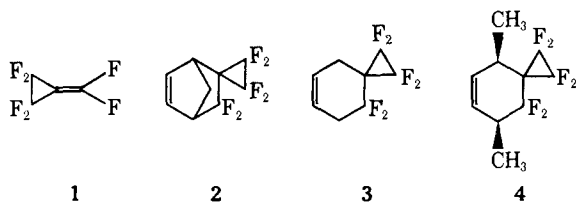## Perfluoromethylenecyclopropane Cycloadditions

*Sir:*

Surprisingly, perfluoromethylenecyclopropane[1] (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, bicyclopropylidene, and fluoroolefin [2 + 2] thermal cycloadditions has been noted.[2-6]

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°.[7,8] Cyclopentadiene reacts with 1 at 0° to give 2: mp 18.5–19.5; ir (neat) 1578 cm$^{-1}$ (very weak C=C); nmr (CCl$_4$) $^1$H $\delta$ 2.0 (unresolved AB m, 2), 3.13 (broad m, 2), 6.32, 6.67 (AB m of m, 2, $J_{AB}$ = 6 Hz); $^{19}$F $\phi^*$ 99.3, 104.7 (AB m of m, 2, $J_{AB}$ = 230 Hz), 147.9, 153 (AB m of m, 2, $J_{AB}$ = 285 Hz), 149.2, 153.4 (AB m of m, 2, $J_{AB}$ = 285 Hz). At 100°, butadiene and 1 afford 3: ir (neat) 1648 cm$^{-1}$ (very weak, C=C); nmr (CCl$_4$) $^1$H $\delta$ 2.3–3.0 (m, 4), 5.22 (m, 2); $^{19}$F $\phi^*$ 99.2 (broad p, 2), 149.5, 153.5 (AA'BB' m of m, 4, $J_{AB}$ = 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



1    2    3    4

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

Perfluoromethylenecyclopropane adds to anthracene at 100° and quadricyclene at 25° to give 5 and 6, re-



5        6
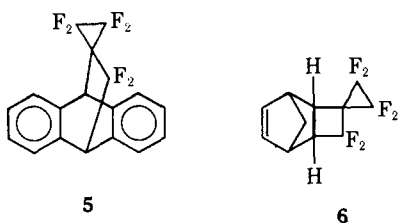
spectively.

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

(1) B. E. Smart, *J. Amer. Chem. Soc.*, **96**, 927 (1974).

(2) W. R. Dolbier, Jr., D. Lomas, and P. Tarrant, *J. Amer. Chem. Soc*, **90**, 3594 (1968).

(3) W. R. Dolbier, Jr., *et al.*, *Tetrahedron*, **28**, 3185 (1972).

(4) D. Kaufmann and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **12**, 159 (1973).

(5) P. Le Perchec and J. M. Conia, *Tetrahedron Lett.*, 1587 (1970).

(6) P. D. Bartlett and R. C. Wheland, *J. Amer. Chem. Soc.*, **94**, 2145 (1972).

(7) W. H. Sharkey, *Fluorine Chem. Rev.*, **2**, 1 (1968).

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

The failure of 1 to [2 + 2] cycloadd is puzzling. Several factors are important for reactivity in the biradical mechanism of cycloaddition:[6] (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[1] suggest that 1 accommodates factors a and b. The similar unreactivity of 1, PFIB, and 1,1-bis(trifluoromethyl)-2,2-dichloroethylene[6] 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.[13,14]

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

(9) D. R. A. Perry, *Fluorine Chem. Rev.*, **1**, 253 (1967).

(10) B. E. Smart, *J. Org. Chem.*, **38**, 2027 (1973).

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

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

(13) A steric limitation in methylenecyclopropane dimerizations has been noted.[3] 2,2-Dimethylmethylenecyclopropane and isopropylidenecyclopropane 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).

**Bruce E. Smart**

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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,[1] 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.[1,2] Minisci and his coworkers have shown that amino radicals generated in redox systems from *N*-chloroamines,[3] hydroxylamine, and hydroxylamino-*O*-sulfonic acid[4] 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).

(2) B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961); C. H. Bamford, *ibid.*, **17** (1939); R. S. Neale, N. L. Marcus, and R. G. Scheppers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).

(3) F. Minisci, R. Galli, and G. Pollina, *Chim. Ind.* (*Milan*), **47**, 736 (1965).

(4) F. Minisci, R. Galli, and M. Cecere, *Chim. Ind.* (*Milan*), **48**, 132 (1966).

Noltes and van den Hurk[5] prepared a complex of tetramethyl-2-tetrazene (TMT) and zinc chloride whose elemental analysis was consistent with the empirical formula $C_4H_{12}N_4ZnCl_2$. On heating between 40 and 60° the complex lost nitrogen. Although no structural data were given for the complex, the authors assumed that it had the structure shown in 1.[6] It seemed likely to us that the loss of nitrogen could yield the biradical species 2. It also seemed likely that 2 could be intercepted by a suitable olefin to give a 1,2-tetramethyldiamine complex 3.
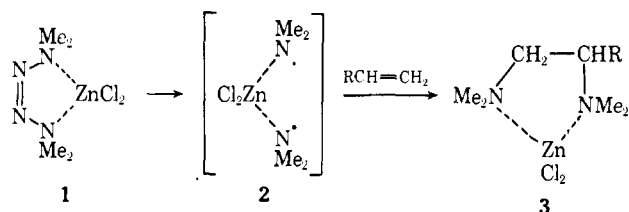


The complex was conveniently prepared in anhydrous THF[7] by mixing anhydrous zinc chloride (in slight excess) with TMT. The complex could be isolated from this solution by precipitation with dry pentane, but for the preparative experiments described in this report the complex was not isolated. The excess olefin was added to the solution and the mixture was heated under reflux (65°) for 2 hr. The basic components of the reaction mixture were extracted and then separated by glc. The olefins tested included styrene, α-methylstyrene, stilbene, 1-octene, cis- and trans-2-butene, cyclohexene, and 3,3-dimethyl-1-butene.

In the absence of oxygen, styrene and α-methylstyrene gave 30% yields of the diamino adduct 4, stilbene gave only a trace of the adduct ($\sim$5%). In the presence of oxygen ($O_2$ passed over the stirred reaction mixture) both styrene and α-methylstyrene gave 30–35% of the amino alcohol 5 and 1-octene gave 10–15% of the amino alcohol 6.[8,9] The other alkenes mentioned
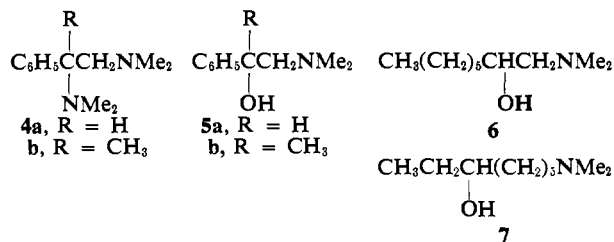


failed to give detectable adducts under the conditions employed. The formation of the amino alcohols can be rationalized by initial formation of a hydroperoxide which is then reduced by one of the easily oxidizable

(5) J. G. Noltes and J. W. G. van den Hurk, *J. Organometal. Chem.*, 1, 377 (1964).

(6) An alternative structure for the complex could be a ten-membered ring dimer. Concerted (or near concerted) loss of two nitrogen molecules from the dimer would also give 2 as an intermediate.

(7) We also used acetone and acetonitrile as solvents. There was no qualitative difference in the reactions in those solvents, except that the complex seemed to be less stable.

(8) All the new compounds had correct elemental analyses and the spectral data (infrared, nmr, and mass spectrometry) were consistent with the assigned structures.

(9) In some runs with 1-octene an important trace (<1%) product was detected. It was N,N-dimethyl-6-hydroxy-1-octylamine (7). This product was probably formed by an intramolecular hydrogen atom transfer in the initial 1-(N,N-dimethylamino)-2-octyl radical, followed by the capture of the rearranged radical by oxygen. This product is important because it is difficult to rationalize its formation by anything but a radical mechanism.

substances present in the reaction mixture. Two likely reducing agents are unreacted TMT and tetramethylhydrazine, which is a product of the decomposition of the original complex.

These data strongly suggest that the intermediate biradical 2 is involved in the reaction and that selected olefins can be used to trap it. The addition of 2 is not concerted as is indicated by the formation of amino alcohols in presence of oxygen.[10] The reaction is very sensitive to steric effects, as is indicated by the lack of addition to internal olefins and to the highly hindered, terminal olefin 3,3-dimethyl-1-butene.

The biradical 2 is a unique species. It is a biradical formed from two monoradicals 'by virtue of complexation to a metallic center. At the present time we have no data to indicate whether 2 is predominantly a triplet or a singlet. The addition reaction seems to be radical in nature, but this fact does not prove the triplet multiplicity of the intermediate.

Experiments on the structure of the tetrazene–metal ion complexes, the structures of the intermediates, the reactivity of the complexes as a function of the metal, the tetrazene, and the substrate are under active investigation.

(10) It may be argued that the addition of two dimethylamino groups to styrene may not, in fact, be *via* a diradical or even a radical mechanism. A stepwise process involving initial addition of one amino radical to styrene followed by a capture of a second amino radical seems unlikely to us. In a previous study of additions of amino radicals to styrene and α-methylstyrene (D. H. Campbell and C. J. Michejda, unpublished), we obtained small yields of monoaddition products (maximum yield 10%) and no diadducts. The fact that the apparent amino radical addition occurs in presence of oxygen simply indicates that oxygen is a poor scavenger of amino radicals. We have observed that fact before, as have others.[11] On the other hand, Roberts and Ingold[12] reported that the highly hindered 2,2,6,6-tetramethylpiperidyl radical was rapidly scavenged by oxygen to give the corresponding nitroxide.

(11) P. W. Jones and H. D. Gesser, *Chem. Ind. (London)*, 566 (1970); *J. Chem. Soc. B*, 1873 (1971).

(12) J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, 95, 3228 (1973).

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## Geometrical Dependences of Carbon–Nitrogen Coupling Constants. Oximes[1]

*Sir:*

We report here (Table I) the first systematic demonstration that $^{13}C$–$^{15}N$ coupling constants are related to nitrogen lone-pair orientation in structurally rigid molecules and that this property can markedly influence values of *one-bond* coupling constants. Isolated examples of the latter phenomenon have been reported for phosphorus[2] and nitrogen;[3] analogous results are well documented for $J_{NH}$.[4,5] Readily available oxime iso-

(1) Presented in part at the 14th Annual Experimental NMR Conference, Boulder, Colo., April 1973.

(2) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, 37, 3470 (1972).

(3) (a) W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Bradley, and D. M. Jerina, *J. Amer. Chem. Soc.*, 94, 8501 (1972); (b) However, see H. C. Yeh, H. Ziffer, D. M. Jerina, and D. R. Boyd, *ibid.*, 95, 2741 (1973).

(4) J. P. Kintzinger and J. M. Lehn, *Chem. Commun.*, 680 (1967).

(5) For reviews, see (a) R. L. Lichter, "Determination of Organic Structures by Physical Methods," Vol. 4, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971, Chapter 4; (b) T. A. Axenrod, "Nitrogen NMR Spectroscopy," G. Webb and M. Witanowski, Ed., Plenum Press, New York, N. Y., 1973, p 261.