Effect of α-cyano groups on neighboring group participation in carbonium ion reactions

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JUNE 1980

Impact Factor: 12.11 · DOI: 10.1021/ja00532a026

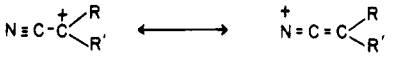
Effect of α-Cyano Groups on Neighboring Group Participation in Carbonium Ion Reactions

Paul G. Gassman* and John J. Talley[1]

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received August 6, 1979*

Abstract: The effect of the addition of an α-cyano substituent on the rates of solvolysis of 7-bicyclo[2.2.1]heptyl, 7-*anti*-bicyclo[2.2.1]heptenyl, and 7-bicyclo[2.2.1]heptadienyl sulfonates has been investigated. Hydrogen/α-cyano rate ratios of 10^2, 10^5, and 10^6 were observed for the three systems, respectively. Product studies indicated that the presence of an α-cyano moiety promoted rearrangements and/or the formation of products with modified carbon skeletons. In general, it appeared that proportionately greater dispersal of positive charge had occurred as a result of neighboring group participation. This charge delocalization was not reflected by the rate data owing to partial delocalization of charge to the nitrogen of the cyano function. As a result of certain rearrangements, the carbon of a ketone carbonyl was eventually converted into a cyano-bearing quaternary center in high yield.

Recently we demonstrated that the effect of an α-cyano function on an incipient carbonium ion center is ambivalent.[2] Inductively, the cyano moiety is strongly destabilizing. Intriguingly, a major portion of this inductive effect is offset by the formation of a resonance hybrid represented by structures **1** and **2**. It has been well established that β-cyano functions

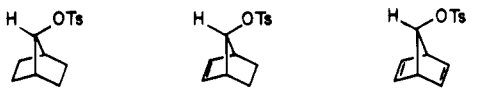


1 **2**

provide rate-retarding effects of 10^4–10^7.[3] On the basis of the Taft relationship[4] an α-cyano rate retardation of 10^{10}–10^{18} might be anticipated. However, for simple systems the balance of inductive and mesomeric effects of the α-cyano function resulted in a fairly constant rate decrease of 10^3 relative to hydrogen.[2] In view of the significant resonance interaction of the α-cyano group in systems such as **3** and **4**, which show

3 **4**

H/α-CN rate ratios of 3.5×10^3 and 1.9×10^3, respectively, we decided to investigate the extent of such ambivalent character of the α-cyano function in systems where neighboring group participation plays a major role in solvolysis. We now wish to present our findings on the effect of a 7-cyano group on the solvolysis of 7-norbornyl *p*-toluenesulfonate (**5**),[5] 7-*anti*-norbornenyl *p*-toluenesulfonate (**6**),[5] and 7-norbornadienyl *p*-toluenesulfonate (**7**).[6,7]

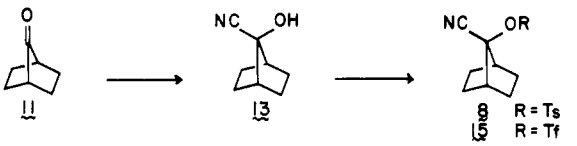


5 **6** **7**

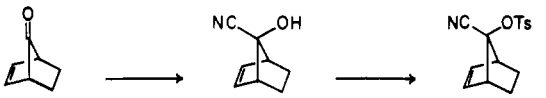
Among the most widely quoted examples of neighboring group participation are those involving the double bonds of **6** and **7**. The 10^{11} and 10^{14} rate accelerations provided by the unsaturated linkages of **6** and **7**, respectively, prompted us to explore the effect of attaching a cyano group to the 7 position. In order to achieve this goal, we set out to prepare **8**–**10**.

Synthesis

The syntheses of **8** and **9** were relatively straightforward. Bicyclo[2.2.1]heptan-7-one (**11**)[8] and bicyclo[2.2.1]hepten-7-one (**12**)[8] were treated with sodium bisulfite followed by



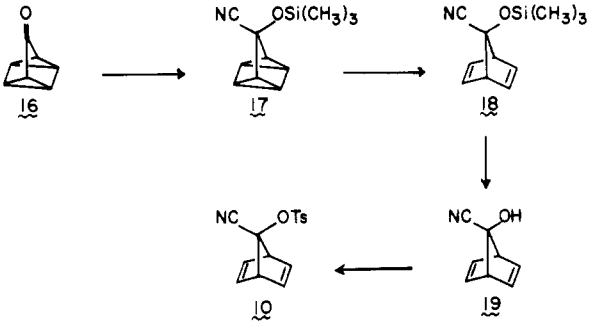
11 **13** **8** R = Ts **15** R = Tf



12 **14** **9**

potassium cyanide to produce the corresponding cyanohydrins **13** and **14** in 58 and 55% yields, respectively. The corresponding sulfonate esters, **8** and **9**, were prepared by standard procedures.[9] While **8** was readily prepared, it proved to be too unreactive in our solvolytic studies; therefore, we prepared the corresponding trifluoromethanesulfonate ester, **15**, for kinetic studies. It is interesting to note that only one isomer was obtained in the formation of the cyanohydrin from **12**. In contrast, addition of trimethylsilyl cyanide to this same ketone produced a mixture of isomers.[10] Presumably, the reversible cyanohydrin process results in the formation of the thermodynamically most stable isomer. The stereochemistry of the hydroxyl function of **14** was established through a lanthanide shift reagent (LSR) study.

The synthesis of **10** was much more difficult because bicyclo[2.2.1]heptadien-7-one is not a stable entity. Fortunately, treatment of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-one (**16**)[11] with trimethylsilyl cyanide[10] gave **17** in 90% yield. Addition of 0.7



16 **17** **18** **19** **10**

mol % of dichloro(bicyclo[2.2.1]heptadiene)palladium(II)[12] to **17** gave an 86% yield of **18**.[11] Hydrolysis of **18** under acidic conditions[10] gave 95% of **19** which was converted to **10** through reaction with 1.1 equiv of *p*-toluenesulfonic anhydride and 1.1 equiv of pyridine in methylene chloride (80% yield).

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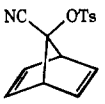
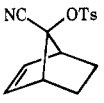
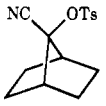
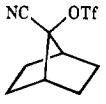
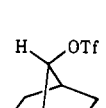
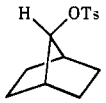
Table I. Rates of Solvolysis of Sulfonate Esters of Cyanohydrins Derived from Bicyclo[2.2.1]heptan-7-one, Bicyclo[2.2.1]hepten-7-one, and Bicyclo[2.2.1]heptadien-7-one

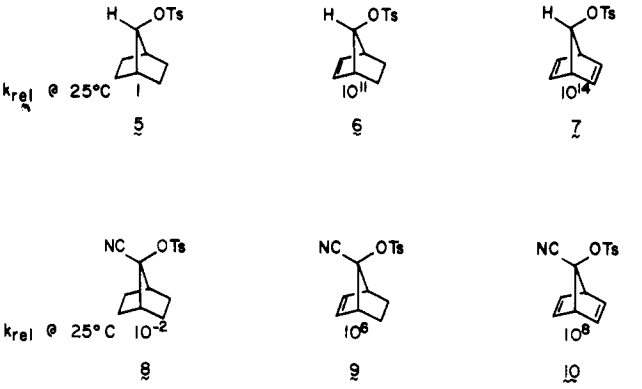
compd	temp (±0.05 °C)	solvent[a]	rate, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S,^{\ddagger}$ eu	k_{rel} in TFE
 **10**	45.00	A	$(2.06 \pm 0.01)10^{-3}$			
	35.00	A	$(7.46 \pm 0.04)10^{-4}$	19.9 ± 0.3	−8.4 ± 1.1	
	25.00	A	$(2.34 \pm 0.02)10^{-4}$			5.4×10^7
 **9**	90.00	A	$(1.59 \pm 0.01)10^{-3}$			
	75.00	A	$(5.12 \pm 0.03)10^{-4}$	18.9 ± 0.1	−19.7 ± 0.5	
	60.00	A	$(1.39 \pm 0.04)10^{-4}$			
	25.0[b]	A	4.34×10^{-6}			1.0×10^6
 **8**	25.0	A	4.30×10^{-14} [c]			1.0×10^{-2}
 **15**	170.00	A	$(7.19 \pm 0.16)10^{-4}$			
	155.00	A	$(3.17 \pm 0.04)10^{-4}$	21.9 ± 0.7	−24.2 ± 1.6	
	140.00	A	$(1.18 \pm 0.03)10^{-4}$			
	25.0[b]	A	2.87×10^{-9}			
 **20**	95.00	A	$(6.22 \pm 0.03)10^{-4}$			
	80.00	A	$(1.51 \pm 0.04)10^{-4}$	23.1 ± 0.2	−10.8 ± 0.7	
	65.00	A	$(3.45 \pm 0.01)10^{-5}$			
	25.0[b]	A	2.90×10^{-7}			
	125.00	B	$(5.17 \pm 0.11)10^{-4}$			
	110.00	B	$(1.18 \pm 0.03)10^{-4}$	29.5 ± 0.4	0.0 ± 0.9	
	95.00	B	$(2.27 \pm 0.04)10^{-5}$			
	25.0[b]	B	1.40×10^{-9} [d]			
 **5**	25.0	B	2.10×10^{-14} [e]			
	25.0	A	4.35×10^{-12} [f]			1

[a] Solvent A was 100% 2,2,2-trifluoroethanol (TFE) buffered with 1.0–1.5 equiv of 2.6-lutidine. Solvent B was anhydrous acetic acid buffered with sodium acetate. [b] Extrapolated from higher temperatures. (c) Rate calculated from the formula $k_8 = k_{15}/k_{20}$). [d] A value of 1.37×10^{-9} s^{-1} has been reported previously. T. M. Su, W. F. Sliwinski, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **91**, 5386 (1969). [e] Reference 6b. [f] Rate calculated from the formula $k_{5\text{-TFE}} = k_{5\text{-HOAc}}$ ($k_{20\text{-TFE}}/k_{20\text{-HOAc}}$). This formula assumes that the rate change observed for the triflate **20** in changing from acetic acid to 2,2,2-trifluoroethanol will be approximately the same for the tosylate **5**.

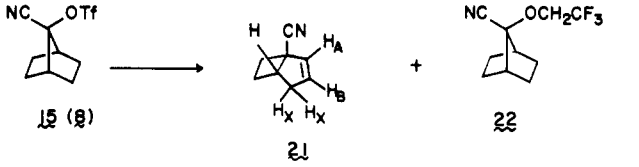
Kinetic Studies

Table I lists the rates of solvolysis of the appropriate derivatives of the three cyanohydrins, **13**, **14**, and **19**. Kinetic studies were carried out in anhydrous 2,2,2-trifluoroethanol (TFE) in order to avoid any hydrolysis of the cyano function or direct S_N2 displacement reactions. Anhydrous TFE seemed ideal for this purpose because of its low nucleophilicity,[13] high ionizing power,[14,15] and relatively weak acidity (pK_a = 12.37).[15] The solvent was buffered with 2,6-lutidine and the rates were determined by the conductometric method.[14,16,17]

As can be seen from a comparison of the rates listed in Table I, in two of the three sets of compounds studied the rate-retarding effect of the α-cyano function was considerably greater than might have been expected in analogy to observations with **3** and **4**.[2] It ranged from 100 for the comparison of **5** to **8** to a difference of 1 000 000 for the rate relationship of **7** to **10**. On the basis of presently available data, which portion of these rate differences is due to mesomeric stabilization by the α-cyano moiety and which portion is due to an increase in neighboring group participation by some portion of the bicyclic skeleton cannot be determined. It has been firmly established that neighboring group participation is a function of the stability of the incipient cationic center.[18] Thus, in situations where massive neighboring group participation is available (for example, in the solvolysis of **10**), mesomeric stabilization of the cationic center by the α-cyano group should be reduced *but not completely eliminated*. In summary, we propose that the observed rate differences are a result of a combination of neighboring group participation, inductive destabilization of the cationic center by the α-cyano function, and mesomeric stabilization of the developing cation by this same group.



Product studies strongly supported the contention that neighboring group participation was important in the solvolysis of **8**–**10**. The 2,2,2-trifluoroethanolysis of **15** gave 86% of **21**



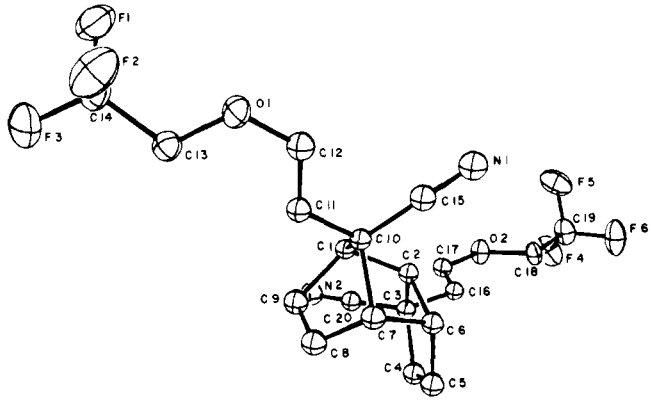
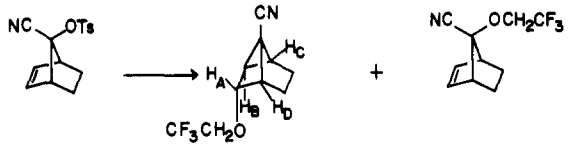


Figure 1. ORTEP drawing of **27**. Hydrogens have been omitted for clarity.

and 8% of **22**.[19] The structure of **21** was based on mass-spectral data and ^1H and ^{13}C magnetic resonance data. The ^1H NMR spectrum ($CDCl_3$) of **21** showed δ 1.95 (2 H, m), 2.25 (2 H, m), 2.60 (2 H, m, allylic methylene, J_{AX} = 2.0, J_{BX} = 2.0 Hz), 3.30 (1 H, m), 5.69 (H_B, J_{AB} = 5.6, J_{BX} = 2.0 Hz), 5.86 (H_A, J_{AB} = 5.6, J_{AX} = 2.0 Hz); ^{13}C NMR ($CDCl_3$) δ 24.6 (t), 31.7 (t), 39.9 (t), 42.2 (d), 44.0 (s), 121.8 (CN, s), 128.8 (d), 135.2 (d). The structure of **22** was based on NMR spectral comparison of **22** with **8** and **15**. It is interesting that the presence of the cyano function at C-7 of **15** provided the driving force for significant rearrangement of the bicyclo[2.2.1]heptyl skeleton to that of the bicyclo[3.2.0]heptyl system. This is in stark contrast to the parent tosylate, **5**, which yields greater than 90% of the product having the starting skeleton intact.[5] Whether anchimeric assistance is involved in the solvolysis of **15** cannot be rigorously determined on the basis of currently available data. However, the large amount of rearranged product would indicate that such assistance was highly probable. The overall net effect of the rearrangement was to convert the carbonyl group of **11** into the cyano-substituted quaternary center of **21**. We believe that this effect of electron-withdrawing groups on incipient cationic centers may have useful applications in the synthesis of complex carbon skeletons through rearrangement processes.

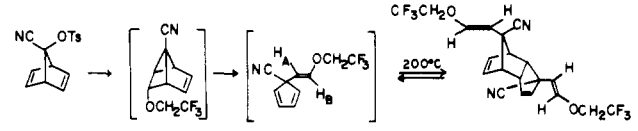
Solvolysis of **9** gave 92% of **23** and 3% of **24**.[19] The structure of **23** was based on mass-spectral data and ^1H and ^{13}C mag-



9 23 24

netic resonance data. The ^1H NMR spectrum ($CDCl_3$) of **23** had δ 1.85 (4 H, m), 2.22 (H_C, m), 2.58 (H_B, J_{AB} = 4.0 Hz), 3.00 (H_D, m, J_{AD} = 7.8 Hz), 3.64 (CF_3CH_2O, q, J_{HF} = 9 Hz), 4.05 (H_A, d of d, J_{AB} = 4.0, J_{AD} = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 14.9 (s), 24.0 (t), 28.2 (t), 33.9 (d), 34.0 (d), 47.8 (d), 66.1 (q of t, J_{CCF} = 34 Hz), 69.7 (d), 119.0 (CN, s), 123.4 (t, J_{CF} = 279 Hz). The proton spectrum of **23** was very diagnostic of this skeleton.[20] The structure of **24** was established by comparison of its spectral data with that of **9**. Again, the isolation of **23** as the overwhelming product demonstrated the ability of the cyano function to direct nucleophilic attack away from its point of attachment.

Product studies for the 2,2,2-trifluoroethanolysis of **10** proved to be more difficult in that a dimer of formula $C_{20}H_{16}F_6N_2O_2$ was formed in 90% yield. Formation of dimers in solvolysis reactions is rare and would appear to require the formation of unusual intermediates. In principle, **10** would be expected to produce **25** in analogy with the formation of **23** and



10 25 26 27

9. We believe that this occurred, but that **25** underwent a retro-Diels–Alder reaction under the reaction conditions to produce **26**. Ample precedent exists for the cleavage of structures similar to **25** in a retro-Diels–Alder fashion.[6a,20b] Dimerization of **26** could then produce **27**. At 200 °C, the dimer was cracked back to the monomer, which showed ^1H NMR ($CDCl_3$) δ 4.06 (2 H, q, J_{HF} = 8.1 Hz), 4.57 (H_A, d, J_{AB} = 12.5 Hz), 6.42 (4 H, 12-line AA'BB' pattern), 6.64 (H_B, d, J_{AB} = 12.5 Hz). This spectral data was consistent with structure **26**. At room temperature, the monomer redimerized to give crystalline **27**, mp 68–69 °C. The dimer showed no evidence for the presence of conjugation by UV spectroscopy. However, the ^1H NMR spectrum ($CDCl_3$) showed δ 3.07–3.32 (3 H, m), 4.01 (2 H, q, J_{HF} = 8.0 Hz), 4.04 (2 H, q, J_{HF} = 8.0 Hz), ca. 4.0 (1 H, m), 4.88 (1 H, d, J = 13.5 Hz), 5.15 (1 H, d, J = 12.7 Hz), 5.52 (2 H, AB q, J_{AB} = 5.6 Hz), 6.05 (1 H, m), 6.30 (1 H, m), 6.49 (1 H, d, J = 13.5 Hz), 6.55 (1 H, d, J = 12.7 Hz). The UV spectrum required that the four double bonds were isolated from each other. This was consistent with the structure **27**.

In order to unequivocally establish the structure of the dimer, a single-crystal X-ray analysis of **27** was carried out. The white crystals of $C_{20}H_{16}F_6N_2O_2$ belonged to the centrosymmetric monoclinic space group $P2_1/n$. The measured cell constants a = 11.006 (6) Å, b = 6.992 (12) Å, c = 26.255 (16) Å, and B = 94.57 (10)° gave a calculated density of 1.419 g/cm^3 for four molecules in the unit cell at ambient temperature. Data were collected on a fully automated Enraf-Nonius CADH diffractometer using variable scan rate ω–2θ scan technique and graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). After Lorentz–polarization corrections, 2403 of the 6043 reflections (40%) with 2θ = 0–60° were observed [$F_o \geq 2\sigma(F_o)$]. A combination of direct methods and Fourier syntheses was used to locate all nonhydrogen atoms.[21,22] Thermal anisotropic refinement was applied to all nonhydrogen atoms. The R factor for the structure was 0.097. Figure 1 is an ORTEP drawing of the dimer with the hydrogens omitted for clarity. Bond lengths and bond angles are given in Tables II and III, respectively.

In summary, we have demonstrated that the presence of an α-cyano group can promote dramatic changes in both the products and rates of solvolysis of bicyclic sulfonates. In all instances, the cyano function is significantly rate retarding. The degree of this retardation would appear to be a function of the stability of the incipient carbonium ion. The largest rate retardation occurs for the most stable ions. In terms of products, the cyano moiety promotes rearrangements which result from charge delocalization to a more stable center through neighboring group participation. In this way, the carbon of a ketone carbonyl can be readily converted into a cyano-bearing quaternary center.

Experimental Section[23]

Bicyclo[2.2.1]heptan-7-one (11). Bicyclo[2.2.1]heptan-7-one was prepared from 7,7-dimethoxybicyclo[2.2.1]heptane according to the method of Gassman and Pape,[8] mp 77–79 °C (lit.[8] mp 77–79 °C).

7-Cyano-7-hydroxybicyclo[2.2.1]heptane (13). A solution of sodium bisulfite (4.15 g, 40 mmol) in water (51 mL) and bicyclo[2.2.1]heptan-7-one (3.12 g, 20 mmol) was stirred at room temperature for 1 h, whereupon the crystalline bisulfite addition product formed. Addition of potassium cyanide (2.60 g, 40 mmol) in water (20 mL) over a period of 10 min resulted in the formation of an oily, yellow liquid. The solution was extracted with three 15-mL portions of ether. The

Table II. Bond Distances (Å) for **27**

atoms	distance	atoms	distance
C(1)-C(2)	1.522(9)	C(11)-C(12)	1.340(10)
C(1)-C(9)	1.513(9)		
C(1)-C(10)	1.569(8)	C(12)-O(1)	1.374(9)
C(2)-C(3)	1.579(9)	C(13)-C(14)	1.491(11)
C(2)-C(6)	1.579(9)	C(13)-O(1)	1.324(9)
C(3)-C(4)	1.511(9)	C(14)-F(1)	1.317(9)
C(3)-C(16)	1.529(9)	C(14)-F(2)	1.336(9)
C(3)-C(20)	1.470(10)	C(14)-F(3)	1.284(9)
C(4)-C(5)	1.342(9)	C(15)-N(1)	1.133(8)
C(5)-C(6)	1.498(10)	C(16)-C(17)	1.334(8)
C(6)-C(7)	1.623(10)	C(17)-O(2)	1.396(8)
C(7)-C(8)	1.432(10)	C(18)-C(19)	1.530(10)
C(7)-C(10)	1.541(9)	C(18)-O(2)	1.393(9)
C(8)-C(9)	1.317(9)	C(19)-F(4)	1.333(9)
		C(19)-F(5)	1.315(11)
		C(19)-F(6)	1.281(10)
C(10)-C(11)	1.500(10)		
C(10)-C(15)	1.438(10)	C(20)-N(2)	1.139(8)

Table III. Bond Angles (deg) for **27**

atoms	angle	atoms	angle
C(2)-C(1)-C(9)	111.6(6)	C(1)-C(2)-C(6)	102.5(5)
C(2)-C(1)-C(10)	100.9(5)	C(3)-C(2)-C(6)	105.2(5)
C(9)-C(1)-C(10)	99.6(5)	C(2)-C(3)-C(4)	103.2(5)
C(1)-C(2)-C(3)	118.2(6)	C(2)-C(3)-C(16)	110.6(5)
C(4)-C(3)-C(20)	111.2(6)	C(7)-C(10)-C(11)	114.4(5)
C(16)-C(3)-C(20)	109.3(5)	C(7)-C(10)-C(15)	112.9(6)
C(3)-C(4)-C(5)	113.4(5)	C(11)-C(10)-C(15)	110.0(6)
C(16)-C(3)-C(20)	109.3(5)	C(7)-H(10)-C(15)	112.9(6)
C(3)-C(4)-C(5)	113.4(5)	C(11)-C(10)-C(15)	110.0(6)
C(4)-C(5)-C(6)	112.0(6)	C(10)-C(11)-C(12)	123.7(7)
C(2)-C(6)-C(5)	104.9(6)	C(11)-C(12)-O(1)	124.1(8)
C(2)-C(6)-C(7)	101.2(6)	C(14)-C(13)-O(1)	110.7(8)
C(5)-C(6)-C(7)	115.4(6)	C(10)-C(15)-N(1)	177.4(8)
C(6)-C(7)-C(8)	105.8(6)	C(3)-C(16)-C(17)	121.7(7)
C(6)-C(7)-C(10)	99.5(5)	C(16)-C(17)-O(2)	124.1(7)
C(8)-C(7)-C(10)	101.4(6)	C(19)-C(18)-O(2)	108.4(7)
C(7)-C(8)-C(9)	111.1(8)	C(3)-C(20)-N(2)	177.9(7)
C(1)-C(9)-C(8)	104.9(8)	C(12)-O(1)-C(13)	119.0(6)
C(1)-C(10)-C(7)	91.4(5)	C(17)-O(2)-C(18)	116.4(5)

combined ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the solvent evaporated at reduced pressure to afford an oil. The oil was taken up in *n*-hexane, decolorized, and allowed to stand. After the oil had stood for several hours, crystals formed which were isolated by filtration. Sublimation at 50 °C (0.02 mm) and a further recrystallization from *n*-hexane gave 3.20 g (58%) of the desired cyanohydrin: mp 110–111 °C; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.50–2.00 (8 H, m), 2.90 (2 H, m), 5.40 (1 H, s); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 26.7 (t), 26.8 (t), 45.5 (d), 78.4 (s), 120.8 (s); IR (CCl_4) 3590, 3400, 2950, 2865, 2225, 1475, 1455, 1375, 1310, 1262, 1208, 1155, 1122, 1085, 1032, 868 cm^{-1}; mass spectrum 110.0756 (calcd for $C_7H_{10}O$ (M − HCN), 110.0731).

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.20. Found: C, 70.18; H, 8.17; N, 10.21.

7-Cyanobicyclo[2.2.1]hept-7-yl *p*-Toluenesulfonate (8). A 125-mL Erlenmeyer flask was charged with 50 mL of dry pyridine, freshly recrystallized tosyl chloride (3.80 g, 20 mmol), and 7-cyano-7-hydroxybicyclo[2.2.1]heptane (1.37 g, 10 mmol), and placed in a refrigerator (5 °C) for 6 days. The contents of the flask were poured into 300 g of ice-water and the aqueous layer was extracted with three 60-mL portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed on a rotary evaporator to give an oil. Low-temperature recrystallization at −78 °C from 30–60 °C petroleum ether afforded 1.37 g (54%) of the desired tosylate, **8**: mp 36–38 °C; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.23–2.30 (8 H, m), 2.47 (3 H, s), 2.78 (2 H, m), 7.69 (4 H, AB quartet, J = 8 Hz); IR (CCl_4) 2965, 2875, 1600, 1375, 1309, 1137, 1126, 1115, 1092, 1010, 852 cm^{-1}; mass spectrum 291.0953 (calcd for $C_{15}H_{17}NO_3S$, 291.0929). An analytical sample was obtained from a further recrystallization from 30–60 °C petroleum ether, mp 36–38 °C.

Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.79; H, 5.92; N, 4.80.

Trifluoromethanesulfonic Anhydride. This anhydride was prepared in 80% yield according to the method of Gramstad and Hazeldine,[24] bp 63–65 °C (lit.[24] bp 64 °C).

***p*-Toluenesulfonic Anhydride.** This anhydride was prepared according to the method of Field.[25]

7-Cyanobicyclo[2.2.1]hept-7-yl Trifluoromethanesulfonate (15). Trifluoromethanesulfonic anhydride (3.10 g, 11.0 mmol) in 15 mL of Freon-11 was placed in a 50-mL, two-necked, round-bottomed flask equipped with a reflux condenser and serum cap. The solution was cooled to 0 °C (ice bath) and a solution of 7-cyano-7-hydroxybicyclo[2.2.1]heptane (1.37 g, 10 mmol) in pyridine (1.00 g, 12 mmol) was added dropwise via syringe. The reaction mixture was stirred for 30 min at 0 °C and then filtered through a 5-cm pad of silica gel. The precipitate was washed with 50 mL of Freon-11; the combined filtrate was then concentrated under a mild vacuum to afford a clear oil. The oil was purified by vacuum transfer to afford pure triflate, **15**: 1.62 g (60%); ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.50 (2 H, m), 1.68 (2 H, m), 1.92 (2 H, m), 2.05 (2 H, m), 2.80 (2 H, m); IR (neat) 2960, 2883, 1412, 1247, 1215, 1135, 970, 875, 863 cm^{-1}; mass spectrum 136.0762 (calcd for $C_8H_{10}NO$ (M − SO_2CF_3), 136.0768); chemical ionization mass spectrum *m/e* 270 (M + H), 298 (M + C_2H_5), 310 (M + C_3H_7) (reagent gas CH_4).[26]

Bicyclo[2.2.1]hepten-7-one (12). This ketone was prepared from 7,7-dimethoxybicyclo[2.2.1]heptene in 90% yield, bp 100–105 °C (120 mm) [lit.[8] bp 96–100 °C (115 mm)] according to the method of Gassman and Marshall.[8,27]

***syn*-7-Cyano-*anti*-7-hydroxybicyclo[2.2.1]heptene (14).** A solution of sodium bisulfite (10.40 g, 0.1 mol) in water (30 mL) and bicyclo[2.2.1]hepten-7-one (5.40 g, 50 mmol) was stirred for 2 h at room temperature and then heated to 80 °C for 3 h. Upon cooling to 0 °C, potassium cyanide (6.50 g, 0.1 mol) in water (20 mL) was added dropwise over a period of 15 min. After stirring at room temperature for 12 h, the solution was extracted with three 50-mL portions of ether. The combined ethereal layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed in vacuo to leave a white solid. Sublimation at 40 °C (0.05 mm) followed by recrystallization from light petroleum gave 3.72 g (55%) of the desired cyanohydrin: mp 54–55 °C; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.00 (2 H, m), 2.00 (2 H, m), 2.90 (2 H, t), 4.30 (1 H, s), 6.15 (2 H, t); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 21.5 (t), 50.0 (d), 82.7 (s), 122.2 (s), 134.7 (d); IR (CCl_4) 3600, 3400, 3000, 2970, 2250, 1423, 1342, 1290, 1130, 1105, 1082, 1055, 1040, 870 cm^{-1}; mass spectrum 135.0691 (calcd for C_8H_9NO, 135.0684). An analytical sample was prepared by a further recrystallization from *n*-hexane, mp 54.5–55.0 °C.

Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.07; H, 6.84; N, 10.24.

Lanthanide Shift Reagent Study of *syn*-7-Cyano-*anti*-7-hydroxybicyclo[2.2.1]heptene (14) with Eu(fod)$_3$. To a 5-mm NMR tube containing 25 μL of a 0.3 M solution of the cyanohydrin **14** in deuteriochloroform/1% tetramethylsilane was added 31.1 mg of Eu(fod)$_3$. A spectrum of this solution was taken. Additional aliquots of the 0.3 M cyanohydrin solution were syringed into the NMR tube and shifts were measured until 150 μL of the solution had been added. A plot of the chemical shift of the protons of **14** vs. the [LSR/[**14**] ratio gave the following slopes: exo hydrogens, 8.4; endo hydrogens, 6.1; vinyl hydrogens, 5.0; bridgehead hydrogens, 11.4.

***syn*-7-Cyanobicyclo[2.2.1]hept-2-en-*anti*-7-yl *p*-Toluenesulfonate (9).** A 125-mL Erlenmeyer flask was charged with 50 mL of dry pyridine, freshly recrystallized tosyl chloride (3.80 g, 20 mmol), and *syn*-7-cyano-*anti*-7-hydroxybicyclo[2.2.1]heptene (**14**, 1.37 g, 10 mmol) at 0 °C. The flask was stoppered and allowed to stand in a refrigerator for 5 days. The solution was then poured into 400 mL of ice water, whereupon the tosylate crystallized. The solid tosylate was taken up in the minimum amount of *n*-hexane and recrystallized at −78 °C to afford 2.05 g (71%) of desired tosylate, **9**: mp 72–73 °C; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.15 (1 H, d), 1.28 (1 H, d), 2.00 (1 H, m), 2.17 (1 H, m), 2.45 (3 H, s), 3.36 (2 H, m), 6.17 (3 H, t), 7.65 (4 H, AB quartet, J = 10 Hz); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 21.3 (t), 21.3 (q), 50.2 (d), 86.5 (s), 127.8 (s), 129.6 (d), 133.5 (d), 145.4 (s); IR (KBr) 2975, 1600, 1375, 1368, 1333, 1172, 1169, 1010, 864, 828, 815 cm^{-1}; mass spectrum 289.0780 (calcd for $C_{15}H_{15}NO_3S$, 289.0772).

Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.22; N, 4.84. Found: C, 62.34; H, 5.25; N, 4.86.

Tetracyclo[3.2.0^{2,7}.0^{4,6}]heptan-3-one (Quadricyclanone, 16). Quadricyclanone was prepared in 51% overall yield (four steps) from 7-acetoxybicyclo[2.2.1]heptadiene by the method of Gassman and Patton,[11] bp 50 °C (1 mm) [lit.[11] bp 50–55 °C (2 mm)].

3-Trimethylsilyloxy-3-cyanotetracyclo[3.2.0^{2,7}.0^{4,6}]heptane (17, Quadricyclanone Trimethylsilyl Cyanohydrin). To a 25-mL, round-bottomed flask equipped with reflux condenser, provisions for magnetic stirring, a serum cap, and a dry nitrogen atmosphere were added tetracyclo[3.2.0^{2,7}.0^{4,6}]heptan-3-one (469 mg, 4.42 mmol), anhydrous zinc iodide (2 mg, 6.3×10^{-3} mmol), and 10 mL of dry nitromethane. To this stirred solution was added, via syringe, trimethylsilyl cyanide (530 mg, 5.31 mmol). After the solution was stirred for an additional 15 min at room temperature the solvent was removed on a rotary evaporator to give 842.4 mg (93%) of a pale yellow liquid. Vacuum distillation gave 815 mg (90%) of **17** as a clear, colorless liquid: bp 85 °C (1 mm); ^{1}H NMR ($CDCl_3$/Me_4Si) δ 0.27 (9 H, s), 1.85 (6 H, m); IR (neat) 2960, 1345, 1256, 1134, 1089, 877, 840, 722 cm^{-1}; mass spectrum 205.0914 (calcd for $C_{11}H_{15}NOSi$, 205.0923). An analytical sample was prepared by preparative GLC on a 10 ft × ¼ in. 14% SE-30 60/80 Chromosorb W column at 200 °C.

Anal. Calcd for $C_{11}H_{15}NOSi$: C, 64.34; H, 7.36; N, 6.82. Found: C, 64.43; H, 7.34; N, 6.76.

Dibenzonitrile Dichloropalladium(II). Benzonitrile was allowed to react with dichloropalladium(II) according to published procedures[28] to yield the title compound.

Dichloro(bicyclo[2.2.1]heptadiene)palladium(II). Bicyclo[2.2.1]-heptadiene was allowed to react with dibenzonitrile dichloropalladium(II) according to published procedures[12] to yield the title compound.

7-Trimethylsilyloxy-7-cyanobicyclo[2.2.1]heptadiene (18). To a 25-mL, round-bottomed flask equipped with provisions for magnetic stirring and a reflux condenser and protected from atmospheric moisture with a nitrogen atmosphere was added a solution of 3-trimethylsilyloxy-3-cyanotetracyclo[3.2.0^{2,7}.0^{4,6}]heptane (1.11 g, 5.41 mmol), dichloro(bicyclo[2.2.1]heptadiene)palladium(II) (10 mg, 0.037 mmol), and 15 mL of chloroform. The solution was heated to reflux for 8 h. The solvent was removed on a rotary evaporator and the residue was vacuum distilled to give 0.95 g (86%) of **18**: bp 85 °C (4 mm); ^{1}H NMR ($CDCl_3$/Me_4Si) δ 0.19 (9 H, s), 3.65 (2 H, m), 6.45 (2 H, t), 6.62 (2 H, t); IR (neat) 2960, 2230, 1307, 1255, 1238, 1204, 1150, 877, 845, 733 cm^{-1}; mass spectrum 205.0922 (calcd for $C_{11}H_{15}NOSi$, 205.0923).

7-Cyano-7-hydroxybicyclo[2.2.1]heptadiene (19). To a 50-mL, round-bottomed flask equipped with provisions for magnetic stirring and a reflux condenser were added 7-trimethylsilyloxy-7-cyanobicyclo[2.2.1]heptadiene (600 mg, 2.93 mmol) and 30 mL of 3 N hydrochloric acid. The solution was heated to 40 °C for 3 h. Upon cooling to room temperature, the contents of the flask were poured into a separatory funnel and extracted with three 15-mL portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed on a rotary evaporator to afford 382 mg of the crude cyanohydrin **19**. The crude product was recrystallized from *n*-hexane to give 370 mg (95%) of analytically pure **19**: mp 83.5–85.0 °C; ^{1}HMR ($CDCl_3$/Me_4Si) δ 3.57 (3 H, m), 6.49 (2 H, t), 6.59 (2 H, t); IR (KBr) 3400, 2240, 1330, 1295, 1225, 1202, 1118, 1005, 812, 733 cm^{-1}; mass spectrum 133.0515 (calcd for C_8H_7NO, 133.0527).

Anal. Calcd for C_8H_7NO: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.23; H, 5.44; N, 10.54.

7-Cyanobicyclo[2.2.1]heptadien-7-yl *p*-Toluenesulfonate (10). To a 10-mL Erlenmeyer flask were added 7-cyano-7-hydroxybicyclo[2.2.1]heptadiene (110 mg, 0.83 mmol), dry pyridine (79 mg, 1.0 mmol), and *p*-toluenesulfonic anhydride (293 mg, 0.9 mmol) in 5 mL of dry methylene chloride. The mixture was stoppered and placed in a refrigerator (5 °C) for 7 days. The solution was then poured into water and the solution extracted with three 10-mL portions of methylene chloride. The combined methylene chloride solution was washed with 3 N hydrochloric acid, water, and brine and dried over anhydrous magnesium sulfate. After filtering, the solvent was removed on a rotary evaporator to give a yellow oil. Low-temperature recrystallization from *n*-hexane gave **10** as white crystals (190 mg, 80%): mp 75–76 °C; ^{1}HMR ($CDCl_3$/Me_4Si) δ 2.45 (3 H, s), 4.05 (2 H, m), 6.51 (2 H, t), 6.75 (2 H, t), 7.60 (4 H, AB quartet, J = 8 Hz); IR ($CHCl_3$) 1600, 1375, 1190, 1180, 1000 cm^{-1}; mass spectrum 171.0131 (calcd for $C_7H_7SO_3$, 171.0115), 132.0460 (calcd for C_8H_6NO, 132.0449), 116.0501 (calcd for C_8H_6N (M − OTs), 116.0500); chemical ionization mass spectrum M + H$^+$ at *m/e* 288 (reagent gas CH_4).[26]

Procedure for Solvolysis of Tosylates and Triflates in Anhydrous 2,2,2-Trifluoroethanol. Anhydrous trifluoroethanol was purchased from Aldrich Chemical Co., distilled through a 12-in., glass-helices packed column from phosphoric anhydride, and stored in glass-stoppered volumetric flasks sealed with Parafilm. Solutions of the appropriate tosylate or triflate were prepared at 0.003–0.005 M. The solutions were buffered with 2,6-lutidine at 0.0045–0.0075 M, respectively. The kinetics were determined conductimetrically in a 2- or 10-mL conductance cell which was sealed for each run. For solvolysis at temperatures greater than 140 °C, the purified tosylates or triflates and dry 2,6-lutidine were dissolved in 10.0 mL of trifluoroethanol to give a solution 0.01 M in substrate and 0.025 M buffer. Approximately 1.2-mL portions were sealed into Pyrex tubes which were immersed in a constant-temperature bath (±0.02 °C). An accurate timer was started when the bath had reequilibrated. The tubes were removed at periodic intervals and the time was recorded (±3 s), followed by immediate quenching in ice-water. The tubes were allowed to come to room temperature and opened, and 1.0 mL of the solution was transferred to a conductivity cell with polished platinum electrodes by means of a constant-delivery pipet. After dilution with 10.0 mL of trifluoroethanol (large cell) or 2.0 mL (small cell) the cell was sealed and then equilibrated at 0 °C in an ice-water bath. Conductance values were obtained with a Barnstead Model PM-70CB conductivity bridge or YSI Model 31 conductivity bridge. After each measurement, the conductivity cell was rinsed four times with acetone (distilled from potassium permanganate) and twice with trifluoroethanol, then dried in a drying oven for at least 30 min. Rate constants were calculated by a least-squares treatment[29] of ln ($C_\infty - C$) vs. time (s). Correlation coefficients greater than 0.999 were obtained. Activation parameters were calculated by a least-squares treatment[29] of ln [K/T (K)] vs. $1/T$ (K). At least two runs were made at each temperature.

Method for Evaluation of Product Stability to Trifluoroethanolysis Reaction Conditions. To a solution of the appropriate solvolysis product (0.1 mmol) in 10 mL of anhydrous trifluoroethanol (0.01 M), previously buffered to 0.005 M in 2,6-lutidine, was added 2,6-lutidinium trifluoromethanesulfonate (26 mg, 0.1 mmol) or 2,6-lutidinium *p*-toluenesulfonate (28 mg, 0.1 mmol).

The resulting solution was heated to the corresponding solvolysis temperature. The reaction was monitored by analytical VPC on a 10 ft × ⅛ in. 10% SE-30 on 45/50 Chromosorb W column and also a 10 ft × 1/8 in. 10% Carbowax 20M on 45/60 Chromosorb W column. All solvolysis products were found to be stable under their respective conditions of generation.

1-Cyanobicyclo[3.2.0]hept-2-ene (21). Trifluoroethanolysis at 170 °C of **15** afforded **21** in 88.5% yield. An analytical sample was obtained by preparative gas chromatography on a 10 ft × ¼ in. 10% SE-30 on 60/80 Chromosorb W column at 170 °C: ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.95 (2 H, m), 2.25 (2 H, m), 2.60 (2 H, m, J_{AX} = 2.0, J_{BX} = 2.0 Hz), 3.30 (1 H, m), 5.69 (H_B, J_{AB} = 5.6, J_{BX} = 2.0 Hz), 5.86 (H_A, J_{AB} = 5.6, J_{AX} = 2.0 Hz); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 24.6 (t), 31.7 (t), 39.9 (t), 42.2 (d) 44.0 (s), 121.8 (s), 128.8 (d), 135.2 (d); IR (neat) 2940, 2250, 1450, 1352, 1276, 1160, 1128, 972 cm^{-1}; mass spectrum 119.0748 (calcd for C_8H_8N, 119.0735).

Anal. Calcd for C_8H_8N: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.51; H, 7.60; N, 11.75.

7-Cyano-7-(2,2,2-trifluoroethoxy)bicyclo[2.2.1]heptane (22). Trifluoroethanolysis of **15** at 170 °C afforded **22** in 7.6% yield. This material was isolated by preparative gas chromatography on a 10 ft × ¼ in. 10% SE-30 on Chromosorb 60/80 column at 170 °C: ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.32 (2 H, m), 1.43 (2 H, m), 1.88 (4 H, m), 2.39 (2 H, m), 3.85 (2 H, q, J_{HF} = 8.0 Hz); IR ($CHCl_3$) 2950, 1456, 1280, 1170, 1130, 1067, 964, 803 cm^{-1}; mass spectrum 219.0723 (calcd for $C_{10}H_{12}F_3NO$, 219.0718).[30]

7-Cyano-*endo*-2-(2,2,2-trifluoroethoxy)tricyclo[4.1.0.0^{3,7}]heptane (23). Trifluoroethanolysis of **9** at 95 °C afforded **23** in 92% yield. An analytical sample was obtained by preparative gas chromatography on a 10 ft × ¼ in. 10% SE-30 on 60/80 Chromosorb W column at 150 °C: ^{1}H NMR ($CDCl_3$/Me_4Si) δ 1.85 (4 H, m), 2.22 (H_C, m), 2.58 (H_B, m, J_{AB} = 4.0 Hz), 3.00 (H_D, m, J_{AD} = 7.8 Hz), 3.64 (2 H, q, J_{HF} = 9.0 Hz), 4.05 (H_A, d of d, J_{AB} = 4.0, J_{AD} = 7.8 Hz); ^{13}C NMR ($CDCl_3$/Me_4Si) δ 14.9 (s), 24.0 (t), 28.2 (t), 33.9 (d), 34.0 (d), 47.8 (d), 66.1 (q of t, J_{CCF} = 34 Hz), 69.7 (d), 119.0 (s), 123.4 (q, J_{CF} =

279 Hz); IR ($CHCl_3$) 2940, 2220, 1460, 1442, 1417, 1307, 1280, 1235, 1165, 1142, 1068, 1018, 969, 820, cm^{-1}; mass spectrum 217.0698 (calcd for $C_{10}H_{10}F_3NO$, 217.0714).

Anal. Calcd for $C_{10}H_{10}F_3NO$: C, 55.33; H, 4.64; N, 6.45. Found: C, 55.29; H, 4.63; N, 6.39.

***syn*-7-Cyano-*anti*-(2,2,2-trifluoroethoxy)bicyclo[2.2.1]hept-2-ene (24).** Trifluoroethanolysis of **9** at 95 °C afforded **24** in 2.6% yield. An analytical sample was obtained by preparative gas chromatography on a 10 ft × ¼ in. 10% SE-30 on 60/80 Chromosorb W column at 150 °C; ^1H NMR ($CDCl_3/Me_4Si$) δ 1.10 (2 H, m), 1.90 (2 H, m), 2.91 (2 H, m), 3.39 (1 H, s), 6.10 (2 H, t); IR ($CHCl_3$) 2972, 2240, 1455, 1331, 1280, 1175, 1128, 1029, 958 cm^{-1}; mass spectrum 217.0711 (calcd for $C_{10}H_{10}F_3NO$, 217.0714).

Anal. Calcd for $C_{10}H_{10}F_3NO$: C, 55.33; H, 4.64; N, 6.45. Found: C, 55.20; H, 4.73; N, 6.58.

***anti*-10-Cyano-*syn*-10-[(*E*)-(2,2,2-trifluoroethyl)vinyl]-*endo*-5-cyano-*exo*-5-[(*E*)-(2,2,2-trifluoroethyl)vinyl]-*endo*-tricyclo[5.2.1.$0^{2,6}$]-deca-3,8-diene (27).** Trifluoroethanolysis of **10** at 25 °C produced the dimer **27** in 90% yield, recrystallized from *n*-hexane: mp 68–69 °C; ^1H NMR ($CDCl_3/Me_4Si$) δ 3.05 (1 H, m), 3.25 (2 H, m), 4.01 (3 H, CF_3CH_2O–, J_{HF} = 8.0 Hz, 1 aliphatic H), 4.04 (2 H, CF_3CH_2O–, J_{HF} = 8.0 Hz), 4.88 (1 H, d, J = 13.5 Hz), 5.15 (1 H, d, J = 12.7 Hz), 5.52 (2 H, q of d, J = 5.6, 1.6 Hz), 6.05 (2 H, m, J = 5.6, 2.9 Hz), 6.49 (1 H, d, J = 13.5 Hz), 6.55 (1 H, d, J = 12.7 Hz); ^{19}F NMR ($CDCl_3/C_6F_6$) δ 53.2 (t, J_{HF} = 8.0 Hz), 52.4 (t, J_{HF} = 8.0 Hz); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 46.4 (s), 52.6 (d), 53.2 (d), 54.1 (d), 54.4 (d), 59.5 (s), 67.2 (q of t, J_{CCF} = 22 Hz), 102.4 (d), 109.5 (d), 119.5 (s), 120.2 (s), 124.2 (q, J_{CF} = 280 Hz), 129.7 (d), 132.6 (d), 132.8 (d), 133.8 (d), 146.5 (d), 149.3 (d); IR (KBr) 2240, 1660, 1285, 1205, 1168, 985, 975, 867, 772, 750 cm^{-1}; mass spectrum 430.1137 (calcd for $C_{20}H_{16}F_6N_2O_2$, 430.1130).

Pyrolysis of the Dimer 27. Preparation of 5-Cyano-5-(*E*)-(2,2,2-trifluoroethoxyvinyl)-1,3-cyclopentadiene (26). A solution of the dimer **27** in deuteriochloroform was injected onto an empty 10 ft × ¼ in. stainless steel VPC column at 200 °C. The product, **26**, and deuteriochloroform were condensed in a glass collector cooled to −78 °C in an isopropyl alcohol/dry ice bath. The solution containing **26** was then examined by ^1H NMR spectroscopy: ^1H NMR ($CDCl_3/Me_4Si$) δ 4.06 (2 H, q, J_{HF} = 8.1 Hz), 4.57 (H_A, d, J_{AB} = 12.5 Hz), 6.42 (4 H, AA′BB′ 12-line pattern), 6.64 (H_B, d, J_{AB} = 12.5 Hz). The redimerization of **26** to give **27** was followed by ^1HMR spectroscopy and was completed within 24 h at room temperature.

Acknowledgments. We are indebted to the National Science Foundation for Grant CHE78-10231 which supported this investigation and for Grant CHE77-28505 which aided in the purchase of an Enraf-Nonius X-ray diffractometer. We wish to thank Mr. M. McGuiggen and Professors J. D. Britton and L. Pignolet for assistance in the X-ray determination.

Supplementary Material Available: Tables of fractional coordinates, structure factors, and bond distances and angles (20 pages). Ordering information is given on any current masthead page.

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