7.72 (ABq, J = 15 Hz, 2 H, vinyl), 8.35 (s, 1 H, arom).

2-(2,4-Dimethoxy-5-(methylcarboxamido)benzoyl)-4-methyl-4-cyclohexenecarboxylic Acid (4c). A mixture of the acrylic acid **3c** (4.0 g, 13.7 mmol) and isoprene (5 mL) in ethanol (100 mL) was refluxed overnight. The adduct **4c** (2.5 g, 50%) was isolated in the same manner as in the previous additions and the solid was collected: mp 190–191 °C (EtOH); IR (KBr) ν_{max} 3400, 1725, 1640, 1600 cm^{-1}; NMR ($(CD_3)_2CO$) δ 1.6 (s, 3 H, C=CCH_3), 2.1 (s, 3 H, $COCH_3$), 2.1–3.0 (m, 6 H), 3.9 (2 s, 6 H, OCH_3), 5.3 (m, 1 H, C=CH), 6.6 (s, 1 H, arom), 7.8 (m, 1 H, arom); λ_{max} (MeOH) 315 nm (ϵ 1200), 270 (3000), 240 (4700); mass spectrum, m/e (relative intensity) 361.1521 (5), 222.0771 (100), 180.0658 (17), 165.0524 (25); m/e calcd for $C_{19}H_{23}NO_6$ (361.1525), $C_{11}H_{12}NO_4$ (222.0767), $C_9H_{10}NO_3$ (180.0661).

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Registry No. 1a, 151-10-0; **1b**, 23042-75-3; **3a**, 78149-70-9; **3b**, 78149-71-0; **3c**, 78149-72-1; **4a**, 78149-73-2; **4b**, 78149-74-3; **4c**, 78149-75-4; **5a**, 78149-76-5; **5b**, 78149-77-6; **6**, 3425-89-6; **8**, 78149-78-7; maleic anhydride, 108-31-6; isoprene, 78-79-5.

Geminal Fluorination of Diazo Compounds

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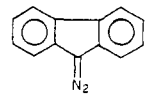
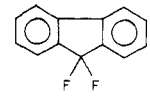
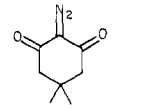
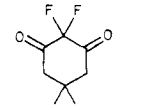
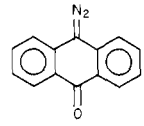
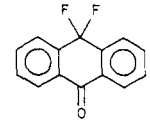
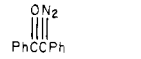
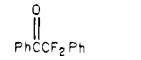
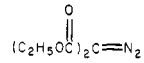
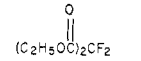
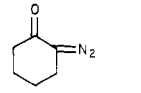
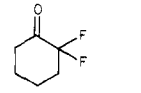
The utility of diazo compounds as intermediates in preparative organic chemistry has proven of great value.[2] Conversion of diazo compounds to halocarbons is a long known process dating back to nearly a century ago when Curtius reported the reaction between diazo compounds and hydrogen halides.[3a] Subsequently, considerable attention has been focused on the halogenation of various diazo substrates with both hydrogen halides and molecular halogen.[3-7]

The preparation of fluorocarbon compounds from diazo precursors has received much less attention. Olah in 1956 first reported the conversion of diazo compounds into fluorocarbons on reaction with hydrogen fluoride.[8a] A few reports on the reaction of hydrogen fluoride with diazo substrates have emerged subsequently, including reactions in the presence of haloamides to produce mixed halofluorocarbon compounds.[8-10] Olah recently introduced the use of pyridinium poly(hydrogen fluoride) as a more effective source of HF in the hydrofluorination of diazo compounds.[8c]

Leroy and Wakselman in 1976 made the only reports on the reaction of diazo compounds with molecular fluorine. However, their studies were mostly concerned with the use of trifluoromethyl hypofluorite as a fluorinating reagent; and their studies with molecular fluorine were less detailed.[11]

We report now an efficient and selective preparation of geminal difluoro compounds by reaction of diazo substrates with dilute molecular fluorine in Freon-11 solution at −70 °C. The results given in Table I show that very respectable yields (65–94%) of geminal difluoro compounds are obtained. Moreover, neither the carbon–hydrogen bonds nor the keto function is affected in the fluorination. The overall enthalpy change of −154 kcal/mol for conversion of a diazo function to a geminal difluoro function would indeed favor the selectivity observed.[12] However, the low

Table I. Fluorination of Diazo Compounds

diazo substrate	product	% yield[a]	^{19}F NMR[b]
$Ph_2C{=}N_2$	Ph_2CF_2	71	87
		88	110
		80	169
		94	81
		79	81
		70	109
		65	111

[a] Isolated yields of pure product. [b] ϕ (ppm) upfield relative to $CFCl_3$.

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temperature and Freon solvent are apparently also important factors in the selectivity. The facility of the reactions is enhanced by the fact that the color of the diazo compound is dissipated during fluorination, and the color change serves as an internal visual indicator for the reaction endpoint.

The selectivity and safety of fluorination with dilute elemental fluorine in Freon solution at low temperature have inspired increased research into this simple fluorination procedure.[13,14] Although Freon is nonpolar and relatively inert, its role in enhancing fluorination selectivity in unclear. Further studies on the synthetic and mechanistic aspects of the fluorination of diazo compounds are in progress in our laboratory.

Experimental Section

General Procedures. Temperature readings are uncorrected. ^{19}F NMR spectra were recorded in $CDCl_3$ solution with internal $CFCl_3$ (ϕ 0.0) on a JEOL FX-90Q spectrometer at 84.6 MHz. Fluorine gas (10%) diluted with nitrogen was purchased from Matheson Gas Company. *Although dilute fluorine gas is much safer than the concentrated gas, the gas cylinder was stored behind a blockade, and all reactions were performed behind a shield in a well-ventilated hood.*

Diazo Compounds. Diphenyldiazomethane,[15] 9-diazofluorene,[15] 9-diazoanthrone,[16] diethyl diazomalonate,[19] diazodeoxybenzoin,[18] diazocyclohexanone,[19] and 2-diazodimedone[15] were prepared by known literature procedures.

Fluorination Procedure. The reaction between diphenyldiazomethane and dilute fluorine exemplifies all of the reactions and is described here as a general procedure. Diphenyldiazomethane (2.0 g, 0.01 mol) in 75 mL of $CFCl_3$ contained in a 100-mL round-bottomed flask cooled to −70 °C in dry ice–acetone was treated with dilute fluorine (10%) delivered from the tank through $^1/_8$ in. copper tubing. The rapidly stirred solution was treated with dilute fluorine at a rate of about six bubbles per second. The mixture became colorless after about 15 min. Pure nitrogen was used to purge the residual fluorine, and the Freon was removed on a rotary evaporator to yield a light yellow oil. Column chromatography on a 20-cm pressurized silica gel column (Silica Gel 60 TLC) with 9:1 hexane–chloroform eluant gave 1.45 g (71%) of pure difluorodiphenylmethane as a colorless liquid: ^1H NMR ($CDCl_3$) δ 7.2 m, aromatic), 7.5 (m, aromatic). Anal. Calcd for $C_{13}H_{10}F_2$: C, 76.47; H, 4.90; F, 18.63. Found: C, 76.60; H, 5.2; F, 18.41.

9,9-Difluorofluorene: mp 37–43 °C; ^1H NMR δ 7.4 (m, aromatic). Anal. Calcd for $C_{13}H_8F_2$: C, 77.23; H, 3.96; F, 18.81. Found: C, 77.02; H, 4.11; F, 19.60.

Diethyl difluoromalonate: colorless liquid; ^1H NMR δ 1.3 (t, CH_3), 4.4 (q, CH_2). Anal. Calcd for $C_7H_{10}O_4F_2$: C, 42.86; H, 5.10; F, 19.39. Found: C, 42.89, H, 5.31; F, 19.60.

Difluorodeoxybenzoin: mp 40–42 °C; ^1H NMR δ 7.2 (m, aromatic). Anal. Calcd for $C_{14}H_{10}OF_2$: C, 72.41; H, 4.31; F, 16.38. Found: C, 72.10; H, 4.53; F, 16.68.

10,10-Difluoroanthrone: mp 140–141 °C (lit.[20] mp 141–142 °C); ^1H NMR δ 7.4 (aromatic); IR 1660 cm^{-1} (C=O).

2,2-Difluorodimedone: mp 104–106 °C; ^1H NMR δ 1.2 (s, CH_3), 2.4 (s, CH_2). Anal. Calcd for $C_8H_{10}O_2F_2$: C, 54.55; H, 5.68; F, 21.59. Found: C, 54.78; H, 5.73; F, 21.91.

2,2-Difluorocyclohexanone: colorless liquid; ^1H NMR δ 2.0, 2.5 (cyclohexane), 3.5 (m, CH_2 next to CF_2); ^{19}F NMR ϕ 111 (t, CF_2); difficult to purify and heat sensitive. Anal. Calcd for $C_6H_8OF_2$: C, 53.37; H, 5.97. Found: C, 53.90; H, 5.79.

Acknowledgment. This research was supported by the Office of Research, SIUE. We thank Mr. Phil James for performing several fluorination experiments.

Registry No. 1,1′-(Diazomethylene)bisbenzene, 883-40-9; 9-diazo-9*H*-fluorene, 832-80-4; 2-diazo-5,5-dimethyl-1,3-cyclohexanedione, 1807-68-7; 10-diazo-9(10*H*)-anthracenone, 1705-82-4; diazodiphenylethanone, 3469-17-8; diethyl diazopropanedioate, 5256-74-6; 2-diazocyclohexanone, 3242-56-6; 1,1′-(difluoromethylene)bisbenzene, 360-11-2; 9,9-difluoro-9*H*-fluorene, 342-58-5; 2,2-difluoro-5,5-dimethyl-1,3-cyclohexanedione, 76185-12-1; 10,10-difluoro-9(10*H*)-anthracenone, 1735-34-8; 2,2-difluoro-1,2-diphenylethanone, 365-01-5; diethyl difluoropropanedioate, 680-65-9; 2,2-difluorocyclohexanone, 29548-93-4.

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1-Bromobenzocyclobutene: A Convenient Entry into the Benzocyclobutene Ring System[1]

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The thermally induced benzocyclobutene–*o*-quinodimethane interconversion has been exploited recently for the construction of complex polycyclic compounds.[2] The synthetic design involves interception of a nascent *o*-quinodimethane by a remote multiple bond in an intramolecular Diels–Alder reaction. The requisite starting material for such a process is a benzocyclobutene appropriately elaborated at the 1-position. Conventional approaches to the benzocyclobutene ring system center around cyclization of exotically substituted acyclic precursors or cycloaddition of benzyne to an olefinic moiety.[3] We describe here a novel, direct route to 1-bromobenzocyclobutene[4] (**1**), a material which may be converted in good yield to 1-substituted benzocyclobutenes of varied functionality.

1-Bromobenzocyclobutene is formed in isolated yields of 18–45% when cycloheptatriene (3 equiv) is allowed to react with bromoform, potassium carbonate, and 18-crown-6 at 140 °C—conditions favoring the formation of dibromocarbene[5] (eq 1). In accord with the literature, starting material is recovered unchanged at lower reaction temperatures or in the absence of the crown ether. Compound **1** is accompanied in the crude reaction mixture by dibromide **2**, several minor unidentified components, and substantial quantities of intractable material. Three additional side products were detected by GC analysis when the higher boiling bromoform was used as the reaction medium (vide infra).

(1) Presented in part at the 12th Central Regional Meeting of the American Chemical Society, Pittsburgh, PA, Nov 12–14, 1980.

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