Free-Radical Additions to Dibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene

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The cyclopropane ring in dibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene (**1**) is opened by inversion by the trichloromethyl radical in the free-radical addition of bromotrichloromethane to **1**. At higher temperatures, thiophenol adds ionically to **1** in the presence or absence of free-radical initiators. Thiophenol also hydrogenates **1** at high temperatures, apparently *via* a diradical intermediate. It is concluded from this study that cyclopropane rings are quite unreactive toward free-radical additions.

A number of studies have been devoted to the chemistry of additions to cyclopropanes. Of particular interest is the stereochemistry of these processes. Nucleophilic ring openings appear to occur always with inversion,[1] whereas electrophilic cyclopropane ring openings may occur with inversion as well as retention. Thus, electrophilic ring opening of quadricycloheptane-2,3-dicarboxylic acid by bromine occurs with inversion at both carbon atoms of the cyclopropane ring.[2] Positive bromine also opens cyclopropanols with inversion.[3] Protonation (deuteration) of cyclopropanes takes place with inversion in the case of *exo*-tricyclo[3.2.1.0^{2,4}]octane,[4] but with retention of configuration in cyclopropanols[5] and bicyclobutanes.[6] 1-Methylnortricyclene is deuterated in acetic acid-d_1 catalyzed by sulfuric acid-*d*, to give a mixture of norbornyl acetates in which the deuterium atom is 62.2% 6-*endo* (retention) and 37.8% 6-*exo* (inversion).[7] Deuterium bromide in acetic acid-d_1 opens the cyclopropane ring of the Diels–Alder adduct of cycloheptatriene–maleic anhydride with retention.[8] Theoretical calculations[9] on the structure of protonated cyclopropanes indicate that the three-membered ring should undergo electrophilic opening with retention.[10]

Free-radical ring openings are encountered far less often than their ionic counterparts. Indeed, one can find few examples of possible free-radical ring openings[12] and closures.[13] These free-radical displacements are very difficult at normal sp^3-hybridized carbon atoms[14] and appear to take place only on highly reactive carbon centers such as Dewar anthracene[15] and cyclopropanes.[12] The stereochemistry of these openings is unknown.[16] Since the stereochemistry of nucleophilic and electrophilic displacements occur in the opposite sense, *i.e.*, nucleophilic displacements (four-electron systems) occur preferentially with inversion and electrophilic displacements (two-electron systems) occur preferentially with retention, free-radical displacements (three-electron systems) should be very much of interest with respect to the stereochemical possibilities.[21]

Results and Discussion

Dibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene (**1**) was chosen for the study of the stereochemistry of free-radical cyclopropane ring opening because of the relative ease of ring openings in the system[22] as well as the fact that the stereochemistry of the resulting *cis*-dibenzobicyclo[3.3.0]-2,7-octadiene could be established by pmr spectroscopy.[1d,22]

When **1** is allowed to react with refluxing (105°) bromotrichloromethane in the presence of benzoyl peroxide (no reaction in the absence of peroxides), a single product is observed in the pmr spectrum up to *ca.* 20% reaction. As the reaction proceeds, considerable darkening is observed and broad multiplets, presumably

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(10) MO calculations indicate that edge-protonated and corner-protonated cyclopropanes are of comparable energy.[11] It might very well be that edge-protonated cyclopropanes result in opening with retention while corner-protonated rings lead to opening with inversion. If this is the case, one might expect subtle changes in steric as well as electronic properties to result in changes in the stereochemistry of electrophilic cyclopropane ring openings.

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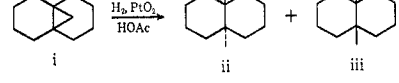
(16) Because of the geometry of the molecule, Dewar anthracene is forced to undergo ring opening with inversion.[15] Highly strained cyclopropanes undergo ring opening with benzyne[17] and maleic anhydride[18] with inversion at each carbon center. Although these latter reactions apparently involve the intermediacy of diradicals,[17,18] how much of this radical character is inherent in the transition state is not clear. Interestingly, the cyclopropane i undergoes nonstereospecific catalytic hydrogenation to give a 50:50 mixture of *cis*- and *trans*-methyldecalins ii and iii,[19] but hydrogenation of bicyclo[2.1.0]pentanes occurs with retention.[20]



i ii iii

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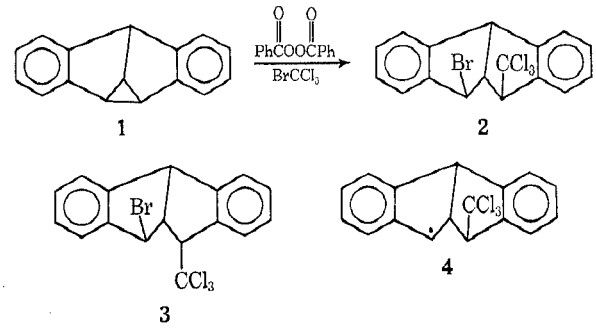
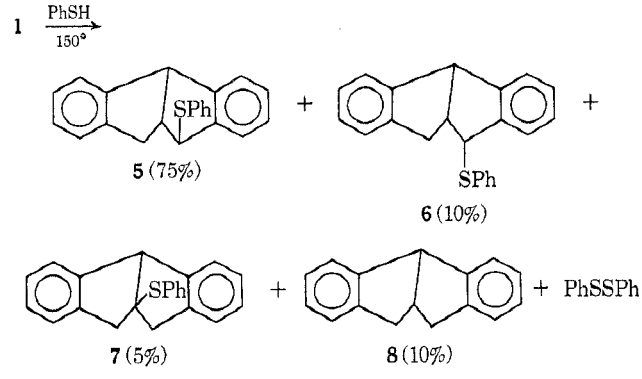
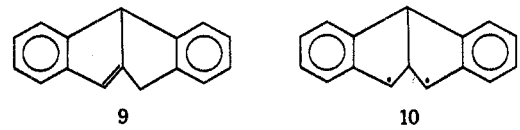
arising from decomposition products, begin appearing in the pmr spectrum. Isolation of the 1:1 adduct of **1** and bromotrichloromethane is hampered not only by these undesired materials, but the adduct itself is sensitive to such things as protic solvents and column chromatography. The most successful manner found for isolating the adduct was chromatography over Florisil (elution with Skellysolve B). The first material off the column was a dark red oil whose ir and pmr spectra, because of the nondescript peaks, were suggestive of a polymeric substance. This material was followed by a light brown oil which when crystallized from *n*-pentane gave *ca.* a 15–20% yield of *anti*-4-trichloromethyl-*anti*-6-bromo-*cis*-dibenzobicyclo[3.3.0]-2,7-octadiene (**2**). When **2** is added to the above reaction mixture at 105°, after a short time the pmr signals attributable to **2** begin to disappear. However, in refluxing bromotrichloromethane (no peroxides added), **2** appears to be stable. If the reaction is stopped after *ca.* 15–20% reaction time, chromatography over Florisil yields 70% recovered **1** and 15% **2** as the only characterizable products. The structure of **2** is supported by an elemental analysis and spectral data. The pmr spectrum is most instructive; outside the aromatic region (8 H from τ 2.3–3.0) lie three doublets (1 H each) at 4.74 (J_{56} = 5.0 Hz), 5.08 (J_{15} = 7.8 Hz), and 5.75 (J_{45} = 3.0 Hz) and a complex multiplet (1 H) from 5.92 to 6.20. The complex multiplet at τ 5.92–6.20 clearly is due to the absorption of the C-5 hydrogen, and the benzhydryl hydrogen at C-1 can be assigned the peak at 5.08, since, in all of the reported compounds in this system, this proton is found always in this region and with J_{15} = 7–8 Hz.[1d,22] The hydrogen α to the bromine atom is assigned the low field signal at τ 4.74, and the proton α to the trichloromethyl group then would be assigned that signal 1 ppm upfield at 5.75; this is consistent with previous observations[23] that the pmr signal for a proton α to a bromine atom is found *ca.* 1 ppm downfield from a proton α to a trichloromethyl group. Since the coupling constants for the *anti* C-4 and C-6 protons are observed to be >7 Hz[1d,22] and the J values for the corresponding *syn* C-4 and C-6 protons are found to be 2–6.4 Hz,[1d,22] clearly the substituents at C-4 and C-6 are in the *anti*-configuration. Thus, the ring has undergone opening by the trichloromethyl radical with inversion. Although none of the corresponding *syn*-trichloromethyl epimer (**3**) was observed, conceivably small amounts of **3** could have been produced but destroyed under the conditions of the reaction. However, it is unlikely that **3** → **2** under the conditions of the reaction. Whether the stereochemistry observed in the opening is characteristic of cyclopropanes in general or whether the *anti* epimer **2** results because of favorable interaction of the aromatic ring in the transition state leading to the radical **4** is not clear. The fact that the bromine atom is transferred from bromotrichloromethane to **4** to yield the *anti*-bromide **2** probably reflects the stereoelectronic requirements of the benzylic radical **4** in the chain-transfer step as well as a definite steric preference for larger groups to occupy the *anti* position.[1d,22] When **1** in bromotrichloromethane is irradiated with uv light, the only adduct observed arises from the electrophilic addition of bromine across the 2,8 bond.[22]



Treatment of **1** with thiophenol at 150° for 1 day gives four compounds along with diphenyl disulfide. In refluxing thiophenol (170°) the ratio of **5**/**6**/**7**/**8** is



11:2:1:7. The percentage of **8** increases dramatically (from 10% at 150° to 30% at 170°). The rate and product distribution of these reactions are unaffected by the presence of free-radical initiators or oxygen. Also, no observable change in the product distribution results when **1** is treated with thiophenol at 170° in the presence of potassium thiophenoxide (heterogeneous reaction). However, the reaction was complete in a few minutes at 110° when a catalytic amount of *p*-toluenesulfonic acid was added. Under these conditions an 85:15 mixture of **5** and **6** results; no **7** or **8** is observed. The proof of structure for the thio ethers **5**–**7** is based on their reactions with Raney nickel to give **8** as well as the pmr spectra of the sulfides and the corresponding sulfones (see Experimental Section). The products from these addition reactions, **5**–**8**, are all stable under the various reaction conditions described above. The thio ethers **5** and **6** are clearly the result of ionic addition of thiophenol across the cyclopropane ring. The formation of small amounts of **7** can be rationalized in terms of protonation of the ring followed by loss of a proton to give the olefin **9**. Under the reaction conditions, **9** should easily undergo free-radical addition of thiophenol to give **7**. This explanation is consistent with the fact that **7** is observed only at high temperatures, a condition which should favor deprotonation of the intermediate carbonium ion.[24]



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Thiophenol apparently is capable of hydrogenating the cyclopropane ring of **1** since relatively large amounts of **8** and diphenyl disulfide are observed (*vide supra*). Thiols are excellent hydrogen atom donors to free radicals; thiophenol is particularly effective.[25] It appears that the 2,8 bond of the cyclopropane ring in **1** undergoes reversible homolysis at higher temperatures to give a diradical (**10**) which is then trapped, *via* hydrogen atom transfer, by thiophenol. Based on previous work of 1,2-diphenylcyclopropanes[26,27] the energy of activation for such homolysis can be expected to be *ca.* 30-35 kcal/mol, a value which is consistent with the large increase in the amount of **8** observed with increasing reaction temperatures. Poorer hydrogen atom transfer reagents are much less effective at trapping the diradical **10**. At temperatures below 200°, fluorene does not reduce **1** after several days. However, dihydroanthracene gives *ca.* 5–10% **8** and 9,9′,-10,10′-tetrahydro-9,9′-bianthryl after 2 days at 200°. Thus, as expected, dihydroanthracene is much less effective at trapping the diradical **10** than is thiophenol, but is more effective than fluorene.[28] Cyclopropanes rearrange *via* 1,2-hydrogen atom shifts in the intermediate diradical to propylenes.[29] In the case of **1** this could give rise to **9** which would then result in the formation of **7**. However, heating **1** in refluxing dimethylacetamide (bp 165°) or *n*-decane (bp 174°) for up to 50 hr gave only recovered starting material. This lack of rearrangement of **1** → **9** appears to be characteristic of 1,2-diphenylcyclopropanes.[26,27]

Treatment of **1** with thiophenol or butanethiol under the influence of uv light gave no reaction after extended periods of time. Treatment of **1** with *n*-butanethiol at 100° in the presence of benzoyl peroxide gave recovered **1** along with varying amounts of *n*-butyl phenyl sulfide. This sulfide could be isolated from the reaction of *n*-butanethiol with benzoyl peroxide in the absence of **1**.

It is clear from these data that **1** and presumably cyclopropanes in general are quite unreactive toward free-radical addition reactions. Whereas protonation of cyclopropanes appears to be somewhat more facile than protonation of the corresponding olefins,[30] free-radical additions to olefins appears to take place far more readily than these additions to cyclopropanes.[31]

Experimental Section[35]

Addition of Bromotrichloromethane to 1.—A solution of 1.0 g (4.9 mmol) of **1**[36] and 50 mg of benzoyl peroxide in 5.0 ml of bromotrichloromethane was held at reflux (105°) under nitrogen. Every hour *ca.* 40 mg of benzoyl peroxide was added to the mixture. The course of the reaction was followed by pmr spectroscopy. After 1 hr the reaction was about 20% complete and the pmr spectrum showed only **1** and **2** to be present. [If the solution is worked up at this point, careful chromatography (*vide infra*) yields first 0.7 g of recovered **1** followed by 0.3 g of **2**.] However, as the reaction proceeded the solution got progressively darker, and the pmr spectrum began to exhibit broadened high field multiplets. The reaction was stopped after 6 hr, and the solvent was removed by rotary evaporation. The resulting dark red oil was chromatographed over 60 g of Florisil packed in Skellysolve B. Elution with Skellysolve B first gave a dark red oil whose pmr and ir spectra, because of the nondescript peaks, were suggestive of a polymeric substance. This material was followed by a light brown oil which when crystallized from *n*-pentane gave 400 mg (20%) of **2**, mp 137–138°.

Anal. Calcd for $C_{17}H_{12}BrCl_3$: C, 50.72; H, 3.01. Found: C, 50.55; H, 3.06.

Although **2** was stable in refluxing bromotrichloromethane under nitrogen, the presence of benzoyl peroxide led to the decomposition of **2**.

Treatment of **1** with bromotrichloromethane under the influence of a high pressure uv light (Vycor filter) gives, as the major products, 4,6-dibromo-*cis*-dibenzobicyclo[3.3.0]-2,7-octadienes in the same ratio as has been observed in the ionic addition of bromine to **1**.[22]

Addition of Thiophenol to 1.—A solution of 2.0 g (9.8 mmol) of **1** in 10 ml of freshly distilled thiophenol was held at reflux under nitrogen for 18 hr. The course of the reaction was followed by tlc (silica gel). The excess thiophenol was removed by distillation at 25 mm and the resulting oil was chromatographed over 120 g of silica gel packed in Skellysolve B. Elution with 3% benzene in Skellysolve B gave 180 mg of diphenyl disulfide followed by 600 mg (30%) of **8**, mp 95–96° (lit.[37] mp 95°). Elution with 5% benzene in Skellysolve B gave the thio ethers **5**, **6**, and **7**. The first fractions were rich in **5** and the latter fractions were rich in **7**. Successive fractional crystallizations from *n*-pentane gave 0.25 g (8%) of *syn*-4-phenylthio-*cis*-dibenzobicyclo[3.3.0]-2,7-octadiene (**6**), mp 113–114°, 1.4 g (46%) of *anti*-4-phenylthio-*cis*-dibenzobicyclo[3.3.0]-2,7-octadiene (**5**), mp 73–74°, and 0.13 g (4%) of 5-phenylthio-*cis*-dibenzobicyclo[3.3.0]-2,7-octadiene (**7**), mp 118–119°.

The pmr spectrum of **5** in carbon tetrachloride shows two overlapping doublets (1 H each, C-1 and C-4 protons) from τ 5.4 to 5.7, a complex multiplet (3 H) from 6.2 to 7.6, and a complex multiplet (13 H) from 2.6 to 3.1.

Anal. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77. Found: C, 83.75; H, 5.91.

Oxidation of 300 mg (0.95 mmol) of **5** in 8 ml of dichloromethane by 500 mg of *m*-chloroperbenzoic acid gave 320 mg (97%) of the corresponding sulfone, mp 161–163°.

The pmr spectrum of the sulfone in chloroform-*d* shows two doublets (1 H each) at τ 5.37 (J_{45} = 1.6 Hz) and 5.77 (J_{15} = 7.6 Hz), a series of complex multiplets (3 H) from 6.0 to 7.6, and a complex multiplet (13 H) from 2.2 to 3.0.

Anal. Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24. Found: C, 76.07; H, 5.28.

The pmr spectrum of **6** in carbon tetrachloride shows two doublets (1 H each) at τ 5.08 (J_{45} = 7.0 Hz) and 5.55 (J_{15} = 7.4 Hz), a complex multiplet (1 H) from 6.1 to 6.6, a complex multiplet (2 H) from 6.8 to 7.1, and a complex multiplet (13 H) from 2.4 to 3.1.

Anal. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77. Found: C, 83.75; H, 5.87.

Oxidation of **6** under the same conditions as that described for **5** gave the sulfone of **6** (90%), mp 183–184°. Treatment of this sulfone with 0.5 *M* sodium ethoxide in ethanol at room temperature for 6 hr gave the sulfone of **5** in quantitative yield.

The pmr spectrum of the sulfone in chloroform-*d* shows two doublets (1 H each) at τ 4.83 (J_{45} = 5.8 Hz) and 5.53 (J_{15} = 6.8 Hz), a complex multiplet (3 H) from 6.2 to 7.2, and a complex multiplet (13 H) from 1.8 to 3.0.

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(26) L. B. Rodewald and C. H. DePuy, *Tetrahedron Lett.*, 2951 (1964).
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(28) E. C. Kooyman, *Discuss. Faraday Soc.*, **10**, 163 (1951).
(29) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).
(30) See, for example, R. T. LaLonde and M. R. Tobias, *J. Amer. Chem. Soc.* **86**, 4068 (1964).
(31) Although cyclopropanes may be protonated more rapidly then analogous alkenes, olefins react far more readily with bromine than do cyclopropanes.[32] This is consistent with the Principal of Hard and Soft Acids and Bases (HSAB Principal).[33] Since olefins are certainly "softer" than cyclopropanes, the olefins should prefer to react with the softer electrophile, bromine. Radicals are believed to be quite "soft"[34] and hence should have an enhanced reactivity toward olefins compared with cyclopropanes.
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(35) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Proton magnetic resonance spectra were measured with a Varian A-60D nmr spectrometer with tetramethylsilane (τ 10.00) as the internal standard. *J* values reported are "observed" ones. Elemental analyses were performed by Dr. Franz J. Kasler, University of Maryland.
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(37) W. Baker, J. F. W. McOmie, S. O. Parfitt, and D. A. M. Watkins, *J. Chem. Soc.*, 4026 (1957).

Anal. Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24. Found: C, 75.99; H, 5.34.

The pmr spectrum of **7** in carbon tetrachloride shows a singlet (1 H) at τ 5.43, a pair of doublets (2 H each, J_{gem} = 16.4 Hz) at 6.62 and 6.83, and a complex multiplet (13 H) from 2.5 to 3.1.

Anal. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77. Found: C, 84.00; H, 5.97.

Oxidation of **7** under the same conditions as that described for **5** gave the sulfone of **7** (95%), mp 178–179°.

The pmr spectrum of the sulfone in chloroform-*d* shows a singlet (1 H) at τ 4.69, a pair of doublets (2 H each, J_{gem} = 17.6 Hz) at 6.10 and 6.78, and a complex multiplet from 2.0 to 3.0.

Anal. Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24. Found: C, 76.40; H, 5.29.

When **1** is treated with thiophenol at 150° for 30 hr, **5**, **6**, **7**, and **8** were isolated in high yield in the ratio of 7.5:1:0.5:1, respectively. The presence of oxygen, benzoyl peroxide, or benzoic acid had no observable effect on the rate or product distribution of the reaction. The reaction of **1** with thiophenol at 110° catalyzed by a trace of *p*-toluenesulfonic acid proceeded very rapidly to give 85% **5** and 15% **6**; no **7** or **8** was observed. Treatment of **1** (500 mg) with 10 ml of thiophenol in which 60 mg of potassium metal had been dissolved at 170° for 18 hr gave essentially identical results with that observed in the absence of potassium thiophenoxide. In all these cases, products **5**–**8** were stable to the conditions of the reactions. Attempts to photoinitiate the addition of thiophenol to **1** with either medium or low pressure mercury uv lamps failed to give any 1:1 adducts.

Treatment of thio ethers **5**–**7** with a 20-fold excess (by weight) of Raney nickel W-2[38] in refluxing ethanol for 14 hr gave an 80–85% yield of hydrocarbon **8** in each case.

Attempted Addition of *n*-Butanethiol to 1.—Treatment of **1** with *n*-butanethiol in the presence of either medium or low pressure mercury uv lamps did not result in any observable addition products. When **1** was treated in refluxing *n*-butanethiol with benzoyl peroxide, **1** was recovered unchanged after several days. Chromatography over silica gel did result in the isolation of *n*-butyl phenyl sulfide (eluted with 10% benzene in Skellysolve B) which proved to be identical (pmr and ir spectra) with an authentic sample.[39] This sulfide could be isolated from a solution of *n*-butanethiol treated with benzoyl peroxide in the absence of **1**.

Treatments of 1 with Fluorene and Dihydroanthracene.—A mixture of 0.50 g of **1** and 5.0 g of fluorene was sealed in a glass tube under nitrogen. The tube was heated at 195–200° in an oil bath for 2 days. The majority of the fluorene was removed by crystallization from methanol, and a pmr spectrum of the mother liquor showed only **1** and fluorene to be present. No **8** could be observed.

This same procedure was employed for 9,10-dihydroanthracene, and a pmr spectrum of the resulting mixture indicated that *ca.* 10% of **1** had been hydrogenated to **8**. This mixture was chromatographed over 60 g of silica gel packed in Skellysolve B. Elution with 3% benzene in Skellysolve B gave 950 mg of 9,10-dihydroanthracene, 45 mg of **8**, 400 mg of **1**, and 70 mg of 9,9′,-10,10′-tetrahydro-9,10-bianthryl, mp 256–258° (lit.[40] mp 255°).

Registry No.—**1**, 2199-28-2; **2**, 23367-54-6; **5**, 23265-33-0; **5** sulfone, 23265-34-1; **6**, 23265-35-2; **6** sulfone, 23265-36-3; **7**, 23288-66-6; **7** sulfone, 23265-37-4.

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Conformational Studies of Perfluoro-2-halo-1,2-oxazetidines Using Nuclear Magnetic Resonance Spectroscopy[1]

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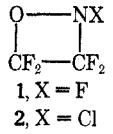
The high-resolution nmr spectra of perfluoro-2-fluoro-1,2-oxazetidine (**1**) and perfluoro-2-chloro-1,2-oxazetidine (**2**) were obtained over the temperature range 85 to −120°. The observed nonequivalence of geminal fluorines was attributed to restricted nitrogen inversion. The temperature dependence of the geminal fluorine–fluorine chemical-shift differences indicated equilibrating nonplanar conformers. The conformational free-energy differences for **1** and **2** were determined to be 900 and 1000 cal/mol, respectively.

The use of nmr spectroscopy to demonstrate the nonplanarity of cyclobutane rings has been reported by Lambert and Roberts.[2] These authors observed that the chemical-shift differences of geminal fluorines in certain substituted cyclobutanes showed temperature dependence. This was attributed to an equilibrium between the two possible puckered-ring conformations. We wish to present nmr evidence indicating similar nonplanarity in a perfluorooxazetidine ring system.

The room-temperature ^{19}F nmr spectra of perfluoro-2-fluoro-1,2-oxazetidine (**1**) and perfluoro-2-chloro-1,2-oxazetidine (**2**) showed AB quartets which were assigned to the CF_2O and CF_2N fluorines. The spectrum of **1** also contained a broad peak owing to the NF fluorine. The chemical shifts and geminal coupling constants are given in Table I. With the temperature varied from 85 to −120°, the same general pattern was obtained in the spectra of **1** and **2** with the geminal coupling constants remaining essentially unchanged. The volatility of the N-halooxazetidines precluded nmr studies above 85°. However, even at this temperature the quartet structures were clearly visible. The NF signal in the spectrum of **1** was detectably sharper at lower temperatures.[3]

The nonequivalence of the geminal fluorines in **1** and **2** results either from restricted oxazetidine ring inversion or from restricted nitrogen inversion. However, it seems very unlikely that the barrier to ring inversion would be sufficient to slow the ring-intercon-



1, X = F
2, X = Cl

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(2) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3710 (1963); **87**, 3884 (1965).

(3) Measurements of $W_{1/2}$ (signal width at half-height) indicate a change from 47 Hz at −120° to 108 Hz at 24° with further broadening to 135 Hz at 85°.