It is quite clear that the reduction process has to involve phenylmercuric cation and not the phenyl cation, and therefore a hydride abstraction by phenyl carbonium ion from toluene to yield benzene and benzyl carbonium ion is ruled out. As regards the difference in the yield of benzene between toluenesulfonate and perchlorate, it perhaps reflects the extent of ionization of the salts.

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A Novel Phenyl Group Migration during Pyrolysis and Photolysis of Bis-(2,3,5,5-tetraphenyl-2-dihydrofuranyl)-hydrazine

Sir:

This rearrangement was discovered during reinvestigation of the cyclic hemiketal, 2,3,5,5-tetraphenyldihydrofuranol-2 (Ia)[1] and its conversion supposedly through the *acyclic cis* hydroxy ketone form into a "hydrazone" for which the *sym,bis cyclic* hydrazine structure II is now suggested on the basis of the following data. The compound gave the correct C, H, and N analyses and molecular weight; it was converted under acid catalysis into the cyclic ketal Ib and dehydratively rearranged to tetraphenylfuran[1b]; it showed λ_{max} 253.5 mμ, (ϵ 28,400) corresponding to two styryl groups, two infrared NH peaks,[2] a narrow one at 3560 cm.$^{-1}$, and a broad one at 3440 cm.$^{-1}$ persisting on dilution and suggestive of intramolecular hydrogen bonding, and no absorption in the 1600 cm.$^{-1}$ range corresponding to NH$_2$ or C=N groups of *gem,bis* hydrazine or *acyclic* azine structures.[2]
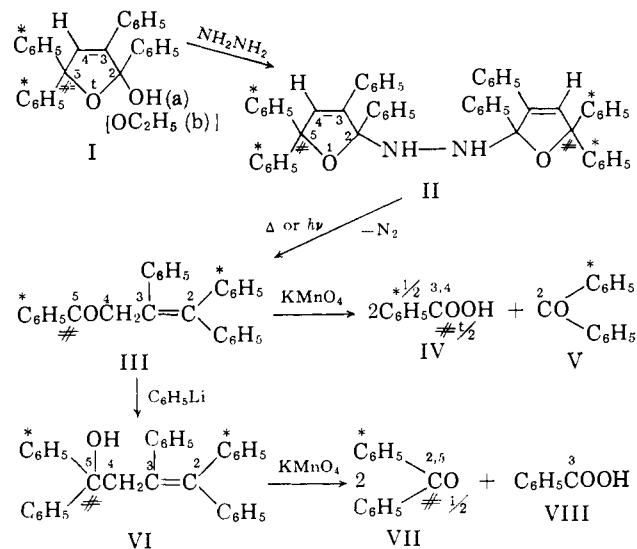
The symbols * and # indicate the respective locations of the C^{14} label in the two tracer experiments. The 2-5 numbering is used throughout to trace the four ring carbons of I and II.

Pyrolysis of II at its melting point (220°), in refluxing decalin (190°), and in dimethylformamide (153°), and photolysis in benzene,[3] caused evolution of nitrogen (identified in one case, v.p.c.) and formation of the β, γ-unsaturated ketone III[4] (50–60%). The *gem*-di-

phenyl group in each moiety of II at position-5 of the numbered four-carbon system is located in the resulting ketone III at carbon-2, the other end of this same four-carbon system. Empirically, therefore, a phenyl group migration has occurred.

Pyrolysis and photolysis of samples of II C^{14}-labeled, respectively, in the *gem*-diphenyl groups (*) and at the 5-carbon atom (#) traced the migration and limited mechanistic possibilities.[5] In the first case (*) the resulting sample of unsaturated ketone III* upon permanganate oxidation gave benzophenone V* and benzoic acid IV* each containing half of the C^{14} activity. Except for the possibility of total scrambling of the locations of the four phenyl groups which would have led to the same result, this showed that carbon-5 of II* had lost one of its two labeled phenyl groups, that carbon-2 had gained one, and that the migration must have been transannular or *cis*-1,4. The mechanistically improbable migration of a 5-phenyl group of II* in successive steps *around* the ring to the 2-position is excluded because it would have led to a 2-*gem*-diphenyl group in the unsaturated ketone III with one-third or less of the C^{14} activity,[5b] depending on the order and reversibility of the steps. That total scrambling of the locations of the *C^{14}-labeled phenyl groups had not occurred was rigorously proved in the case of dimethylformamide pyrolysis by addition of phenyllithium to the unsaturated ketone III* and oxidation of the resulting pentaphenylbutenol VI* to benzophenone VII* containing all of the *C^{14} and benzoic acid VIII containing none (scrambling would have led to *C^{14} contents of 75 and 25%, respectively[5b]).

The pyrolysis and photolysis reactions can be expressed stoichiometrically as intramolecular oxidation of the hydrazo group to molecular nitrogen and reduction of the two ring moieties by hydrogen transfer from the hydrazo group.[5b] The drive for furanization existing before this reaction is absent afterward because of the lower oxidation stage of the nitrogen-free products (*e.g.*, III, IX–XI). Initial formation of a carbene-like transition is suggested, *e.g.*, IX, followed by 5–2 migration of a phenyl group[6] and formation of the unsaturated ketone III, either through its diene-ol or through the cyclobutenol X.[5b,7]
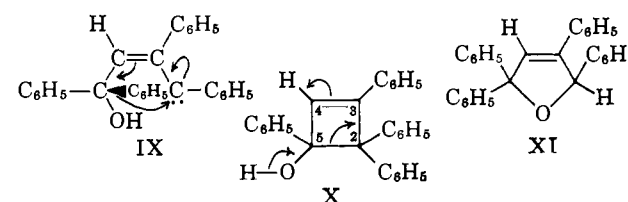
Preliminary study of the dihydrofuran, presumably XI, which has been made by lithium aluminum hydride reduction of Ia to a glycol and subsequent cyclodehydration [m.p. 94–95°; analyzed; λ_{max} 254 mμ, (ϵ

(1) (a) S. Salkind and V. Teterin, *J. prakt. Chem.*, **133**, 195 (1932); (b) R. E. Lutz, C. L. Dickerson, and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 3062 (1962); (c) further studies in these areas are in progress.

(2) Determined in CCl$_4$ (Perkin-Elmer 421 grating spectrophotometer) and interpreted by W. L. Truett, duPont Co., Waynesboro, Va.

(3) Hanovia 450-watt high pressure mercury arc lamp, Pyrex filter.

(4) Erroneously formulated (a) as a butenol[1a] and (b) as a cyclic enol ether

[K. Scholtis, *Ann.*, **557**, 82 (1945)]. For structure proof see (c) R. E. Lutz and C. L. Dickerson, *J. Org. Chem.*, **27**, 2040 (1962).

(5) (a) Samples of C^{14}-labeled II, * and #, were prepared from samples of Ia made from acetophenone labeled, respectively, in the phenyl group and at the carbonyl carbon. To be certain that there had been no rearrangement in going from Ia to II, C^{14}-labeled II* was converted into Ib, which upon chromic acid oxidation gave benzophenone carrying all of the C^{14}; (b) details and mechanistic discussion will appear in the forthcoming paper.

(6) *Cf.* (a) 1,3-Methyl shift [P. Yates and S. Danishefsky, *J. Am. Chem. Soc.*, **84**, 879 (1962)]; 1,3-, 1,4- and 1,5-phenyl shifts [(b) M. Stiles and A. J. Libbey, Jr., *J. Org. Chem.*, **22**, 1243 (1957); (c) P. T. Lansbury and R. L. Letsinger, *J. Am. Chem. Soc.*, **81**, 940 (1959)]; (d) *cf. cis*-1,5 phenyl shift in photolysis of *cis*-dibenzoylethylene [G. W. Griffin and E. J. O'Connell, *ibid.*, **84**, 4148 (1962)]; *cf.* references cited in a–c.

(7) *Cf.* (a) P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **28**, 1160 (1963); *cf.* (b) R. E. Lutz, L. T. Slade, and P. A. Zoretic, *ibid.*, **28**, 1358 (1963); work in this field is under further investigation, and the reactions are subject to possible reinterpretation in terms of carbene intermediates [*cf.* (c) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99, (1963)].

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 X[8] *before* phenyl group migration, was excluded by the second group ot tracer experiments designed to test this point, starting from II# C[14]-labeled at carbon-5. Oxidation of the resulting samples of unsaturated ketone III# gave benzophenone V carrying none of the #C[14] 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 #C[14] and benzoic acid VIII containing none. This showed that all of the C[14] of the ketone III# had been located at position-5 as demanded by the mechanism II → IX or X → 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-(benzhydryl)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).

(10) (a) Work supported in part by a National Science Foundation Research Grant; (b) Shell Co. Fellow, 1961–1962; (c) Shell Co. Fellow 1962–1963. (d) Ph.D. Dissertation, University of Virginia, October, 1962.

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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 $C_6F_6N_2$: 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-

(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.

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

$$X = RO^-, RS^-, p\text{-}ROC_6H_4^-$$
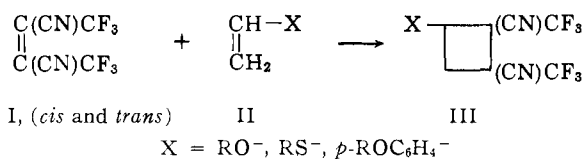
Reactions of *trans*-I with the alkenes II in the absence of solvent give exclusively the cyclobutane diastereomers IIIa and IIIb; reactions of *cis*-I give a different set of diastereomers, IIIc and IIId. Similar stereospecificity is observed in reactions of *trans*-I with *cis*- and *trans*-propenyl *n*-propyl ether.
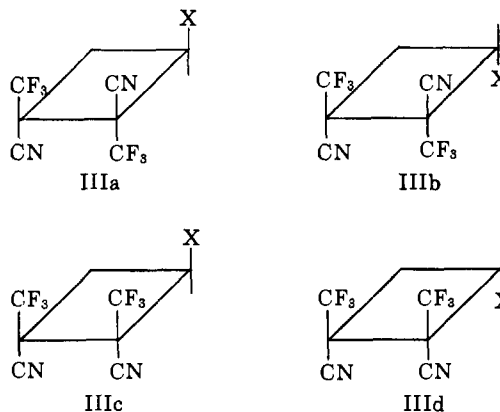
The cyclobutane structures for the products were confirmed by elemental and spectral analyses. Comparative fluorine n.m.r. spectroscopy was particularly useful for determining the number and kinds of diastereomers formed. For example, the cyclobutane diastereomer mixture IIIa + IIIb resulting from the 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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