J. Org. Chem. 1991, 56, 5143-5146 5143

Synthesis of Perfluoroalkylated Indenes

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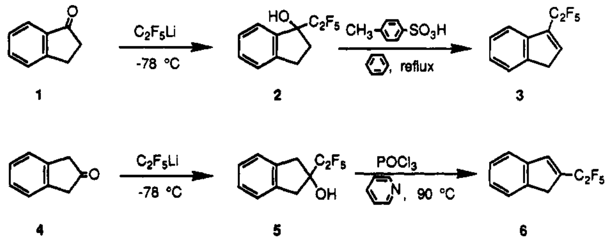
Received March 18, 1991

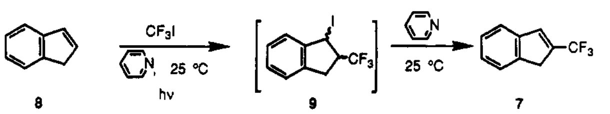
A series of perfluoroalkylated indenes has been synthesized using four different synthetic pathways. 1-(Pentafluoroethyl)indene and 2-(pentafluoroethyl)indene were prepared by the addition of (pentafluoroethyl)lithium to the appropriate ketones and subsequent dehydration. 2-(Trifluoromethyl)indene was synthesized through the photoinduced addition of trifluoromethyl iodide to indene, followed by dehydroiodination. 1-(Trifluoromethyl)indene was prepared by the addition of (trifluoromethyl)trimethylsilane to 1-indanone followed by deprotection and dehydration and by the sigmatropic cyclization of the appropriate phenylvinyl carbocation. This latter approach was also used to synthesize 1,3-bis(trifluoromethyl)indene and 1,2,3-tris(trifluoromethyl)indene.

Derivatives of perfluoroalkylated cyclopentadienes have been of interest to organic chemists for many years.[3-6] Unfortunately, synthetic procedures that would permit the synthesis of a variety of such compounds were not readily available. Our interest,[7] and those of others,[5,8] in using perfluoroalkylated cyclopentadiene derivatives as electron-withdrawing ligands for transition metals prompted us to develop new synthetic pathways to these compounds. We now wish to report four new synthetic methods for preparing perfluoroalkylated indenes. The most mechanistically intriguing of these approaches involves the sigmatropic cyclization of perfluoroalkylated phenylvinyl carbocations.[9]

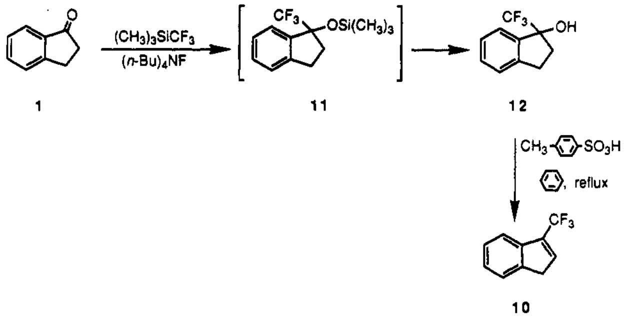
Treatment of 1-indanone (1) with (pentafluoroethyl)lithium[10] in diethyl ether gave an 88% yield of 1-(pentafluoroethyl)-1-indanol (2). Treatment of 2 with a catalytic amount of p-toluenesulfonic acid in refluxing benzene for 12 h gave an 85% yield of 1-(pentafluoroethyl)indene (3). Similar treatment of 2-indanone (4) with (pentafluoroethyl)lithium gave 63% of 5, which on treatment with phosphorus oxychloride in pyridine at 90 °C gave a 76% yield of 6.



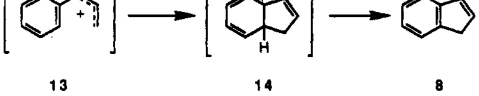
The synthesis of 2-(trifluoromethyl)indene (7) was achieved by the photochemical addition of trifluoromethyl iodide[11] to indene (8) in pyridine. Under the basic conditions provided by the pyridine solvent, the initial addition product 9 was not observed, since it underwent spontaneous base-promoted dehydroiodination under the reaction conditions to give 7 in 37% yield. Only 7 could be detected in the reaction mixture. Thus, 1-(trifluoromethyl)indene (10) was not accessible by this approach.



Two approaches were taken in the synthesis of 10. The first involved the addition of (trifluoromethyl)trimethylsilane[12,13] to 1 in the presence of tetra-n-butylammonium fluoride[13] to give 11, which was desilylated under the reaction conditions to give 12 in 67% yield. Dehydration of 12 with p-toluenesulfonic acid in refluxing benzene, in a procedure similar to that used in the preparation of 3, gave only small amounts of 10.



In view of the limitations encountered in the preparation of 10, both in terms of low yields and the limited generality of the process in terms of the preparation of polyperfluoroalkylated indenes, an alternate route to 10 was explored. It is well known that phenyl-substituted allyl cations such as 13 readily cyclize to give intermediates of



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[1] Petroleum Research Fund Scholar, summer, 1988.

[2] Petroleum Research Fund Scholar, summer, 1989.

[3] Olsson, T.; Wennerström, O. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 293.

[4] Laganis, E. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 6633.

[5] Burk, M. J.; Arduengo, A. J., III; Calabrese, J. C.; Harlow, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 8938. Janulis, E. P., Jr.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1983**, *105*, 3563.

[6] Chambers, R. D.; Greenhall, M. P. *J. Chem. Soc., Chem. Commun.* **1990**, 1128.

[7] Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228.

[8] Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406. Cheong, M.; Basolo, F. *Organometallics* **1988**, *7*, 2041. Lichtenberger, D. L.; Renshaw, S. K.; Basolo, F.; Cheong, M. *Organometallics* **1991**, *10*, 148.

[9] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie GmbH: Weinheim/Bergstr., 1970; pp 58-59. Cohen, S. *J. Am. Chem. Soc.* **1957**, *79*, 1499.

[10] Gassman, P. G.; O'Reilly, N. J. *J. Org. Chem.* **1987**, *52*, 2481.

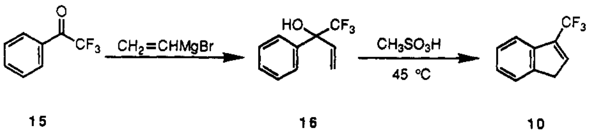
[11] Rasmusson, G. H.; Brown, R. D.; Arth, G. E. *J. Org. Chem.* **1975**, *40*, 672.

[12] Ruppert, I.; Schlich, K.; Volbach, W. *Tetrahedron Lett.* **1984**, *25*, 2195.

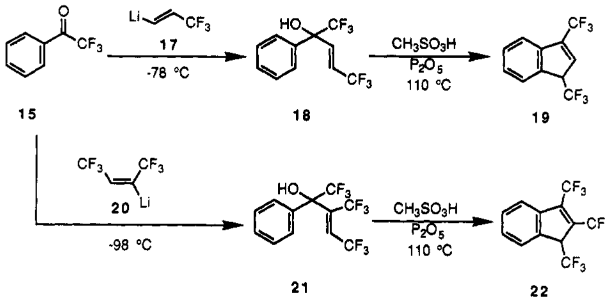
[13] Prakash, G. K. S.; Krishnamurti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393. Krishnamurti, R.; Bellew, D. R.; Prakash, G. K. S. *J. Org. Chem.* **1991**, *56*, 984. Stahly, G. P.; Bell, D. R. *J. Org. Chem.* **1989**, *54*, 2873.

0022-3263/91/1956-5143$02.50/0

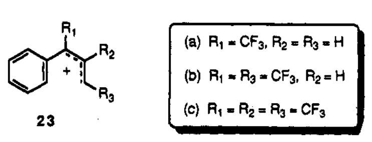
the general formula 14 via electrocyclic ring closure, followed by proton loss to produce indenes of general formula 8.[14] It is also well established that trifluoromethyl substitution severely inhibits allyl cation formation.[15] Thus, the questions were whether trifluoromethyl-substituted phenylallyl cations could be generated, and, once generated, whether cyclization would occur. In order to answer these questions, vinylmagnesium bromide was added to 2,2,2-trifluoroacetophenone (**15**) to give **16** in 84% yield. When **16** was treated with methanesulfonic acid (solvent) at 45 °C for 10 min, a 53% yield of **10** was obtained.



The successful preparation of **10** via an electrocyclic rearrangement suggested that a variety of trifluoromethyl-substituted indenes might be accessible by this path. This proved to be the case. Metal–halogen exchange between methyllithium and 1-iodo-3,3,3-trifluoropropene[16] gave **17**. Addition of **17** to **15** at −78 °C in ether gave a 92% yield of **18**. When **18** was treated with phosphorus pentoxide in methanesulfonic acid (solvent) at 110 °C, **19** was obtained in 76% yield. Similarly, metal–halogen exchange between methyllithium and 2-bromo-1,1,1,4,4,4-hexafluoro-2-butene[17] at −98 °C gave **20**, which on addition of **15** gave an 86% yield of **21**. Exposure of **21** to phosphorus pentoxide in methanesulfonic acid as solvent at 110 °C gave a 63% yield of **22**.



The successful preparation of **10**, **19**, and **22** via electrocyclic rearrangements indicates that phenylallyl cations of general formula **23** bearing one, two, or three trifluoromethyl groups can be generated under strongly acidic conditions. The trifluoromethyl group has been shown to retard the formation of the allyl cation by 10^4–10^6.[15] Solvolysis studies have shown that an α-trifluoromethyl group gives a rate retardation of 10^5–10^7 for tertiary sulfonate esters and 10^3–10^5 for the analogous secondary systems.[18] In view of the significant rate retardation of carbocation formation that is observed when the trifluoromethyl moiety is present, it is significant that an ion such as **23c** can be generated and used productively in a synthetic procedure.



In summary, we have developed synthetic paths to a variety of perfluoroalkylated indenes. Studies designed to evaluate these compounds as electron-withdrawing ligands for transition metals are in progress.

Experimental Section

General. All NMR spectra were recorded on IBM NR/300 FT or Nicolet NIC 1180E nuclear magnetic resonance spectrometers with ^{1}H NMR and ^{13}C NMR referenced to TMS in ppm (δ) and ^{19}F NMR referenced to $CFCl_3$ in ppm (δ). Boiling and melting points are uncorrected. Preparative-scale GLC (10% OV101, 10 ft × 0.25 in. column, 130–200 °C) afforded analytical samples.

All reactions were run under purified Ar or N_2. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under Ar. CH_2Cl_2 was distilled from CaH_2 under Ar.

1-(Pentafluoroethyl)-1-indanol (2). Pentafluoroethyl iodide (13.2 g, 53.7 mmol) was condensed into 40 mL of anhydrous diethyl ether, which was stirred and cooled to −78 °C under N_2. Methyllithium (1.4 M in diethyl ether, 27 mL, 37.8 mmol) was added dropwise with stirring. The reaction mixture was diluted with 50 mL of diethyl ether and stirred at −78 °C for 1 h. A solution of 1-indanone (3.32 g, 25.1 mmol) in 30 mL of diethyl ether was then added dropwise, and the reaction mixture was stirred for an additional 1 h at −78 °C. The reaction mixture was poured into 120 mL of 1 N HCl for quenching. The layers were separated, and the aqueous layer was extracted with three 30-mL portions of diethyl ether. The combined ethereal extracts were washed with 50 mL of distilled water, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed from the filtrate under reduced pressure and the residue was purified by Kugelrohr distillation [pot temperature 99–103 °C (0.7 mm)] to yield 5.58 g (88%) of **2**: ^{1}H NMR ($CDCl_3$) δ 7.55–7.25 (m, 4 H), 3.16–2.94 (m, 2 H), 2.76–2.67 (m, 1 H), 2.44 (s, 1 H), 2.29–2.20 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 144.74, 139.76, 130.10, 127.06, 125.20, 124.91, 119.76 (qt, J_{CF} = 251.6 Hz, J_{CCF} = 36.5 Hz), 115.28 (tq, J_{CF} = 246.7 Hz, J_{CCF} = 34.8 Hz), 83.96 (t, J_{CCF} = 24.2 Hz), 35.62, 29.75; ^{19}F NMR ($CDCl_3$) δ −120.78 (J_{FF} = 278.2 Hz), −124.61 (J_{FF} = 278.1 Hz), −78.49; IR (neat) 3429, 3077, 3033, 2994, 2956, 2864, 1483, 1462, 1343, 1211, 1193, 1153, 1139, 1075, 1064, 887, 761, 742 cm^{-1}; MS *m/e* calcd for $C_{11}H_9F_5O$ 252.0574, found 252.0579. Anal. Calcd for $C_{11}H_9F_5O$: C, 52.39; H, 3.60. Found: C, 52.37; H, 3.67.

1-(Pentafluoroethyl)indene (3). A solution of 50 mL of benzene, 5.43 g (21.5 mmol) of **2**, and a catalytic amount of *p*-toluenesulfonic acid was added to a flask fitted with a Dean–Stark trap and refluxed overnight. The reaction mixture was cooled, diluted with diethyl ether, extracted with three 50-mL portions of a saturated $NaHCO_3$ solution, washed with 60 mL of distilled water, and dried (anhyd Na_2SO_4). After filtration, the solvent was removed under reduced pressure, and the residue was purified by Kugelrohr distillation [pot temperature 100–105 °C (20 mm)] to yield 4.29 g (85%) of **3**. An analytical sample was prepared by MPLC using hexane as solvent: ^{1}H NMR ($CDCl_3$) δ 7.61–7.26 (m, 4 H), 7.06 (t, 1 H), 3.57 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.59, 139.48, 138.98 (t, J_{CCCF} = 7.4 Hz), 133.94 (t, J_{CCF} = 24.9 Hz), 126.89, 126.18, 124.19, 121.44, 119.74 (qt, J_{CF} = 249.4 Hz, J_{CCF} = 39.5 Hz), 112.52 (tq, J_{CF} = 251.2 Hz, J_{CCF} = 39.5 Hz), 38.67; ^{19}F NMR ($CDCl_3$) δ −113.34 (q, J_{FF} = 2.40 Hz), −83.83 (t, J_{FF} = 2.42 Hz); IR (neat) 3076, 1613, 1607, 1463, 1391, 1337, 1261, 1207, 1192, 1126, 1098, 1054, 969, 915, 764, 717 cm^{-1}; MS *m/e* calcd for $C_{11}H_7F_5$ 234.0468, found 234.0465. Anal. Calcd for $C_{11}H_7F_5$: C,

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[14] Olah, G. A.; Asensio, G.; Mayr, H. *J. Org. Chem.* **1978**, *43*, 1518. Deno, N. C.; Pittman, C. U., Jr.; Turner, J. O. *J. Am. Chem. Soc.* **1965**, *87*, 2153.

[15] Poulter, C. D.; Rilling, H. C. *Acc. Chem. Res.* **1978**, *11*, 307. Poulter, C. D.; Satterwhite, D. M.; Rilling, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 3376. Gassman, P. G.; Harrington, C. K. *J. Org. Chem.* **1984**, *49*, 2258. See, also: Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4400.

[16] Haszeldine, R. N. *J. Chem. Soc.* **1950**, 3037.

[17] Haszeldine, R. N. *J. Chem. Soc.* **1952**, 3490.

[18] Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279. Allen, A. D.; Ambidge, I. C.; Che, C.; Micheal, H.; Muir, R. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983**, *105*, 2343. Allen, A. D.; Shahidi, F.; Tidwell, T. T. *J. Am. Chem. Soc.* **1982**, *104*, 2516. Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *J. Am. Chem. Soc.* **1981**, *103*, 3863. Koshy, K. M.; Roy, D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1979**, *101*, 357. Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216. Liu, K.-T.; Kuo, M.-Y.; Shu, C.-F. *J. Am. Chem. Soc.* **1982**, *104*, 211. Liu, K.-T.; Sheu, C.-F. *Tetrahedron Lett.* **1980**, *21*, 4091.

56.42; H, 3.01. Found: C, 56.44; H, 3.04.

2-(Pentafluoroethyl)-2-indanol (5). The synthesis of **5** was achieved by a process analogous to that used in the preparation of **2**. From 3.33 g (25.2 mmol) of 2-indanone (**4**) was obtained 4.01 g (63%) of **5** after purification by Kugelrohr distillation [pot temperature 100–107 °C (2.0 mm)]. An analytical sample was prepared by MPLC using 4% ethyl acetate–96% hexane as solvent: ^{1}H NMR ($CDCl_3$) δ 7.27 (s, 4 H), 3.53 (d, J = 16.8 Hz, 2 H), 3.03 (d, J = 16.8 Hz, 2 H), 2.22 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 138.42, 127.45, 125.13, 119.48 (qt, J_{CF} = 287.2 Hz, J_{CFF} = 36.3 Hz), 113.75 (tq, J_{CF} = 216.4 Hz, J_{CCF} = 35.5 Hz), 82.38 (t, J_{CCF} = 24.9 Hz), 42.40; IR (near) 3445, 3030, 2928, 1748, 1736, 1349, 1220, 1209, 1191, 1142, 1085, 1069, 957, 744, 728 cm^{-1}; MS m/e calcd for $C_{11}H_9F_5O$ 252.0574, found 252.0581. Anal. Calcd for $C_{11}H_9F_5O$: C, 52.39; H, 3.60. Found: C, 52.25; H, 3.63.

2-(Pentafluoroethyl)indene (6). A solution of 5.32 mL (8.75 g, 57.1 mmol) of $POCl_3$ was stirred and cooled at 0 °C, and 27 mL of dry pyridine was added. A solution of 2.66 g (10.5 mmol) of **5** in 53 mL of pyridine was added dropwise at 0 °C. The reaction mixture was warmed to rt and stirred at that temperature for 1 h. The reaction mixture was heated and stirred at 90 °C for 5 h and then cooled to rt. After 12 h, ice was added followed by pouring the reaction mixture into 10% aqueous HCl and ice. The reaction mixture was extracted with diethyl ether, and the aqueous layer was back extracted with three 40-mL portions of diethyl ether. The combined ethereal extracts were washed with 50-mL portions of 10% aqueous HCl, water, and brine. The organic phase was dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation [pot temperature 105–110 °C (20 mm)] to yield 1.88 g (76%) of **6**. An analytical sample was prepared by preparative GLC on a 10-ft OV-101 column at 150 °C to give **6**: ^{1}H NMR ($CDCl_3$) δ 7.52 (m, 2 H), 7.38 (m, 3 H), 3.65 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.37, 141.81, 136.79 (t, J_{CCCF} = 7.9 Hz) 133.38 (t, J_{CFF} = 24.9 Hz), 127.08, 126.97, 124.01, 122.79, 119.70 (qt, J_{CF} = 243.6 Hz, J_{CCF} = 40.6 Hz), 112.82 (tq, JC_F = 263.9 Hz, J_{CCF} = 36.5 Hz), 37.51; IR (neat) 3078, 1618, 1604, 1578, 1463, 1400, 1326, 1200, 1191, 1123, 1071, 972, 882, 852, 754, 733, 716 cm^{-1}; MS m/e calcd for $C_{11}H_7F_5$ 234.0468, found 234.0471. Anal. Calcd for $C_{11}H_7F_5$: C, 56.42, H, 3.01. Found: C, 56.40; H, 3.06.

2-(Trifluoromethyl)indene (7). A thick-walled, resealable tube was charged with 15 mL of dry pyridine and the tube was cooled to −78 °C. Trifluoromethyl iodide (8.6 g, 43.9 mmol) was condensed into the tube. Indene (**8**) (3 mL, 2.98 g, 25.7 mmol) was added under Ar. The tube was sealed, allowed to warm to rt, placed in a Rayonet reactor equipped with eight 3500-Å fluorescent bulbs, and irradiated for 2 weeks. The tube was cooled to −78 °C, opened, and allowed to warm to rt. The contents were poured into 75 mL of cold 3 N HCl, and the product was extracted with three 50-mL portions of diethyl ether. The combined ethereal extracts were washed with 60 mL of distilled water, 60 mL of 10% sodium thiosulfate solution, and 60 mL of saturated brine. The organic phase was dried (anhyd $MgSO_4$) and filtered. The filtrate was concentrated under reduced pressure and the product was purified by Kugelrohr distillation [pot temperature 103–109 °C (20 mm)] to yield 1.76 g (37%) of **7**. This olefin was further purified by preparative GLC on a $^1/_4$ in. × 10 ft column containing 10% SE-30 on Chromosorb W at 130 °C: ^{1}H NMR ($CDCl_3$) δ 7.53 (m, 2 H), 7.36 (m, 3 H), 3.64 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.09, 141.83, 134.83 (q, J_{CCF} = 34.4), 134.66 (q, J_{CCCF} = 5.7 Hz), 127.57, 127.11, 124.27, 123.38 (q, J_{CF} = 268.4 Hz), 123.00, 36.85; ^{19}F NMR ($CDCl_3$) δ −62.00; IR (neat) 3070, 2918, 2899, 1622, 1578, 1463, 1369, 1356, 1257, 1152, 1115, 1030, 926, 885, 867, 715 cm^{-1}; MS m/e calcd for $C_{10}H_7F_3$ 184.0500, found 184.0491. Anal. Calcd for $C_{10}H_7F_3$: C, 65.22; H, 3.83. Found: C, 65.40; H, 3.95.

1-(Trifluoromethyl)-1-indanol (12). A Schlenk flask, equipped for magnetic stirring, was charged with a solution of 2.60 g (20 mmol) of 1-indanone (**1**) in 20 mL of THF. (Trifluoromethyl)trimethylsilane (4.70 g, 33 mmol) was added via syringe. A catalytic amount (10 mg) of tetra-*n*-butylammonium fluoride was added with stirring at rt. Additional tetra-*n*-butylammonium fluoride was added periodically over 10 h, until a total of 250 mg was added. The solution was stirred for an additional 10 h and then 20 mL of 1:1 water/concentrated aqueous HCl was added. This reaction mixture was stirred for 12 h and then diluted with 50 mL of distilled water and 100 mL of diethyl ether. The organic phase was separated, and the aqueous phase was extracted three times with 40-mL portions of diethyl ether. The combined ethereal solutions were washed with 50 mL of water, dried (anhyd $MgSO_4$), and filtered. The filtrate was concentrated under reduced pressure and the residual oil was fractionally distilled to give 2.72 g (67%) of **12**: bp 44–46 °C (0.25 mm). An analytical sample was prepared by preparative GLC at 200 °C: ^{1}H NMR ($CDCl_3$) δ 7.50–7.25 (m, 4 H), 3.14–2.94 (m, 2 H), 2.70–2.60 (m, 1 H), 2.47 (s, 1 H), 2.28–2.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 144.83, 139.15, 130.18, 127.23, 125.93 (q, J_{CF} = 279.0 Hz), 125.21, 124.08, 83.58 (q, J_{CCF} = 30.3 Hz), 35.40, 29.55; IR (neat) 3396, 3076, 3033, 2952, 2861, 1441, 1361, 1236, 1161, 967, 946, 918, 868, 848, 763, 740, 728 cm^{-1}; MS m/e calcd for $C_{10}H_9F_3O$ 202.0606, found 202.0605. Anal. Calcd for $C_{10}H_9F_3O$: C, 59.41; H, 4.49. Found: C, 59.15; H, 4.53.

1-(Trifluoromethyl)indene (10). A solution of 40 mL of benzene, 395 mg (1.93 mmol) of **12**, and a catalytic amount of *p*-toluenesulfonic acid was refluxed for 24 h in a flask equipped with a Dean–Stark trap. The solution was diluted with 50 mL of diethyl ether and washed with 50 mL of saturated $NaHCO_3$ solution. The aqueous wash was back extracted twice with 30-mL portions of diethyl ether and the combined ethereal solutions were washed with 50 mL of water. The organic phase was dried (anhyd $MgSO_4$) and filtered. The solvent was removed under reduced pressure and the residue was vacuum transferred to afford **10**. This material gave spectral data identical with that of **10** prepared by an alternate method (vide post).

2-Phenyl-1,1,1-trifluorobut-3-en-2-ol (16). A solution of 200 mL of anhydrous THF, and 12.53 g (72.0 mmol) of 2,2,2-trifluoroacetophenone (**15**) under Ar, was cooled to 0 °C and 90 mL (90 mmol) of a 1 M THF solution of vinylmagnesium bromide was added dropwise. The reaction mixture was stirred at 0 °C for 90 min and quenched by pouring into 200 mL of 2 N aqueous HCl. The mixture was extracted three times with 75-mL portions of diethyl ether. The combined organic fractions were washed successively with 75 mL of saturated $NaHCO_3$ solution, 75 mL of water, and 75 mL of brine and dried (anhyd $MgSO_4$). The solution was filtered and the solvent was removed under reduced pressure. Vacuum distillation of the residue afforded 12.15 g (84%) of **16** as a clear, colorless liquid: bp 85 °C (8 mm). An analytical sample was prepared by preparative GLC at 150 °C: ^{1}H NMR ($CDCl_3$) δ 7.60 (m, 2 H), 7.41 (m, 3 H), 6.45 (m, 1 H), 5.56 (m, 2 H), 2.63 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 137.01, 135.64, 128.78, 128.35, 126.69, 124.88 (q, J_{CF} = 286.0 Hz), 118.45; IR (neat) 3555, 3478, 3065, 3035, 1451, 1412, 1345, 1326, 1271, 1165, 1096, 1079, 1062 cm^{-1}; MS m/e calcd for $C_{10}H_9F_3O$ 202.0605, found 202.0603. Anal. Calcd for $C_{10}H_9F_3O$: C, 59.41; H, 4.49. Found: C, 59.25; H, 4.67.

1-(Trifluoromethyl)indene (10). A solution of 200 mL of methanesulfonic acid and 6.67 g (33 mmol) of **16** under Ar was heated at 45 °C for 10 min and then quenched by pouring into 500 mL of cold water. The aqueous solution was then extracted three times with 75-mL portions of diethyl ether. The combined ethereal extracts were washed twice with 50-mL portions of saturated $NaHCO_3$ solution, 50 mL of water, and 50 mL of brine and dried (anhyd $MgSO_4$). The solution was filtered and the solvent was removed under reduced pressure. Vacuum distillation of the residue afforded 3.2 g (53%) of **10** as a clear, colorless liquid: bp 54 °C (1.8 mm). An analytical sample was prepared by preparative GLC at 130 °C: ^{1}H NMR ($CDCl_3$) δ 7.63–7.51 (m, 2 H), 7.40–7.29 (m, 2 H), 7.00 (q, J_{HF} = 1.8 Hz, 1 H), 3.53 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.47, 138.88, 136.07 (q, J_{CCCF} = 5.6 Hz), 135.12 (q, J_{CCF} = 34.1 Hz), 126.84, 126.15, 124.18, 122.47 (q, J_{CF} = 269.6 Hz), 120.57, 38.12; IR (neat) 3075, 1461, 1384, 1270, 1224, 1200, 1167, 1118, 1024 cm^{-1}; MS m/e calcd for $C_{10}H_7F_3$ 184.0500, found 184.0498. Anal. Calcd for $C_{10}H_7F_3$: C, 65.22; H, 3.83. Found: C, 65.45; H, 3.94.

2-Phenyl-1,1,1,5,5,5-hexafluoropent-3-en-2-ol (18). A solution of 200 mL of anhydrous diethyl ether and 12.44 g (56.0 mmol) of 1-iodo-3,3,3-trifluoropropene under Ar was cooled to −78 °C and 37.1 mL (52.0 mmol) of a 1.4 M methyllithium–diethyl ether solution was added via cannula from a graduated Schlenk tube. After 5 min, 7.69 g (44.2 mmol) of 2,2,2-trifluoroacetophenone (**15**) was added and stirring was continued for 60 min. The reaction was quenched by pouring onto 100 mL of 1 N aqueous HCl. The ether layer was separated and the aqueous layer was extracted three times with 75-mL portions of diethyl ether. The combined ethereal extracts were washed with 50 mL of saturated $NaHCO_3$ solution, 50 mL of water, and 50 mL of brine and dried (anhyd $MgSO_4$). The solution was filtered and the solvent was removed under reduced pressure. Vacuum distillation of the residue afforded 11.0 g (92%) as a clear, colorless liquid: bp 95 °C (8 mm). An analytical sample was prepared by preparative GLC at 130 °C: ^1H NMR ($CDCl_3$) δ 7.63 (m, 2 H), 7.50 (m, 3 H), 6.95 (d, J = 15.7 Hz, 1 H), 6.32 (dq, J_{HH} = 15.6 Hz, J_{HF} = 6.3 Hz, 1 H), 3.05 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 136.57 (q, J_{CCCF} = 6.3 Hz), 135.58, 129.56, 128.88, 126.33, 124.37 (q, J_{CF} = 271.5 Hz), 122.76 (q, J_{CF} = 268.7 Hz), 122.23 (q, J_{CCF} = 35.2 Hz); IR (neat) 3605, 3478, 3069, 1315, 1263, 1159 cm^{-1}; MS *m/e* calcd for $C_{11}H_8F_6O$ 270.0479, found 270.0464. Anal. Calcd for $C_{11}H_8F_6O$: C, 48.90; H, 2.98. Found: C, 48.83; H, 3.20.

1,3-Bis(trifluoromethyl)indene (19). A solution of 200 mL of methanesulfonic acid, 5 g of phosphorus pentoxide, and 4.79 g (17.8 mmol) of **18** under Ar was heated to 110 °C for 2 h and then quenched by pouring into 400 mL of cold water. The aqueous solution was then extracted three times with 75-mL portions of diethyl ether. The combined ethereal extracts were washed four times with 100 mL of water and 50 mL of brine and dried (anhyd $MgSO_4$). The solution was filtered and the solvent was removed under reduced pressure. Vacuum distillation of the residue afforded 3.4 g (76%) of **19** as a clear, colorless liquid: bp 37 °C (1.5 mm). An analytical sample was prepared by preparative GLC at 130 °C: ^1H NMR ($CDCl_3$) δ 7.71 (d, J = 7.3 Hz, 1 H), 7.62 (d, J = 7.5 Hz, 1 H), 7.53–7.41 (m, 2 H), 6.90 (m, 1 H), 4.28 (q, J_{HF} = 9.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 139.31 (q, J_{CCF} = 34.9 Hz), 138.82, 137.67, 130.22 (q, J_{CCCF} = 2.2 Hz), 129.10, 127.65, 125.23 (q, J_{CF} = 278.3 Hz), 124.93, 121.70 (q, J_{CF} = 270.3 Hz), 121.35, 52.88 (q, J_{CCF} = 30.4 Hz); IR (neat) 3078, 1462, 1300, 1261, 1196, 1145, 1108 cm^{-1}; MS *m/e* calcd for $C_{11}H_6F_6$ 252.0372, found 252.0375. Anal. Calcd for $C_{11}H_6F_6$: C, 52.40; H, 2.40. Found: C, 52.51; H, 2.42.

1,1,1,5,5,5-Hexafluoro-2-phenyl-3-(trifluoromethyl)pent-3-en-2-ol (21). A solution of 300 mL of anhydrous diethyl ether and 13.60 g (55.9 mmol) and 2-bromo-1,1,1,4,4,4-hexafluoro-2-butene under Ar was cooled to −98 °C and 30.7 mL (43.0 mmol) of a 1.4 M methyllithium–diethyl ether solution was added via cannula from a graduated Schlenk tube. After 5 min, 5.22 g (30 mmol) of 2,2,2-trifluoroacetophenone (**15**) was added and stirring was continued for 60 min (while warming to −40 °C). The reaction was quenched by pouring onto 100 mL of 1 N aqueous HCl. The ether layer was separated and the aqueous layer was extracted three times with 75-mL portions of diethyl ether. The combined ethereal extracts were washed with 50 mL of saturated $NaHCO_3$ solution, 50 mL of water, and 50 mL of brine and dried (anhyd $MgSO_4$). The solution was filtered and the solvent was removed under reduced pressure. Vacuum distillation of the residue afforded 8.70 g (86%) of **21** as a clear, colorless liquid: bp 64 °C (1.7 mm). An analytical sample was prepared by preparative GLC at 130 °C: ^1H NMR ($CDCl_3$) δ 7.56 (m, 2 H), 7.45 (m, 3 H), 6.69 (qq, J_{HF} = 8.8 Hz, J_{HF} = 1.3 Hz, 1 H), 2.87 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 139.66 (qq, J_{CCF} = 28.6 Hz, J_{CCCF} = 5.9 Hz), 136.47, 129.98, 129.80 (qq, J_{CCF} = 41.1 Hz, J_{CCF} = 6.3 Hz), 129.04, 126.49, 123.55 (q, J_{CF} = 286.9 Hz), 121.43 (q, J_{CF} = 277.4 Hz), 120.94 (q, J_{CF} = 271.3 Hz), 79.27 (q, J_{CCF} = 31.4 Hz); IR (neat) 3617, 3545, 3070, 1262, 1182 cm^{-1}; MS *m/e* calcd for $C_{12}H_7F_9O$ 338.0353, found 338.0340. Anal. Calcd for $C_{12}H_7F_9O$: C, 42.62; H, 2.09. Found: C, 42.67; H, 2.17.

1,2,3-Tris(trifluoromethyl)indene (22). A solution of 200 mL of methanesulfonic acid, 5 g of phosphorus pentoxide, and 4.7 g (13.9 mmol) of **21** under Ar was heated to 110 °C for 2 h and then quenched by pouring into 400 mL of cold water. The aqueous solution was then extracted three times with 100-mL portions of diethyl ether. The combined ethereal extracts were washed four times with 75-mL portions of water and 50 mL of brine and dried (anhyd $MgSO_4$). The solution was filtered and the solvent was removed on a rotary evaporator. Vacuum distillation of the residue afforded 2.8 g (63%) of **22** as a clear, colorless distillable solid, bp 55 °C (1.5 mm); mp 38–40 °C. An analytical sample was prepared by preparative GLC at 130 °C: ^1H NMR ($CDCl_3$) δ 7.73–7.67 (m, 2 H), 7.56–7.51 (m, 2 H), 4.59 (q, J_{HF} = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 141.68 (qq, J_{CCF} = 36.5 Hz, J_{CCCF} = 3.6 Hz), 137.67, 136.40, 131.33 (q, J_{CCF} = 39.4 Hz), 129.79, 125.37, 124.09 (q, J_{CF} = 280.6 Hz), 123.70, 123.67, 120.84 (q, J_{CF} = 271.3 Hz), 120.59 (q, J_{CF} = 273.2 Hz), 53.65 (q, J_{CCF} = 30.5 Hz); IR (neat) 3083, 2929, 1642, 1588, 1341, 1226, 1162 cm^{-1}; MS *m/e* calcd for $C_{12}H_5F_9$ 320.0247, found 320.0248. Anal. Calcd for $C_{12}H_5F_9$: C, 45.02; H, 1.57. Found: C, 44.96; H, 1.63.

Acknowledgment. We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for grants that supported this investigation.

Registry No. 1, 83-33-0; 2, 134391-51-8; 3, 134391-52-9; 4, 615-13-4; 5, 134391-53-0; 6, 134391-54-1; 7, 134391-55-2; 8, 95-13-6; 10, 134391-57-4; 12, 121692-27-1; 15, 434-45-7; 16, 134418-70-5; 17, 134391-60-9; 18, 134391-61-0; 19, 134391-56-3; 20, 134391-59-6; 21, 134391-58-5; 22, 134418-69-2; C_2F_5Li, 91935-83-0; CF_3I, 2314-97-8; $(CH_3)_3SiCF_3$, 81290-20-2.