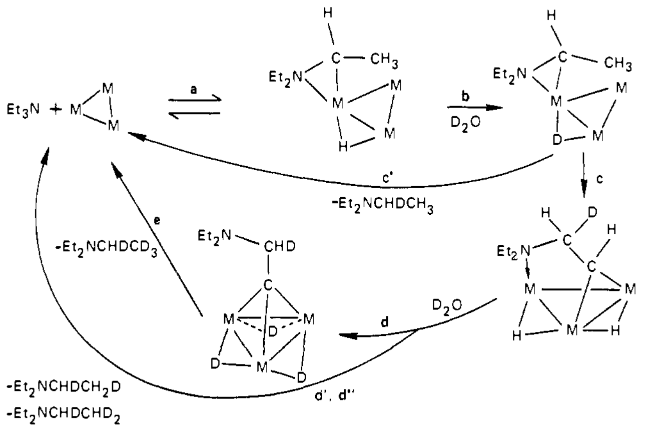

Figure 1. A possible mechanism accounting for the $\alpha\beta\beta\beta$ deuterium for hydrogen exchange pattern catalyzed by either Pd black, $Ru_3(CO)_{12}$, or $Os_3(CO)_{12}$ where Et_3N is the substrate. Step c′ will give α-d_1 products. Depending on the rate of deuterium for hydrogen exchange vs. Et_3N reconstitution, d′ will give $\alpha\beta$-d_2 product, d″ will give $\alpha\beta$-d_3 product, and e will give $\alpha\beta\beta$-d_4 product. The reverse sequence of steps may provide a route for the $\beta\beta\beta\alpha$ substitution pattern; however, our previously proposed mechanism remains viable.[5]

as the tertiary amine is varied. These changes in catalyst behavior are not purely a consequence of the increased steric bulk on going from Et_3N to Bu_3N, because catalyst activity (turnover frequency) should decrease as the alkyl groups become larger rather than increase as is observed. The anomaly lies in the Pr_3N reactions, which consistently have lower turnover frequencies and $\alpha{:}\beta$ ratios than would be expected from the Bu_3N results. At this point, we have insufficient information to either offer a satisfactory explanation of the changes in catalyst behavior or explain this anomaly; however, it is important to note that the anomaly is found for reactions catalyzed by both palladium black and ruthenium. One other point of interest is the fact that the ruthenium-catalyzed Et_3N exchange exhibits two different exchange pathways ($\beta\beta\beta\alpha$ and $\alpha\beta\beta\beta$). As steric hindrance increases, the $\alpha\beta\beta\beta$ exchange mechanism is favored. Figure 1 shows a plausible mechanism for the $\alpha\beta\beta\beta$ exchange.

The above observations indicate that three different catalyst–amine reaction parameters change in the same way and with much the same relative rates of change. These facts are strong support for reliable modeling. Moreover, if the modeling concept is indeed valid, it seems logical that the homogeneous catalysts should be capable of catalyzing other reactions of tertiary amines found to be catalyzed by Pd black. In this respect, we have recently reported[9a] that reactions similar to reaction 2 (with Et_3N and Pr_3N) can be very effectively catalyzed by homogeneous catalysts deriving from $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$. These results represent a fourth reaction parameter. Initial modeling studies of reaction 2 with the ruthenium catalyst have resulted in a fifth parameter. Both the ruthenium and palladium black catalysts require catalytic amounts of water for catalysis of reaction 2.[9b]

We believe that in the homogeneous catalysis of reactions 1 and 2 the active species are clusters. Our beliefs are based on the following reasons. First, as the CO pressure is decreased, the rate of deuterium for hydrogen exchange increases rapidly for all of the active catalysts.[10] Second, a bridging carbene complex similar to that formed in step c of Figure 1 has been isolated and a crystal structure obtained from the reaction of Et_3N with $Os_3(CO)_{12}$.[11,12] Third, Deeming has shown that the reactions of $C_6H_5CH_2N(CH_3)_2$ with $Os_3(CO)_{12}$ produce only amine cluster complexes of osmium,[13] and, fourth, we have isolated from reactions similar to (1) and (2) the cluster $(\eta^2\text{-}CH_3C{=}NEt)Ru_3(CO)_9H$.[9b] Finally, we cannot describe a mononuclear catalysis mechanism for deuterium–hydrogen exchange that successfully accounts for all the observed exchange patterns.[5,14] Unfortunately, definitive proof of cluster catalysis must await isolation of active intermediates.

The amine catalysis studies described above appear to be valuable model systems useful for delineation of the catalytic mechanism(s) of hydrodenitrogenation and may be of value in understanding the mechanisms by which amines poison catalysts.[15]

Acknowledgment. We thank Dr. Karl F. Kuhlmann for running the ^2H NMR MR spectra and Maria Buyco for her assistance with the manuscript. This work was supported by National Science Foundation Grant 78-25069.

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[9] (a) Shvo, Y.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753. (b) Shvo, Y.; Laine, R. M., unpublished results.

[10] We have recently described criteria for identifying cluster-catalyzed reactions (Laine, R. M. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1980**, *25*, 399) wherein one criterion is that the occurrence of increased catalytic activity under conditions that favor cluster formation (low CO pressures and third-row carbonyl complexes, e.g., $Os_3(CO)_{12}$) is suggestive of cluster catalysis. The CO pressures used in the present studies are used solely to inhibit reaction 2.

[11] (a) Shapley, J. R.; Tachikawa, M.; Churchill, M. R.; Lashewyck, R. A. *J. Organomet. Chem.* **1978** *167*, C32. Note that reconstitution of Et_3N from the Shapeley complex in the presence of D_2O will give either $Et_2NCHDCH_2D$ or $Et_2NCHDCHD_2$ depending on whether or not the metal hydride exchanges with D_2O. These are the only d_2 and d_3 products found with the osmium-catalyzed exchange. (b) Note also that steps c and d are similar to reactions found for $HCOs_3(CO)_9H_3$. Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

[12] Similar amine reactions are also reported by: Adams, R. D.; Selegue, J. P. *Inorg. Chem.* **1980**, *19*, 1795.

[13] Yin, C. C.; Deeming, A. J. *J. Organomet. Chem.* **1977**, *133*, 123. The reaction conditions reported in this paper are more severe than those we employ.

[14] The key features that are difficult to explain with mononuclear catalysis are (1) no d_5 as $-CD_2CD_3$ is found; (2) in the rhodium reaction d_4 is $-CHDCD_3$ and d_3 is always $-CH_2CD_3$, and (3) osmium is the best catalyst of all the group 8 metals at low CO pressures.

[15] These relationships will be discussed in future publications.

Stabilization of α-Keto Cations by Carbonyl Conjugation

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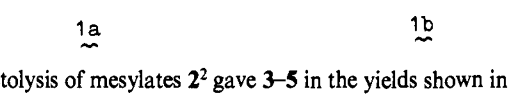
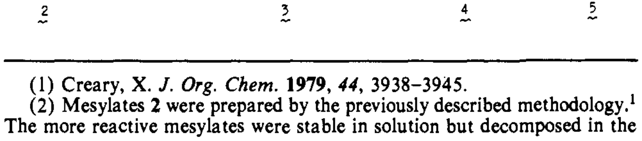
Received February 2, 1981

We have previously reported that solvolytically generated α-keto cations are viable, although they are relatively unstable intermediates.[1] Evidence for this instability included their slow rate of formation, rearrangement propensity, a large α-CH_3/α-CD_3 isotope effect, and large reaction constant in a Hammett study. We now wish to report experimental evidence that the α-keto cation **1** can derive significant stabilization by a conjugative interaction as represented by **1b**.



1a 1b

Acetolysis of mesylates **2**[2] gave **3–5** in the yields shown in Table I. Increasing amounts of the rearranged acetate **4** and the tricyclic



2 3 4 5

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[1] Creary, X. *J. Org. Chem.* **1979**, *44*, 3938–3945.

[2] Mesylates **2** were prepared by the previously described methodology.[1] The more reactive mesylates were stable in solution but decomposed in the pure state at rom temperature.

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Table I. Product Yields in the Acetolysis of Mesylates 2

substituent	**3**, %	**4**, %	**5**, %
3,5-$(CH_3)_2$	97		
m-CH_3	95		
p-H	92		
m-SCH_3	95		
m-F	95		trace
m-Cl	90		2
m-CF_3	83	7	6
p-CF_3	64	17	14
3,5-Cl_2	55	21	20
3,5-$(CF_3)_2$	27	25	42[a]

[a] Small amount of an unidentified product also produced.

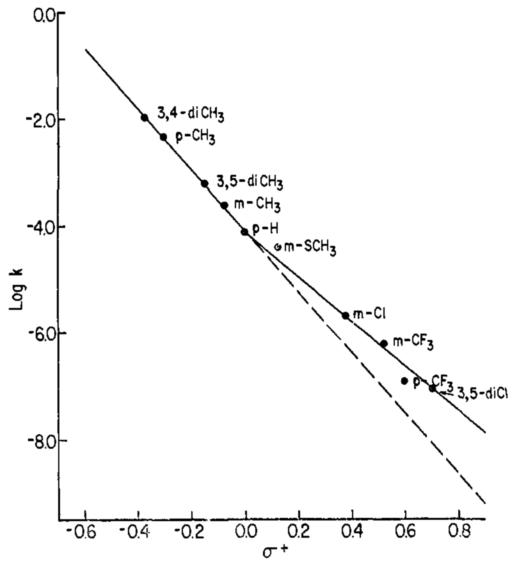


Figure 1. A plot of log k vs. σ^+ for solvolysis of **2** in ethanol at 25 °C.

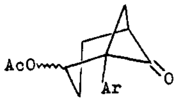
ketone **5** are formed as substituent electronegativity increases. The results of a rate study in ethanol[3] are given in Table II and in Figure 1. A break in the plot is seen. The reaction constant, ρ, is -5.69 ($r = 0.999$) for the electron donor substituents and ρ is -4.15 ($r = 0.999$, excluding the *m*-SCH_3 and *p*-CF_3 substituents) for the electron-withdrawing substituents.

Table II. Rates of Ethanolysis of Mesylates 2 at 25 °C

substituent	k, s^{-1}	$\sigma^{+\,f}$
3,4-$(CH_3)_2$	$1.09 \times 10^{-2\,a}$	-0.378^c
p-CH_3	$4.61 \times 10^{-3\,a}$	-0.305^c
3,5-$(CH_3)_2$	$6.06 \times 10^{-4\,a}$	-0.154
m-CH_3	$2.39 \times 10^{-4\,a}$	-0.077
p-H	$7.64 \times 10^{-5\,a}$	0.000
m-SCH_3	$3.90 \times 10^{-5\,d}$	0.125
m-Cl	$2.06 \times 10^{-6\,a,b}$	0.377
m-CF_3	$6.38 \times 10^{-7\,a,b}$	0.517
p-CF_3	$1.21 \times 10^{-7\,a,b}$	0.596
3,5-Cl_2	$8.86 \times 10^{-8\,b,d}$	0.701^e

[a] Determined spectrophotometrically; 5×10^{-4} M NaOAc. [b] Extrapolated from data at higher temperatures. [c] Determined from spectrophotometric rate constant for solvolysis of the appropriate cumyl chloride. [d] Determined titrimetrically; 0.025 M 2,6-lutidine. [e] Determined from titrimetric rate constant for solvolysis of 3,5-dichlorocumyl chloride. [f] Reference 4.

The break in Figure 1 is reminiscent of benzyl tosylate solvolyses which also gives a nonlinear Hammett plot.[5] Additionally, recent studies on 1-aryl-1-(trifluoromethyl)ethyl tosylates[6] also show a nonlinear Hammett plot. The reasons for these nonlinear plots may or may not be related. Potential reasons for the break in Figure 1 are now examined. A break in a Hammett plot usually indicates a mechanistic change. In solvolytic studies, this test, termed the tool of increasing electron demand,[7] has been used often to indicate a mechanistic change from k_c to k_Δ as substituents become more electronegative. This mechanistic change (from k_c to k_Δ) has been *ruled out* in the solvolysis of **2**. Stereochemical constraints require that the k_Δ process in the solvolysis of **2** involve C_1–C_7 participation. However products such as **6** or **4**, which would result from this k_Δ process, are not seen. The products



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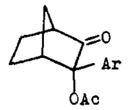

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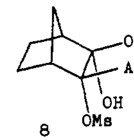
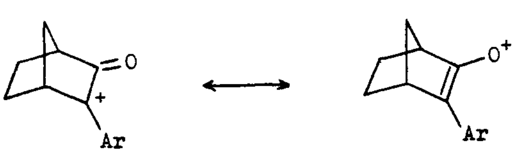


8

3–**5** can all be explained in terms of descrete α-keto cations which can undergo subsequent rearrangement.[1] The C_1–C_7 k_Δ process is not viable.

A second mechanistic possibility involves the reversible addition of solvent to the carbonyl group of **2**, giving **8**, followed by solvolysis of **8**. This process does not appear likely.[8] We have shown that stable analogues of **8** solvolyze only slightly faster than **2**.[8] Therefore unreasonably large equilibrium constants for solvent addition to **2** would be required to account for the observed enhanced rates when **2** carries electronegative substituents. Additionally, stable analogues of **8** solvolyze giving much more rearrangement than does **2**. Therefore it is unlikely that **8** is involved in the solvolysis of **2**.

An intriguing possibility which could account for the break in Figure 1 involves carbonyl group stabilization of the α-keto cation via conjugation as in **1b**. Gassman[9] has suggested that α-cyano carbocations derive an analogous type of stabilization. We suggest that in the electron-withdrawing portion of the plot, contribution of forms such as **9b** become important and lend increased stability to the cationic intermediate. In the electron donor portion of the plot, forms such as **9b** are not important and the carbonyl effect is mainly inductive. Increasing electron demand results in the onset of "neighboring carbonyl group conjugation" as a stabilizing feature and a resultant break in the plot. Stated differently, increasing carbonyl conjugation partially offsets the decreased aryl stabilization when the substituent is electronegative. The result is a faster solvolysis rate than expected simply based on σ^+ values.



9a **9b**

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(3) Rates were monitored in ethanol since σ^+ values have been determined in this solvent[4] and not in acetic acid. Brown[4] has shown that σ^+ values can vary with solvent. Additionally, use of ethanol permits determination of rapid rates spectrophotometrically when it is not possible to measure titrimetric rate constants as is usually done in acetic acid. A limited product study in ethanol gives similar product trends. However, less rearranged products are formed in this solvent. Mesylate **2** (Ar = Ph) gives exclusively unrearranged product. Mesylate **2** (Ar = *m*-$CF_3C_6H_4$) gives 92% unrearranged ethoxy ketone and only traces of the rearranged ethoxy ketone and **5**. Mesylate **2** (Ar = 3,5-$Cl_2C_6H_3$) gives 85% unrearranged ethoxy ketone and 7% rearranged products.

(4) Okamoto, Y.; Inukai, T.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 4972–4976.

(5) (a) Kochi, J. K.; Hammond, G. S. *J. Am. Chem. Soc.* **1953**, *75*, 3445–3451. (b) Okamoto, Y.; Brown, H. C. *J. Org. Chem.*, **1957**, 22, 485-94.

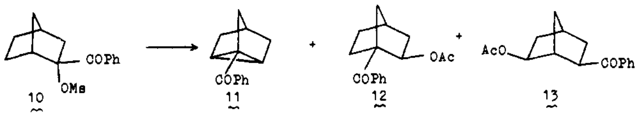
(6) Liu, K.-T.; Sheu, C.-F. *Tetrahedron Lett.* **1980**. 4091–4094.

(7) (a) Gassman, P. G.; Fentiman, A. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 2549–2551. (b) Brown, H. C. "The Nonclassical Ion problem"; Plenum Press: New York, 1977.

(8) Full details on the solvolysis of stable analogues of **8** (3,3-dimethoxy-2-aryl-*endo*-2-norbornyl tosylates) will be presented subsequently. Details of arguments against the involvement of **8** are given as supplementary material.

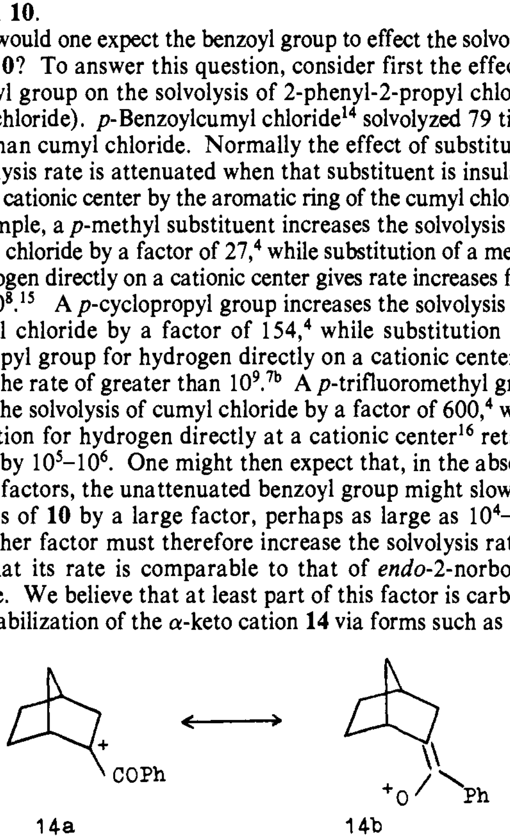
(9) (a) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214–1216. (b) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *Ibid.* **1980**, *102*, 3957–3958. (c) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 7613–7615. (d) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *Ibid.* **1980**, *102*, 6640–6441.

In support of this hypothesis, mesylate **10** has been prepared.[10] Acetolysis of **10** ($k = 1.35 \times 10^{-5}$ s^{-1} at 75 °C) gave the products shown and strongly suggests the involvement of an α-keto cation.



However, in terms of rate, the effect of the benzoyl group relative to hydrogen is quite small.[12] Solvolysis rates of **10** and *endo*-2-norbornyl mesylate ($k = 2.6 \times 10^{-5}$ s^{-1} at 75 °C)[13] are comparable, despite the inductively electron-withdrawing benzoyl group in **10**.

How would one expect the benzoyl group to effect the solvolysis rate of **10**? To answer this question, consider first the effect of a benzoyl group on the solvolysis of 2-phenyl-2-propyl chloride (cumyl chloride). *p*-Benzoylcumyl chloride[14] solvolyzed 79 times slower than cumyl chloride. Normally the effect of substituents on solvolysis rate is attenuated when that substituent is insulated from the cationic center by the aromatic ring of the cumyl chloride. For example, a *p*-methyl substituent increases the solvolysis rate of cumyl chloride by a factor of 27,[4] while substitution of a methyl for hydrogen directly on a cationic center gives rate increases from 10^5 to 10^8.[15] A *p*-cyclopropyl group increases the solvolysis rate of cumyl chloride by a factor of 154,[4] while substitution of a cyclopropyl group for hydrogen directly on a cationic center increases the rate of greater than 10^9.[7b] A *p*-trifluoromethyl group retards the solvolysis of cumyl chloride by a factor of 600,[4] while substitution for hydrogen directly at a cationic center[16] retards the rate by 10^5–10^6. One might then expect that, in the absence of other factors, the unattenuated benzoyl group might slow the solvolysis of **10** by a large factor, perhaps as large as 10^4–10^5. Some other factor must therefore increase the solvolysis rate of **10** so that its rate is comparable to that of *endo*-2-norbornyl mesylate. We believe that at least part of this factor is carbonyl group stabilization of the α-keto cation **14** via forms such as **14b**.



This suggestion, on the basis of our experimental results, is in agreement with the recent theoretical study of Houk and Paddon-Row[17] which indicates that a formyl group in a conjugating conformation can stabilize a cationic intermediate relative to a nonconjugating (perpendicular) formyl group.

Acknowledgment is made to the donors of the Petroleum Research fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Details of arguments against the involvement of **8** (4 pages). Ordering information is given on any current masthead page.

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[10] Reaction of norcamphor with diethyl-1-(trimethylsiloxy)-1-phenylmethanephosphonate carbanion[11] followed by hydrolysis gave the alcohol precursor to **10**. Treatment with CH_3SOCl-Et_3N followed by *m*-chloroperbenzoic acid oxidation gave **10**.

[11] Koenigkramer, R. E.; Zimmer, H. *J. Org. Chem.* **1980**, *45*, 3994-3998.

[12] Our previous study[1] found a rate ratio of $10^{7.3}$ in the solvolysis of *exo*-2-methylbicyclo[2.2.1]heptan-*endo*-2-yl tresylate and carbonyl analogue *exo*-3-methylbicyclo[2.2.1]heptan-2-on-*endo*-3-yl tresylate. This is the α-CH_2/α-keto ratio and *not* the α-H/α-keto ratio as has been implied in the various references to our work. These systems are not suitable for determining the effect of the carbonyl group relative to hydrogen. The present system, **10**, gives such an α-H/α-keto ratio.

[13] Estimated from the tosylate rate assuming the tosylate rate is 2 times the mesylate rate. See: Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375-376.

[14] This chloride was prepared by reaction of the grignard reagent derived from 4-bromobenzophenone dimethyl ketal with acetone followed by treatment with concentrated hydrochloric acid.

[15] Fry, J. L.; Harris, J. M.; Bingham, C. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540-2542.

[16] Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216-1218.

[17] Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561-6563.

Syntheses of Trifluoromethylated Thiadiphosphanorbornadiene and Thiadiphosphole[1]

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Received January 5, 1981

Previously, we reported that 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (**2**) was obtained by thermolysis of 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-7,8-dihydro-1,4-diphosphabarrelene (**1**) and that **2** was thermally stable but reactive to dienophiles and oxygen.[2] Now, we have used this high reactivity of **2** for the synthesis of a new ring system, thiadiphosphanorbornadiene (**3**), which was further converted to a thiadiphosphole. Since **2** is very sensitive to air, we thermolyzed **1** in situ in this experiment.

Thermolysis of **1** with excess of sulfur in pentane in a sealed tube at 100 °C for 48 h gave an adduct of **2** with sulfur, 2,3,5,6-tetrakis(trifluoromethyl)-7-thia-1,4-diphosphanorbornadiene (**3**), which was purified by preparative GLC.[3] **3**: an air-stable yellow oil; $\nu_{C{=}C}$ 1610 cm^{-1}; ^{19}F NMR (pentane) δ[4] -6.8 ($J_{PF} = 24.8$ Hz); high-resolution MS, *m/e* 418 (M^+). Anal. Calcd. for $C_7F_9P_2S$ ($M - CF_3$): 348.905. Found: 348.906. In the attempted desulfurization of **3** with triphenylphosphine, the formation of **2** was confirmed by ^{19}F NMR spectroscopy. Treatment of **2** with 0.5 molar equiv of cyclohexene thioxide gave **3** and a cycloadduct (**4**) of **2** with cyclohexene in nearly quantitative yields, estimated by ^{19}F NMR spectroscopy, both of which were separated by preparative GLC.[3] **4**: mp 130–132 °C (pentane); ν_{C-H} 2950, 2870, ν_{C-F} 1240, and 1140 cm^{-1}; *m/e* 468 (M^+). This reaction shows that **2** has a high affinity for sulfur.

Compound **3** seemed likely to react with **2** as a dienophile, since hexakis(trifluoromethyl)diphosphabarrelene (**5**) was known to be a good dienophile.[5] The adduct **6** could be a good precursor for the thiadiphosphole compound **7**, since dihydrodiphosphabarrelene **1** was easily cleaved to **2** and the ethylene compound. Therefore, we thermolyzed **1** with 0.5 molar equiv of sulfur and obtained the thiadiphosphole **7** and **5** in nearly quantitative yields, estimated by ^{19}F NMR spectroscopy. The reaction mixture was cooled, the precipitate of **5** was filtered off, and the solvent was removed under vacuum to give a very air-sensitive oil which was nearly pure **7** by ^{19}F NMR spectroscopy. **7**: ν_{C-F} 1238, 1175 cm^{-1}; ^{19}F NMR (pentane) δ -12.8 ($J_{PF} = 51$ Hz); λ_{max} (hexane) 248 ($\epsilon > 1100$), 322 nm ($\epsilon > 850$). The air sensitivity of **7** is comparable to that of **2**, both of which have planar structures. This is very interesting, since **3** and **5** of the cage structure are stable to air. Compound **7** was found to be a good diene in the Diels–Alder reaction. Thus the reaction of **7** with hexafluoro-2-butyne gave **3** quantitatively. Further, the treatment of **7** with maleic anhydride in pentane gave an adduct (**8**) in 57% yield, which was precipitated from the reaction mixture. **8**: mp 135–136°C (hexane–C_6H_6); ν_{C-H} 2980,

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[1] A part of this work was presented at 9th International Symposium on Fluorine Chemistry, Sept. 1979, Avignon, France.

[2] Y. Kobayashi, I. Kumadaki, A. Ohsawa, and H. Hamana, *Tetrahedron Lett.*, **1976**, 3715.

[3] Ohkura gas chromatograph, Model 701. Column DEGS 3-mm i.d., 3-m long, at 70 °C. Isolation yield 7.4% (58% based on ^{19}F NMR spectroscopy).

[4] Benzotrifluoride as an external standard: higher field is shown by +.

[5] Y. Kobayashi, I. kumadaki, H. Hamana, and S. Fujino, *Tetrahedron Lett.*, **1976**, 4815.

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