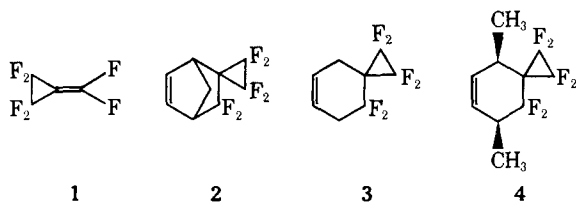


## Perfluoromethylenecyclopropane Cycloadditions

Sir:

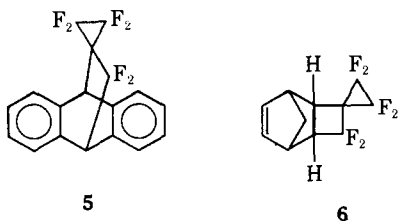
Surprisingly, perfluoromethylenecyclopropane<sup>1</sup> (**1**) fails to undergo thermal [2 + 2] cycloadditions although facile [4 + 2] cycloadditions are observed. The increased p character of the carbon orbitals in C–F and cyclopropane C–C bonds weakens the double bond, and biradical cycloaddition in analogy with tetrafluoroethylene was anticipated. The similarity of dichloromethylenecyclopropane, methylenecyclopropane, bicyclopopylidene, and fluoroolefin [2 + 2] thermal cycloadditions has been noted.<sup>2–6</sup>

No cyclodimer is formed when **1** is heated at 150° for 24 hr. Styrene and acrylonitrile fail to cycloadd **1** at 150–175°. Tetrafluoroethylene readily undergoes these cycloadditions and dimerizes at 150°.<sup>7,8</sup> Cyclopentadiene reacts with **1** at 0° to give **2**: mp 18.5–19.5; ir (neat) 1578 cm<sup>-1</sup> (very weak C=C); nmr (CCl<sub>4</sub>) <sup>1</sup>H δ 2.0 (unresolved AB m, 2), 3.13 (broad m, 2), 6.32, 6.67 (AB m of m, 2, J<sub>AB</sub> = 6 Hz); <sup>19</sup>F φ\* 99.3, 104.7 (AB m of m, 2, J<sub>AB</sub> = 230 Hz), 147.9, 153 (AB m of m, 2, J<sub>AB</sub> = 285 Hz), 149.2, 153.4 (AB m of m, 2, J<sub>AB</sub> = 285 Hz). At 100°, butadiene and **1** afford **3**: ir (neat) 1648 cm<sup>-1</sup> (very weak, C=C); nmr (CCl<sub>4</sub>) <sup>1</sup>H δ 2.3–3.0 (m, 4), 5.22 (m, 2); <sup>19</sup>F φ\* 99.2 (broad p, 2), 149.5, 153.5 (AA'BB' m of m, 4, J<sub>AB</sub> = 185 Hz). No [2 + 2] cycloadduct is formed in either reaction. Perfluoromethylenecyclopropane fails to react with *cis,cis*- or *cis,trans*-2,4-hexadiene at 100°, although **4** is readily formed from



*trans,trans*-2,4-hexadiene under these conditions.

Perfluoromethylenecyclopropane adds to anthracene at 100° and quadricyclene at 25° to give **5** and **6**, respectively.



spectively.

The dienophilicity of **1** is exceptional. Simple fluoroolefins require temperatures in excess of 100° for facile

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- (4) D. Kaufmann and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **12**, 159 (1973).
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- (8) All reactions were performed by heating the appropriate olefin or diene and a 5–10% excess of **1** with a trace of *d*-limonene in sealed glass ampoules. The product mixture was examined by vpc and isolated products gave satisfactory combustion and/or mass spectral analyses in all cases. Complete detailed structure identifications by nmr and ir will be discussed in the forthcoming full paper.

cycloaddition to cyclopentadiene.<sup>9</sup> Comparison of the reactivity of **1** with its acyclic analog, perfluoroisobutylene (PFIB), is illustrative. Facile addition of PFIB to cyclopentadiene requires 150°;<sup>10</sup> less than 5% cycloaddition to butadiene is observed at 200°;<sup>11</sup> and addition to anthracene requires ca. 200°.<sup>12</sup> The ease of [4 + 2] cycloaddition of **1** further reflects the reactivity of the difluoromethylene double bond.<sup>1</sup>

The failure of **1** to [2 + 2] cycloadd is puzzling. Several factors are important for reactivity in the biradical mechanism of cycloaddition:<sup>5</sup> (a) accommodation of an odd electron on the potential biradical; (b) exothermicity of the double bond opening; and (c) ease of approach of reactants. The reactivity of **1** in [4 + 2] cycloadditions and ease of polymerization<sup>1</sup> suggest that **1** accommodates factors a and b. The similar unreactivity of **1**, PFIB, and 1,1-bis(trifluoromethyl)-2,2-dichloroethylene<sup>6</sup> suggests that the failure of **1** to [2 + 2] cycloadd, when compared to other methylene cyclopropanes, is a result of steric repulsion from the cyclopropane ring fluorines toward incoming cycloaddend at the site of initial bond formation.<sup>13,14</sup>

Partially fluorinated methylenecyclopropanes are in preparation to further elucidate the factors which control [2 + 2] and [4 + 2] cycloadditions in methylenecyclopropanes.

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(11) B. E. Smart, unpublished results.

(12) J. E. Nottke, unpublished results.

(13) A steric limitation in methylenecyclopropane dimerizations has been noted.<sup>3</sup> 2,2-Dimethylmethylenecyclopropane and isopropylidene-cyclopropane fail to dimerize under conditions which are amenable to methylenecyclopropane dimerization.

(14) The importance of steric control by fluorine relative to hydrogen substituents has been demonstrated in other reactions, see ref 10 and B. E. Smart, *J. Org. Chem.*, **38**, 2035, 2039 (1973).

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## Complexed Radicals. I. Decomposition of Tetramethyl-2-tetrazene-Zinc Chloride Complex in Presence of Olefins

Sir:

In our continuing studies of the reactivity of amino radicals,<sup>1</sup> we became intrigued by the modification of that reactivity by complexation of the radicals by metal ions. Unprotonated or uncomplexed amino radicals are notably unreactive toward unsaturation.<sup>1,2</sup> Minisci and his coworkers have shown that amino radicals generated in redox systems from *N*-chloroamines,<sup>3</sup> hydroxylamine, and hydroxylamino-*O*-sulfonic acid<sup>4</sup> added well to alkenes. It is reasonable to assume that these amino radicals were coordinated by the metal ions involved in the redox processes, at least when the reactions were carried out in neutral media.

(1) Cf. C. J. Michejda and W. P. Hoss, *J. Amer. Chem. Soc.*, **92**, 6298 (1970); S. Shih, R. J. Buenker, S. D. Peyerimhoff, and C. J. Michejda, *ibid.*, **94**, 7620 (1972).

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