PF_2$ in equilibrium with F_2PPF_2: (a) M. S. Wei, J. H. Current, and J. Gendell, *J. Chem. Phys.*, **52**, 1592 (1970), and (b) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, 88, 3729 (1966). It has also been suggested that the $\cdot PF_2$ radicals have been involved in chemical reactions: (c) K. W. Morse and R. W. Parry, *ibid.*, **89**, 172 (1967), (b) above, (d) G. Bokerman, Ph.D. Thesis, University of Michigan, 1968, and (e) H. W. Schiller and R. W. Rudolph, *Inorg. Chem.*, **50**, 2500 (1971). However, no studies have been reported on the photochemistry of P_2F_4.