from benzonorbornadiene (2) in four steps with an overall yield of ca. 70%.

The presently described synthesis offers several advantages over previous methods. Although relatively lengthy, it begins with a readily available starting material (2), and the subsequent steps are all efficient and readily amenable to large scale-up, since there are no troublesome purifications necessary. However, in addition to simply offering a means of preparing large quantities of the parent 1, this route offers several possibilities for isotopically labeling the bicyclic skeleton. For example, the use of ^{13}C- or ^{12}C-labeled chloroform in the phase-transfer method[9] for carbene generation would lead to 1 selectively labeled at C(2). Alternatively, several deuterated benzonorbornadienes are known,[10] which could serve as precursors to deuterated 1. Finally, this route allows straightforward synthesis of aromatic-substituted benzobarrelenes.[11]

Experimental Section

Addition of Dichlorocarbene to Benzonorbornadiene (2). A mixture of benzonorbornadiene (19.0 g, 0.133 mol), sodium methoxide (32.3 g, 0.597 mol), and dry hexane (150 mL) was cooled in an ice bath and vigorously stirred while ethyl trichloroacetate (100.4 g, 0.545 mol) was added dropwise during 3 h. The reaction temperature was maintained below 5 °C throughout the addition. After an additional 4 h at 0 °C, the mixture was allowed to warm gradually to ambient temperature and was stirred overnight, before being poured into ice water (500 mL). The organic layer was separated and the water layer was extracted with ether (3 × 100 mL). Combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated at reduced pressure to afford a brown oil. Distillation at reduced pressure, then under vacuum, yielded adduct 3 (29.02 g, 96.5%) as a viscous yellow oil (bp 98–105 °C at 0.7 mm), which crystallized on standing.

Recrystallization of a small sample from pentane afforded slightly yellow crystals: mp 75–75.5 °C (lit.[5b] 68–69 °C). The ^{1}H NMR spectrum was as reported.

Benzo[6,7]bicyclo[3.2.1]octa-2,6-diene (4). Metallic sodium (28.5 g, 1.24 mol) was cut into small pieces and combined with 300 mL of anhydrous ether. This was mechanically stirred at gentle reflux under a nitrogen atmosphere while a mixture of dichloride 3 (29.02 g, 0.129 mol), *tert*-butyl alcohol (74.0 g, 1.0 mol), and ether (50 mL) was added dropwise during 3 h. After stirring at reflux overnight, heating was discontinued and methanol (50 mL) and then water (100 mL) were added dropwise. The mixture was poured into water (200 mL), the organic layer was separated, and the water layer was extracted with ether (3× 100 mL). Combined organic layers were washed with water and brine, dried ($MgSO_4$), and concentrated. Distillation afforded alkene 4 (16.42 g, 83.5%) as a colorless oil: bp 45 °C (0.1 mm); ^{1}H NMR was as reported;[5b] ^{13}C NMR ($CDCl_3$) 151.8, 146.2, 134.2, 126.0, 125.9, 123.4, 123.3, 120.3, 41.2, 40.7, 40.3, 32.3 ppm.

***anti,anti*-2,7-Dibromobenzo[5,6]bicyclo[2.2.2]oct-5-ene (5).** A solution of alkene 4 (7.58 g, 48.6 mmol) in dichloromethane (20 mL) was stirred at −20 °C while a solution of bromine in dichloromethane (ca. 10% solution) was added dropwise until no further reaction was noted. Warming to ambient temperature and solvent removal at reduced pressure yielded dibromide 5 (15.22 g, 99.2%) as slightly orange crystals.

Recrystallization of a small sample from hexane afforded white crystals: mp 133.5–134.5 °C; IR (KBr) prominent maxima at 2900, 1470, 1322, 1267, 1235, 951, 835, 767 and 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.20–2.60 (apparent d of d, 2 H_3, 2 H_8), 3.04 (quint J = 3.0 Hz, H_4), 3.69 (t, J = 2.4 Hz, H_1), 4.12 (t of d, J = 8.0, 2.4 Hz, H_2, H_7), 7.25 (s, four aromatics); ^{13}C NMR ($CDCl_3$) 140.8, 139.8, 128.1, 127.0, 124.7, 123.9, 48.2 (C(1)), 44.8 (C(2), C(7), 38.7 (C(3), C(8)), 35.6 (C(4)).

Anal. Calcd for $C_{12}H_{12}Br_2$: C, 45.61; H, 3.82; Br, 50.57. Found: C, 45.66; H, 3.98; Br, 50,47.

Benzobarrelene (1). The crude dibromide 5 from above (15.22 g, 0.048 mol) was dissolved in dry tetrahydrofuran (60 mL) and added dropwise during 30 min to a stirring ambient temperature solution of potassium *tert*-butoxide (27.2 g, 0.243 mol) in dry tetrahdyrofuran (200 mL), maintained under a nitrogen atmosphere. After 3 h more, the mixture was heated at gentle reflux for 1.5 h, then cooled, quenched by dropwise water addition (100 mL), and poured into cold water (600 mL). The mixture was extracted with pentane (4× 125 mL) and combined extracts were washed with water and brine, dried ($MgSO_4$), and concentrated at reduced pressure to afford 7.48 g of off-white crystals. Sublimation at 80 °C (0.7 mm) yielded benzobarrelene (6.77 g, 91.1%) as white needles: mp 63–65 °C. Recrystallization from pentane and resublimation gave material with mp 65–66 °C (lit.[1] 65.5–66 °C). The ^{1}H NMR spectrum was as reported.[1]

Registry No.—**1,** 7322-47-6; **2,** 4453-90-1; **3,** 54647-00-6; **4,** 2409-43-1; **5,** 63216-61-5; dichlorocarbene, 1605-72-7.

References and Notes

(1) (a) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **85**, 1798 (1963); (b) L. Friedman, *ibid.*, **89**, 3071 (1967).

(2) (a) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Am. Chem. Soc.*, **90**, 6096 (1968); (b) K. Kitahonoki and Y. Takano, *Tetrahedron Lett.*, 1597 (1963).

(3) N. J. Hales, H. Heaney, and J. H. Hollinshead, *Synthesis*, 707 (1975).

(4) T. F. Mich, E. J. Nienhouse, T. E. Farina, and J. J. Tufariello, *J. Chem. Educ.*, **45**, 272 (1968).

(5) (a) H. Tanida, K. Tori, and K. Kitahonoki, *J. Am. Chem. Soc.*, **89**, 3212 (1967); (b) Z. Goldschmidt and U. Gutman, *Tetrahedron*, **30**, 3327 (1974); (c) R. C. Hahn and L. J. Rothman, *J. Am. Chem. Soc.*, **91**, 2409 (1969).

(6) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(7) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32**, 893 (1967).

(8) R. P. Johnson, Ph.D. Dissertation, Syracuse University, 1976.

(9) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461 (1972).

(10) (a) J. R. Edman, *J. Am. Chem. Soc.*, **91**, 7103 (1969); (b) G. R. Buske and W. T. Ford, *J. Org. Chem.*, **41**, 1998 (1976).

(11) For example, nitration of dibromide **5** with Ac_2O/HNO_3 afforded a 94% yield of mixed β and β'-NO_2 derivatives. Treatment of this isomeric mixture with potassium *tert*-butoxide in THF gave β-nitrobenzobarrelene. Classical transformations of this nitro derivative and use of an appropriate base for dehydrohalogenation should allow preparation of a variety of aromatic substituted benzobarrelenes.

The First Observation of Splitting by a "Peripheral" Substituent in a Radical Cation Containing a Tetravalent Phosphorus Atom

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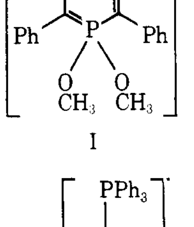
Recently, a number of stable radicals containing tetravalent phosphorus have been reported.[2–6] In all of these cases, coupling was not observed from groups attached to phosphorus which were not part of the delocalized π system containing the unpaired electron. This is best illustrated through examples. In I hyperfine splittings are observed from the phenyl substituents on the hetrocyclic ring and from the two protons on the ring, but no splittings are observed from the methoxy substituents.[4] Similarly, in the spectrum of II there are splittings from R′ and the ring protons, but no evidence is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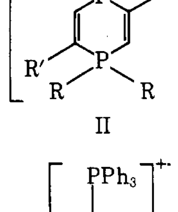
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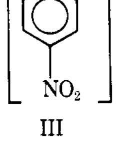
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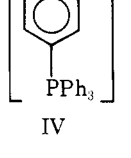
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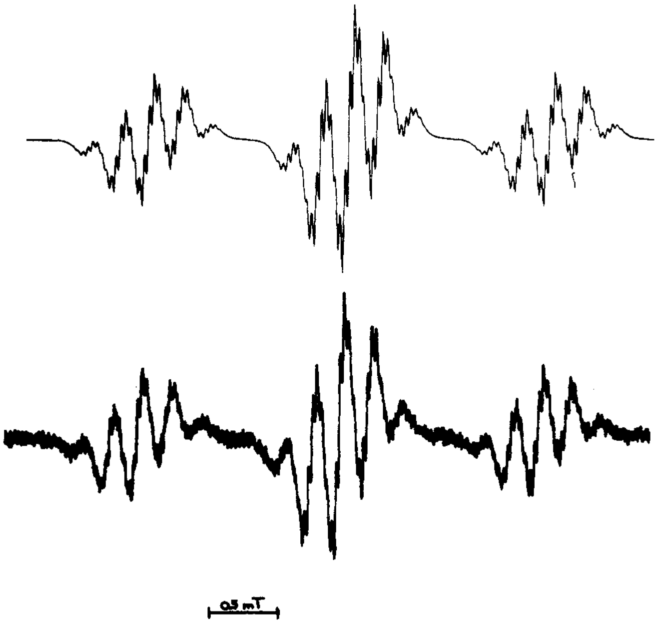


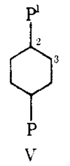
Figure 1. ESR spectrum of the radical cation of V. Upper, calculated spectrum using a line width of 0.030 mT; lower, experimental spectrum in DMF at −47 °C.

Table I. Hyperfine Splitting Constants of $V^{+\cdot}$

Atom	hfsc[b] (mT[a])
Phosphorus (c)	1.508
Phenyl protons (d)	0.213
Methylene (b)	0.035
Methyl (a)	0.000

[a] 1 mT = 10 G. [b] ±0.001 mT.

Table II. Hückel Molecular Orbital Calculations[b] of the Odd Electron Density in $V^{+\cdot}$



V

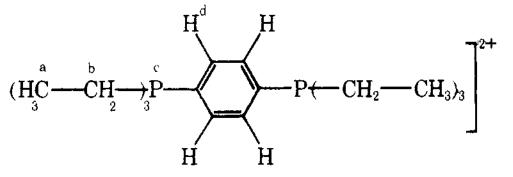
Atom	C^2	hfsc(calcd)[a]	hfsc(obsd)
1	0.2040		
2	0.161		
3	0.0675	0.160	0.213

[a] $a^H = Q\rho$, where Q = 2.37 mT. [b] Parameters from ref 6: $\alpha' = \alpha^0 + h|\beta|\beta' = k\beta^0$; $h_d = +0.6\, h\alpha_c = -0.6$; $h_{\beta c} = -0.3k_{dp} = 0.5$.

observed for couplings from R whether it is alkyl or aryl.[2,7] In fact, if R is *p*-fluorophenyl no coupling is observed from the fluorine atom.[2,7] In III and IV there are no couplings from the "peripheral" phenyl substituents of phosphorus.[3,6] All these radicals have large (0.5–1.8 mT) phosphorus hyperfine splitting constants. We wish to report the first observation of coupling by a group not directly attached to the unpaired-electron-bearing moiety of a stable radical containing tetravalent phosphorus.

Results

Reduction of V in the electron paramagnetic resonance (EPR) cavity at potentials corresponding to the first reduction



V

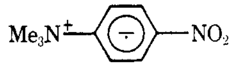
wave results in the EPR spectrum shown in Figure 1. Along with this spectrum is the computer simulation using the hyperfine splitting constants (hfsc) given in Table I. The line width used in the simulation was 0.030 mT.

Hückel molecular orbital (HMO) calculations were carried out on the molecule and the results are given in Table II. The parameters used for the phosphorus atoms assume a conjugative interaction as well as inductive effects on the α-carbon atom rather than just inductive effects alone. These parameters have been shown to correlate EPR and electrochemical data for a large number of phosphorus-containing radicals.[6]

Discussion

The question of whether the phosphorus atom of a phosphonium group can interact with a π system in a combined conjugative and inductive manner or just in an inductive manner has received considerable attention. Recently, convincing evidence has been presented that in certain cases conjugative interaction is, in fact, important.[2-7,11] In this paper, we have presented the first example of an observed hyperfine splitting of a peripheral methylene group attached to a tetravalent phosphorus atom. It is likely that coupling is, in fact, occurring in radicals I–IV as the line widths are typically large (>0.1 mT).[2-8] Only in the case of $IV^{+\cdot}$ is the line width relatively small (0.035 mT);[6] however, in $V^{+\cdot}$ the line width is only 0.030 mT. Computer simulation of the EPR spectrum of $V^{+\cdot}$ using a line width of 0.035 mT showed no signs of coupling of the methylene protons other than the broad line width. Thus, the experimental line width is just small enough to allow observation of the methylene hfsc.

The relatively large coupling of the methylene protons (0.035 mT) represents additional evidence of the conjugative interaction of the phosphorus atom. It is doubtful that such a large coupling could be observed via a spin-polarization mechanism through the phosphorus atom. Also, one would have expected to see coupling in radicals such as II where R is either an ethyl or methyl group. Thus, it would seem that the odd electron is delocalized onto the phosphorus atoms. Further evidence against a spin-polarization mechanism is the observation that the methyl groups of VI do not couple.[3] In



VI

this case, only a spin-polarization mechanism could be involved. Thus, we feel that the observed splittings of the methylene groups of $V^{+\cdot}$ are strong evidence for the conjugative interaction of a tetravalent phosphorus atom.

Experimental Section

Melting points were taken with a Thomas-Hoover oil-bath melting-point apparatus and were corrected. Infrared spectra were obtained with a Perkin-Elmer 257 spectrometer. NMR spectra were recorded on a Varian XL-100 instrument. EPR spectra were recorded on a JEOL JES-ME instrument with temperatures determined with a copper–constantan thermocouple. Computer simulation of theoretical EPR spectra was done using a Fortran IV program for mixtures employing Lorentzian line shapes written by R. G. Griffin.[9] The program used for the Hückel MO calculations was written by Munch and Rieke[10] and modified by T. H. Ridgeway for simplified input. Elemental analyses were obtained from Galbraith Laboratories (Knoxville, Tenn.). The electrochemical and EPR equipment and techniques used in this study have been previously described.[3,6]

1,4-Bis(triethylphosphonium)benzene (V). Triethylphosphine (pressure chemical, 8.4 g) and *p*-dibromobenzene (Aldrich, 8.25 g) were heated in a sealed tube for 185 h at 190–210 °C. The mixture was allowed to cool and the solid triturated with anhydrous ethyl ether, filtered, and washed with ethyl ether. The residue was dissolved in the minimum amount of water and the salt precipitated by the addition of a copious quantity of acetone. This suspension was filtered and dried to yield crude light-brown V (8.25 g, 50%). Crude V was decolorized with activated carbon and recrystallized from isopropyl alcohol to give colorless needles: mp >330; NMR (F_3CCO_2H) δ 8.24 (AA′BB′ system, 4 H), 2.70 (oct, 12 H, J = 12.8 Hz), 1.36 (hex, 18 H, J = 19 Hz); IR (KBr) 1450, 1115 cm^{-1}, characteristic of a phosphonium salt. Anal. ($C_{18}H_{34}P_2Br_2$) P, Br.

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Registry No.—V dibromide, 63216-62-6; $V^{+\cdot}$, 63216-63-7; triethylphosphine, 554-70-1; *p*-dibromobenzene, 106-37-6.

References and Notes

(1) Alfred P. Sloan Fellow 1973–1975. Present address: Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebr. 68588.
(2) R. D. Rieke and R. A. Copenhafer, *J. Chem. Soc., Chem. Commun.*, 1130 (1972).
(3) R. D. Rieke, C. K. White, and C. M. Milliren, *J. Am. Chem. Soc.*, **98**, 6872 (1976).
(4) K. Dimroth, *Colloq. Int. C.N.R.S.*, **182**, 139 (1970).
(5) K. Dimroth, *Fostschr. Chem. Forsch.*, **38**, 1 (1973).
(6) C. K. White, Ph.D. Dissertation, University of North Carolina at Chapel Hill, Chapel Hill, N.C. (1974).
(7) R. A. Copenhafer, R. D. Rieke, C. K. White, A. M. Aguiar, M. S. Chattha, and J. C. Williams, Jr., submitted for publication.
(8) F. Gerson, G. Plattner, A. J. Ashe, III, and G. Maerkl, *Mol. Phys.*, **28**, 601 (1974).
(9) R. G. Griffin, Ph.D. Dissertation, Washington University, St. Louis, Mo. (1968).
(10) R. D. Rieke, Ph.D. Dissertation, University of Wisconsin, Madison, Wis. (1966).
(11) W. Schafer, A. Schweig, K. Dimroth, and H. Kanter, *J. Am. Chem. Soc.*, **98**, 4410 (1976).

Quantitative Dealkylation of Alkyl Ethers via Treatment with Trimethylsilyl Iodide. A New Method for Ether Hydrolysis

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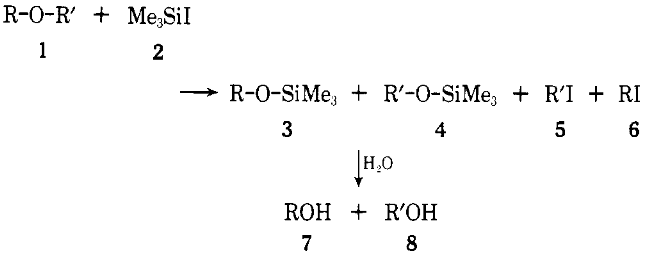
Many alkyl ethers have found extensive use in organic chemistry as protecting groups for alcohols.[1] Foremost among these are *tert*-butyl, triphenylmethyl (trityl), and benzyl ethers, all of which can be removed under relatively mild conditions, i.e., nonaqueous acid, mild aqueous acid, and hydrogenation, respectively.[2] Certain other alkyl ethers have also been employed to advantage on occasion, e.g., allyl,[3] tritylone,[4] *p*-halophenyl,[5] and similar systems.[6] However, simple methyl ethers have found little use in the protection of aliphatic hydroxyl groups (although they are quite extensively utilized for the protection of phenols) due to the difficulties associated with their removal. This fact has promoted the following statement which appeared in a recent review[1a] on protecting groups for aliphatic alcohols: "the methyl group is too stable to be used for the routine protection of alcohols". We report now observations which are contrary to the above statement, namely, the simple and efficient dealkylation of methyl and other alkyl ethers by trimethylsilyl iodide in both aliphatic and aromatic systems, the overall process affording ether hydrolysis in high yields.

Recently, several new modifications of long-standing procedures have been published which increase somewhat the usefulness of aliphatic alkyl ethers as protecting groups. These include the generation of HI in situ[7] and the use of acetic anhydride–Lewis acid media.[8] Boron trihalides have been used occasionally to cleave aliphatic methyl ethers,[9] although the yields in these cases are somewhat lower than with aromatic methyl ethers.[10] However, these methods do not solve the problem of clean and efficient demethylation of alkyl methyl ethers, since they often result in mixtures of dealkylated products.

We have very recently reported the simple and quantitative dealkylation of alkyl carboxylic esters by treatment with trimethylsilyl iodide to afford trimethylsilyl carboxylates, which upon addition of water furnish carboxylic acids.[11] We find that alkyl methyl ethers **1** (R′ = Me) also react with trimethylsilyl iodide **2** to afford mixtures of dealkylated products, the trimethylsilyl ethers **3** and **4** and the alkyl iodides **5** and **6**, in which, in general, the demethylation products **3** and **5** (methyl iodide) greatly predominate.[12] For example, cyclohexyl methyl ether **1a** when treated with 1.1 equiv of trimethylsilyl iodide **2** at 25 °C for 6 h affords 95% of the demethylation products, cyclohexyl trimethylsilyl ether **3a** and methyl iodide **5**, with only 5% of cyclohexyl iodide **6a** and methyl trimethylsilyl ether **4** being formed. It is interesting that at a somewhat higher temperature (50 °C) the reaction is complete in only 2 h, but now affords a 90:10 mixture of cyclohexyl silyl ether and methyl silyl ether. Aryl alkyl ethers (**1q–z**) are all cleaved unidirectionally when treated with trimethylsilyl iodide to afford only the aromatic trimethylsilyl ethers (**3q–z**) and the alkyl iodides (**5q–z**) in very high yields. In all cases, the silyl ethers **3** and **4** can be easily converted into the alcohols or phenols **7** and **8** in high yield upon simple hydrolysis.



$$\underset{1}{\text{R-O-R}'} + \underset{2}{\text{Me}_3\text{SiI}} \longrightarrow \underset{3}{\text{R-O-SiMe}_3} + \underset{4}{\text{R}'\text{-O-SiMe}_3} + \underset{5}{\text{R}'\text{I}} + \underset{6}{\text{RI}}$$

$$\xrightarrow{\text{H}_2\text{O}} \underset{7}{\text{ROH}} + \underset{8}{\text{R}'\text{OH}}$$

The results with a series of methyl ethers and other alkyl ethers **1a–z** are listed in Table I. Several conclusions can be made from this data: (1) trityl, benzyl, and *tert*-butyl ethers are cleaved at a very much faster rate than the other alkyl ethers (methyl, ethyl, isopropyl, cyclohexyl, etc.), thus permitting the former to be selectively hydrolyzed in the presence of the latter; (2) aryl alkyl ethers (e.g., anisole) react with trimethylsilyl iodide at a significantly slower rate than dialkyl ethers (e.g., cyclohexyl methyl ether), so that dialkyl ethers can, in general, be cleaved completely under conditions which cause only 5–10% clevage of phenolic ethers; (3) the rates of dealkylation are such that alkyl methyl ethers can be cleaved cleanly in the presence of methyl esters[11] by conducting the reaction with just slightly more than 1 equiv of the silyl iodide at room temperature or below; (4) as was the case with alkyl esters,[11] many functional groups are stable to the conditions for ether hydrolysis, including acetylenes, olefins, ketones, amines, aromatic halides; (5) by careful variation of solvent, one can cleanly demethylate methyl ethers of straight-chain secondary alcohols, e.g., methyl 2-octyl ether **1g**, since the use of a propene–acetonitrile solution permitted the production of predominately 2-octanol.

As in the case of dealkylation of esters,[11] the possibility that the observed reactions are due entirely to catalytic amounts of HI present in the trimethylsilyl iodide cannot be totally discounted. However, we believe that trimethylsilyl iodide itself is causing dealkylation because, in the presence of 15 mol % pyridine or 2,6-di-*tert*-butyl-4-methylpyridine,[15] ether