

18,200) (styryl); n.m.r., τ ca. 2.7, 3.10, 3.65 p.p.m. (intensities ca. 20:1:1), indicates that this compound is not an intermediate (through cyclization of IX) because it behaves differently under reaction conditions.^{5b}

A mechanism involving intermediate ring contraction to a 2-hydroxy-2,3,5,5-tetraphenyl isomer of the cyclobutenol X⁸ before phenyl group migration, was excluded by the second group of tracer experiments designed to test this point, starting from II# C¹⁴-labeled at carbon-5. Oxidation of the resulting samples of unsaturated ketone III# gave benzophenone V carrying none of the #C¹⁴ activity and benzoic acid IV# containing all of it; and oxidation of the pentaphenylbutenol VI# obtained by adding phenyllithium to these samples of the ketone III# gave benzophenone VII# containing all of the #C¹⁴ and benzoic acid VIII containing none. This showed that all of the C¹⁴ of the ketone III# had been located at position-5 as demanded by the mechanism II \rightarrow IX or X \rightarrow III.^{5b}

The drive for the rearrangement seems to be furnished by the extraordinary coincidence of steric pressure at the quaternary carbon-5 and strain release by ring cleavage with formation of the acyclic ketone III. The reaction bears some analogy to the pinacol rearrangement.⁹

Studies of these and related reactions are in progress to gain more detailed understanding of the scope, by-products and mechanisms.

(8) Cf. Also N. C. Yang, A. Morduchowitz, and D.-D. H. Yang, *ibid.*, **85**, 1017 (1963); cf. also ref. 7b.

(9) Cf. (a) G. W. Griffin and R. B. Hager, *J. Org. Chem.*, **28**, 599 (1963); cf. Also the pinacol-like rearrangements of (b) 1,2-di-(benzhydridyl)cyclopropane to an acyclic unsaturated ketone [R. A. Darby and R. E. Lutz, *ibid.*, **22**, 1353 (1957)] and of (c) *trans*-(C₆H₅)₂C(OH)CH=CHC(C₆H₅)₂OH to C₆H₅COCH(C₆H₅)CH=C(C₆H₅)₂, an isomer of III [R. E. Lutz and R. G. Bass, unpublished results (see Dissertation, University of Virginia, 1961)].

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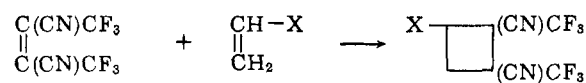
Stereochemistry of the Cycloaddition Reaction of 1,2-Bis-(trifluoromethyl)-1,2-dicyanoethylene and Electron-Rich Alkenes

Sir:

It has been emphasized that few quantitative data about the stereochemistry of additions to form cyclobutanes are available.¹ We wish to report on the stereochemistry of a type of cycloaddition recently discovered,² in which strongly electrophilic olefins, such as tetracyanoethylene, undergo cyclization with electron-rich alkenes, *e.g.*, II, under very mild conditions. Such reactions involve a highly colored charge-transfer complex and exhibit reaction rates that are markedly dependent on solvent polarity. For tetracyanoethylene, the relative rates for cyclobutane formation vary by as much as 8×10^4 depending on solvent, with nitromethane being one of the fastest and cyclohexane one of the slowest.³

We have prepared 1,2-bis-(trifluoromethyl)-1,2-dicyanoethylene (I) by pyrolysis of 1-cyano-2,2,2-trifluoroethyl chlorosulfite. *Anal.* Calcd. for C₆F₆N₂: C, 33.66; F, 53.25; N, 13.09. Found: C, 33.91; F, 53.43; N, 12.81. The pure *cis* and *trans* isomers of this strongly electrophilic olefin react at room tempera-

ture with electron-rich alkenes to form 1,2-bis-(trifluoromethyl)-1,2-dicyanocyclobutanes (III) with complete stereospecificity over a wide range of solvent polarity.



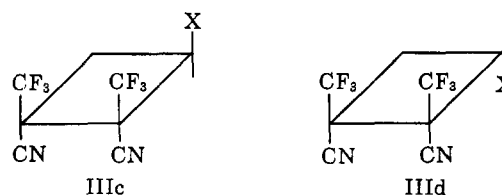
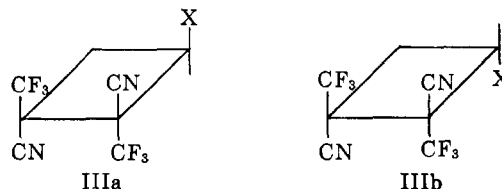
I, (*cis* and *trans*)

II

III

X = RO⁻, RS⁻, *p*-ROC₆H₄⁻

Reactions of *trans*-I with the alkenes II in the absence of solvent give exclusively the cyclobutane diastereomers IIIa and IIIb; reactions of *cis*-I give a different set of diastereomers, IIIc and IIId. Similar stereospecificity is observed in reactions of *trans*-I with *cis*- and *trans*-propenyl *n*-propyl ether.



The cyclobutane structures for the products were confirmed by elemental and spectral analyses. Comparative fluorine n.m.r. spectroscopy was particularly useful for determining the number and kinds of diastereomers formed. For example, the cyclobutane diastereomer mixture IIIa + IIIb resulting from the reaction of *trans*-I and *t*-butyl vinyl sulfide (II, X = SCMe₃) exhibits a fluorine n.m.r. spectrum consisting of four singlet resonances appearing as two pairs whose components are of equal intensity. The fluorine n.m.r. spectrum of diastereomer mixture IIIc + IIId (X = SCMe₃), prepared from *cis*-I and *t*-butyl vinyl sulfide, also exhibits two pairs of resonances whose components are of equal intensity, but the chemical shifts are different from those obtained from the mixture IIIa + IIIb, and the resonances appear as quadruplets (due to mutual splitting of the CF₃ groups) rather than singlets. A further verification of isomer composition was also obtained in certain cases by chromatographic separation of the diastereomers.

The rate of cycloaddition of I to *t*-butyl vinyl sulfide is strongly influenced by solvents. Qualitative measurements based on observation of the disappearance of color of the charge-transfer complex gave reaction times ranging from less than 1 min. in methanol to 4320 min. in carbon tetrachloride for *cis*-I and 1.5 min. in methanol to 17,280 min. in carbon tetrachloride for *trans*-I. The stereospecificity of the reaction was, however, maintained throughout the whole range of solvents tested.

These observations place some stringent requirements on the mechanism of this type of cycloaddition which will be discussed in detail in a forthcoming paper.

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(1) J. D. Roberts and C. M. Sharts, "Cyclobutane Derivatives from Thermal Cycloaddition Reactions" in "Organic Reactions," Vol. 12, John Wiley and Sons, Inc., New York, N. Y., 1962.

(2) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962); A. T. Blomquist and Y. C. Meinwald, *ibid.*, **79**, 5316 (1957); **81**, 667 (1959).

(3) D. W. Wiley, private communication.

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