Studies on Organic Fluorine Compounds. 29.[1] Cycloaddition Reactions of Hexakis(trifluoromethyl)-1,4-diphosphabarrelene[2]

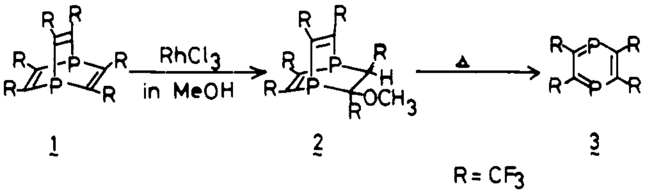
Yoshiro Kobayashi,* Hiroshi Hamana, Shomi Fujino, Akio Ohsawa, and Itsumaro Kumadaki

Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan

Received July 27, 1979

Cycloaddition reactions of hexakis(trifluoromethyl)-1,4-diphosphabarrelene (1) were examined. The primary adducts of diazomethane and phenyl azide with 1 were not isolated, but they dissociated to 3,4-bis(trifluoromethyl)pyrazole (4) and 1-phenyl-4,5-bis(trifluoromethyl)-1,2,3-triazole (9), respectively. Photolysis of 9 gave 2,3-bis(trifluoromethyl)indole (10). The reaction of 1 with cyclobutadiene gave *exo*- and *endo*-2,7,9,10,11,12-hexakis(trifluoromethyl)-1,8-diphosphatetracyclo$[6.2.2.0^{2,7}.0^{3,6}]$dodeca-4,9,11-triene (11 and 12), only the latter of which was cyclized by photolysis to a new cage compound, 2,5,7,10,11,12-hexakis(trifluoromethyl)-1,6-diphosphahexacyclo$[4.4.2.0^{2,5}.0^{3,9}.0^{4,8}.0^{7,10}]$dodec-11-ene (13). Compound 1 did not react with other cyclic dienes but reacted with butadiene and 2,3-dimethylbutadiene, while the primary adducts were not isolated in these cases either. Thermolysis of 11 and 12 is also described.

A diphospha analogue of barrelene, 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene (1), had been reported to be stable to atmospheric oxygen or bromine dissolved in chloroform because of the steric hindrance of the trifluoromethyl groups.[3] However, in the previous papers[1] we reported that methanol adds to the double bond of 1 in the presence of rhodium trichloride and the adduct 2 thus formed is transformed by thermolysis to a new heteroaromatic ring system, 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (3). Formation of the methanol adduct (2) suggests that the double bond moiety in compound 1 is appreciably reactive. From this point of view, we tried the reactions of 1 with 1,3-dipolar compounds (phenyl azide and diazomethane) and dienes (cyclobutadiene) and found that both cycloaddition reactions occurred smoothly. Further, we obtained a new cage compound containing two phosphorus atoms at the bridgeheads by the photolysis of the adduct of 1 with cyclobutadiene; the structure of this new cage compound was confirmed by X-ray analysis.

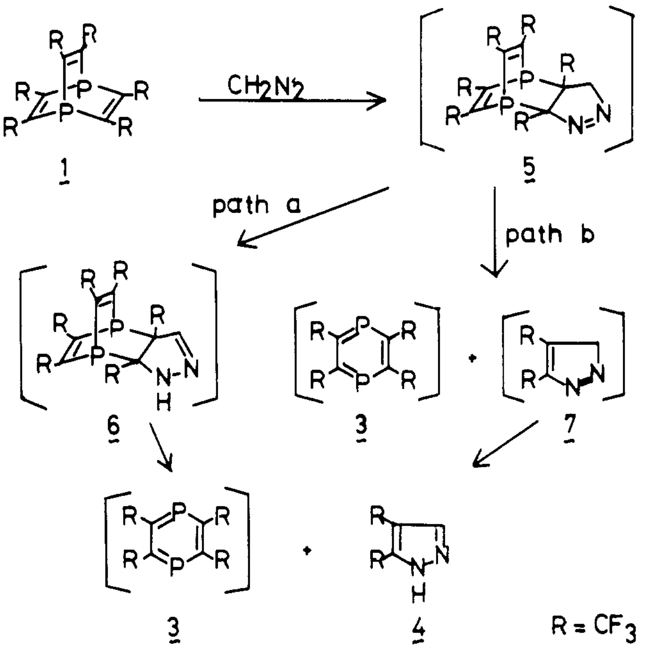


1. **1,3-Dipolar Reactions.** Reaction of 1 with diazomethane gave 3,4-bis(trifluoromethyl)pyrazole (4) quantitatively. The fact that 1 did not react with dimethylacetylene even at 200 °C shows that there is no equilibrium between 1 and 3 and hexafluorobutyne-2. Therefore, 1 must have reacted at first with diazomethane to give 1,3-dipolar adduct (5), and then 5 dissociated readily into 3 and 4 via path a or path b (Scheme I).

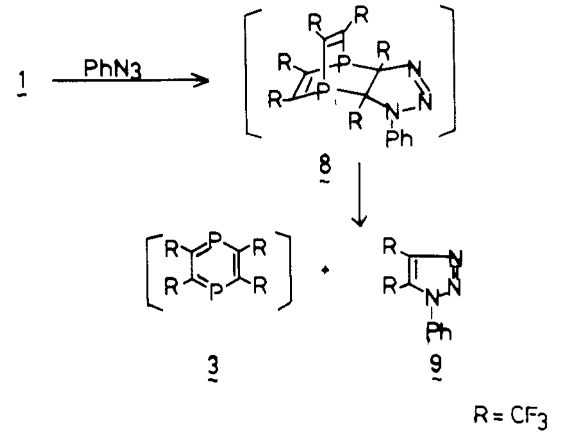
This cycloreversion is attributed to the steric hindrance of the adduct 5 or 6 and the aromaticity of diphosphabenzene (3) and pyrazole (4) produced. This reaction is one of the rare examples[4] of mild cycloreversion of 1,3-dipolar adduct obtained from diazoalkanes.

Similarly, the reaction of 1 with phenyl azide at 80 °C gave not the primary adduct 8 but 1-phenyl-4,5-bis(trifluoromethyl)-1,2,3-triazole (9) quantitatively (Scheme II).

Scheme I



Scheme II



The structures of 4 and 9 were determined by comparison with the authentic samples obtained by the reactions of hexafluorobutyne-2 with diazomethane[5] and

---

[1] Part 28: Y. Kobayashi, H. Hamana, S. Fujino, A. Ohsawa, and I. Kumadaki, *J. Am. Chem. Soc.*, in press.

[2] Parts of this work were preliminarily published in *Tetrahedron Letts.*, 4815 (1976); 867 (1977).

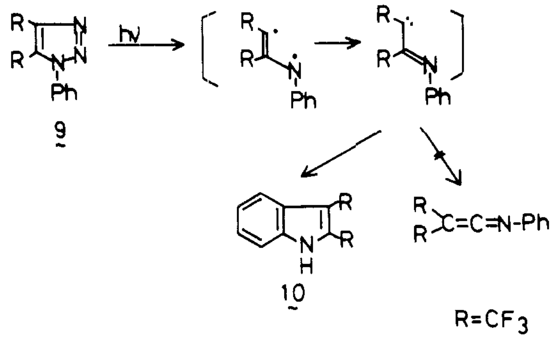
[3] C. G. Krespan, *J. Am. Chem. Soc.*, 83, 3432 (1961).

[4] R. Paulissen, *J. Chem. Soc., Chem. Commun.*, 219 (1976).

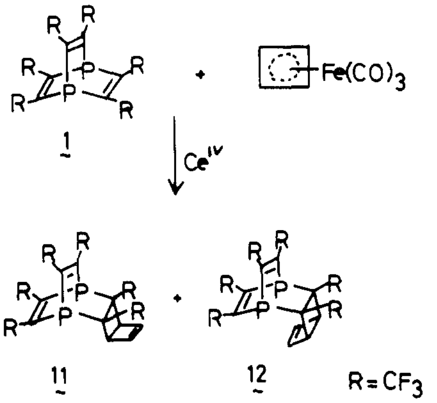
[5] J. H. Atherton and R. Fields, *J. Chem. Soc. C*, 1507 (1968).

0022-3263/79/1944-4930$01.00/0

Scheme III



Scheme IV



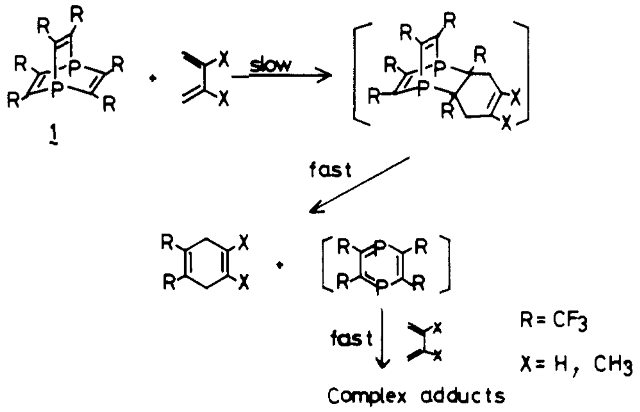
phenyl azide, respectively. In the reaction of 1 with an equimolar amount of 1,3-dipolar compounds, the primary adducts were not isolated, and 4 or 9 was obtained with the recovery of the starting material 1. This fact suggests that the rate-determinating step is the 1,3-dipolar cycloaddition reaction, and the following cycloreversion step is very rapid. The primary adducts 6 and 8 were very unstable and easily dissociated into 3, 4, and 9. Compound 3 is very reactive and seemed to be decomposed by the reaction with excess 1,3-dipolar compounds.

Further, irradiation of 9 in *n*-pentane solution gave 2,3-bis(trifluoromethyl)indole (10) (43.9%) with the recovery of the starting material (22.6%) (see Scheme III). The structure of 10 was determined by comparison with the authentic sample.[6] Photochemical decomposition of 1-phenyl-1,2,3-triazole derivatives was reported to give indole derivatives and ketenimine derivatives,[7] but in this case the ketenimine derivative was not obtained, possibly because of the electronic effect of the trifluoromethyl groups.

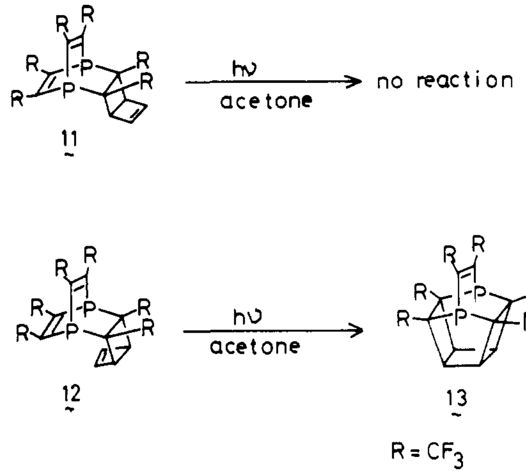
2. Diels–Alder Reaction. The primary cycloadducts could not be isolated by the reaction of 1 with 1,3-dipolar compounds, as shown above.

Diels–Alder reaction of 1 with diene was subsequently investigated in the hope of isolating the cycloadduct. As 1 did not react with furan, 2,5-dimethylfuran, or tetraphenylcyclopentadienone even at 160 °C for 20 h, the reaction of a less bulky diene was attempted. In fact, 1 reacted with cyclobutadiene, generated from cyclobutadieneiron tricarbonyl at room temperature, in acetone to give two isomeric 1:1 Diels–Alder adducts (11 and 12). The structures of these compounds were determined by their photolysis, which will be discussed later (see Scheme IV).

Scheme V



Scheme VI



Dimethylbutadiene and butadiene also reacted with 1 to give 1,4-cyclohexadiene derivatives and complex products composed of these dienes and 1,4-diphosphabenzene (3) (Scheme V). These reactions were similar to those of 1 with 1,3-dipolar compounds.

3. New Cage Compounds Containing Two Phosphorous Atoms. In order to establish the configuration of the two isomers obtained from the reaction of 1 with cyclobutadiene, the photolysis of two isomers (11 and 12) was followed by NMR. Irradiation of 12 in acetone caused a peak of vinylic protons to disappear and a single peak of four equivalent methyne protons to appear in the ^{1}H NMR spectrum, showing the formation of a new cage compound (13), while photolysis of the other isomer 11 did not proceed under the same conditions, the starting material being recovered. This fact shows that 12 is an endo isomer and that 11 is an exo one. Kobayashi[8] and coworkers and Eberbach[9] have reported that even an exo isomer gave intramolecular cycloadducts through exo-endo isomerization in special cases. If our photochemical reaction proceeded with the isomerization, a cycloadduct must have been obtained from both isomers. Therefore, this photochemical reaction seems to be a concerted intermolecular $[_\pi 2_s + _\pi 2_s]$ cycloaddition reaction.

There are a few examples of cage compounds containing a phosphorus atom,[10] but this cage compound is the first example which contains two trivalent phosphorus atoms at its bridgeheads.

---

[6] Y. Kobayashi, I. Kumadaki, and T. Yoshida, *Heterocycles*, 8, 387 (1977).

[7] E. M. Burgess, R. Carithers, and L. McCullagh, *J. Am. Chem. Soc.*, **90**, 1923 (1968).

[8] Y. Kobayashi, I. Kumadaki, A. Ohsawa, and Y. Sekine, *Tetrahedron Lett.*, 2841 (1974).

[9] W. Eberbach, *Chem. Ber.*, **107**, 3287 (1974).

[10] E. W. Turnblom and T. J. Katz, *J. Am. Chem. Soc.*, **95**, 4292 (1973).

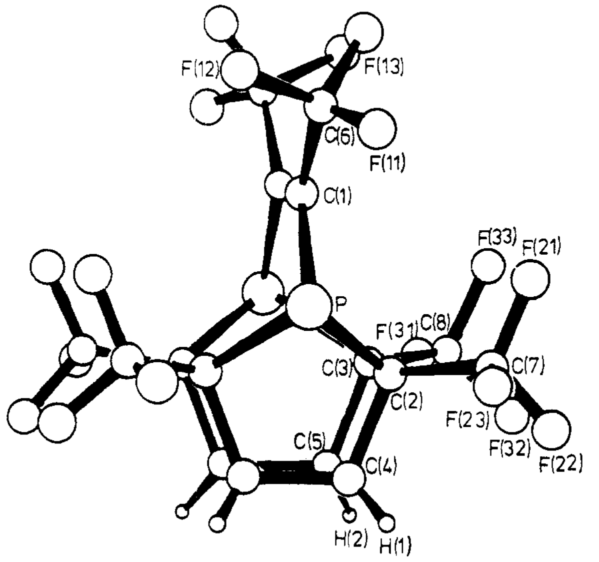
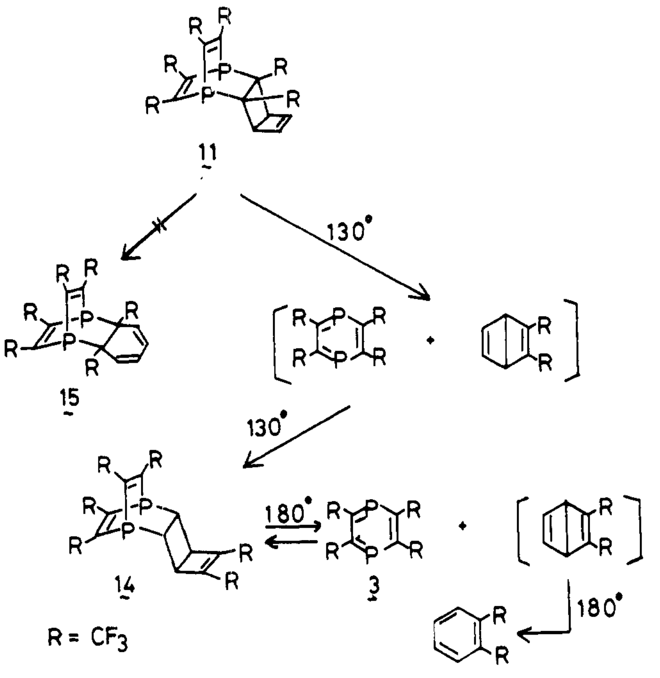


Figure 1.

Scheme VII



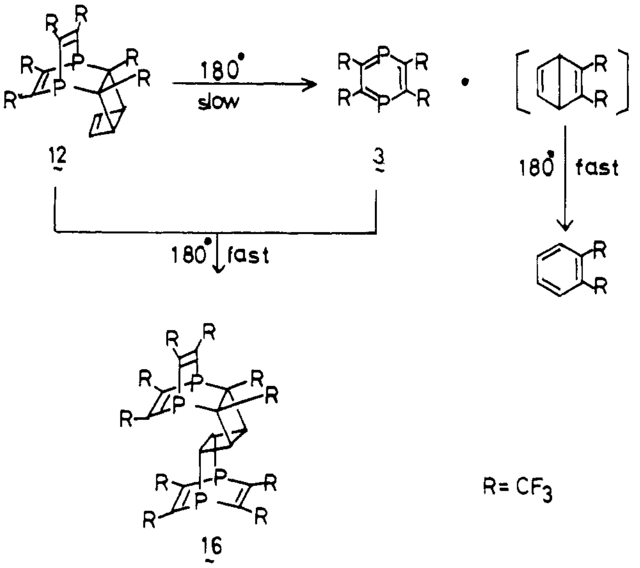
X-ray analysis of the compound **13** shown in Figure 1[11] supports the structure of **13**.

4. Thermal Reactions of Adducts 11 and 12. The primary adducts of **1** with compounds of the 4π system were found to be very unstable. Therefore, the adducts **11** and **12** were the only examples of isolated 1:1 adducts, and their thermal stability seemed to be worth examining.

Exo isomer **11** was heated at 130 °C for 16 h in a sealed tube to give 4,5,9,10,11,12-hexakis(trifluoromethyl)-1,8-diphosphatetracyclo[$6.2.2.0^{2,7}.0^{3,6}$]dodeca-4,9,12-triene (**14**). No partially ring-opened product (**15**) was observed. Moreover, this isomer (**14**) was heated at 180 °C for 3 h to produce diphosphabenzene (**3**) and 1,2-bis(trifluoromethyl)benzene. These facts suggest that PC bond cleavage is preferred to CC bond cleavage. The mechanism of these thermolyses is proposed as shown in Scheme VII.

Endo isomer **12** did not react on heating at 130 °C in a sealed tube with the recovery of the starting material, but heating at 180 °C gave the one-to-two adduct, which was assumed to be 2,6,7,11,13,14,15,16,17,18-decakis(trifluoromethyl)-1,5,8,12-tetraphosphahexacyclo[$10.2.2.2^{5,8}.0^{2,11}.0^{3,10}.0^{4,9}$]octadeca-6,13,15,17-tetraene (**16**) and 1,2-bis(trifluoromethyl)benzene. A probable mechanism of this reaction is formulated in Scheme VIII.

Scheme VIII



Unexpectedly, the endo isomer **12** was more stable than the exo isomer **11**. This might be ascribed to the difference between the lengths of PC and CC bonds. The PC bond length (1.84 Å in trimethylphosphine) is much larger than the CC bond length (1.50–1.51 Å in barrelene[12]). In order to elucidate the details of this fact, as well as the structure of **16**, further work is in progress.

Experimental Section[13]

3,4-Bis(trifluoromethyl)pyrazole (4). To the solution of **1** (110 mg) in AcOEt (0.1 mL), the solution of CH_2N_2 in Et_2O was added dropwise, until the yellow color of CH_2N_2 persisted for a few minutes. After the mixture was kept at room temperature overnight, solvents were evaporated with a vacuum line, and the residue was chromatographed over SiO_2 (10 g) in *n*-pentane solution. The effluent with *n*-pentane–Et_2O (20:1) was sublimed at 90 °C (6 mmHg) to give colorless needles (**4**): 48 mg (quantitative); mp 122 °C. This compound was identified with the authentic sample[5] by the comparison of IR spectra and the mixture melting point.

1-Phenyl-4,5-bis(trifluoromethyl)-1,2,3-triazole (9). (a) The solution of **1** (119 mg) and phenyl azide (125 mg) in C_6H_6–CH_3CN (1:1, 0.5 mL) was sealed in a Pyrex tube (diameter = 3 mm) and heated at 80 °C for 50 h. After evaporation of solvents with a vacuum line, the residue was extracted with *n*-pentane. The extract was chromatographed over SiO_2 (10 g). The effluent with Et_2O–*n*-pentane (5:3) gave pale yellow oil (**9**), 60 mg (quantitative), which was identified with the authentic sample by comparison of IR and NMR spectra.

(b) The solution of hexafluorobutyne-2 (1.5 mL) and phenyl azide (0.94 g) in benzene (30 mL) was kept in a Pyrex tube with a stopcock at room temperature for 3 days. After evaporation of solvent with a vacuum line, the residue was chromatographed over SiO_2 in *n*-pentane–Et_2O (3:2) to give pale yellow oil (**9**): 1.7 g; ^1H NMR ($CDCl_3$) δ 7.8–7.2 (aromatic H); ^{19}F NMR ϕ −8.0, −3.8 (both q, $J_{FF} = 6.8$ Hz, CF_3); mass m/e 281 (M^+), 253 ($M - N_2$).

2,3-Bis(trifluoromethyl)indole (10). The solution of **9** (113 mg) in *n*-hexane was sealed in a quartz tube (diameter = 3 mm) and irradiated with a low-pressure Hg lamp for 11 days. The mixture was concentrated with a vacuum line, and the residue

---

(11) Detailed data of X-ray analysis will be published by Dr. Schonburg elsewhere.

(12) O. Ermer, *Tetrahedron*, 30, 3103 (1974).

(13) General notices are the same as those that appeared in ref 1.

was purified by the preparative TLC on SiO_2 plate developed by *n*-pentane–Et_2O (10:3) to give pale yellow needles (**10**), mp 49–52 °C, which were identified with the authentic sample[6] by the comparison of IR and NMR spectra and the mixture melting point.

2,7,9,10,11,12-Hexakis(trifluoromethyl)-1,8-diphosphatetracyclo[6.2.2.0^{2,7}.0^{3,6}]deca-4,9,11-triene (11 and 12). The solution of cerium(IV) ammonium nitrate (14 g) in H_2O–EtOH (7:3, 5 mL) was added dropwise to the solution of **1** (2.23 g) and cyclobutadieneiron tricarbonyl (0.763 g) in acetone (100 mL) at 0 °C for 20 min. After the solution was stirred at room temperature for 3 h, H_2O (100 mL) was added, and the reaction mixture was extracted with Et_2O. After the Et_2O layer was washed with H_2O and dried over Na_2SO_4, Et_2O was evaporated with a vacuum line. The residue was chromatographed over SiO_2 (150 g) in *n*-pentane. The first effluent with *n*-pentane was recrystallized from *n*-pentane to give colorless plates (**11**): 410 mg (23.7%); mp 97–8 °C (in a sealed tube); IR (KBr) $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.00 (2 H, m, >CH), 6.22 (2 H, s, C=CH); ^{19}F NMR ϕ −5.40 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 40.6$ Hz, CF_3], −6.06 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 38.4$ Hz, CF_3], −6.16 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 33.8$ Hz, CF_3]; mass *m/e* 600 (M^+); high mass calcd for $C_{16}H_4F_{18}P_2$ 599.950, found 599.949.

The second effluent was recrystallized from *n*-pentane to give colorless plates (**12**): 560 mg (33.2%); mp 111–112 °C (in a sealed tube); IR (KBr) $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.95 (2 H, b, >CH), 6.00 (2 H, b, C=CH); ^{19}F NMR ($CDCl_3$) ϕ −2.84 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 41.7$ Hz, CF_3], −6.04 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 39.5$ Hz, CF_3], −6.08 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 39.5$ Hz, CF_3]; mass *m/e* 600 (M^+); high mass calcd for $C_{16}H_4F_{18}P_2$ 599.950, found 599.949.

2,5,7,10,11,12-Hexakis(trifluoromethyl)-1,6-diphosphahexacyclo[4.4.2.0^{2,5}.0^{3,9}.0^{4,8}.0^{7,10}]dodec-11-ene (13). The solution of **12** (350 mg) in acetone (5 mL) was sealed in a Pyrex tube (diameter = 7 mm) under vacuum and irradiated with a high-pressure mercury lamp for 16 h. After evaporation of acetone with a vacuum line, the residue was recrystallized from acetone to give colorless plates (**13**): 247 mg (73%); mp 201–203 °C (in a sealed tube); IR (KBr) $\nu_{C=C}$ 1610; ^{1}H NMR [$(CD_3)_2CO$] δ 3.96 (4 H, s); ^{19}F NMR [$(CD_3)_2CO$] ϕ −1.06 [12 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 41.3$ Hz, 4CF_3], −4.80 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 38.6$ Hz, 2CF_3]; mass *m/e* 600 (M^+); high mass, calcd for $C_{16}H_4F_{18}P_2$ (M^+) 599.950, found 599.950.

Similar irradiation of **11** in a Pyrex NMR tube caused no change of the ^{1}H and ^{19}F NMR.

Reaction of 1 wtih 2,3-Dimethylbutadiene. The solution of **1** (1 g) and 2,3-dimethylbutadiene (0.66 g) in CH_3CN (20 mL) was shaken at 100 °C in a stainless steel tube for 5 h. After evaporation of solvent with a vacuum line, the residue was chromatographed over SiO_2 (50 g) in *n*-pentane solution. The first effluent with *n*-pentane was sublimed at 30 °C (15 mmHg) to give colorless needles [1,2-dimethyl-4,5-bis(trifluoromethyl)-1,4-cyclohexadiene]: 120 mg (22.2%); mp 49–50 °C (in a sealed tube); ^{1}H NMR ($CDCl_3$) δ 1.73 (6 H, s, 2CH_3), 2.97 (4 H, bs, 2CH_2); ^{19}F NMR −5.0 (s); mass *m/e* 244 (M^+). This compound was identified with the authentic sample obtained by the reaction of hexafluorobutyne-2 and dimethylacetylene.

The second effluent from the SiO_2 column mentioned above was recrystallized from *n*-pentane to give colorless plates: 194 mg (19.1%); mp 119–122 °C (in a sealed tube); IR (KBr) $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.75 (12 H, m, 4CH_3), 2.08–3.50 (8 H, bm, 4CH_2); ^{19}F NMR ϕ −3.40 (3 F, m, CF_3), −8.00 to −12.10 (9 F, bm, 3CF_3); mass *m/e* 556 (M^+); high mass, calcd for $C_{20}H_{20}F_{12}P_2$ (M − 16) 550.085, found 550.085.

These data show that this product consists of 2 mol of dimethylbutadiene, 1 mol of diphosphabenzene, and one oxygen atom, but its structure is not fully assigned.

Thermolysis of the Exo Adduct (11). (a) The solution of **11** (150 mg) in *n*-pentane (0.5 mL) was sealed in a Pyrex tube (diameter = 3 mm) under vacuum and heated at 130 °C for 16 h. The crystals precipitated on cooling were filtered and recrystallized from acetone. Colorless needles, 148 mg (quantitative), were obtained: mp 175–176 °C (in a sealed tube); IR (KBr) $\nu_{C=C(cyclobutene)}$ 1715, $\nu_{C=C}$ 1590 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 3.32 (2 H, m, >CH), 3.54 [2 H, d, $^{1}/_{2}(J_{PH} + J_{PH'}) = 24$ Hz, PCCH]; ^{19}F NMR [$(CD_3)_2CO$] ϕ 2.36 (6 F, s, C=CCF_3), −5.66 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 40.6$ Hz, 2CF_3], −6.22 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 40.6$ Hz, 2CF_3]; mass *m/e* 600 (M^+), high mass calcd for $C_{16}H_4F_{18}P_2$ (M^+) 599.950, found 599.949.

(b) The solution of **11** (100 mg) in *n*-pentane (0.5 mL) was sealed in a Pyrex tube (diameter = 3 mm) under vacuum and heated at 180 °C for 3 h. ^{19}F NMR of the reaction mixture showed that equimolar amounts of 1,2-bis(trifluoromethyl)benzene and **3** were formed quantitatively. The former product was identified with the authentic sample by GLC.

Thermolysis of the Endo Adduct (12). The endo adduct (**12**, 70 mg) and *n*-pentane (0.5 mL) were sealed in a Pyrex tube (diameter = 3 mm) under vacuum and heated at 180 °C for 3 h. The crystals precipitated on cooling were collected by filtration and recrystallized from acetone (−78 °C) to give colorless plates (**16**): 52 mg (quantitative); mp over 200 °C; IR (KBr) $\nu_{C=C}$ 1595 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 2.80 (2 H, m, >CH), 3.00 (2 H, m, >CH); ^{19}F NMR [$(CD_3)_2CO$] ϕ −2.72 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 40.6$ Hz, 2CF_3], −5.73 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 37.2$ Hz, 2CF_3], −5.97 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 37.2$ Hz, 2CF_3], −6.32 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 40.6$ Hz, 2CF_3], −7.38 [6 F, d, $^{1}/_{2}(J_{PF} + J_{PF'}) = 38.6$ Hz, 2CF_3]; mass *m/e* 600 [M^+ − 386, $(CF_3)_4C_4P_2$]. Extremely high volatility prevented determination of the accurate molecular weight. Therefore, the structure of **16** is a speculative one.

Acknowledgment. We express our sincere gratitude to Dr. D. Schonburg of Technische Universitat, Braunschweig, for X-ray analysis of compound **13**.

Registry No. **1**, 2925-91-9; **3**, 62218-19-3; **4**, 19968-19-5; **9**, 63790-89-6; **10**, 63790-90-9; **11**, 62839-77-4; **12**, 62929-10-6; **13**, 62839-78-5; **14**, 71901-72-9; **16**, 71901-73-0; diazomethane, 334-88-3; phenyl azide, 622-37-7; 2,3-dimethylbutadiene, 513-81-5; 1,2-dimethyl-4,5-bis(trifluoromethyl)-1,4-cyclohexadiene, 781-87-3; 1,2-bis(trifluoromethyl)benzene, 433-95-4.

Synthesis of Some Tetrahydrochrysenes as Potential Ultraviolet Laser Dyes[1-3]

Terry A. Lyle and Guido H. Daub*

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Received June 19, 1979

A general synthetic pathway employed in the synthesis of 5,6,11,12-tetrahydrochrysene and six of its benzo- and phenyl-substituted derivatives is described. Development of an efficient synthesis of the required starting materials 2-(3-biphenylyl)ethyl bromide and 6-phenyl-3,4-dihydro-1(2*H*)-naphthalenone is also presented. Preliminary laser performance data of the tetrahydrochrysenes have been included.

A number of *trans*-1,2-diarylethylenes (**1**) which have been synthesized in our laboratory during the past 15 years as liquid scintillator solutes[4] have recently shown promise as potential UV laser dyes when irradiated at 337 nm with