Reactions of 1,3-Dibromo-1,1-difluoro Compounds with 1,8-Diazabicyclo[5.4.0]undec-7-ene

Seth Elsheimer,* Christopher J. Foti, and Michael D. Bartberger

Department of Chemistry, University of Central Florida, Orlando, Florida 32816

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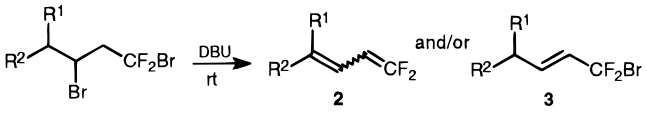
Difluorodienes result from the double dehydrobromination of 4-aryl-1,3-dibromo-1,1-difluorobutanes with DBU. Attempted syntheses of analogous 4-alkyl or 4-alkoxy dienes yield monoelimination products under mild conditions and unexpected trifluoro compounds under more vigorous conditions. 4-Aryl-1,1-difluoro-1,3-butadienes react rapidly with 4-phenyl-1,2,4-triazoline-3,5-dione in Diels−Alder reactions, but these dienes are unreactive toward several other electron-deficient and electron-rich dienophiles.

Diels−Alder reactions are widely used for the synthesis of various six-membered rings,[1] and although fluorinated dienophiles and/or perfluorinated dienes have been used in these cycloadditions, partially fluorinated dienes have received little attention.[2,3] As part of our interest in the chemistry of 1,3-dibromo-1,1-difluoro compounds,[4] we sought a general procedure for the preparation of 1,1-difluorodienes involving double dehydrobromination of **1**. One would expect the product dienes to find utility in [4 + 2] cycloadditions thus providing a source of geminally-fluorinated six-membered rings.

The previous observation that compounds **1** react with hydroxide to yield α,β-unsaturated carboxylates[4c] led us to use the non-nucleophilic base 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU).[5] The room temperature results are summarized in eq 1. When the forming diene bears an



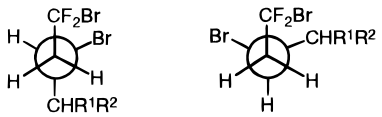
1a: R^1 = H, R^2 = Ph
1b: R^1 = H, R^2 = 3,4-dimethoxyphenyl
1c: R^1 = H, R^2 = pentyl
1d: R^1 = H, R^2 = butoxy
1e: R^1 R^2 = -$(CH_2)_5$-
1f: R^1 R^2 = -$(CH_2)_7$-
1g: R^1 = H, R^2 = 1-hydroxycyclohexyl
1h: R^1 = H, R^2 = 1-cyclohexenyl

(1)

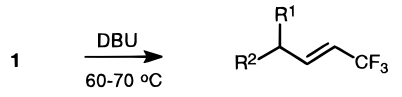
aryl substituent (**2a** and **2b**), the anticipated double dehydrobromination proceeds as expected. If, however, the substituent is alkyl, cycloalkyl, or alkoxy, the reaction stops at monoelimination to yield (*E*)-1,1-difluoro-1-bromo-2-alkenes (**3c**−**g**).

Apparently conjugation with an aryl group lowers the activation energy for formation of difluoro dienes **2**. In order to determine if conjugation with an alkenyl substituent would produce a similar result, we carried out the reaction with DBU on **1h**. After 15 min at room temperature, triene **2h** was observed along with the monoelimination product **3h**. Slightly more vigorous conditions (30 min, 38 °C) gave **2h** as the major product.

The dehydrobrominations of **1** to **3** with DBU were highly stereoselective yielding only the *E* isomers with no *Z* visible by NMR. This probably reflects a conformational preference for *anti*-**1,** which provides maximum separation for the bulky CHR^1R^2 and trihalomethyl groups, over more congested alternatives such as *gauche*-**1**.



The possibility that more vigorous conditions might force a second elimination on compounds **3** led to the treatment of compounds **1c**−**e** with excess DBU at 60−70 °C overnight. Under these conditions, the trifluoromethyl compounds **4c**−**e** were the major organic products obtained[6] (eq 2). This unexpected observation is not



4c: R^1 = H, R^2 = pentyl
4d: R^1 = H, R^2 = butoxy
4e: R^1 R^2 = -$(CH_2)_5$-

(2)

without precedent[7] and is likely the result of fluoride

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(6) Under similar conditions **1a** was converted into (*E*)-4,4,4-trifluoro-1-phenyl-1-butene which has been synthesized by a different route (Burdon, J.; Coe, P. L.; Marsh, C. R.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1967**, 1259), but no spectral data were reported. [^{1}H NMR δ 7.35 (m, 5H), 6.61 (d, J = 15.8 Hz, 1H), 6.11 (dt, J = 15.8 Hz, J' = 7.2 Hz, 1H), 2.98 (qdd, J = 10.6, Hz, J' = 7.2 Hz, J'' = 1.3 Hz, 2H); ^{13}C NMR δ 137.2, 136.7, 129.2, 128.6, 127.0, 126.4 (q, J = 284.1 Hz), 117 (q, J = 3.6 Hz); IR 3000, 2975, 2925, 2850, 1487, 1450, 1425, 1375, 1250, 1050, 950, 912, 875, 812, 750, 687, 650, 612 cm^{-1}.] The atypical regiochemistry of this alkene presumably reflects the thermodynamic advantage of conjugation with the aromatic ring. The isomerization of (*E*)-1,1,1-trifluoro-4-phenyl-2-butene to (*E*)-4,4,4-trifluoro-1-phenyl-1-butene is estimated to be exothermic by 2.09 kcal/mol (Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976).

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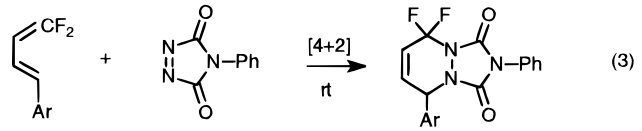
attack on dienes **2c**−**e**. Fluoride ion is generated by partial alkaline hydrolysis (trace moisture and DBU) of the intermediate dienes **2** by a pathway we reported previously.[4d] Attempts to employ an added fluoride source to make this a viable procedure for the preparation of trifluoromethyl compounds **4** have met with some success.[8] Investigations continue toward that end.

Diene **2a** was found to be unreactive toward several electron-deficient dienophiles including maleic anhydride,[9] diethyl malonate,[10] dimethyl acetylenedicarboxylate, dimethyl maleate, *cis*-1,2-bis(phenylsulfonyl)ethylene, and DDQ. Diene **2a** was also inert toward electron-rich dienophiles including butyl vinyl ether, vinyltrimethylsilane, and 1,4-cyclohexadiene. These observations are perhaps surprising in that photoelectron spectroscopy and theoretical studies indicate that vinylic fluorine substituents do not significantly alter the HOMO or LUMO energies.[11]

Unique among the dienophiles examined was 4-phenyl-1,2,4-triazoline-3,5-dione (**5**),[12] which reacted quickly with **2a** or **2b** at room temperature to yield the cycloadducts **6a** and **6b**, respectively (eq 3). To support the hypothesis



(3)

2a: Ar = Ph
2b: Ar = 3,4-dimethoxyphenyl

5 **6**

that **6** results from an electrocyclic process, we monitored by ^{1}H NMR the reaction of a mixture of (*Z*)- and (*E*)-**2a** with incrementally-added **5**. Since (*Z*)-**2a** cannot readily adopt the *s-cis* conformation required for a concerted [4 + 2] cycloaddition, its reaction with dienophiles should be much slower than that of (*E*)-**2a**. As expected, at room temperature in the presence of **5**, (*E*)-**2a** disappears to yield **6a** while (*Z*)-**2a** persists.

Experimental Section

General. Except where otherwise specified, reagents were commercial samples obtained from Aldrich Chemical Co. and used without purification. Analytical and preparative GC was carried out on a 8 ft × 0.25 in. Cu column packed with 10% SE 30 on Chromosorb WHP (He flow = 60 mL/min). All NMR spectra were run in $CDCl_3$ on a Varian Gemini 200 spectrometer operating at 200 MHz for ^{1}H and 50 MHz for ^{13}C. All new compounds were found to be >95% pure by NMR. Infrared spectra were run as capillary films of neat liquids or KBr pellets unless otherwise noted. Melting points are uncorrected.

1,3-Dibromo-1,1-difluoro Compounds 1. General Procedure. Dibromodifluoromethane was added to alkenes in the presence of CuCl and ethanolamine in *tert*-butyl alcohol using a modification of a literature method.[4b,13] The preparation of **1b** is representative.

4-(2,4-Dibromo-4,4-difluorobutyl)-1,2-dimethoxybenzene (1b). A mixture of *tert*-butyl alcohol (15 mL), ethanolamine (2.39 g, 39.1 mmol), CuCl (0.389 g, 3.93 mmol), 1,2-dimethoxy-4-allylbenzene (14.0 g, 78.5 mmol), and dibromodifluoromethane (32.8 g, 156 mmol) was stirred and heated at 85−90 °C in a 185-mL pressure tube for 48 h. The cooled mixture was decanted, leaving behind a black resin which was extracted with 20 mL of hexane. The hexane extract was combined with the decanted reaction mixture, and the resulting solution was filtered through 50 cm^3 of silica gel with 40 mL of hexane. The filtrate was condensed by rotary evaporation, and unreacted olefin was removed by distillation at 0.25 Torr and 80−100 °C leaving 10.32 g of **1b** as a red viscous liquid residue (34%): ^{1}H NMR δ 6.85−6.64 (m, 3H), 4.35 (quintet, J = 6.6 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.15 (m, 1H), 3.11 (m, 1H), 2.95 (td, J = 13.4 Hz, J' = 6.6 Hz, 2H); ^{13}C NMR δ 149.5, 148.8, 129.9, 122.0, 121.2 (t, J = 308 Hz), 112.7, 111.6, 56.2, 56.1, 51.6 (t, J = 21.6 Hz), 46.5, 44.8; IR 1181 cm^{-1}.

1,3-Dibromo-4-butoxy-1,1-difluorobutane (1d). A mixture of *tert*-butyl alcohol (10 mL), ethanolamine (0.800 g, 13.1 mmol), CuCl (0.026 g, 0.26 mmol), 90% allyl butyl ether (3.00 g, 23.6 mmol), and dibromodifluoromethane (11.0 g, 52.4 mmol) was heated for 48 h. Fractional distillation of the crude liquid gave two fractions: (1) bp 50−60 °C (0.4 Torr), 1.10 g of unreacted olefin with some **1d**; (2) bp 63−66 °C (0.3 Torr), 1.04 g (14%) of **1d**. For **1d**: ^{1}H NMR δ 4.25 (quintet, 1H), 3.66 (m, 2H), 3.49 (t, 2H), 3.22 (m, 1H), 2.86 (m, 1H), 1.55 (quintet, J = 7 Hz, 2H), 1.38 (sextet, J = 7 Hz, 2H), 0.9 (t, J = 7 Hz, 3H); ^{13}C NMR δ 121.2 (t, J = 308 Hz), 73.9, 71.5, 49.0 (t, J = 22.0 Hz), 42.7 (t, unresolved), 31.8, 19.4, 14.1; IR 1190 cm^{-1}.

(1,3-Dibromo-3,3-difluoropropyl)cyclohexane (1e). A mixture of *tert*-butyl alcohol (10 mL), ethanolamine (0.831 g, 13.6 mmol), CuCl (0.027 g, 0.273 mmol), vinylcyclohexane (3.00 g, 27.2 mmol), and dibromodifluoromethane (11.5 g, 54.8 mmol) was heated for 18 h. Distillation of the crude liquid product (67−69 °C, 0.3 Torr) gave 4.71 g (54%) of **1e**: ^{1}H NMR δ 4.18 (m, 1H), 2.98 (m, 2H), 1.9−1.6 (m, 5H), 1.6−1.5 (m, 1H), 1.45−1.0 (m, 5H); ^{13}C NMR δ 121.6 (t, J = 308 Hz), 53.7, 50.6 (t, J = 21.3 Hz), 44.1, 31.3, 28.1, 26.3, 26.1, 25.9; IR 1196 cm^{-1}.

(1,3-Dibromo-3,3-difluoropropyl)cyclooctane (1f). A mixture of *tert*-butyl alcohol (10 mL), ethanolamine (0.659 g, 10.8 mmol), CuCl (0.0215 g, 0.217 mmol), vinylcyclooctane (3.00 g, 21.7 mmol), and dibromodifluoromethane (9.17 g, 43.7 mmol) was heated for 24 h. Distillation of the crude liquid (bp 100−106 °C, 0.3 Torr) gave 3.78 g (50%) of **1f**: ^{1}H NMR δ 4.23 (td, J = 6.2 Hz, J' = 2.9 Hz, 1H), 2.95 (m, 2H), 1.85 (m, 1H), 1.75−1.15 (m, 14H); ^{13}C NMR δ 121.5 (t, J = 308.3 Hz), 56.2 (t, unresolved), 50.5 (t, J = 21.2 Hz), 43.2, 33.0, 29.5, 26.8, 26.2, 26.0; IR 1198 cm^{-1}.

1-(2,4-Dibromo-4,4-difluorobutyl)cyclohexanol (1g). A mixture of *tert*-butyl alcohol (15 mL), ethanolamine (3.48 g, 57.0 mmol), CuCl (0.564 g, 5.70 mmol), 1-allylcyclohexanol (16.0 g, 114 mmol), and dibromodifluoromethane (47.6 g, 227 mmol) was heated for 48 h. Fractional distillation of the crude liquid gave two fractions: (1) bp 44−46 °C (0.6 Torr), 5.0 g of unreacted 1-allylcyclohexanol; (2) bp 90−100 °C (0.3 Torr), 10.02 g (25%) of **1g**: ^{1}H NMR δ 4.42 (quintet, J = 6.4, 1H), 3.31 (m, 1H), 2.96 (m, 1H), 2.15 (m, 2H), 1.85 (br s, 1H), 1.7−1.1 (m, 10H); ^{13}C NMR δ 121.3 (t, J = 308.3 Hz), 72.1, 53.6 (t, J = 21.0 Hz), 50.4, 41.6, 38.7, 37.2, 25.7, 22.2, 22.1; IR 1187 cm^{-1}.

1-(2,4-Dibromo-4,4-difluorobutyl)cyclohexene (1h). Phosphorus oxychloride (2.63, 17.2 mmol), contained in a 25-mL addition funnel, was slowly added (*caution!*) to a stirring mixture of **1g** (3.00 g, 8.57 mmol) and pyridine (15 mL) contained in a 50-mL, three-necked flask equipped with a condenser. The mixture was warmed to 50 °C for 5 min, cooled to room temperature, slowly poured over ice, and extracted with diethyl ether (2 × 15 mL). The ether solution was washed twice with 20-mL portions of 3 M HCl, once with water, and then dried over anhydrous calcium chloride. All volatile material was removed by rotary evaporation leaving 2.5 g (88%) of red liquid **1h**: ^{1}H NMR δ 5.5 (m, 1H), 4.3 (m, 1H), 2.9 (m, 2H), 2.55 (d, J = 7 Hz, 2H), 2.3−1.9 (m, 4H), 1.9−1.3 (m, 4H); ^{13}C NMR δ 134.0, 126.8, 121.4 (t, J = 308.1 Hz), 52.0 (t, J = 21.4 Hz), 48.3, 43.8, 28.0, 25.9, 23.2, 22.4; IR 1202 cm^{-1}.

(8) Elsheimer, S.; Foti, C. J.; Foti, M. J. Unpublished results.
(9) The hydrocarbon analog of **2** reacts with maleic anhydride in toluene at 100 °C in 5 h (Grummit, O.; Christoph, F. J. *J. Am. Chem. Soc.* **1951**, *73*, 3479), but **2a** did not react with maleic anhydride in $CDCl_3$ at 60 °C after 24 h.
(10) The roughly analogous 1,1-dimethoxy-1,3-butadiene yields a cycloadduct with diethyl malonate in CCl_4 at 25 °C in 1 h (van Balen, H. C. J. G.; Broekhuis, A. A.; Scheeren, J. W.; Nivard, R. J. F. *Recl. Trav. Chim.* **1979**, *98*, 36), but no reaction was observed for **2a** with diethyl malonate in $CDCl_3$ after 2 days at 61 °C.
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(12) Cookson, R. C.; Gilani, S. S. H.; Stevens, I. D. R. *Tetrahedron Lett.* **1962**, 615.
(13) Burton, D. J.; Kehoe, L. J. *J. Org. Chem.* **1970**, *45*, 1339.

Reactions of 1 with DBU at Room Temperature. General procedure. A 3-fold excess of DBU was added to a stirring ether solution of **1**. The preparation of **2a** is representative.

(4,4-Difluoro-1,3-butadienyl)benzene (2a). DBU (4.17 g, 27.4 mmol) was slowly added to a stirring solution of **1a**[4c] (3.00 g, 9.15 mmol) in 15 mL of ether at a rate that maintained the temperature below 30 °C. Solid DBU hydrobromide salt formed during the addition. The resulting mixture was stirred for an additional 15 min, diluted with 10 mL of ether, and washed with two 20-mL portions of 3 M HCl to dissolve the salt. The ether phase was separated and dried over anhydrous calcium chloride. Rotary evaporation of the volatile material left 0.84 g (55%) of pale yellow liquid **2a**. The *E*/*Z* ratio was determined by GC (column = 150 °C) to be 9:1. The *E* and *Z* isomers were separated by preparative GC. Note: the purified dienes should be stored in solution in the dark below room temperature to prevent polymerization. For (*E*)-**2a**: ^{1}H NMR and IR spectra were consistent with those previously reported:[14] ^{13}C NMR δ 157.4 (dd, J = 298.2 Hz, J' = 292.5 Hz), 137.4, 131.6 (dd, J = 11.7 Hz, J' = 3.4 Hz), 129.2, 128.2, 126.7, 118.3 (dd, J = 4.2 Hz, J' = 2.2 Hz), 83.3 (dd, J = 27.8 Hz, J' = 17.0 Hz). For (*Z*)-**2a**: ^{1}H NMR δ 7.27 (m, 5H), 6.44 (d, J = 11.2 Hz, 1H), 6.14 (t, J = 11.2 Hz, 1H), 5.46 (ddm, J = 23.8 Hz, J' = 11.2 Hz, 1H); ^{13}C NMR δ 158.5 (dd, J = 298.9 Hz, J' = 292.6 Hz), 137.3, 130.3 (dd, J = 11.2 Hz, J' = 7.6 Hz), 128.9, 128.5, 128.0, 119.1 (dd, unresolved), 79.7 (dd, J = 27.8 Hz, J' = 15.6 Hz); IR ($CHCl_3$) 1708 cm^{-1}.

1,2-Dimethoxy-4-(4,4-difluoro-1,3-butadienyl)benzene (2b). In a procedure similar to that used for the preparation of **2a**, a mixture of DBU (5.00 g, 32.8 mmol), **1b** (4.26 g, 11.0 mmol), and diethyl ether (14 mL) was stirred for 10 min at room temperature to yield 1.40 g (56%) of red liquid which was mostly (*E*)-**2b** (<5% *Z* by ^{1}H NMR). Note: to prevent polymerization, **2b** should be stored cold in solution. For (*E*)-**2b**: ^{1}H NMR δ 6.95−6.75 (m, 3H), 6.51 (dd, J = 15.9 Hz, J' = 9.5 Hz, 1H), 6.38 (d, J = 15.9 Hz, 1H), 5.10 (ddd, J = 24.1 Hz, J' = 9.5 Hz, J'' = 1.6 Hz), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR δ 157.2 (dd, J = 297.6, J' = 291.6 Hz), 149.6, 149.4, 131.3 (dd, J = 11.6 Hz, J' = 3.3 Hz), 130.5, 120.0, 116.4 (dd, unresolved), 111.5, 108.7, 83.3 (dd, J = 27.7, J' = 17.0 Hz), 56.2, 56.1; IR 1719 cm^{-1}.

Reaction of 1h with DBU. Preparation of (*E*)-1-(4,4-Difluoro-1,3-butadienyl)cyclohexene (2h) and (*E*)-1-(4-Bromo-4,4-difluoro-2-butenyl)cyclohexene (3h). A mixture of DBU (3.57 g, 23.4 mmol), **1h** (2.50 g, 7.53 mmol), and diethyl ether (15 mL) was reacted at room temperature for 10 min. Workup of a small sample of the reaction mixture showed 19% **2h**, 55% **3h**, and 26% unreacted **1h**. Further reaction at 38 °C for 30 min gave 0.90 g of a yellow liquid that is 75% **2h** and 25% **3h**. Pure samples of **2h** and **3h** were obtained by preparatory GC (column = 150 °C). For **2h**: this unstable compound decomposes rapidly unless stored cold in solution; ^{1}H NMR δ 6.12 (d, J = 15.8 Hz, 1H), 5.95 (dd, J = 15.8 Hz, J' = 10.3 Hz, 1H), 5.73 (m, unresolved, 1H), 4.96 (ddd, J = 24.5 Hz, J' = 10.4 Hz, J'' = 1.8 Hz, 1H), 2.2−2.0 (m, 4H), 1.85−1.5 (m, 4H); ^{13}C NMR δ 156.9 (dd, J = 297.0 Hz, J' = 290.9 Hz), 136.0, 135.6 (dd, J = 11.1 Hz, J' = 3.3 Hz), 130.6, 114.3 (dd, unresolved), 83.2 (dd, J = 27.3 Hz, J' = 17.3 Hz), 26.1, 24.5, 22.6, 22.5; IR 1696, 1613 cm^{-1}. For **3h**: ^{1}H NMR δ 6.20 (dtt, J = 15.5 Hz, J' = 6.8 Hz, J'' = 1.9 Hz, 1H), 5.86 (dtt, J = 15.5 Hz, J' = 9.9 Hz, J'' = 1.4 Hz, 1H), 5.6−5.4 (m, unresolved, 1H), 2.9−2.6 (m, 2H), 2.2−1.94 (m, 2H), 1.94−1.8 (m, 2H), 1.8−1.4 (m, 4H); ^{13}C NMR δ 136.0 (t, J = 7.3 Hz), 134.5, 128.4 (t, J = 23.0 Hz), 124.3, 117.5 (t, J = 301 Hz), 40.0, 28.3, 24.6, 22.5, 22.1; IR 1737, 1666, 1231 cm^{-1}.

(*E*)-1-Bromo-1,1-difluoro-2-nonene (3c). DBU (4.77 g, 31.3 mmol) and **1c**[4b] (3.37 g, 10.5 mmol) in 20 mL of diethyl ether yielded 1.37 g (54%) of colorless liquid **3c**: ^{1}H NMR δ 6.23 (dtt, J = 15.5 Hz, J' = 6.8 Hz, J'' = 1.9 Hz, 1H), 5.86 (dtt, J = 15.5 Hz, J' = 9.8 Hz, J'' = 1.4 Hz, 1H), 2.1 (m, 2H), 1.5−1.2 (m, 8H), 0.9 (t, J = 6.5 Hz, 3H); ^{13}C NMR δ 136.5 (t, J = 7.3 Hz), 126.0 (t, J = 23.3 Hz), 116.4 (t, J = 301.9 Hz), 30.6, 30.2, 27.8, 27.0, 21.6, 13.1; IR 1660, 1225 cm^{-1}.

(*E*)-1-Bromo-4-butoxy-1,1-difluoro-2-butene (3d). A mixture of DBU (0.74 g, 4.9 mmol), **1d** (0.50 g, 1.5 mmol), and diethyl ether (10 mL) yielded 0.19 g (52%) of yellow liquid **3d**: ^{1}H NMR δ 6.35−5.98 (m, 2H), 4.15−3.95 (m, 2H), 3.43 (t, J = 7 Hz, 2H), 1.57 (m, 2H), 1.4 (m, 2H), 0.9 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 133.6 (t, J = 7.0 Hz), 127.0 (t, J = 24.1 Hz), 117.4 (t, J = 301.5 Hz), 71.3, 68.5, 31.9, 19.5, 14.0; IR 1672, 1231 cm^{-1}.

(*E*)-(3-Bromo-3,3-difluoropropenyl)cyclohexane (3e). DBU (1.43 g, 9.39 mmol) and **1e** (1.00 g, 3.12 mmol) in 10 mL of diethyl ether yielded 0.30 g (40%) of colorless liquid **3e**: ^{1}H NMR δ 6.15 (ddt, J = 15.7 Hz, J' = 6.5 Hz, J'' = 1.9 Hz, 1H), 5.75 (dtd, J = 15.7 Hz, J' = 9.8 Hz, J'' = 1.3 Hz, 1H), 2.2−1.9 (m, 1H), 1.8−1.6 (m, 5H), 1.4−1.0 (m, 5H); ^{13}C NMR δ 142 (t, J = 7.0 Hz), 125 (t, J = 23.3 Hz), 118 (t, J = 302 Hz), 39.6, 31.9, 26.1, 25.9; IR 1660, 1230 cm^{-1}.

(*E*)-(3-Bromo-3,3-difluoropropenyl)cyclooctane (3f). A mixture of DBU (1.31 g, 8.60 mmol), **1f** (1.00 g, 2.87 mmol), and diethyl ether (10 mL) reacted to yield 0.30 g (39%) of colorless liquid **3f:** ^{1}H NMR δ 6.15 (ddt, J = 15.7 Hz, J' = 6.5 Hz, J'' = 1.9 Hz, 1H), 5.78 (dtd, J = 15.6 Hz, J' = 9.9 Hz, J'' = 1.3 Hz, 1H), 2.3 (unresolved m, 1H), 1.8−1.3 (m, 14H); ^{13}C NMR δ 143.5 (t, J = 6.7 Hz), 124.7 (t, J = 24.3 Hz), 118 (t, J = 302 Hz), 39.8, 30.8, 27.4, 26.0, 25.0; IR 1660, 1231 cm^{-1}.

(*E*)-1-(4-Bromo-4,4-difluoro-2-butenyl)cyclohexanol (3g). Reaction of DBU (1.91 g, 12.5 mmol), **1g** (1.46 g, 4.17 mmol), and diethyl ether (10 mL) yielded 0.75 g (67%) of yellow liquid **3g**: ^{1}H NMR δ 6.27 (dtt, J = 15.5 Hz, J' = 7.7 Hz, J'' = 1.9 Hz, 1H), 5.88 (dtt, J = 15.5 Hz, J' = 9.8 Hz, J'' = 1.3 Hz, 1H), 2.25 (dt, J = 7.6 Hz, J' unresolved, 2H), 2.0−1.8 (br s, 1H), 1.7−1.0 (m, 10H); ^{13}C NMR δ 133.2 (t, J = 7.4 Hz), 129.9 (t, J = 23.4 Hz), 117.2 (t, J = 302.0 Hz), 71.8, 44.2, 37.6, 25.7, 22.2; IR 1660, 1225 cm^{-1}.

Trifluoromethyl Compounds 4. General Procedure. These compounds are the unexpected products from the reactions of the corresponding dibromides (**1**) with 3 equiv of DBU in dioxane at 60−65 °C for 12−14 h. The preparation of **4c** is representative.

(*E*)-1,1,1-Trifluoro-2-nonene (4c). DBU (2.83 g, 18.6 mmol) contained in a 25-mL addition funnel is slowly added to a stirred mixture of **1c** (2.0 g, 6.21 mmol) in 15−20 mL of dioxane in a three-necked, round-bottomed flask connected to a reflux condenser. During the slow addition of DBU at room temperature, a precipitate of DBU hydrobromide salt is clearly visible. After the addition of DBU was complete, the reaction mixture was heated at 65 °C for 12 h. The dark brown reaction mixture was cooled, diluted with 15 mL of diethyl ether, and washed twice with 15-mL portions of 3 M HCl, at which point the solids dissolved. The organic phase was separated, dried over anhydrous calcium chloride, and then concentrated under reduced pressure to yield 0.35 g of crude liquid **4c**. GC and ^{1}H NMR showed minor contamination by **3c** and two other minor products which were not characterized but had ^{1}H NMR signals consistent with (*E*)- and (*Z*)-**2c** A pure sample of **4c** was isolated by preparative GC (column T = 150 °C): ^{1}H NMR δ 6.38 (dtq, J = 15.8 Hz, J' = 6.8 Hz, J'' = 2.1 Hz, 1H), 5.61 (dqt, J = 15.8 Hz, J' = 6.4 Hz, J'' = 1.6 Hz, 1H), 2.13 (m, 2H), 1.5−1.15 (m, 8H), 0.89 (t, 6.6 Hz, 3H); ^{13}C NMR δ 141.3 (q, J = 6.5 Hz), 123.6, (q, J = 269.9 Hz), 118.6 (q, J = 33.1 Hz), 31.7, 31.6, 28.8, 28.0, 22.7, 14.1; IR 1678, 1273, 1190, 1132 cm^{-1}.

(*E*)-4-Butoxy-1,1,1-trifluoro-2-butene (4d). A stirred mixture of DBU (4.24 g, 27.9 mmol) and **1d** (3.0 g, 9.3 mmol) in 10 mL of dioxane was heated at 65 °C for 12 h. Workup gave 0.49 g of crude product **4d**. A pure sample of **4d** was isolated by preparative GC (column T = 120 °C): ^{1}H NMR δ 6.42 (dm, J = 15.8 Hz, 1H), 5.92 (dqt, J = 15.8 Hz, J' = 6.5 Hz, J'' = 1.9 Hz, 1H), 4.08 (m, 2H), 3.48 (t, J = 6.6 Hz, 2H), 1.6 (m, 2H), 1.4 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 137.5 (q, J = 6.3 Hz), 123.6, (q, J = 269.7 Hz), 118.8 (q, J = 34.1 Hz), 71.3, 68.7, 31.9, 19.5, 14.0.

(*E*)-(3,3,3-Trifluoro-1-propenyl)cyclohexane (4e). A stirred mixture of DBU (4.29 g, 28.2 mol) and **1e** (3.0 g, 9.4 mmol) in 10 mL of dioxane was heated at 60 °C for 14 h.

(14) (a) Burton, D. J.; Wheaton, G. A. *J. Org. Chem.* **1983**, *48*, 917. (b) Hayashi, S.; Nakai, T.; Ishikawa, N.; Burton, D. J.; Naae, D. G.; Kesling, H. S. *Chem. Lett.* **1979**, *8*, 983.

Workup gave 0.50 g of crude liquid **4e**. A pure sample of **4e** was isolated by preparative GC (column T = 120 °C): ^{1}H NMR δ 6.33 (ddq, J = 15.9 Hz, J' = 6.5 Hz, J'' = 1.9 Hz, 1H), 5.54 (dq, J = 15.9 Hz, J' = 6.3 Hz, 1H), 2.2−2.0 (m, 1H), 1.8−1.6 (m, 5H), 1.4−1.1 (m, 5H); ^{13}C NMR δ 146.3 (q, J = 6.2 Hz), 124.0, (q, J = 269.8 Hz), 116.5 (q, J = 33.4 Hz), 39.9, 31.9, 26.0, 25.8; IR 1678, 1289, 1125 cm^{-1}.

Attempted Diels−Alder Reactions of 2 with Various Dienophiles. Preliminary experiments were carried out with excess dienophile in $CDCl_3$ in sealed NMR tubes. The samples were periodically examined by ^{1}H NMR for disappearance of starting material. If no apparent reaction was observed at room temperature the sample was warmed to 60 °C and reexamined after several hours.

Reaction of 2a with 5. A solution of dichloromethane and **5** (1.05 g, 6.00 mmol) was slowly dripped into a stirring solution of **2a** (1.00 g, 6.02 mmol) in 15 mL of dichloromethane at room temperature. The carmine color of **5** quickly disappeared as the reaction occurred. The solvent was removed under vacuum yielding 2.10 g of crude solid, which was purified by column chromatography (silica gel 230−400 mesh, 60 Å, 50:50 hexane:ethyl acetate). A white solid, **6a**, was obtained (1.30 g, 63%, mp = 184−187 °C): ^{1}H NMR δ 7.48−7.28 (m, 10H), 6.47 (dd, J = 10.3 Hz, J' = 4.8 Hz, 1H), 6.22 (ddm, J = 10.2, J' = 5.9 Hz, 1H), 5.72 (t, J = 4.8 Hz, 1H); ^{13}C NMR δ 150.4, 150.0, 134.0, (dd, J = 9.2 Hz, J' = 6.9 Hz), 132.7, 130.7, 130.4, 129.7, 129.2, 127.4, 126.0, 120.8 (dd, J = 31.5 Hz, J' = 29.0 Hz), 120.6, 114.4 (dd, J = 265.6 Hz, J' = 238.6 Hz), 56.9; IR 1790, 1737, 1490, 1420, 1290, 1132, 1061 cm^{-1}; HRMS calcd for $C_{18}H_{13}F_2N_3O_2$ M^+ = 341.0977, found M^+ = 341.0965 (intensity = 78%), base peak = 166 amu.

Reaction of 2b with 5. The procedure described above for reaction of **2a** with **5** was followed. A mixture of **5** (0.790 g, 4.51 mmol) and **2b** (1.02 g, 4.51 mmol) in 15 mL of dichloromethane was reacted at room temperature. Column chromatography yielded 1.35 g (75%) of the white solid **6b** (mp = 130−134 °C): ^{1}H NMR δ 7.5−7.3 (m, 5H), 6.97 (dd, J = 10.2 Hz, J' = 2 Hz, 1H), 6.94 (d, J = 2 Hz, 1H), 6.84 (d, J = 10.2 Hz, 1H), 6.48 (dd, J = 10.2 Hz, J' = 4.8 Hz, 1H), 6.21 (ddm, J = 10.2 Hz, J' = 6.2 Hz, 1H), 5.67 (tm, J = 4.8 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H); ^{13}C NMR δ 150.7, 150.5, 150.0 (d, J < 2 Hz), 149.7, 134.1 (dd, J = 9.1 Hz, J' = 6.7 Hz), 130.7, 129.7, 129.2, 126.0, 124.8, 121.8, 120.8 (dd, J = 31.5 Hz, J' = 28.6 Hz), 114.4 (dd, J = 264.6 Hz, J' = 236.4 Hz), 112.1, 111.6, 56.7, 56.2. IR 1784, 1719, 1584, 1519, 1419, 1290, 1266, 1237, 1167, 1143, 1055, 1020 cm^{-1}; HRMS calcd for $C_{20}H_{17}N_3O_4F_2$ M^+ = 401.1188, found M^+ = 401.1161.

Relative Reactivity of (*E*)-2a versus (*Z*)-2a with Dienophile 5. A small sample of the 9:1 isomeric mixture of **2a** was enriched in *Z* isomer by isolating some (*Z*)-**2a** from another run and adding it to a sample of the original mixture. The enriched mixture was dissolved in a small volume of $CDCl_3$ and the *E*/*Z* ratio was determined to be 1.7:1 by ^{1}H NMR integration of the C(2) hydrogens of the *E* and *Z* isomers (δ 5.12 and 5.46, respectively). The NMR sample was sequentially treated with four small aliquots of **5** in $CDCl_3$ and examined by ^{1}H NMR after each addition. The relative areas of peaks corresponding to each isomer of **2a** revealed that the *Z* isomer persisted while the *E* isomer progressively disappeared as **6a** was formed.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **1b**, **1d**−**h**, (*E*)-**2a**, (*Z*)-**2a**, (*E*)-**2b, 2h**, **3c**−**h**, **4c**−**e**, **6a,** and **6b**, and the ^{1}H NMR study of the relative reactivity of (*E*)- and (*Z*)-**2a** with **5** (44 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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