eight scans stored (on resonance). After approximately 100 cycles of this acquisition sequence, two 16K data blocks of on-resonance and off-resonance spectra resulted. Subtraction of the 16K data blocks produced the difference NOE spectrum. $CDCl_3$ stored over K_2CO_3 was used in the initial NMR experiments, but hydrolysis of some of the enol ethers was observed and C_6D_6 was found to be a more suitable solvent. The NMR spectra were calibrated vs. $CHCl_3$ at δ 7.24 or C_6D_6 at δ 7.15.

The trimethylsilyl enol ethers **1**, **2**, **3a**, and **3b** were prepared according to published procedures (see above). All reactions were carried out in flame-dried glassware under a N_2 atmosphere. Ratios of enol ethers were determined by capillary GC on a 12-m SE-30 or Carbowax column.

(*E*)-9-[(Trimethylsilyl)oxy]-8-tetradecen-13-olide (6a). The enone **4** (50 mg, 0.21 mmol) was dissolved in 5 mL of THF and the resultant mixture cooled to −78 °C. Lithium tri-*sec*-butylborohydride (0.21 mL, 0.21 mmol) was then injected in one portion. After being stirred at −78 °C for 15 min, a filtered mixture of Me_3SiCl (0.053 mL, 0.42 mmol) and Et_3N (0.030 mL, 0.21 mmol) in 1 mL of THF was added. The reaction mixture was allowed to warm to room temperature, evaporated, and flash chromatographed on silica gel, eluting with hexane–ethyl acetate (9:1, v/v). The appropriate fractions were evaporated to afford 33 mg of a 97:3 mixture of **6a** and **6b** and 29 mg of the 1,2-reduction products.

6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 1.25 (d, 3 H, J = 7 Hz), 1.30–1.75 (m, 13 H), 1.85–2.05 (m, 2 H), 2.15–2.50 (m, 3 H), 4.48 (dd, 1 H, J = 5.0, 11.2 Hz), 4.93 (m, 1 H, J = 3.5, 7, 10.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.41 (q), 20.26 (q), 22.57 (t), 24.44 (t), 25.49 (t), 25.54 (t), 25.58 (t), 26.16 (t), 26.87 (t), 28.17 (t), 30.56 (t), 35.21 (t), 35.81 (t), 69.23 (d), 107.42 (d), 151.97 (s), 173.69 (s); MS, M^+ = 312.2119, calcd for $C_{17}H_{32}O_3Si$ 312.2120.

(*Z*)-9-[(Trimethylsilyl)oxy]-8-tetradecen-13-olide (6b). Trimethylsilyl triflate (93.9 mg, 0.42 mmol) was added dropwise to a solution of ketone **5** (100 mg, 0.42 mmol) and Et_3N (34 mg, 0.33 mmol) in 5 mL of dry ether at 0 °C. The reaction mixture was stirred overnight at room temperature and then diluted with ether, washed with ice-cold aqueous NH_4Cl, dried ($MgSO_4$), and filtered, and the solvent was evaporated. The crude product was filtered through a short silica gel column to yield 97 mg (94%) of four isomeric silyl enol ethers in a ratio of 85:5:4:6 (**6b**:**6a**:**6c**:**6d**).[12]

6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 1.17 (d, 3 H, J = 6.5 Hz), 1.18–2.10 (m, 16 H), 2.25 (m, 2 H), 4.40 (t, 1 H, J = 8 Hz), 5.05 (m, 1 H, J = 3.5, 6.5, 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.63 (q), 13.67 (q), 21.0 (t), 24.47 (t), 24.67 (t), 27.31 (t), 28.40 (t), 28.62 (t), 33.30 (t), 34.36 (t), 34.69 (t), 69.23 (d), 109.65 (d), 149.76 (s), 173.87 (s); MS, M^+ = 312.2119, calcd for $C_{17}H_{32}O_3Si$ 312.2120.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

(12) Isomers **6c** and **6d** were the $\Delta^{9,10}$ silyl enol ethers.

3,3-Difluorocyclobutene. Synthesis and Reaction with Diazomethane

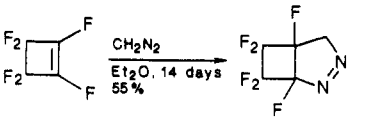
William R. Dolbier, Jr.,* and Dheya M. Al-Fekri[1]

Department of Chemistry, University of Florida, Gainesville, Florida 32611

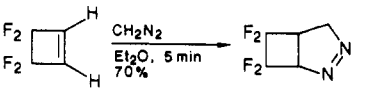
Received August 18, 1986

Recently, Chambers and co-workers completed a systematic study of the effects of fluorine and perfluoroalkyl substituents on the reactivity and regiochemistry of alkenes in their reactions with diazomethane.[2] From their results, they concluded that the reactivity of such alkenes increases with increasing presence of perfluoroalkyl groups as follows: $(R_F)_2C{=}C(R_F)_2 \gg (R_F)_2C{=}CFR_F \gg (R_F)_2C{=}CF_2$, $R_FCF{=}CFR_F$, and $CF_3CH{=}CHCF_3 > CF_3CF{=}CHCF_3 \gg CF_3CF{=}CFCF_3$

While perfluoroalkenes of the type $R_FCF{=}CFR_F$, including perfluorocyclohexene, were found to be essentially unreactive, perfluorocyclopentene and perfluorocyclobutene (**1**) underwent reaction, albeit reluctantly. In an earlier study,[3] we found that 3,3,4,4-tetrafluorocyclobutene (**2**) as expected from the Chambers study was considerably more reactive than **1**, providing further evidence that *vinyl* fluorine substituents are not enhancing to the dipolarophilicity of olefins.

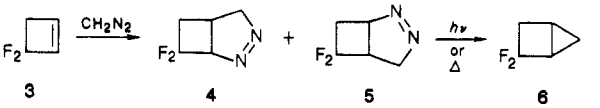


1



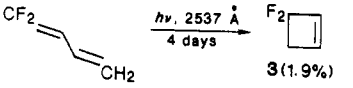
2

We were interested in the unsymmetrically fluorine-substituted pyrazolines **4** and **5** in the hope that they might act as precursors to 2,2-difluorobicyclopentane (**6**).

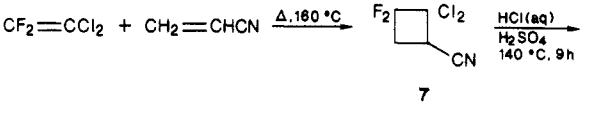


3 **4** **5** **6**

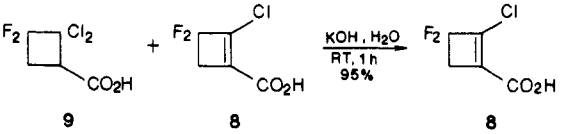
Therefore, a synthesis of 3,3-difluorocyclobutene (**3**) was required. Initially, a photochemical scheme involving the photolysis of 1,1-difluoro-1,3-butadiene was envisaged.



Indeed, small amounts of the desired product could be obtained, but the method was deemed inappropriate for synthesis of gram quantitites of **3**. Our method of choice for the synthesis of **3** began with the regiospecific [2 + 2] cycloaddition of 1,1-dichloro-2,2-difluoroethylene with acrylonitrile, which proceeded almost quantitatively.[4]



7



9 **8** **8**

Acidic hydrolysis of the adduct **7** led to a mixture of carboxylic acid products comprised largely of cyclobutene **8**, plus some **9**. The crude mixture was converted cleanly to 2-chloro-3,3-difluorocyclobutene carboxylic acid (**8**) by treatment with base.

(1) Taken from the Ph.D. Dissertation of D.M.A.-F., University of Florida, 1985.

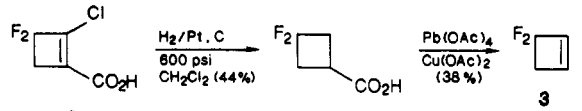
(2) Bryce, M. R.; Chambers R. D.; Taylor, G. *J. Chem. Soc., Perkin Trans. 1* **1984**, 509.

(3) (a) Dolbier, W. R., Jr.; Al-Fekri, D. M. *Tetrahedron Lett.* **1983**, *24*, 4047. (b) Dolbier, W. R., Jr.; Al-Fekri, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 6349.

(4) Bartlett, P. D.; Montgomery, L. K.; Siedel, B. *J. Am. Chem. Soc.* **1964**, *86*, 616.

0022-3263/87/1952-1872$01.50/0

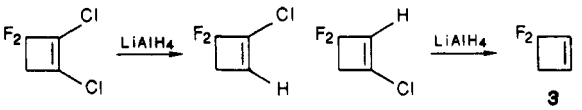
Then in an unexpectedly clean step, **8** underwent conversion directly to 3,3-difluorocyclobutanecarboxylic acid (**10**) under catalytic hydrogenation conditions via a one-pot dehydrohalogenation and hydrogenation. Interestingly,



8 **10** **3**

attempts to carry out a direct conversion of **9** under similar conditions were unsuccessful. Conversion of **10** to the desired 3,3-difluorocyclobutene was accomplished via an oxidative decarboxylation procedure using $Pb(OAc)_4$ with $Cu(OAc)_2$ catalysis.[5,6]

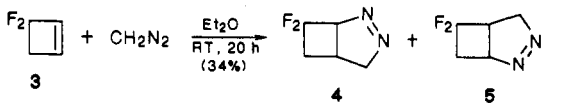
A number of interesting aspects of cyclobutene NMR spectra were encountered during the course of this work.



11 **12** **13** **3**

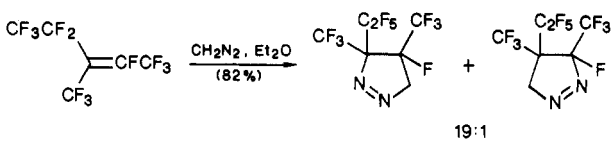
^{19}F spectra of **3** and **12** indicated clearly an unexpectedly large four-bond coupling (J = 14 Hz) between the fluorine substituents and the diagonally located vinylic protons. In contrast, the three-bond coupling between fluorine and the adjacent vinyl protons of **3** and **13** was only 1.5 Hz. There are other examples in the literature consistent with these observations.[7]

Addition of a diazomethane solution in ether to **3** resulted in formation of a 2.4 to 1 ratio of pyrazolines **4** and **5** in 34% isolated yield. The observed regioselectivity of



3 **4** **5**

this reaction is consistent with observations of the Chambers group[2] wherein they found that one can readily predict the regiochemical outcome of such reactions by considering the diazomethane additions, although no doubt concerted in nature, to be like a carbanion addition. Frontier molecular orbital considerations also lead to the same predictions.[2]



Pyrolysis of the mixture of pyrazolines **4** and **5** surprisingly led to the formation of *no detectable amount* of 2,2-difluorobicyclopentane (**6**). The results from this pyrolysis and discussion thereof will appear elsewhere.[8]

Experimental Section

NMR spectra were run in $CDCl_3$, with ^1H and ^{13}C chemical shifts reported (ppm) upfield from internal standard Me_4Si and ^{19}F chemical shifts (ppm) downfield from internal standard $CFCl_3$.

1,1-Difluoro-1,3-butadiene. The preparation was as earlier reported.[9] The diene was obtained in 56% and was isolated by trap-to-trap distillation and purified by prep GC (20 ft by $^1/_4$ in. in 20% DNP at 60 °C, 30 mL/min. NMR: ^1H, δ 4.92–5.21 (complex m, 3 H), 6.2–6.33 (complex m, 1 H); ^{19}F, ϕ 86.07 (dd, $^2J_{FF}$ = 28.09 Hz, $^3J_{FH}$ = 24 Hz), 88.59 (d, J_{FF} = 28.4 Hz).

3,3-Difluorocyclobutene (3) (by Photolysis). 1,1-Difluoro-1,3-butadiene (0.5 g, 5.7 mmol) in 20 g of cyclohexane was photolyzed in a 60-mL quartz bulb for 4 days at 38 °C by a Rayonet photoreactor (2537 Å) to give 10 mg (0.11 mmol, 1.9%) of 3,3-difluorocyclobutene (**3**), isolated from the solution by preparative GC using the DNP column at 80 °C. NMR: ^1H, δ 3.03 (tdd, $^3J_{H_4F}$ = 3.18 Hz, $^3J_{H_4H_2}$ = 0.98 Hz, $^4J_{H_4H_2}$ = 0.49 Hz, 2 H), 6.126 (pm, $^3J_{H_2F}$ = 1.8 Hz, 1 H), 6.705 (tdt, $^4J_{H_1F}$ = 14.4 Hz, $^3J_{H_1H_2}$ = 2.19 Hz, $^3J_{H_1H_4}$ = 0.98 Hz, 1 H); ^{19}F, ϕ 104.52 (dtd, $^4J_{FH_1}$ = 14.21 Hz, $^3J_{FH_4}$ = 3.1 Hz, $^3J_{FH_2}$ = 1.84 Hz); ^{13}C, δ 45.17 (t, $^2J_{CF}$ = 23.19 Hz), 134.16 (t, $^2J_{CF}$ = 24.37 Hz), 142.74 (t, $^3J_{CF}$ = 17.09 Hz), no CF_2 carbon seen. Mass spectrum: m/e (rel base %) 90 (M^+, 2.5), 64 ($M^+ - C_2H_2$, 0.3), 26 ($M^+ - C_2H_2F_2$, 0.1), 59 (22), 45 (6), 31 (100), 29 (22).

2,2-Dichloro-3,3-difluorocyclobutanecarbonitrile (7). The title compound was prepared by a modified published procedure.[4]

Into a 60-mL autoclave were introduced 20 g (25 mL, 0.377 mol) of acrylonitrile and 0.5 g of hydroquinone. Then 25 g (0.18 mol) of 1,1-dichloro-2,2-difluoroethylene was condensed via vac line transfer into the autoclave. The mixture was heated at 140–160 °C for 20 h. The procedure was repeated, and the combined crude product was distilled to give 72 g (0.38 mol) of **7**. Bp: 57 °C (17 mm). IR (neat film): 3035, 2960, 2255, 2235, 1725, 1615, 1420, 1350, 1300, 1150, 1040, 910, 790, 640, 625 cm^{-1}. NMR: ^1H, δ 2.7–3.4 (m, 2 H), 3.6–4.1 (m, 1 H); ^{19}F, ϕ 100.5 (midpoint AB, J_{AB} = 200 Hz, downfield, F, dt, J_{FF} = 200 Hz, $^3J_{FH}$ = 8 Hz, highfield F, dtd, J_{FF} = 200 Hz, $^3J_{FH}$ = 14 Hz, J_{FH} = 3 Hz, $\Delta\nu$ = 480 Hz).

2,2-Dichloro-3,3-difluorocyclobutanecarboxylic Acid (9) and 2-Chloro-3,3-difluorocyclobutenecarboxylic Acid (8). A mixture of 50 mL of hydrochloric acid (38%) and 30 mL of sulfuric acid (98%) was combined in a 500-mL one-necked flask with 75 g (0.389 mol) of **7**. The mixture was refluxed at 140 °C for 9 h. The mixture was neutralized with KOH/H_2O (40%) and the organic layer extracted with ether and dried over anhydrous $CaCl_2$. The ether was removed by distillation to leave a yellow solid, mp 90–100 °C (**8**), as the major product and small amount of a yellow liquid (**9**). The total weight was 65 g (0.3809 mol 97.6%). Spectral data for **9** follow. NMR: ^1H, δ 2.6–3.15 (m, 2 H), 3.4–3.95 (m, 1 H), 11 (s, 1 H); ^{19}F, ϕ 101 (midpoint) AB, J_{AB} = 200 Hz, $\Delta\nu$ = 550 Hz, downfield F, ddd, J_{FF} = 200 Hz, $^3J_{FH}$ = 10 Hz, $^3J_{FH}$ = 4 Hz, upfield F, dddd, J_{FF} = 200 Hz, $3J_{FH}$ = 20 Hz, $^3J_{fH}$ = 14 Hz, $^4J_{FH}$ = 2 Hz).

The above mixture of **8** and **9** was stirred with excess KOH/H_2O (40%) for 1 h at room temperature and then acidified with 38% HCl. The organic layer was extracted with ether and the ether removed, giving 62 g (0.369 mol) (94.8%) of **8**. BP 90 °C (15 mm). NMR: ^1H, δ 3.2 (t, $^3J_{HF}$ = 3 Hz, 2 H), 11 (s, 1 H); ^{19}F, ϕ 114.5 (t, $^3J_{FH}$ = 3 Hz). Mass spectrum: M^+ 168.9784 ± 0.0023, calcd for $C_5H_3O_2F_2Cl$ 168.9789 ± 0.004 (2.9 ppm).

3,3-Difluorocyclobutanecarboxylic Acid (10). A 1-L bomb equipped with gas inlet and outlet valves and mechanical stirrer was charged with 62 g (0.369 mol) of **8**, 400 mL of methylene chloride, and 1 g of Pt/C. The bomb was purged with dry N_2 for 10 min and then it was pressurized with H_2 up to 600 psi. The mixture was stirred at 60–80 °C for 1 h (exothermic reaction). The solvent was removed by simple distillation, and the crude acid was distilled to give a colorless liquid, bp 85–90 °C (4–5 mm), that then solidified at 0 °C to give 21.9 g (0.161 mol, 43.6%) of needlelike white crystals. MP: 48–50 °C. IR: 3500–2500 (br), 1680 cm^{-1}. NMR: ^1H, δ 2.803–2.937 (complex m, 4 H), 2.97–3.03 (complex m, 1 H), 8 (br s, 1 H); ^{19}F, ϕ 90.84 (midpoint, AB, J_{AB} = 193.53 Hz, $\delta\nu$ = 37.6387 Hz, downfield F, dm, J_{FF} = 193.53 Hz, $^4J_{FH}$ = 3 Hz, upfield F, dp with fine splitting, J_{FF} = 193.53 Hz, J_{FH} = 14.4 Hz); ^{13}C, δ 26.6 (dd, $^3J_{CF}$ = 15 Hz, $^3J_{CF}$ = 5 Hz), 39.0 (t, $^2J_{CF}$ = 23 Hz), 118.7 (midpoint, AB, $^1J_{AB}$ = 270 Hz, $\delta\nu$ = 91.24 Hz), 180.4 (s, carbonyl C). Mass spectrum: m/e (rel base %) 136 (M^+, 0.45), 91 ($M^+ - CO_2H$, 9.6), 64 ($M^+ - CH_2CHCO_2H$, 100).

3,3-Difluorocyclobutene (3). The synthesis of **3** was based upon a published procedure.[5]

(5) Tobe, Y.; Fukuda, Y.; Kakiuchi, K.; Odaira, Y. *J. Org. Chem.* **1984**, *49*, 2012.

(6) Kinstle, T. H.; Loo, D.; Beight, D. W. Paper presented at the 187th National Meeting of the American Chemical Society, St. Louis, MO, April 1984; ORGN 0050.

(7) Newmark, R. A.; Apai, G. R.; Michael, R. O. *J. Magn. Reson.* **1969**, *1*, 418.

(8) Dolbier, W. R., Jr.; Al-Fekri, D. M. *Tetrahedron* **1987**, *43*, 39.

(9) Tarrant, P.; Lovelace, A. M. *J. Am. Chem. Soc.* **1954**, *76*, 3466.

Into a 100-mL three-necked flask, equipped with an N_2 inlet and a reflux condenser connected to a trap kept at −78 °C during the reaction, was introduced $Cu(OAc)_2 \cdot H_2O$ (0.1 g, 0.5 mmol), pyridine (1.16 g, 0.0147 mol), **10** (2. g, 0.0147 mol), and 15 mL of chlorobenzene. The mixture was stirred magnetically for 40 min at room temperature. To the resulting homogeneous solution was added 97% lead(IV) tetraacetate (2.5 g, 5.7 mmol, freshly recrystallized) and 15 mL more of chlorobenzene. The resulting mixture was stirred in the dark for 1 h at room temperature, and then it was heated gradually up to 80 °C and refluxed for 1 h. The product was mostly condensed in the trap at −78 °C, and more of the product was obtained by distilling it from the chlorobenzene. The total amount of the product obtained was 0.5 g (0.0055 mol, 37.7%). The spectroscopic data for **3** are identical with those described above.

1,1,2,2-Tetrachloro-3,3-difluorocyclobutane. This compound was prepared by similar procedure as for **7**, using 100 g (0.751 mol) of 1,1-dichloro-2,2-difluoroethylene and 70.1 g (60 mL, 0.73 mol) of vinylidene chloride at 180 °C for 9 h to give 34 g (0.147 mmol 20.1%) of the adduct, a white solid. Mp: 53–55°C. Bp: 60 °C (20 mm). NMR: ^1H, δ 3.59 (t, J_{HF} = 10 Hz); ^{19}F, ϕ 101.5 (t, J_{FH} = 10 Hz).

1,2-Dichloro-3,3-difluorocyclobutene (11). Dechlorination was carried out in refluxing ethanol (280 mL) using 29 g (0.126 mol) of 1,1,2,2-tetrachloro-3,3-difluorocyclobutane and 75 g (1.134 mol) of zinc powder to give 11 g (0.0691 mol, 55%) of **11**, a colorless liquid. Bp: 82–84.5 °C. NMR: ^1H, δ 3.2 (t, J_{HF} = 3 Hz); ^{19}F, ϕ 114 (t, J_{FH} = 3 Hz); ^{13}C, δ 48.5 (t, $^2J_{CF}$ = 29 Hz), 116.8 (t, $^1J_{CF}$ = 342 Hz), 122.5 (t, $^2J_{CF}$ = 34.2 Hz), 136.8 (t, $^3J_{CF}$ = 29 Hz).

1-Chloro-4,4-difluorocyclobutene (12). According to a published procedure,[10] 3 g (0.0188 mol) of **11** was reduced with 0.75 g (0.0197 mol) of lithium aluminum hydride in 100 mL of ether to give 0.3 g (0.0024 mol, 13%) of **12**. NMR: ^1H, δ 2.66 (t, $^3J_{HF}$ = 3 Hz), 6.3 (t, $^4J_{HF}$ = 13 Hz); ^{19}F, ϕ 114 (dt, $^4J_{FH}$ = 13 Hz, $^3J_{FH}$ = 3.0 Hz).

1,1,2-Trichloro-3,3-difluorocyclobutane. The procedure followed was similar to that described for **7**. 1-Chloro-2,2-difluoroethylene (26 g, 0.264 mol) and 21.34 g (0.22 mol) of vinylidene chloride were heated at 220 °C for 22 h, giving 1.45 g (0.0074 mol, (3%) of product, a colorless liquid. Bp: 80–84 °C (40 mm). NMR: ^1H, δ 3.51 (dd, midpoint AB, J_{AB} = 6 Hz, $\Delta\nu$ = 16 Hz, 2 H), 5.1 (td, $^3J_{HF}$ = 9 Hz, J_{HF} = 2 Hz, 1 H); ^{19}F, ϕ 102 (midpoint AB, J_{AB} = 210 Hz, $\Delta\nu$ = 1410 Hz, upfield F, d of octet, J_{FF} = 210 Hz, $^3J_{FH}$ = 10 Hz, $^3J_{FH}$ = 6 Hz, downfield F, d of sextet, J_{FF} = 210 Hz, J_{FH} = 10 Hz).

1-Chloro-3,3-difluorocyclobutene (13). The procedure was similar to that described for **11**. 1,1,2-Trichloro-3,3-difluorocyclobutane 1.4 g, 0.0071 mol) was utilized along with 4.3 g (0.064 mol) of powdered zinc in 30 mL of ethanol to give 0.2 g (0.0016 mol) (22.6%) of **13**. NMR: ^{19}F, ϕ 106.92 (td, $^3J_{FH}$ = 2.83 Hz, $^3J_{FH(vinylic)}$ = 1.39 Hz).

3,3-Difluorocyclobutene (3) by Reduction of 13. The reduction was achieved by a procedure similar to that used for **12**. The reaction of 0.2 g (0.0016 mol) of **13** and 0.8 g (0.021 mol) of lithium aluminum hydride in 20 mL of ether at room temperature for 22 h gave **3** with spectral data as described above.

7,7- and 6,6-Difluoro-2,3-diazabicyclo[3.2.0]hept-2-ene. An ether solution of diazomethane (70 mL) was prepared from 7.14 g (0.0285 mol) of *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide and was allowed to react with 0.828 g (0.0111 mol) of 3,3-difluorocyclobutene for 20 h at room temperature to give 0.335 g (0.00372 mol, 33.5%) of an oily faint yellow liquid. IR: 2945, 1545 cm^{-1} (main peaks). NMR: ^1H, δ 5.8 (m, 1 H), 5.2 (m, 1 H, **5**), 4.6 (br s with fine splitting, 2 H), 1.5–2.9 (m, 3 H); ^{19}F, ϕ 95.55 (midpoint AB, **4**, J_{AB} = 207.73 Hz, $\Delta\nu$ = 1055.48 Hz, upfield F, dddd, J_{FF} = 207.73 Hz, J_{FH} = 20 Hz, J_{FH} = 10.5 Hz, J_{FH} = 4.51 Hz, downfield F, ddddd, J_{FF} = 207.73 Hz, J_{FH} = 18.99 Hz, J_{FH} = 9.99 Hz, J_{FH} = 3.42 Hz, J_{FH} = 1.79 Hz), 93.98 (midpoint AB, **5**, J_{AB} = 197.39 Hz, $\Delta\nu$ = 2486.46 Hz, upfield F, dddd, J_{FF} = 197.39 Hz, $^3J_{FH}$ = 21.26 Hz, $^3J_{FH}$ = 11.11 Hz, $^4J_{FH}$ = 4.34 Hz, downfield F, dm, J_{FF} = 197.39 Hz, J_{FH} = 18.84, 14.94, 7.33, and 4.86 Hz).

Acknowledgment. We acknowledge with thanks support of this research in part by the National Science Foundation.

Registry No. **3**, 29507-09-3; **4**, 107496-59-3; **5**, 107496-58-2; **7**, 107496-53-7; **8**, 1735-42-8; **9**, 1801-08-7; **10**, 107496-54-8; **11**, 14851-11-7; **12**, 107496-55-9; **13**, 107496-57-1; $ClHC{=}CF_2$, 359-10-4; $F_2C{=}CHCH{=}CH_2$, 590-91-0; $H_2C{=}CH_2CN$, 107-13-1; $Cl_2C{=}CF_2$, 79-35-6; $H_2C{=}CCl_2$, 75-35-4; 1,1,2-trichloro-3,3-difluorocyclobutane, 107496-56-0; 1,1,2,2-tetrachloro-3,3-difluorocyclobutane, 697-16-5; CH_2N_2, 334-88-3.

Supplementary Material Available: ^1H, ^{13}C, and ^{19}F NMR for compounds **10** and **3** (10 pages). Ordering information is given on any current masthead page.

(10) Fuller, G.; Tatlow, J. C. *J. Chem. Soc.* **1961**, 3198.

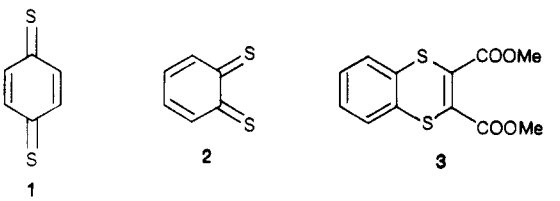
Thioquinones. A Reinvestigation of Perkin and Green's Diaminodithioquinone

M. V. Lakshmikantham, Maynard S. Raasch, Michael P. Cava,* Simon G. Bott, and Jerry L. Atwood*

Chemistry Department, University of Alabama, University (Tuscaloosa), Alabama 35486

Received December 15, 1986

In contrast to the vast and rich chemistry of the quinones, the chemistry of their thione analogues remains practically unexplored.[1,2] Although the first futile attempt to synthesize *p*-dithiobenzoquinone (1) was reported in



1 2 3

1909,[3] this highly labile molecule was successfully generated only in 1983 using a flash pyrolysis reaction; it was studied spectroscopically in a frozen argon matrix, but it was observed to decompose in an unknown manner, on moderate warming of the matrix.[4] The isomeric *o*-dithiobenzoquinone (**2**) has proven to be even more elusive. Two attempts have been recorded to generate this compound by either a photochemical or a thermal fragmentation of an appropriate precursor. The matrix-isolated product from the pyrolysis route showed an ultraviolet spectrum suggestive of the unknown benzodithiete rather than that expected of dithione **2**.[5] The photolysis route also did not afford **2** as an isolable product, but its transient generation was proven by trapping it with DMAD to give adduct **3** in modest yield.[6]

As a part of a broad program concerning thioquinone chemistry,[7,8] we have been interested in the possibility of

(1) Klamann, D., Ed. *Methoden der Organischen Chemie*; George Thieme Verlag: Stuttgart, 1985; Vol. E 11.
(2) Patai, S., Ed. *The Chemistry of Quinonoid Compounds*; Wiley: New York, 1974.
(3) Zincke, Th.; Frohneberg, W. *Ber Dtsch. Chem Ges.* **1909**, *42*, 2721.
(4) Bock, H.; Mohmand, S.; Hirabayashi, J.; Maier, G.; Reisenauer, H. P. *Chem. Ber.* **1983**, *116*, 273.
(5) Breitenstein, M.; Schulz, R.; Schweig, A. *J. Org. Chem.* **1982**, *47*, 1981.
(6) DeMayo, P.; Weedon, A. C.; Wong, G. S. K. *J. Org. Chem.* **1979**, *44*, 1977.
(7) Orahovatz, A.; Levinson, M. I.; Carroll, P. J.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1985**, *50*, 1550.

0022-3263/87/1952-1874$01.50/0