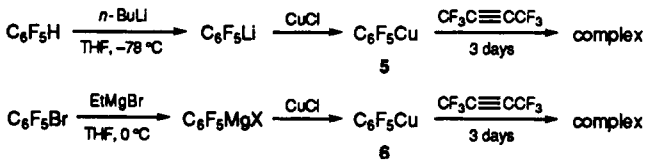
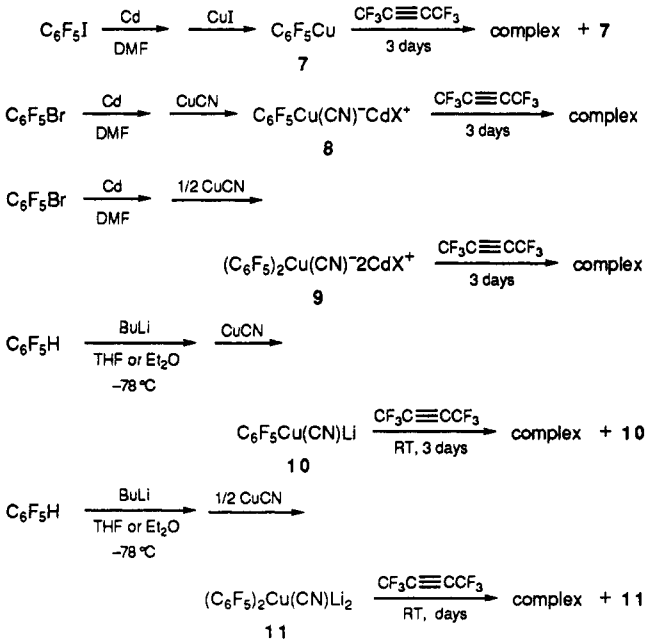
Attempts to add C_6F_5Cu to various other alkynes were unsuccessful. For example, no reaction occurred with diphenylacetylene, whereas terminal alkynes, such as phenylacetylene and $CF_3C{\equiv}CCH$ underwent an acid–base reaction in the presence of the arylcopper reagent to give pentafluorobenzene and the corresponding copper acetylide.

Furthermore, we explored the utility of the addition of C_6F_5Cu to *F*-2-butyne when the arylcopper reagent was prepared by the two procedures of Tamborski,[16,17] in order to ascertain the effect, if any, of solvent and metal salts on the system.

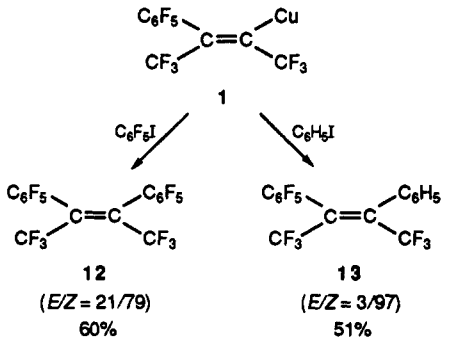


In both cases, the intermediate complex was detected by ^{19}F NMR, but no further rearrangement to 1 was observed. Since these systems required ethereal solvents, we surmised that the addition was hindered by the absence of the highly-coordinating solvent DMF. Accordingly, we repeated the arylcopper synthesis from the Grignard reagent and performed a solvent exchange from ether to DMF. Although the ^{19}F NMR spectrum of the resulting solution was remarkably similar to that of the C_6F_5Cu prepared from the corresponding cadmium species, the arylcopper was inert toward hexafluorobutyne and unreacted copper reagent still remained after a period of 3 days. These observations suggest that the nature of the inorganic salts in solution is a key element of the synthesis. Other C_6F_5Cu syntheses and the results of hexafluoro-2-butyne addition are summarized in the following reactions.

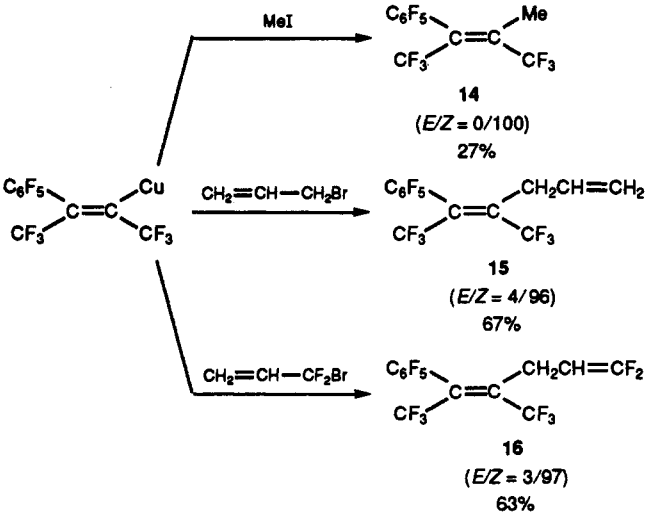


The syntheses of copper reagents 8–11 were designed according to the "lower and higher order mixed cuprate" chemistry that has been developed by Lipshutz *et al.*[27] As illustrated in the above reactions, none of the alternative methods of (pentafluorophenyl)copper preparation proved to be synthetically viable in the carbocupration reaction; therefore, it would appear that the addition of C_6F_5Cu to *F*-2-butyne is a reaction that is unique to the novel arylcopper reagent which we have developed.

Functionalization of 1. Vinylcopper reagent 1 can be coupled with a variety of organic electrophiles to afford the corresponding substituted alkenes in moderate to good yields. For example, arylation reactions take place readily under mild conditions. When 1 equiv of iodopentafluorobenzene (C_6F_5I) is added at room temperature to the reaction mixture containing 1, compound 12 is obtained. Similarly, 1 and iodobenzene afford compound 13.



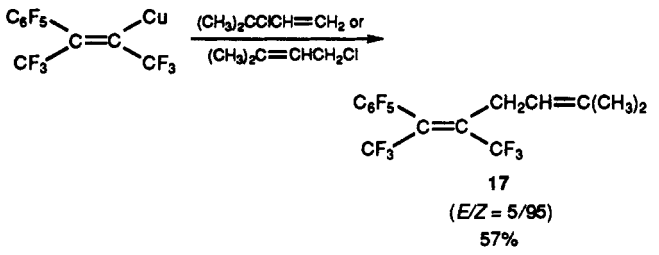
Reagent 1 can also be readily alkylated. When 1 is heated to 60 °C overnight with iodomethane, 14 is obtained, though in low yield. Alkylation can also be effected with allyl halides in a regiospecific manner. Allyl bromide reacts with 1 at 0 °C to give diene 15 in good yields; with 3-bromo-3,3-difluoro-1-propene, where more than one regioisomer is possible, the coupling is regiospecific to afford 16, the isomer which results from a formal S_N2' attack. The



regiochemistry was assigned on the basis of two vinyl fluorines in the ^{19}F NMR spectrum of the product, as well as the characteristic $=CF_2$ stretch of 1765 cm^{-1} in the FTIR spectrum.

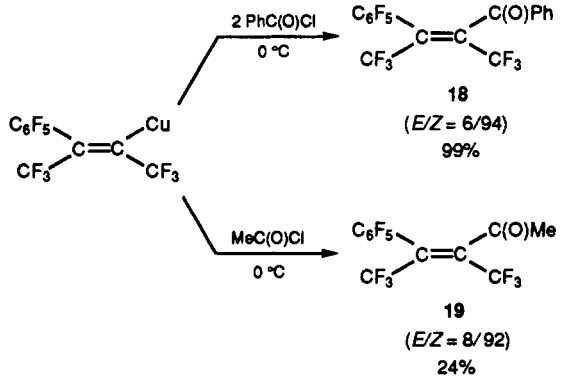
Further evidence for the regiospecificity observed in the functionalization of 1 was provided by reactions with 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene, both of which gave the same product, 17, exclusively:

(27) Lipshutz, B. H. *Synlett* **1990**, *3*, 119.



With 3-chloro-3-methyl-1-butene, the formation of **17** resulted from a formal S_N2'-type pathway, which is presumably favored due to the hindered steric environment of carbon 3.

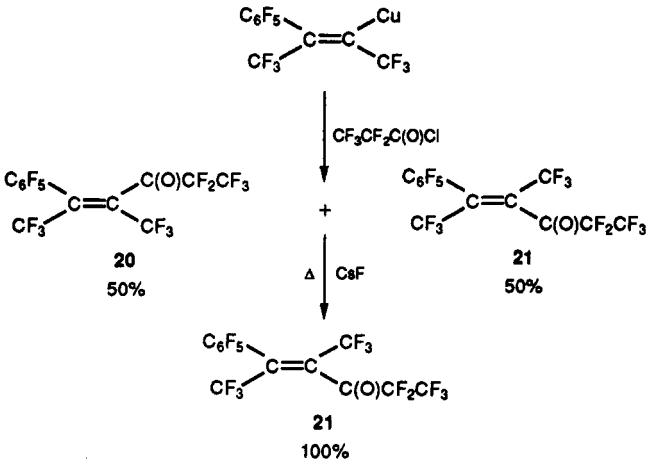
The vinylcopper species can also be efficiently quenched with an acyl halide. This transformation is demonstrated by the reaction of **1** with benzoyl chloride or acetyl chloride at 0 °C. Interestingly, if only 1 equiv of PhC(O)Cl is added



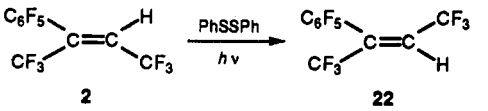
to the reaction mixture that contains **1**, only a 50% conversion to **18** is observed, with half of the starting material remaining unreacted. However, if a second equivalent of benzoyl chloride is added, the mixture proceeds to completion, and, in fact, results in a nearly quantitative isolated yield of the desired, α,β-unsaturated ketone **18**. The reason for this peculiar stoichiometric requirement is not known, although it seems to be quite common for coupling reactions between benzoyl chloride and other organometallic reagents in our laboratories.

In nearly all of the preceding functionalization reactions, coupling occurred with good-to-excellent stereoselectivity. For the reaction of **1** with iodopentafluorobenzene, however, 21% isomerization occurred, and a similar phenomenon is observed in the reaction of **1** with a *perfluorinated* acid halide. For example, when **1** was stirred with $CF_3CF_2C(O)Cl$ at 0 °C, it was observed that, in addition to the expected product **20**, approximately 50% of the isolated material consisted of the *E* isomer **21**, which presumably resulted from a halide-induced rotation about the carbon–carbon double bond. Although attempts to isolate **20** with a greater stereochemical integrity met with little success, it was subsequently discovered that further isomerization of the mixture of isomers can be induced to afford only the *E* isomer **21**. This isomerization can be effected chemically by the simple addition of a fluoride ion source, such as CsF, and gentle heating (50–100 °C).

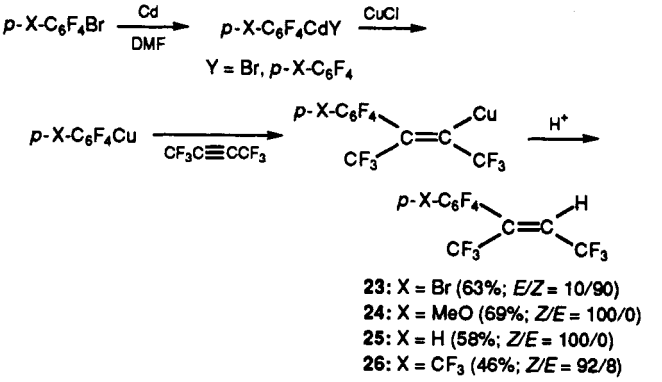
We then attempted a fluoride ion-induced isomerization of a stereochemically pure alkene that we had already isolated. Protonated alkene **2** was treated with a fluoride ion source and subjected to prolonged heating; however, no change was observed in the ^{19}F NMR spectrum of the treated sample. Compound **2** was then irradiated with a UV lamp. After 24 h, a significant amount (24–37%) of



isomerization occurred, but no further isomerization was noted during the course of four more days of photolytic exposure. Finally, a catalytic amount of the radical initiator PhSSPh was added to the irradiated sample, and complete isomerization to **22** was achieved within 5 h.

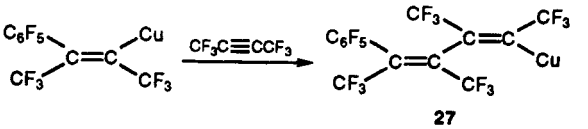


The generality of the addition reaction of hexafluoro-2-butyne with arylcopper reagents was demonstrated with copper reagents substituted in the *para* position. As



demonstrated by the preceding examples, arylcopper reagents that contain either electron-withdrawing or electron-releasing groups in the *para* position can undergo the addition to hexafluoro-2-butyne.

Finally, we describe another phenomenon that was observed in the addition reaction. It is important that the stoichiometry of the addition reaction is reasonably accurate, and that only a slight excess of butyne is added. If two or more equivalents of the alkyne are utilized, the vinylcopper reagent initially produced may undergo a second addition to the butyne to afford the conjugated dienylcopper reagent **27**.



Our preliminary results indicate that the "double addition" is affected by temperature, pressure, and time, and that either the vinylcopper reagent **1** or the dienyl-

copper reagent 27 can be produced exclusively depending on the choice of reaction conditions. Detailed discussion concerning the scope of this double addition will be included in future reports.

Conclusion

We have described a novel, efficient procedure for the preparation of (pentafluorophenyl)copper in high yields. The thermally stable copper reagent thus produced undergoes regio- and stereospecific *syn* addition to hexafluoro-2-butyne to afford the corresponding vinylcopper reagent 1 in ^{19}F NMR yields of 60–80%. Once formed, the vinylcopper species can be coupled with a variety of electrophiles to give highly substituted fluoroalkenes. The functionalization reaction typically proceeds with excellent retention of stereochemistry, and in those cases where it does not, fluoride ion-induced isomerization can be performed in order to obtain one stereoisomer exclusively. Partial success has also been achieved with photolytic isomerization of a pure alkene product. The generality of the addition reaction has been demonstrated by successfully utilizing *para*-substituted arylcopper reagents in place of (pentafluorophenyl)copper.

Experimental Section

General. All reactions were performed in an oven-dried apparatus that consisted of a two- or three-necked flask equipped with a Teflon-coated magnetic stir bar and a nitrogen tee connected to a nitrogen source and mineral oil bubbler. Reported boiling points were determined during fractional distillation by means of a partial immersion thermometer and are uncorrected. ^{19}F NMR, ^1H NMR, and ^{13}C NMR spectra were generated on JEOL FX90Q 90 MHz and Bruker AC 300-MHz multinuclear spectrometers. ^{19}F NMR spectra were referenced against internal $CFCl_3$, ^1H and ^{13}C NMR spectra were referenced against internal TMS, and all chemical shifts are reported in parts per million downfield of the standard. FT-IR spectra were recorded as CCl_4 solutions on a Mattson Cygnus 100 FT-IR and absorbance frequencies reported in cm^{-1}, and GC-MS spectra were obtained at 70 eV, in the electron impact mode. HIgh resolution mass spectral data were collected on a VG Analytical ZAB-HF Mass Spectrometer, operated at 70 eV in the electron impact mode. GLPC analyses were performed on a 5% OV-101 column with a thermal conductivity detector. Where indicated, final purifications were performed on a Varex Preparative Scale Gas Chromatograph using a 1 m × $^1/_2$ in. OV-101 column.

Materials. Cadmium powder was activated by stirring with dilute acid, washing with water and acetone, and drying *in vacuo* overnight. DMF was purified and dried by vacuum distillation from calcium hydride. Cuprous chloride was purified by dissolving in concentrated HCl, diluting with 1 L of water, suction filtration, rinsing with acetone, and removing the acetone *in vacuo*. C_6F_5Br, $CF_3C{\equiv}CCF_3$, C_6F_5I, and *p*-Br-C_6F_4Br were obtained from PCR Specialty Chemicals, Gainesville, FL, and utilized without further purification. *p*-H-C_6F_4Br was prepared according to the method of Tamborski and Soloski.[28] Alkyl, acyl, and allyl halides were obtained from Aldrich Chemical Co. and were distilled from CaH_2 prior to use. *p*-MeO-C_6F_4Br was prepared by treatment of C_6F_5Br with NaOMe/MeOH, washing with water, and drying over 4A molecular sieves.

p-CF_3-C_6F_4Br was prepared by the following method: CF_3-CdX was synthesized according to the procedure by Burton and Wiemers.[29] C_6F_5Br and CuCl were added, and the mixture was heated at 60 °C for 2 days. The reaction mixture was steam distilled, and the resulting organic material was dried over 4A molecular sieves and distilled. The $CF_3C_6F_5$ was combined with $AlBr_3$ and heated to reflux. The resulting *p*-CF_3-C_6F_4Br was isolated by fractional distillation.

All other chemicals were obtained from Aldrich Chemical Co. and were used without further purification.

Preparation of 1. (Pentafluorophenyl)cadmium was prepared on a 100-mmol scale according to the procedure reported by Burton and Heinze.[26] The solid material in the flask was allowed to settle, and the remaining liquid was carefully decanted *via* syringe and added to another flask. To the stirred cadmium reagent was added 9.9 g (100 mmol) of CuCl. The ^{19}F NMR yield of the resultant (pentafluorophenyl)copper reagent was 88%, based on bromopentafluorobenzene. ^{19}F NMR (DMF): −112.4 (m, 2F), −164.0 (t, $^3J_{F,F}$ = 19 Hz, 1F), −165.3 (m, 2F). The reaction flask was fitted with a condenser containing methanol that was cooled to −100 °C with a Neslab Cryocool low temperature probe. The hexafluoro-2-butyne (17.8 g, 110 mmol) was condensed into the reaction mixture. After a period of 2–3 days at ambient temperature, the resulting vinylcopper species 1 was present in an 80% ^{19}F NMR yield. ^{19}F NMR (DMF): −54.9 (q, $^5J_{F,F}$ = 12 Hz, 3F), −61.1 (q, $^5J_{F,F}$ = 12 Hz, 3F), −142.9 (m, 2F), −159.0 (t, $^3J_{F,F}$ = 19 Hz, 1F), −165.5 (m, 2F).

Preparation of 2. To a flask containing 120 mL of a 0.5 *M* solution of 1 (60 mmol) was added aqueous HCl (20 mL, 6 *M*) *via* syringe. The resultant precipitate was removed by filtration, and the bottom layer of the filtrate was washed with water and dried over 4A molecular sieves. Distillation of the crude product resulted in 8.5 g (43%) of 2: GLPC purity = 92%; bp 152–153 °C; ^{19}F NMR ($CDCl_3$) −59.9 (qd, $^5J_{F,F}$ = 11 Hz, $^3J_{F,H}$ = 8 Hz, 3F), −61.5 (qt, $^5J_{F,F}$ = 11 Hz, $^5J_{F,F}$ = 5 Hz, 3F), −139.3 (m, 2F), −149.9 (tt, $^3J_{F,F}$ = 21 Hz, $^4J_{F,F}$ = 2 Hz, 1F), −160.4 (m, 2F); ^1H NMR ($CDCl_3$) 6.4 (q, $^3J_{H,F}$ = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$): 107.9 (m), 119.9 (q, $^1J_{C,F}$ = 273 Hz), 133.0 (q, $^2J_{C,F}$ = 40 Hz), 136.3–146.4 (m); FT IR (CCl_4) 2932 (w), 1682 (s), 1502 (s), 1279 (s), 1195 (s); MS 330 (25.1), 261 (78.2), 192 (45.7), 123 (15.5), 117 (12.9), 69 (100.0); high resolution MS calcd 329.9903, obsvd 329.9871.

Preparation of 3. To a flask containing 120 mL of a 0.5 *M* solution of 1 (60 mmol) was added iodine (15.2 g, 60 mmol). After 1 h, the volatile components of the reaction mixture were removed by vacuum transfer, and the organic portion of the distillate was washed with saturated aqueous $NaHSO_3$ and water and dried over 4A molecular sieves. Distillation of the crude product resulted in 12.6 (46%) of 3: GLPC purity = 95%; bp 40–42 °C (1.65 mmHg); ^{19}F NMR ($CDCl_3$) −58.3 (qt, $^5J_{F,F}$ = 12 Hz, $^5J_{F,F}$ = 3 Hz, 3F), −58.3 (qt, $^5J_{F,F}$ = 12 Hz, $^6J_{F,F}$ = 2 Hz, 3F), −139.6 (dqq, $^4J_{F,F}$ = 3 Hz, $^5J_{F,F}$ = 3 Hz, $^6J_{F,F}$ = 2 Hz, 2F), −149.7 (tt, $^3J_{F,F}$ = 21 Hz, $^4J_{F,F}$ = 3 Hz, 1F), −160.0 (m, 2F); ^{13}C NMR ($CDCl_3$) 110.0 (q, $^2J_{C,F}$ = 40 Hz), 110.3 (m), 118.9 (q, $^1J_{C,F}$ = 277 Hz), 119.7 (q, $^1J_{C,F}$ = 275 Hz), 136.3–145.3 (m); FT IR (CCl_4) 1504 (s), 1177 (s), 1140 (s), 1079 (m), 1027 (s); MS 456 (38.2), 260 (40.2), 241 (100.0), 141 (36.6), 127 (37.6), 69 (50.7); high resolution MS calcd 455.8869, obsvd 455.8891.

Preparation of 4. Five millimoles of C_6F_5Cu was combined with $C_6F_{13}C{\equiv}CCF_2H$ (1.97 g, 5 mmol) in a flask. The mixture was stirred for 2 h, after which time 5 mL of 6 *M* HCl was added. The lower, organic layer was removed by pipet, washed with water, and dried over 4A molecular sieves. Distillation of the crude product resulted in 1.5 g (53%) of 4: GLPC purity = 99%, bp 85–88 °C (12 mmHg); ^{19}F NMR ($CDCl_3$) −81.5 (t, $^4J_{F,F}$ = 8.5 Hz, 3F), −107.2 (m, 2F), −116.0 (ddt, $^2J_{F,H}$ = 54 Hz, $^3J_{F,H}$ = 15 Hz, $^5J_{F,F}$ = 8.5 Hz, 2F), −121.8 (m, 2F), −123.4 (m, 4F), −126.6 (m, 2F), −139.2 (m, 2F), −151.5 (tt, $^3J_{F,F}$ = 20 Hz, $^4J_{F,F}$ = 2 Hz, 1F), −161.5 (m, 2F); ^1H NMR ($CDCl_3$) 6.10 (t, $^3J_{H,H}$ = 15 Hz, 1H), 6.80 (t, $^2J_{H,F}$ = 54 Hz, 1H); ^{13}C NMR ($CDCl_3$) 108.4 (tt, $^1J_{C,F}$ = 239 Hz, $^3J_{C,F}$ = 7 Hz), 113.8 (t, $^2J_{C,F}$ = 32 Hz), 115.6 (t, $^2J_{C,F}$ = 33 Hz), 116.6 (t, $^2J_{C,F}$ = 33 Hz), 118.8 (t, $^2J_{C,F}$ = 33 Hz), 128.5 (tt, $^2J_{C,F}$ = 26 Hz, $^3J_{C,F}$ = 7 Hz), 134.4 (t, $^2J_{C,F}$ = 26 Hz), 136.2–146.0 (m); FT IR (CCl_4) 3058 (w), 1503 (m), 1237 (s), 1117 (s), 1066 (s); MS 562 (12.4), 293 (100.0), 243 (51.8), 224 (21.8), 223 (21.7), 205 (15.3); high resolution MS calcd: 561.9837, obsvd 561.9818.

Preparation of 12. To a flask containing 90 mL of a 0.5 *M* solution of 1 (45 mmol) was added C_6F_5I (13.2 g, 45 mmol) *via* syringe. The mixture was stirred overnight, and the contents of the flask were poured into water and filtered. The lower, organic layer was removed by pipet, washed with water, and dried over 4A molecular sieves. Distillation of the crude product resulted in 13.75 g (60%) of 12: GLPC purity = 100%, bp 68–71 °C (1.65

(28) Tamborski, C.; Soloski, E. *J. Org. Chem.* **1966**, *31*, 746.
(29) Burton, D.; Wiemers, D. *J. Am. Chem. Soc.* **1985**, *107*, 5014.

mmHg); ^{19}F NMR ($CDCl_3$) −60.1 (tt, $^5J_{F,F}$ = 2 Hz, $^6J_{F,F}$ = 2 Hz, 6F), −137.7 (m, 4F), −147.8 (tt, $^3J_{F,F}$ = 21 Hz, $^4J_{F,F}$ = 3 Hz, 2F), −159.3 (m, 4F); ^{13}C NMR ($CDCl_3$) 106.7 (m), 119.9 (q, $^1J_{C,F}$ = 277 Hz), 133.0 (q, $^2J_{C,F}$ = 43 Hz), 136.4–146.2 (m); FT IR (CCl_4) 1656 (m), 1184 (s), 1134 (s), 1052 (s); MS: 496 (67.2), 427 (67.2), 358 (100.0), 289 (28.1), 69 (76.6); high resolution MS calcd 495.9745, obsvd 495.9752.

Preparation of 13. A volume of 50 mL of a 0.5 *M* solution of 1 (25 mmol) was combined with C_6H_5I (5.6 g, 25 mmol) in a flask. The mixture was heated overnight, poured into water, and filtered. The lower organic layer was removed by pipet, washed with water, and dried over 4A molecular sieves. Distillation of the crude product resulted in 5.2 g (51%) of **13**: GLPC purity = 96%, bp 72–75 °C (1.65 mmHg); ^{19}F NMR ($CDCl_3$) −59.9 (qm, $^5J_{F,F}$ = 12 Hz, 3F), −60.5 (qm, $^5J_{F,F}$ = 12 Hz, 3F), −138.5 (m, 2F), −151.2 (tt, $^3J_{F,F}$ = 20 Hz, $^4J_{F,F}$ = 3 Hz, 1F), −161.5 (m, 2F); ^{1}H NMR ($CDCl_3$) 7.12–7.58 (m, 5H); ^{13}C NMR ($CDCl_3$) 108.6 (t, $^2J_{C,F}$ = 20 Hz), 120.6 (q, $^1J_{C,F}$ = 275 Hz), 120.9 (q, $^1J_{C,F}$ = 275 Hz), 127.4 (s), 128.9 (s), 130.2 (s), 132.2 (s), 135.7–145.8 (m); FT IR (CCl_4) 3066 (w), 1274 (s), 1200 (s), 1171 (s), 993 (m); MS 406 (79.9), 337 (90.5), 317 (100.0), 268 (77.5), 158 (15.0); high resolution MS calcd 406.0216, obsvd 406.0185.

Preparation of 14. To an ice-cooled flask containing 100 mL of a 0.5 *M* solution of 1 (50 mmol) was added iodomethane (7.1 g, 50 mmol) dropwise *via* syringe. The mixture was heated at 60 °C overnight, after which time the volatile components were removed by vacuum transfer and poured into water. The lower, organic layer was removed by pipet, washed with water, and dried over 4A molecular sieves. Distillation of the crude product, followed by preparative gas chromatography, resulted in 4.6 g (27%) of **14**: GLPC purity = 99%; bp 169–173 °C; ^{19}F NMR ($CDCl_3$) −59.1 (q, $^5J_{F,F}$ = 12 Hz, 3F), −63.3 (q, $^5J_{F,F}$ = 12 Hz, 3F), −138.9 (m, 2F), −150.4 (t, $^3J_{F,F}$ = 20 Hz, 1F), −160.3 (m, 2F); ^{1}H NMR ($CDCl_3$) 1.9 (s, 3H); ^{13}C NMR ($CDCl_3$) 17.4 (s), 107.8 (m), 117.4 (s), 120.4 (q, $^1J_{C,F}$ = 275 Hz), 121.4 (q, $^1J_{C,F}$ = 276 Hz), 136.2–145.9 (m); FT IR (CCl_4) 2958 (w), 1503 (s), 1278 (s), 1176 (vs), 1140 (s); MS 344 (27.7), 275 (47.0), 255 (65.5), 205 (100.0), 187 (40.2), 69 (75.9); high resolution MS calcd 344.0059, obsvd 344.0059.

Preparation of 15. To an ice-cooled flask containing 100 mL of a 0.5 *M* solution of 1 (50 mmol) was added allyl bromide (6.0 g, 50 mmol) dropwise *via* syringe, and the mixture was stirred overnight. The volatile components were removed by vacuum transfer and poured into water. The lower, organic layer was removed by pipet, washed with water and dried over 4A molecular sieves. Distillation of the crude product resulted in 12.4 g (67%) of **15**: GLPC purity = 96%, bp 101–104 °C (54 mmHg); ^{19}F NMR ($CDCl_3$) −59.2 (q, $^5J_{F,F}$ = 12 Hz, 3F), −59.9 (q, $^5J_{F,F}$ = 12 Hz, 3F), −139.2 (m, 2F), −151.5 (tt, $^3J_{F,F}$ = 20 Hz, $^4J_{F,F}$ = 3 Hz, 1F), −161.1 (m, 2F); ^{1}H NMR ($CDCl_3$) 2.91 (d, $^2J_{H,H}$ = 6 Hz, 2H), 4.96 (dd, $^3J_{H,H}$ = 17 Hz, $^2J_{H,H}$ = 1 Hz, 1H), 5.12 (dd, $^3J_{H,H}$ = 10 Hz, $^2J_{H,H}$ = 1 Hz, 1H), 5.61 (m, 1H); ^{13}C NMR ($CDCl_3$) 35.8 (s), 107.6 (m), 119.4 (s), 120.4 (q, $^1J_{C,F}$ = 275 Hz), 121.5 (q, $^1J_{C,F}$ = 277 Hz), 130.3 (s), 136.4–146.0 (m); FT IR (CCl_4) 3091 (w), 2941 (w), 1501 (s), 1273 (s), 1140 (s), 993 (m); MS 370 (71.8), 301 (100.0), 231 (78.6), 205 (80.8), 181 (70.1), 59 (67.1); high resolution MS calcd 370.0216, obsvd 370.0243.

Preparation of 16. A volume of 60 mL of a 0.5 *M* solution of 1 (30 mmol) was combined with 3-bromo-3,3-difluoro-1-propene (4.7 g, 30 mmol) in a flask. The mixture was stirred overnight, poured into water, and filtered. The lower, organic layer was removed by pipet, washed with water, and dried over 4A molecular sieves. Distillation of the crude product resulted in 7.67 g (63%) of **16**: GLPC purity = 96%, bp 60–61 °C (1.65 mmHg); ^{19}F NMR ($CDCl_3$) −60.2 (q, $^5J_{F,F}$ = 12 Hz, 3F), −61.1 (q, $^5J_{F,F}$ = 12 Hz, 3F), −85.2 (d, $^2J_{F,F}$ = 39 Hz, 1F), −88.5 (dd, $^2J_{F,F}$ = 39 Hz, $^3J_{F,H}$ = 23 Hz, 1F), −138.7 (m, 2F), −149.7 (tt, $^3J_{F,F}$ = 20 Hz, $^4J_{F,F}$ = 3 Hz, 1F), −160.0 (m, 2F); ^{1}H NMR ($CDCl_3$) 2.85 (d, $^3J_{H,H}$ = 8 Hz, 2H), 4.17 (dt, $^3J_{H,F}$ = 23 Hz, $^3J_{H,H}$ = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$) 25.4 (m), 73.0 (dd, $^2J_{C,F}$ = 28 Hz, $^2J_{C,F}$ = 20 Hz), 107.1 (m), 120.3 (q, $^1J_{C,F}$ = 275 Hz), 121.3 (q, $^1J_{C,F}$ = 278 Hz), 136.3–145.9 (m), 157.4 (t, $^1J_{C,F}$ = 290 Hz); FT IR (CCl_4) 3401 (w), 1504 (s), 1277 (s), 1176 (s), 994 (m); MS: 406 (18.0), 337 (100.0), 268 (86.6), 95 (31.6), 77 (33.6), 69 (23.2); high resolution MS calcd 406.0027, obsvd 406.0023.

Preparation of 17. To an ice-cooled flask containing 100 mL of 0.5 *M* solution of 1 (50 mmol) was added either 3-chloro-3-methyl-1-butene or 1-chloro-3-methyl-2-butene (5.2 g, 50 mmol) dropwise *via* syringe. The mixture was stirred at room temperature for 2 h, after which time the volatile components were removed by vacuum transfer and poured into water. The lower, organic layer was removed by pipet, washed with water, and dried over 4A molecular sieves. Distillation of the crude product resulted in 11.3 g (57%) of **17**: GLPC purity = 94%, bp 102–104 °C (22 mmHg); ^{19}F NMR ($CDCl_3$) −58.9 (q, $^5J_{F,F}$ = 15 Hz, 3F), −59.8 (q, $^5J_{F,F}$ = 15 Hz, 3F), −139.1 (m, 2F), −151.5 (t, $^3J_{F,F}$ = 21 Hz, 1F), −161.2 (m, 2F); ^{1}H NMR ($CDCl_3$) 1.41 (s, 3H), 1.67 (d, $^4J_{H,H}$ = 1 Hz, 3H), 2.86 (d, $^3J_{H,H}$ = 7 Hz, 2H), 4.86 (t, $^3J_{H,H}$ = 7 Hz, 1H); ^{13}C NMR ($CDCl_3$) 17.5 (s), 25.6 (s), 31.0 (s), 107.9 (m), 116.1 (s), 120.5 (q, $^1J_{C,F}$ = 275 Hz), 121.7 (q, $^1J_{C,F}$ = 277 Hz), 122.9 (q, $^2J_{C,F}$ = 37 Hz), 136.4–146.2 (m); FT IR (CCl_4) 2976 (w), 1504 (s), 1274 (s), 1179 (s), 993 (m); MS 398 (0.2), 181 (54.0), 69 (18.8), 61 (100.0), 55 (26.7), 41 (25.0); high resolution MS calcd 398.0529; obsvd 398.0555.

Preparation of 18. To an ice-cooled flask containing 120 mL of a 0.5 *M* solution of 1 (60 mmol) was added benzoyl chloride (16.9 g, 120 mmol) dropwise *via* syringe. The mixture was stirred overnight, poured into water, and extracted with CH_2Cl_2. The organic material was dried over $MgSO_4$, filtered, concentrated, and purified on a silica gel column using 2% ethyl acetate in hexane as the eluent. Distillation of the crude product resulted in 28.0 g (100%) of **18**: GLPC purity = 99%, bp 90–92 °C (1.65 mmHg); ^{19}F NMR ($CDCl_3$) −57.3 (q, $^5J_{F,F}$ = 12 Hz, 3F), −61.1 (qt, $^5J_{F,F}$ = 12 Hz, $^5J_{F,F}$ = 5 Hz, 3F), −136.6 (m, 2F), −148.8 (tt, $^3J_{F,F}$ = 20 Hz, $^4J_{F,F}$ = 4 Hz, 1F), −160.8 (m, 2F); ^{1}H NMR ($CDCl_3$) 7.47–7.80 (m, 5H); ^{13}C NMR ($CDCl_3$) 105.3 (t, $^2J_{C,F}$ = 20 Hz), 119.5 (q, $^1J_{C,F}$ = 277 Hz), 120.1 (q, $^1J_{C,F}$ = 277 Hz), 126.3 (q, $^2J_{C,F}$ = 40 Hz), 129.2–135.8 (m), 139.2–146.1 (m), 186.8 (s); FT IR (CCl_4) 3090 (w), 1689 (m), 1507 (m), 1275 (s), 1151 (s); MS 434 (1.0), 241 (44.4), 105 (72.1), 77 (100.0), 69 (26.3), 51 (33.9); high resolution MS calcd 434.0165, obsvd 434.0168.

Preparation of 19. To an ice-cooled flask containing 100 mL of a 0.5 *M* solution of 1 (50 mmol) was added acetyl chloride (3.9 g, 50 mmol) dropwise *via* syringe. The mixture was stirred at room temperature for 2 h, after which time the volatile components were removed by vacuum transfer and poured into water. The lower, organic layer was removed by pipet, washed with water, and dried over 4A molecular sieves. Distillation of the crude product, followed by preparative gas chromatography, resulted in 4.5 g (24%) of **19**: GLPC purity – 99%; bp 50–53 °C (10 mmHg); ^{19}F NMR ($CDCl_3$) −58.2 (q, $^5J_{F,F}$ = 12 Hz, 3F), −61.4 (q, $^5J_{F,F}$ = 12 Hz, 3F), −138.0 (m, 2F), −148.5 (tt, $^3J_{F,F}$ = 20 Hz, $^4J_{F,F}$ = 3 Hz, 1F), −159.7 (m, 2F); ^{1}H NMR ($CDCl_3$) 2.30 (s); ^{13}C NMR ($CDCl_3$) 29.2 (s), 105.0 (m), 119.5 (q, $^1J_{C,F}$ = 277 Hz), 136.2–145.9 (m), 193.3 (s); FT IR (CCl_4) 2941 (w), 1509 (s), 1274 (s), 1174 (s), 995 (m); MS 373 (24.4), 357 (14.1), 241 (30.3), 217 (18.4), 141 (9.9), 69 (19.6); high resolution MS calcd 372.0008, obsvd 372.0010.

Preparation of 20 and 21. To a dry ice/2-propanol-cooled flask containing 100 mL of a 0.5 *M* solution of 1 (50 mmol) was added pentafluoropropionyl chloride (8.3 g, 50 mmol) dropwise *via* syringe, and the mixture was allowed to warm to room temperature. The mixture was filtered, and the lower layer was washed with water and dried over 4A molecular sieves. Distillation of the crude product resulted in 14 g (59%) of a 50:50 mixture of **20** and **21**: GLPC purity = 99%; bp 30–32 °C (1.5 mmHg). ^{19}F NMR ($CDCl_3$) of **20**: −57.0 (m, 3F), −62.5 (qm, $^5J_{F,F}$ = 12 Hz, 3F), −83.6 (s, 3F), −119.3 (s, 2F), −136.1 (m, 2F), −146.2 (t, $^3J_{F,F}$ = 21 Hz, 1F), −158.9 (m, 2F). ^{19}F NMR ($CDCl_3$) of **21**: −59.2 (s, 3F), −64.7 (s, 3F), −82.0 (s, 3F), −120.0 (s, 2F), −137.4 (m, 2F), −147.1 (t, $^3J_{F,F}$ = 20 Hz, 1F), −159.7 (m, 2F). ^{13}C NMR ($CDCl_3$) of **21**: 106.6 (t), 119.4 (q, $^1J_{C,F}$ = 278 Hz), 120.5 (q, $^1J_{C,F}$ = 277 Hz), 131.1 (m), 136.8–146.7 (m), 180.9 (t, $^2J_{C,F}$ = 33 Hz; FT IR (CCl_4) of **20** and **21**: 1759 (w), 1507 (s), 1270 (s), 1186 (s), 996 (m). MS of **20**: 476 (3.5), 357 (33.2), 241 (42.7), 217 (31.5), 119 (39.0), 69 (100.0). MS of **21**: 476 (14.0), 357 (100.0), 279 (26.5), 241 (52.5), 217 (49.3), 69 (31.2); high resolution MS calcd: 475.9694, obsvd 475.9720 (**20**), 475.9719 (**21**).

Preparation of 22. A neat sample of **2** (0.66 g, 2 mmol) was syringed into a quartz NMR tube that contained PhSSPh (0.04 g, 10 mol%), and the the tube was irradiated in a Rayonet

Photochemical Reactor (254 nm) for 5 h. Distillation of the crude product resulted in 0.59 g (89%) of **22**: GLPC purity = 94%; bp 127–129 °C; ^{19}F NMR ($CDCl_3$) –62.5 (d, $^3J_{F,H}$ = 7 Hz, 3F), –69.5 (d, $^4J_{F,H}$ = 1 Hz, 3F), –138.4 (m, 2F), –149.5 (t, $^3J_{F,F}$ = 21 Hz, 1F), –160.7 (m, 2F); ^{1}H NMR ($CDCl_3$) 6.87 (qq, $^3J_{H,F}$ = 7 Hz, $^4J_{H,F}$ = 1 Hz); ^{13}C NMR ($CDCl_3$) 103.7 (m), 120.7 (q, $^1J_{C,F}$ = 272 Hz), 121.0 (q, $^1J_{C,F}$ = 275 Hz), 130.0 (qq, $^2J_{C,F}$ = 37 Hz, $^3J_{C,F}$ = 5 Hz), 136.2–146.2 (m); FT IR (CCl_4) 3093 (w), 1654 (m), 1301 (s), 1003 (s), 858 (m); MS 330 (66.3), 311 (33.6), 261 (100.0), 241 (17.1), 192 (42.9), 69 (71.4); high resolution MS calcd 329.9903, obsvd 329.9875.

General Procedure for the Preparation of 23–26. A flask was charged with DMF (10 mL), Cd (1.4 g, 12 mmol), and *p*-X-C_6F_4Br (10 mmol). The mixture was stirred overnight, after which time the solid material was allowed to settle out of the resulting green solution. The supernatant liquid was removed *via* syringe and added to another flask. The cadmium reagent was present in an ^{19}F NMR yield of 76–78%. ^{19}F NMR (DMF) *p*-Br-C_6F_4-CdX: –112.3 (m, 2F), –136.7 (m, 2F); *p*-MeO-C_6F_4CdX: –115.0 (m, 2F), –158.7 (m, 2F); *p*-H-C_6F_4CdX: –115.7 (m, 2F), –141.8 (m, 2F). *p*-CF_3-C_6F_4CdX: –57.5 (t, $^4J_{F,F}$ = 21 Hz, 3F), –112.6 (m, 2F), –144.1 (m, 2F).

To the stirred cadmium reagent was added CuCl (0.99 g, 10 mmol), to result in an ^{19}F NMR yield of 72–81%. ^{19}F NMR (DMF) *p*-Br-C_6F_4Cu: –111.2 (m, 2F), –138.4 (m, 2F). *p*-MeO-C_6F_4Cu: –113.7 (m, 2F), –160.0 (m, 2F); *p*-H-C_6F_4Cu: –114.7 (m, 2F), –143.1 (m, 2F). *p*-CF_3-C_6F_4Cu: –57.1 (m, 3F), –112.1 (m, 2F), –145.7 (m, 2F).

The reaction flask was fitted with a condenser containing methanol that was cooled to –100 °C with a Neslab Cryocool low temperature probe. The hexafluoro-2-butyne (1.78 g, 11 mmol) was condensed into the mixture. After 2–3 days at ambient temperature the resulting vinylcopper reagent was present in an overall ^{19}F NMR yield of 50–62%. ^{19}F NMR (DMF) *p*-Br: –53.8 (m, 6F), –135.4 (m, 2F), –138.1 (m, 2F). *p*-MeO: –54.2 (q, $^5J_{F,F}$ = 12 Hz, 3F), –59.9 (q, $^5J_{F,F}$ = 12 Hz, 3F), –144.7 (m, 2F), –160.7 (m, 2F). *p*-H: –54.2 (q, $^5J_{F,F}$ = 10 Hz, 3F), –59.7 (q, $^5J_{F,F}$ = 10 Hz, 3F), –141.7 (m, 2F), –143.3 (m, 2F). *p*-CF_3: –55.0 (bs, 3F), –58.1 (m, 6F), –137.6 (bs, 2F), –140.8 (bs, 2F).

10% HCl (2 mL) was added dropwise to the flask *via* syringe, and the resulting precipitate was removed by filtration. The bottom layer of the filtrate was washed with water and dried over 4A molecular sieves. Distillation of the crude product gave the desired compounds. **23**: 63%, GLPC purity = 94%; bp 52–53 °C (10 mmHg); ^{19}F NMR ($CDCl_3$) –59.2 (qd, $^5J_{F,F}$ = 10 Hz, $^3J_{F,H}$ = 8 Hz, 3F), –60.6 (qt, $^5J_{F,F}$ = 10 Hz, $^5J_{F,F}$ = 5 Hz, 3F), –132.9 (m, 2F), –139.0 (m, 2F); ^{1}H NMR ($CDCl_3$) 7.15 (q, $^3J_{H,F}$ = 8 Hz); ^{13}C NMR ($CDCl_3$) 103.1 (t, $^2J_{C,F}$ = 22 Hz), 111.9 (t, $^2J_{C,F}$ = 18 Hz), 119.8 (q, $^1J_{C,F}$ = 274 Hz), 132.5 (q, $^2J_{C,F}$ = 40 Hz), 142.5–147.1 (m); FT IR (CCl_4) 3085 (w), 1490 (s), 1278 (s), 1154 (s), 637 (m); MS 392 (87.1), 390 (84.7), 323 (68.6), 321 (68.6), 242 (74.2), 69 (100.0); high resolution MS calcd 389.9102, obsvd 389.9085.

24: 69%, GLPC purity = 97%, bp 66–68 °C (10 mmHg); ^{19}F NMR ($CDCl_3$) –60.5 (qd, $^5J_{F,F}$ = 12 Hz, $^3J_{F,H}$ = 9 Hz, 3F), –62.1 (qt, $^5J_{F,F}$ = 12 Hz, $^5J_{F,F}$ = 6 Hz, 3F), –143.3 (m, 2F), –158.9 (m, 2F); ^{1}H NMR ($CDCl_3$) 4.10 (t, $^5J_{H,F}$ = 2 Hz, 3H), 6.30 (q, $^3J_{H,F}$ = 9 Hz, 1H); ^{13}C NMR ($CDCl_3$) 62.4 (s), 105.7 (t, $^2J_{C,F}$ = 18 Hz), 120.3 (q, $^1J_{C,F}$ = 272 Hz), 120.4 (q, $^1J_{C,F}$ = 276 Hz), 132.5 (q, $^2J_{C,F}$ = 39 Hz), 139.4–146.8; FT IR (CCl_4) 2950 (w), 1651 (m), 1500 (s), 1271 (s), 1155 (s); MS 343 (9.5), 342 (100.0), 323 (21.7), 273 (89.9), 249 (20.7), 230 (18.4); high resolution MS calcd 342.0102, obsvd 342.0103.

25: 58%, GLPC purity = 93%; bp 47–49 °C (10 mmHg); ^{19}F NMR ($CDCl_3$) –59.9 (q, $^5J_{F,F}$ = 10 Hz, 3F), –61.5 (qd, $^5J_{F,F}$ = 10 Hz, $^3J_{F,H}$ = 8 Hz, 3F), –137.5 (t, $^3J_{F,F}$ = 10 Hz, 2F), –140.1 (m, 2F); ^{13}C NMR ($CDCl_3$) 108.4 (t, $^2J_{C,F}$ = 22 Hz), 119.8 (q, $^1J_{C,F}$ = 273 Hz), 119.9 (q, $^1J_{C,F}$ = 277 Hz), 132.5 (q, $^2J_{C,F}$ = 40 Hz), 142.3–147.9 (m), 162.6 (s); FT IR (CCl_4) 2932 (w), 1512 (s), 1374 (s), 1236 (s), 1133 (s); MS 312 (67.7), 293 (28.2), 243 (85.1), 223 (29.4), 174 (56.2), 69 (100.0); high resolution MS calcd 311.9997, obsvd 311.9982.

26: 46%, GLPC purity = 92%; bp 75–81 °C (40 mmHg); ^{19}F NMR ($CDCl_3$) –57.1 (tm, $^4J_{F,F}$ = 22 Hz, 3F), –60.0 (dq, $^5J_{F,F}$ = 10 Hz, $^3J_{F,H}$ = 10 Hz, 3F), –61.3 (qm, $^5J_{F,F}$ = 10 Hz, 3F), –137.5 (bs, 2F), –139.0 (m, 2F); ^{1}H NMR ($CDCl_3$) 6.89 (q, $^3J_{H,F}$ = 10 Hz); ^{13}C NMR ($CDCl_3$) 111.8 (t, $^2J_{C,F}$ = 13 Hz), 116.3 (t, $^2J_{C,F}$ = 18 Hz), 119.4 (q, $^1J_{C,F}$ = 272 Hz), 120.2 (q, $^1J_{C,F}$ = 273 Hz), 132.9 (q, $^2J_{C,F}$ = 40 Hz), 142.5 (t, $^2J_{C,F}$ = 12 Hz), 145.9 (t, $^2J_{C,F}$ = 12 Hz); FT IR (CCl_4) 2932 (w), 1677 (s), 1502 (s), 1343 (s), 1155 (s); MS 381 (6.0), 380 (62.9), 361 (42.2), 311 (58.6), 73 (100.0), 44 (54.3); high resolution MS calcd 379.9871, obsvd 379.9850.

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Supplementary Material Available: Copies of ^{13}C NMR spectra (42 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Mechanism of Thermal Z/E Isomerization of Substituted N-Benzylideneanilines. Nature of the Activated Complex with an sp-Hybridized Nitrogen Atom

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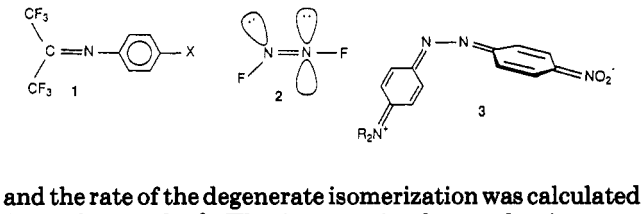
In order to study the mechanism of thermal geometrical isomerization involving a sp^2-hybridized nitrogen atom, kinetic effects of substituent, solvent, and pressure were studied in substituted N-benzylideneanilines. The effect of the substituent on the aniline moiety was almost independent of the electronic nature of the benzylidene group, and the results could be described satisfactorily by $\log (k/k_0) = \rho[\sigma^\circ + r^+(\sigma^+ - \sigma^\circ) + r^-(\sigma^- - \sigma^\circ)]$, except for the 4-(dimethylamino) group. The r^- values were more than twice as large as r^+, suggesting strongly that the aniline ring is in conjugation not with the carbon–nitrogen π bond but with the nitrogen lone pair in the transition state. The lower activation enthalpies and fairly large negative activation entropies observed in N-(4-X-benzylidene)-4-nitroanilines also support this view. When a dimethylamino group exists in the 4-position of the aniline ring, the rate constants observed were larger than that expected from the above equation. This deviation suggests the existence of a reaction route where the two phenyl groups become coplanar in the transition state. *Ab initio* calculations on selected N-phenylformaldimines and N-benzylideneanilines were performed to characterize the actual relation between both reaction possibilities as alternative and parallel routes, respectively. On the basis of the experimental data, the rate constants for the two inversion isomerizations were estimated by assuming parallel reactions for three cases.

Introduction

The mechanism of Z/E-type thermal isomerization involving sp^2-hybridized nitrogen(s) continues to impose challenging problems on organic chemists. Such reactions are well-known for a variety of azoarenes and azomethines. For example, (Z)-azobenzene was first isolated by Hartley in 1937,[1] and it was shown to regenerate the E-isomer in several hours at room temperature in solution.[2] Similarly, a relatively slow spectral change observed after the xenon-flash irradiation of solution of substituted azobenzenes[3] or N-benzylideneanilines[4,5] was attributed to thermal Z to E isomerization. Coalescence of ^{19}F-NMR signal was also observed in N-(hexafluoroisopropylidene)anilines 1,



and the rate of the degenerate isomerization was calculated from the results.[6] The interest in the mechanism was aroused by the proposal of nitrogen inversion by Binenboym and his co-workers for difluorodiazene (transition state 2).[7] Now it is generally agreed that their conclusion is applicable to most of the cases.[8] One notable exception is the reaction of push–pull-substituted azobenzenes such as 4-(dialkylamino)-4′-nitroazobenzene. Involvement of a highly polar rotational transition state 3 was proposed by Whitten[3] on the basis of the kinetic effects of solvent, and it was shown later that the mechanism depends upon the polarity of the reaction medium, i.e., inversion (*via* 4) in nonpolar solvents and rotation in polar ones.[13,17-19] The two-route mechanism was unequivocally proved by concave-up Arrhenius plots observed in benzene, 1,4-dioxane,

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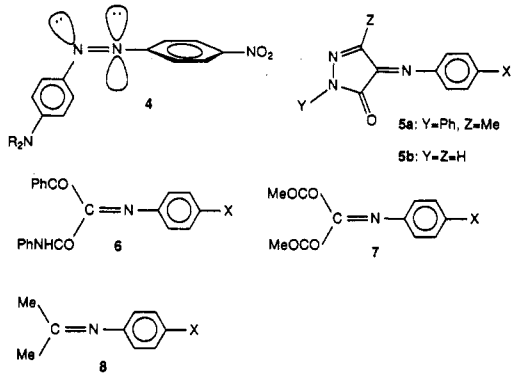
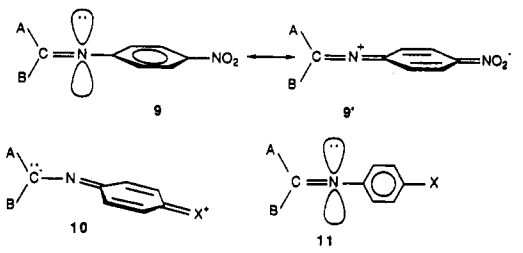
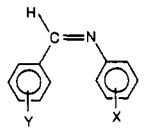
and other solvents with medium polarity. A similar two-route mechanism was proposed for some N-arylazomethines such as 1, 5a, 6, 7, and 8, on the basis of the



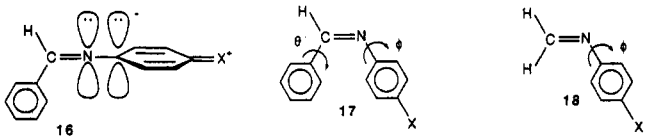
kinetic effects of the substituent X on the aniline moiety.[6,20-23] In all of these compounds, the isomerization was accelerated both by electron donation and attraction by the substituent X. While the acceleration by electron-attracting substituents was rationalized by an increase in contribution of a canonical structure 9′ in the (perpendicular) inversion transition-state 9, the electron-donating



substituents were believed to accelerate the reaction by inducing the rotation mechanism. Since most of these compounds carry electronegative substituent(s) on the imino carbon, considering a dipolar transition state such as 10 was seemingly justifiable. However, the examination of the kinetic effects of solvent and pressure revealed that in 1 and 5a, the polarity of the reactant decreased slightly even in the case of X = NMe_2.[24,25] The results could not be reconciled with a highly polar rotation transition state, and the acceleration by electron-release from X had to be rationalized in the framework of the inversion mechanism. Therefore, the existence of a conformationally different (planar) inversion transition state 11 where the aryl group is in conjugation with the carbon–nitrogen π bond was assumed for the strongly electron-donating substituents. This conclusion was supported by *ab initio* calculations on 1 and 5b.[26,27] In these compounds, the perpendicular inversion was energetically favored for X = NO_2 and H, while the planar inversion was preferred for X = NH_2 both in the gas phase and in water. However, the intervention of the planar inversion mechanism was yet to be proven for a compound that is most closely related to azobenzene, i.e., N-benzylideneaniline. Therefore, the effects of the substituent X were studied experimentally and theoretically for N-arylazomethines 12–15, 17, and 18 to shed light on the electronic and structural features of the species with an sp-hybridized nitrogen atom.



12: Y=4-NMe_2 a: X=4-NMe_2 b: X=4-MeO c: X=4-PhO d: X=4-Me
13: Y=4-NO_2 e: X=4-F f: X=4-Cl g: X=4-Br h: X=4-CF_3
14: Y=2,4-$(NO_2)_2$ i: X=4-COOEt j: X=4-NO_2 k: X=3-MeO l: X=3-Me
15: Y=2,4,6-$(NO_2)_3$ m: X=3-F n: X=3-Cl o: X=3-CF_3 p: X=3-NO_2 q: X=H



Methods

Materials. N-Benzylideneanilines (12–15) were prepared from the corresponding benzaldehyde and aniline. They were purified by recrystallization from benzene, hexane, or a mixture of the two. Column chromatography (silica gel/benzene) was also used in the case of 4-(dimethylamino)-N-(2,4,6-trinitrobenzylidene)aniline 15a. All of the isolated products gave satisfactory elemental analyses. The melting/decomposition points (in °C) are as follows: 12a, 238–9 (lit.[28] 239–40); 12b, 142.5–3 (lit.[29] 143); 12c, 151–2; 12d, 124–5 (lit.[29] 123); 12e, 139.5–4 (lit.[29] 137); 12f, 154–5 (lit.[29] 153); 12g, 161–2 (lit.[29] 162); 12h, 155–5.5 (lit.[29] 151); 12i, 120–22 (lit.[29] 121); 12j, 208.5–9.5 (lit.[30] 207); 12k, 92 (lit.[31] 82); 12l, 80 (lit.[31] 79); 12m, 86–7; 12n, 81–1.5; 12o, 94–5 (lit.[32] 81–2); 12p, 112–3 (lit.[29] 112); 12q, 101.5–2.5 (lit.[29] 100); 13a, 226 (lit.[30] 223–4); 13b, 137 (lit.[29] 134); 13c, 146–7 (lit.[33] 143–5); 13d, 127–7.5 (lit.[29] 124); 13e, 114–4.5 (lit.[29] 112); 13f, 134–5 (lit.[29] 132); 13g, 166–7 (lit.[29] 164); 13h, 126–7 (lit.[29] 128); 13i, 183.5–4 (lit.[29] 180); 13j, 205–5.5 (lit.[34] 203); 13k, 97–8; 13l, 98–9 (lit.[29] 98); 13m, 89.5–90; 13n, 110 (lit.[35] 107–9); 13o, 81–2; 13p, 155–6 (lit.[29] 152); 13q, 92–2.5 (lit.[34] 93); 14a, 216–7 (lit.[36] 211); 14b, 133–3.5 (lit.[37] 129); 14d, 155 (lit.[38] 152); 14e, 122; 14f, 164–5 (lit.[39] 161.5); 14h, 106; 14j, 173 (lit.[37] 169.5); 14l, 135–5.5 (lit.[40] 130); 14n, 144–5.5 (lit.[41] 137); 14o, 138.5–9; 14p, 141 (lit.[37] 138); 14q, 133–4.5 (lit.[42] 133); 15a, no clear melting point (lit.[36] 268); 15b, 184 (lit.[43] 182); 15f, 181–2 (lit.[43] 180); 15j 179–80. The structures of newly reported compounds and the ones with an inconsistent melting point were confirmed by ^{1}H- and ^{13}C-NMR spectra (supplementary material) except 15a. It was not possible to obtain satisfactory spectra for this compound because of its poor

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