J_{AB} = 143 Hz, 2 F), 170.0 (m, 1 F) ppm. In addition, ~5% of monosubstituted olefins **14**, ~1.5% of disubstituted olefin **15**, and ~10% of carboxylate of **16** were present. Percentages are relative to the major product. Methylation with dimethyl sulfate (5.3 mL, 56 mmol) at room temperature was followed by workup with ice water (~400 mL). The product layer that separated was dissolved in ether, washed, and dried. The brownish liquid thus obtained was fractionated to yield 7.8 g (25.8 mmol, 46%) of ester **18**, bp 45-47°/0.01 mm. ^{19}F NMR (282.2 MHz, $CDCl_3$): 74.30 (q, J = 8.6 Hz, 3 F), 76.87, 77.99 (subsplit AB q, J_{AB} = 142 Hz, 2 F), 180.45 (m, 1 F) ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.16 aromatic m, 5 H), 4.00 (s, 3 H). IR ($CHCl_3$): 3030 (w), 2960 (w), 1780 (s), 1600 (w), 1500 (m), 1450 (w), 1270 (vs), 1190 (s), 1160 (s), ~1100 (s), 1030 (s) cm^{-1}. MS: m/e 302 (M^+), 209 ($M^+ - C_6H_5O$), 131 ($CF_2CFCF_2^+$), 81 (CF_2CF^+), 77 ($C_6H_5^+$), 59 ($CO_2CH_3^+$, base). Anal. Calcd for $C_{11}H_8F_6O_3$: C, 43.71; H, 2.65. Found: C, 44.24; H, 2.72.

Acknowledgment. We thank PPG Industries, Inc., for generously supporting this work.

Carbonyl Chemistry of Tetrafluorocyclopentadienone

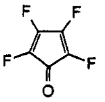
David M. Lemal,* David L. Klopotek,[1] Janet L. Wilterdink, and W. Daniel Saunders

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

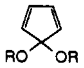
Received August 22, 1989

In order to control the Diels-Alder reactivity of the very labile title compound **1**, experiments designed to modify the carbonyl group have been carried out. With methanol a hemiketal (**4**) is formed reversibly at low temperatures, but conjugate addition to give 3-methoxy derivatives **5** and **6** occurs at ordinary temperatures. Diazomethane reacts with **1** in cold methanol to give a spirooxirane (**9**) which undergoes Diels-Alder dimerization orders of magnitude slower than dienone **1** at room temperature. Hydrogen cyanide gives a cyanohydrin (**15**) with **1** at low temperatures, but the compound decomposes at 0 °C. Trimethylsilyl cyanide yields the trimethylsilyl cyanohydrin **16**, a stable derivative of **1** that dimerizes only at elevated temperatures, yet retains reactivity as a Diels-Alder diene.

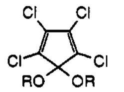
When tetrafluorocyclopentadienone (**1**) was first synthesized in our laboratory,[2] we hoped that it could serve as a building block for incorporating the 1,2,3,4-tetrafluorobutadienediyl unit (—CF=CFCF=CF—) into various perfluoroannulenes and their valence isomers. In principle this could be accomplished via Diels-Alder addition across the diene followed by extrusion of carbon monoxide from the resulting 7-norbornenones. Not surprisingly, **1** undergoes very facile Diels-Alder dimerization, which makes addition of most other dienophiles impractical. Dimerization of **1** is much slower than that of the extraordinarily labile parent cyclopentadienone,[3] however. The orange vapor can be stored for hours at room temperature at pressures below 1 Torr, and it is thus feasible to carry out reactions with the compound in cold, dilute solution.



1



2



3

R = CH_3, C_2H_5, $(CH_2CH_2)_{1/2}$, etc.

Since the diene's tendency to dimerize is attributable to a very narrow HOMO-LUMO gap, and since the carbonyl is largely responsible for the low-lying LUMO, we anticipated that derivatization of the carbonyl group could dramatically inhibit dimerization and brighten the prospects for carrying out other Diels-Alder reactions.[4] The Diels-Alder chemistry of ketals of cyclopentadienone (**2**)[5] and tetrachlorocyclopentadienone (**3**)[6] constitutes excellent precedent for this idea. Ketals **2** and **3** were prepared by routes that bypassed the labile dienones;[7] unfortunately, these routes do not seem adaptable to the synthesis of the corresponding derivatives of **1**. Treatment of hexachlorocyclopentadiene with alkoxides leads smoothly to **3**, for example, but nucleophilic attack on hexafluorocyclopentadiene tends to give products of addition/elimination in which the germinal difluoro group remains intact.[8] This is a consequence of the mutual bond-strengthening effect characteristic of two or more fluorines linked to the same carbon.[9]

Here we describe experiments designed to derivatize directly the carbonyl group of tetrafluorocyclopentadienone. At the outset there was no assurance that this could be accomplished, as all five carbons are highly electron deficient and activated for attack by nucleophilic reagents.

Results and Discussion

Attempts to prepare the semicarbazone and hydrazones of **1** by treatment of cold solutions of the dienone with various hydrazine derivatives yielded unpromising mixtures. Initial observations of the reaction of dienone **1** with methanol revealed only addition of the alcohol across one of the carbon-carbon double bonds. Closer scrutiny of the

---

[1] Department of Chemistry, St. Norbert College, DePere, WI 54115.

[2] Grayston, M. W.; Saunders, W. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 413.

[3] Chapman, O. L.; McIntosh, C. L. *J. Chem. Soc., Chem. Commun.* **1971**, 770.

[4] Garbisch, E. W.; Sprecher, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6785; **1966**, *88*, 3433, 3434.

[5] Eaton, P. E.; Hudson, R. F. *J. Am. Chem. Soc.* **1965**, *87*, 2769.

[6] See, for example: Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 4456. Lemal, D. M.; Gosselink, E. P.; McGregor, S. D. *J. Am. Chem. Soc.* **1966**, *88*, 582.

[7] DeJongh, D. C.; Brent, D. A.; Van Fossen, R. Y. *J. Org. Chem.* **1971**, *36*, 1469.

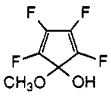
[8] Soelch, R. R., Ph.D. Dissertation, Dartmouth College, 1984.

[9] Dolbier, W. R., Jr.; Medinger, K. S.; Greenberg, A.; Liebman, J. F. *Tetrahedron* **1982**, *38*, 2415. Dill, J. D.; Schleyer, P. v. R.; Pople, J. *J. Am. Chem. Soc.* **1976**, *98*, 1663.

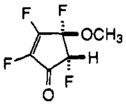
0022-3263/91/1956-0157$02.50/0

latter reaction, however, exposed a dichotomy in the mode of addition. When the dienone was dissolved at −78 °C in methanol containing a catalytic quantity of sodium methoxide, a colorless solution resulted with a ^{19}F NMR spectrum very different from that of the orange starting material. Both were AA′XX′ spectra, but that of the dienone (methylene chloride, −90 °C) had chemical shifts of 136.9 and 173.4 ppm ($\Delta\delta$ = 36.5 ppm)[2] while the new spectrum comprised multiplets at 160.5 and 164.9 ppm ($\Delta\delta$ = 4.4 ppm). The 2-fold molecular symmetry required by this spectrum is compatible only with addition of methanol across the carbonyl double bond of **1**, giving hemiketal **4**. Though such an adduct would not form to an appreciable extent from a typical conjugated ketone, fluorination greatly enhances the tendency of a carbonyl group to add water and other nucleophiles.[10a] At higher concentrations of **1**, the cold methanol solution remains yellow, indicating that hemiketal formation is significantly reversible.

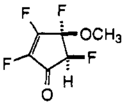
When a solution of **4** in methanol containing a trace of methoxide was allowed to warm gradually to room temperature, the spectrum slowly disappeared and was replaced by six widely spaced signals at 117.3 (m), 127.7 (m), 161.7 (m), 162.3 (m), 204.1 (d, J_{HF} = 52 Hz), and 205.7 ppm (dd, J_{HF} = 50 Hz). The new spectrum was explicable in terms of two nearly identical isomers present in a ratio of about 3:2. While the two lowest field resonances were common to both, those at 161.7 and 204.1 ppm belonged to the minor isomer, and the 162.3 and 205.7 ppm signals arose from the major isomer. The structures of the isomers were revealed by the pair of highest field signals. Their large coupling constants were characteristic of fluorines geminal to hydrogen; their simplicity bespoke fluorines vicinal to (no more than) one other fluorine; and the doublet subsplitting of one but not the other indicated a difference in geometrical relationship for this vicinal pair of fluorines in the two isomers. These observations point uniquely to structures **5** and **6**. On the tentative assumption that the coupled pair of vicinal fluorines is cis,[11] the major isomer is assigned the cis configuration **5**.



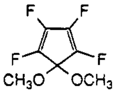
4



5



6

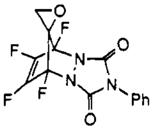


7

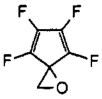
Clearly, hemiketal **4** is the product of kinetic control in the methoxide-initiated addition of methanol to **1**, and the formation of thermodynamic products **5** and **6** requires reversion of **4** to starting materials and readdition in 1,4-fashion with both suprafacial and antarafacial stereochemistry. The fact that comparable quantities of cis and trans isomer are found suggests that the enolate ion generated by methoxide addition has a finite lifetime before protonation.

Since the skeleton of hemiketal **4** is fluorinated, the hydroxyl group is expected to be unusually acidic.[10b] This thought encouraged us to try transforming the labile **4** into the presumably stable dimethyl ketal **7** by treatment with diazomethane.[13] Excess diazo compound was added to a methanol solution of the dienone in methanol/catalytic methoxide at −78 °C and reaction was completed by warming in stages to room temperature. Though some of the dimer of **1** was formed, a new compound was produced in good yield. As expected for the desired ketal, the unknown product displayed an AA′XX′ ^{19}F NMR spectrum; it featured doublets with 12.2-Hz separation at 151.6 and 168.3 ppm in methylene chloride. The UV maximum at 273.5 nm (cyclohexane), which was virtually identical with that of hexafluorocyclopentadiene,[14] confirmed that the diene system was intact. Comprising a singlet at δ 3.45, the ^{1}H NMR spectrum (deuteriochloroform) supported the dimethyl ketal structure.

The compound reacted in seconds at room temperature with 4-phenyl-1,2,4-triazoline-3,5-dione to give a nicely crystalline Diels–Alder adduct. Its ^{19}F NMR spectrum (acetone-d_6), singlets at 148.4 (vinyl F's) and 180.6 ppm (bridgehead F's), gave no cause for concern, but the proton spectrum was inconsistent with the presumed structure. The aryl proton signal at δ 7.47 was about 2.5 times as intense as the sole upfield resonance, a singlet at 3.44 ppm in deuteriochloroform. This clue indicated that the two methyls in the postulated structure should be replaced by a single methylene group and suggested the structure **8** for the triazolinedione adduct (stereochemistry at C_7 designated arbitrarily). Microanalysis confirmed that the adduct had this composition, and its mass spectrum displayed prominent peaks for both the corresponding parent ion and the ion derived from **9** (generated by *retro*-Diels–Alder reaction).



8



9

Thus spiro diene **9**, not a ketal, is the product of the reaction of diazomethane with dienone in methanol. The diazo compound clearly attacks the dienone in preference to the hemiketal, giving a type of product that is familiar in the reactions of diazomethane with ketones.[15] One might jump to the conclusion that methanol just provides an impediment to the reaction, but in fact the spiro diene fails to form in significant amount in the absence of methanol due to competing reactions. Probably the role of methanol is to keep the concentration of ketone low, thereby slowing its dimerization reaction sufficiently to allow the diazo compound to compete for it. The fragile hemiketal **4** may therefore play a role similar to that which we had anticipated for the ketal, but by controlling the concentration of the dienone instead of attenuating its reactivity. Because the slower, less readily reversed reaction of **1** with methanol discussed above also occurs, however, this strategem for directing the reactivity of the dienone can be expected to be useful only for rather facile transformations. It is interesting that diazomethane chooses to form an oxirane with **1** in preference to ring expanding the molecule or adding to a carbon–carbon double bond to give a pyrazoline,[15] a reaction that could occur with either **1** or **4**.

A less conventional reaction course was also possible a priori. Shimizu and Bartlett[16] observed that aryldiazomethanes react with penta- and hexafluoroacetone at −20

---

(10) Chambers, R. D. *Fluorine in Organic Chemistry*; John Wiley and Sons: New York, 1973; (a) pp 219–25; (b) pp 65–6.

(11) Though vicinal F–F coupling constants deviate badly from Karplus-type behavior (ref 12), model compounds provide some for support this assignment (Merritt, R. F.; Johnson, F. A. *J. Org. Chem.* **1966**, *31*, 1859.

(12) Emsley, J. W.; Phillips, L.; Wray, V. *Fluorine Coupling Constants*; Pergamon Press: Oxford, 1977; pp 115–6.

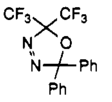
(13) We have subsequently learned that Krespan has made ketals of hexafluoroacetone this way (Krespan, C. G., personal communication).

(14) Burdon, J.; Hodgins, T. M.; Perry, D. R. A.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc.* **1965**, 808.

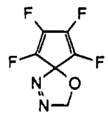
(15) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; John Wiley and Sons: New York, 1978; Part 2, Chapter 18.

(16) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 4260.

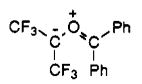
°C to give 1,3,4-oxadiazoles such as **10**. While the regiochemistry of this cycloaddition can be rationalized solely on steric grounds, it may also reflect the unusual polarization of highly fluorinated ketones. The oxadiazoles decomposed with nitrogen loss at temperatures ≥25 °C to oxiranes. If the analogous 1,3,4-oxadiazole **11** is formed in the reaction of diazomethane with **1**, it must be much more labile because it has gone undetected. When Bartlett and Shimizu chose methanol as the solvent for decomposition of their oxadiazoles, ketals were formed, in several cases almost quantitatively. This observation implicated carbonyl ylide intermediates such as **12**, trappable by methanol to give **13**, on the decomposition pathway to oxiranes. The formation of oxirane **9** instead of a ketal in the dienone–diazomethane reaction in methanol therefore consitutes further evidence against the intermediacy of oxadiazole **11**. Presumably diazomethane adds to **1** with conventional regiochemistry, giving zwitterionic intermediate **14**, which eliminates nitrogen in S_N2 fashion. The polarity of the carbonyl group of **1** may well resemble that of hexafluoroacetone's C=O function both because of the fluorine substitution and because of the electronic character of cyclopentadienones, but steric hindrance to C–C bond formation is obviously much smaller in our reaction than in those of Shimizu and Bartlett.



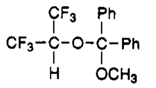
10



11

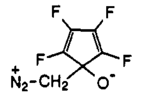


12



$CF_3-\overset{CF_3}{\underset{H}{C}}-O-\overset{Ph}{\underset{OCH_3}{C}}-Ph$

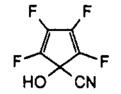
13



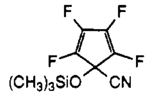
14

Spiro diene **9** reacts readily with *N*-phenylmaleimide in ether to give a Diels–Alder adduct analogous to **8** in high yield. As a neat liquid the diene dimerizes at room temperature, but fairly slowly ($t_{1/2} \approx 3$ h). The compound thus meets the original objective in derivatizing **1** of diminishing the tendency to dimerize while maintaining reactivity as a Diels–Alder diene. Spiro diene **9** is not suitable as a tetrafluorobutadienediyl synthon, though, because there is no easy way to extrude the one-carbon bridge in its Diels–Alder adducts.[17]

Success in adding methanol and diazomethane at the carbonyl carbon of **1** implied that other nucleophilic reagents would show similar selectivity. Base-catalyzed addition of hydrogen cyanide was an attractive possibility. A methanol solution of the dienone and hydrogen cyanide containing a catalytic amount of benzyltrimethylammonium hydroxide was prepared at -78 °C and monitored by ^{19}F NMR starting at -70 °C. At this temperature two new signals at 155.7 and 160.7 ppm with splittings similar to those of **1** developed very slowly at the expense of the two dienone signals. The temperature was gradually raised to -20 °C and maintained there until the starting material was gone and the new signals, corresponding to the cyanohydrin **15**, had reached maximum intensity. As required of an AA′XX′ spectrum, each half had mirror symmetry and the two halves were mirror-related except that the multiplet at higher field was distinctly broader than its lower field counterpart.[18] As the solution was warmed further to 0 °C, the cyanohydrin resonances collapsed and a very complex spectrum resulted. No trace of **15** was observable at room temperature. Both promising and disappointing, this experiment indicated that cyanide addition occurs smoothly but that the resulting cyanohydrin is too reactive to be useful.

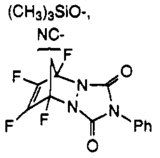


15

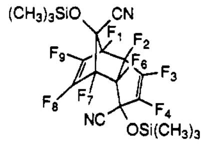


16

"Capping" the cyanohydrin offered promise of the requisite stability. Accordingly, trimethylsilyl cyanide was substituted for hydrogen cyanide in the reaction with dienone **1**, again with catalysis by benzyltrimethylammonium hydroxide. Trimethylsilyl cyanohydrin **16** was formed quite cleanly, presumably via attack on **1** by cyanide generated by hydrolysis of trimethylsilyl cyanide. Its AA′XX′ spectrum, with resonances at 152.7 and 161.3 ppm (methylene chloride), resembled that of the cyanohydrin closely except for its greater $\Delta\delta$ and absence of broadening in the X part. Analysis and computer simulation[19] of the spectrum revealed these coupling constants: $J_{AX}, J_{AX'} = \pm 14.9, \mp 5.4$; $|J_{AA'}|, |J_{XX'}| = 17.8, 5.5$ Hz. This diene reacted rapidly with 4-phenyl-1,2,4-triazoline-3,5-dione to give a ~3:1 mixture of Diels–Alder adducts **17** differing in configuration at the one-carbon bridge. The major isomer displayed ^{19}F NMR signals (methylene chloride) at 144.6 and 172.3 ppm; the minor isomer gave 149.2 and 170.7 ppm signals. In each case the resonances represent vinyl fluorines and bridgehead fluorines, respectively. Probably the major isomer has the cyano group proximal to the heterocyclic ring as a result of preferential addition to the less hindered face of **16**.



17



18

Diene **16** also dimerized, but in contrast to spiro diene **9** the reaction was not rapid even at 110 °C. As judged from ^{19}F NMR spectra, only one of the eight possible stereoisomeric Diels–Alder dimers was formed. The configuration that appears to be the most likely on steric grounds is **18**. The ^{19}F NMR spectrum (deuteriochloroform), assigned by analogy to that of tetrafluorocyclopentadienone dimer,[2] displayed signals at 135.4, 138.0 (F_3, F_4); 146.1, 150.8 (F_8, F_9); 171.8, 182.3 (F_2, F_6); 207.5, 211.6 ppm (F_1, F_7). This dimer proved difficult to purify fully and its characterization was not completed.

The ability of trimethylsilyl cyanohydrin **16** to function as a Diels–Alder diene, its reluctance to dimerize, and the ease with which the potential carbonyl group in its adducts should be regenerable together suggest that this derivative of dienone **1** will find use as a building block for higher

---

(17) An alternative approach to a ketal derivative of 1 was attempted. In the hope of generating a hemiketal which could be cyclized in S_N2 fashion to give an ethylene ketal, 2-bromoethanol was substituted for methanol. Hemiketal formation did not occur spontaneously, and introduction of 1,8-bis(dimethylamino)naphthalene (Proton Sponge) to catalyze the addition and effect the cyclization led instead to extensive decomposition.

(18) Cyanohydrin formation is not very fast even at this temperature, so this is not exchange broadening caused by rapidly reversible HCN addition. Long-range spin coupling to the hydroxyl proton is probably the origin of the differential broadening, and the high field multiplet can thus be assigned tentatively to F_1 and F_4.

(19) Spectra simulation was carried out by using the LAOCOON 3 program of A. A. Bothner-By and S. Castellano.

perfluoroannulenes and their valence isomers.

Experimental Section

Melting points were determined in capillary tubes and are uncorrected. The ^{19}F NMR spectra were obtained at 56.26 MHz on a JEOL FX60Q Fourier transform instrument with trichlorofluoromethane (Freon 11) as an internal standard. Chemical shifts are reported in parts per million upfield from the reference. ^{1}H NMR spectra were determined on a Varian EM360 spectrometer and mass spectra were measured with a Finnigan Model 4023 quadrupole mass spectrometer. Analytical gas chromatograms were obtained with a Hewlett-Packard Model 5880A gas chromatograph with a 25-m methylsilicone capillary column, flame ionization detector, and electronic integration. Preparative gas chromatography was performed on a Hewlett-Packard Model 5750 instrument with a thermal conductivity detector.

Solvents and reagents used in this work were reagent grade. Perfluorobenzene was purchased from Fairfield Chemical and other organic chemicals from Aldrich Chemical Company. Microanalytical data were obtained from Galbraith Laboratories, Knoxville, TN.

4,5,6,7-Tetrafluoro-1-oxaspiro[2.4]hepta-4,6-diene (9). Tetrafluorocyclobutenedicarboxylic anhydride (50 mg, 0.26 mmol) was subjected to flow pyrolysis at 585 °C and 1.0 Torr in a 2 ft × 10 mm (i.d.) quartz tube. The dienone product[20] was caught at 77 K in a trap containing 4 mL of methanol and 10 mg of sodium methoxide. With the system under nitrogen, 10 mL of a precooled 2% solution of diazomethane (from Diazald) in ether was added all at once and the mixture was allowed to stand at −78 °C for 2 h. [In other experiments the dienone was allowed to equilibrate with hemiketal **4** prior to the addition of the diazomethane solution.] After an additional hour at −12 °C (ethylene glycol slush bath) and an hour at room temperature, the mixture was analyzed by GC and ^{19}F NMR. The product comprised **9** (72%) and the dimer of tetrafluorocyclopentadienone (28%); spiro diene **9** was isolated as a crystalline derivative in 64% yield, as described below. Excess diazomethane was destroyed with isophthalic acid, and the solution was washed with water (2 × 10 mL) and dried over magnesium sulfate. Dynamic vacuum transfer of 90% of the solution (8.7 mL) served to separate **9** from the dimer of tetrafluorocyclopentadienone (as its hydrate). At this stage the spiro diene was either isolated by preparative GC on a 15′ ft × $^1/_4$ in. Carbowax 20M-on-Chromasorb WHP column or derivatized. IR (vapor): 1752, 1405, 1037, 905 cm^{-1}.

4-Phenyl-1,2,4-triazoline-3,5-dione (29 mg, 0.17 mmol) was added to the above solution. The red dienophile was rapidly decolorized, and after 5 min the ether solvent was removed by rotary evaporation. After washing with ether (3 mL), the resulting white cyrstals of **8** (56 mg, 0.16 mmol, 64% from the starting anhydride) melted at 208 °C. The compound was sublimed for microanlaysis. IR (KBr): 1745 (br, structured), 1591, 1503, 1406, 1368, 1343, 1202, 1152, 1021, 999, 975, 894 cm^{-1}. MS: *m/e* 341 (M$^+$), 166 (**9**$^+$), 138 (**9**$^+$ − CO), 119 (PhNCO$^+$, base). Anal. Calcd for $C_{14}H_7F_4N_3O_3$: C, 49.28; H, 2.07; F, 22.27; N, 12.31. Found: C, 49.42; H, 2.29; F, 21.98; N, 12.22.

To an ether solution of **9** prepared as above from 50 mg of anhydride was added *N*-phenylmaleimide (29 mg, 0.17 mmol), and the solution was heated under reflux for 8 h. The solvent was removed by rotary evaporation and the resulting crystals were washed with cold ether (0 °C). Yield: 56 mg, 0.17 mmol, 65%; mp 240 °C. A sample was sublimed for microanalysis. ^{1}H NMR (CDCl$_3$); δ 7.46 (m, 3 H, aryl), 7.19 (m, 2 H, aryl), 4.05 (m, 2 H, bridgehead), 3.37 (s, 2 H, methylene). IR (KBr): 3030, 3005, 1782, 1723, 1592, 1491, 1387, 1364, 1202, 1187, 1045, 900, 802, 790, 697 cm^{-1}. MS: *m/e* 339 (M$^+$), 173 (*N*-phenylmaleimide$^+$), 119 (PhNCO$^+$, base). Anal. Calcd for $C_{16}H_9F_4NO_3$: C, 56.65; H, 2.67; F, 22.40; N, 4.13. Found: C, 56.66; H, 2.65; F, 22.61; N, 4.07.

5-Cyano-5-(trimethylsiloxy)-1,2,3,4-tetrafluorocyclopentadiene (16). Dienone **1** prepared from 420 mg (2.14 mmol) of anhydride was washed out of the cold trap with 2 mL of methylene chloride that had been precooled to −78 °C. To this was added a solution of trimethylsilyl cyanide (0.7 mL, 0.5 g, 5 mmol) in 1 mL of methylene chloride and 3 drops of a 5:1 mixture of methylene chloride and Triton B (40% benzyltrimethylammonium hydroxide in methanol), all at −78 °C. Warmed to room temperature, the brown reaction solution showed the AA′XX′ ^{19}F NMR spectrum of adduct **16**. Vacuum transfer gave a colorless methylene chloride solution (3.92 g), 10% of which was the adduct as estimated by GC analysis uncorrected for differential detector response. A sample was isolated by preparative GC. IR (vapor): 2970, 1408, 1256, 1064, 843, 714 cm^{-1}.

To 0.25 mL of the above solution of **16** was added 4-phenyl-1,2,4-triazoline-3,5-dione slowly in portions until the pink color of the dienophile persisted (20 mg, 0.11 mmol). The solution was stripped and cooled to 0 °C. Addition of a few drops of ether induced crystallization of the adduct, which was recrystallized from methylene chloride-hexanes (1:20) with substantial loss to give **17** as a colorless mixture of stereoisomers in ~10% yield based on anhydride, mp 144–7 °C. ^{1}H NMR (CDCl$_3$): δ 0.41 (s), 0.46 (shoulder). IR (KBr): 2970, 1822, 1756, 1380, 1255, 980, 854 cm^{-1}. MS *m/e* 354 (M$^+$ − C_3H_8Si), 327 (M$^+$ − C_3H_9SiCN), 299 (M$^+$ − C_3H_9SiCN, CO), 119 (PhNCO$^+$, base). Anal. Calcd for $C_{17}H_{14}F_4N_4O_3Si$: C, 47.79; H, 3.31; N, 13.14; F, 17.71. Found: C, 47.46; H, 3.35; N, 13.04; F, 17.23.

An aliquot of the methylene chloride solution of **16** described above was concentrated to remove most of the solvent and then sealed in vacuo in a heavy-walled Pyrex ampule. This was placed in a steel tube wrapped with heating tape and heated at 110 °C for 8.5 h. The ^{19}F NMR spectrum of the brown solution revealed only the dimer **18** of **16**. Volatile material was removed by vacuum transfer, and attempts were made to purify the residue by a variety of methods. The most successful was a sublimation (50–60 °C, 0.05 Torr), which gave white crystals with mp 48–50 °C. ^{1}H NMR (CDCl$_3$): δ 0.36 ppm (s). IR (KBr): 2965, 1753, 1359, 1241, 966, 910, 842 cm^{-1}. MS: *m/e* 502 (M$^+$), 487 (M$^+$ − CH$_3$), 73 ((CH$_3$)$_3$Si$^+$, base).

Acknowledgment. We wish to thank the Air Force Office of Scientific Research and the National Science Foundation for supporting this research.

---

[20] On this scale the dienone is formed in about 90% yield (ref 2). When the reaction is run on a large scale, yields are lower.