Steric Course in Cycloaddition of Chlorotrifluorethylene

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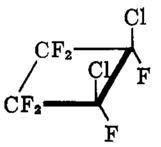
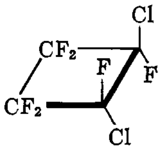
The thermal dimerization of chlorotrifluoroethylene has been discussed by several workers.[1-3] Certain mechanistic usefulness has been derived from the fact that only 1,2-dichlorohexafluorocyclobutane is formed in this reaction.[2] In addition, a knowledge of the ratios of *cis* and *trans* isomers (I and II, respectively) of the 1,2-dichloro compound should have very specific implications.



I



II

Other work in these laboratories has necessitated the availability of a quantity of relatively pure I. Thus, the literature indicates that the cycloaddition reaction should lead mainly to this material.[4] Several cycloadditions have been carried out in stainless steel cylinders at temperatures ranging from 150 to 300° concommitant with pressures of 1500 and 2800 p.s.i. Curiously, infrared spectral analysis indicates that a considerable amount of *trans*-1,2-dichlorohexafluorocyclobutane is formed if the reaction is carried out under these conditions.[4,6] Separation of I and II has been achieved by means of gas–solid chromatography (activated alumina), and measurement of peak areas provides a product ratio of 44% *trans* and 56% *cis*. Integration of the F^{19} n.m.r. spectra of the unseparated reactions confirms the 44 to 56% isomer ratio. Thus, a composite spectrum (Cl_3CF solvent) consists of two partially superimposed AB patterns for each of the two *gem* fluorines of the individual isomers, and well-separated singlets (*cis*, 137.6 p.p.m.; *trans*, 128.9 p.p.m.) for F^{19} *gem* to chlorine.[7]

Since our results are not in accord with those of the previous workers, it was suspected that either the *cis* isomer is unstable under the reaction conditions, or that these conditions lead to products of thermodynamic rather than kinetic control. An identical isomer ratio is obtained in stainless steel when the reaction proceeds only 3% to completion. Both I and II maintain isomeric integrity for 3 hr. in stainless steel under normal reaction conditions. Dimerizations which are carried out in glass (both above and below ambient pressure) produce this same isomer ratio. We, therefore, conclude that the invarient product ratio results from a kinetically controlled reaction, and that it is the normal result of cycloaddition. Similar work on the cycloaddition of bromotrichloroethylene provides a 55:45 *cis–trans* dimer ratio.[8]

The argument of Wilson and Goldhammer that a concerted kind of mechanistic process would lead to stereospecific addition is not very compelling.[3] However, the fact that some stereospecificity has been noted is interesting when a diradical with unpaired spins is considered. Ring closure in some cycloaddition reactions[9] is more rapid than rotation about carbon–carbon bonds.[10] A change in multiplicity must be a relatively slow process compared to such a ring closure, and would seem not to occur.[11] This argument, when taken with the fact that a slight stereoselectivity is found for the cycloaddition is not consistent with a triplet transition state. Our observations can be accommodated by the "virtual" diradical mechanism (a diradical with paired spins), which has been suggested by Roberts and Sharts,[2] or a concerted process. In either case, the orientation of the product is decided in the first step rather than in any subsequent phase of the reaction. The present findings, in which truly free diradicals are probably not formed, are in accord with the recent, elegant studies of Bartlett[12] and his associates, whose work concerns relatively long-lived diradicals.

Experimental

Isomer Separation and Analysis.—Attempts to separate *cis*- and *trans*-1,2-dichlorohexafluorocyclobutane through use of the usual gas–liquid partition chromatographic substrates came to repeated failure. However, gas chromatography on specially prepared powdered alumina was successful. Alcoa F-20 alumina was sieved to 80–100 mesh, heated to 650° for 1 hr., and cooled; 2% by weight Kel-F-90 grease (Minnesota Mining and Manufacturing Co.) in Freon-11 solvent was added. This was used to pack a 6 ft. × 0.375 in. copper column which was maintained at 100° and through which the helium flow rate was measured at 100 cc./min.[13] Once-distilled cyclo adduct (b.p. 55.5–56.5°) was chromatographed over this column, and two peaks with retention times of 17 and 19 min. were found. Integration of these two peaks resulted in an area ratio of 0.44 and 0.56, respectively. These relative areas proved to be constant regardless of the manner in which cycloaddition had been carried out. The material was first off the column had infrared and n.m.r. spectra which were identical with those obtained from an authentic sample of *trans*-1,2-dichlorohexafluorocyclobutane.[5] The n.m.r. spectra of the separated isomers showed AB patterns for each, and integration of the portion (due to the uncoupled nuclei) of the unseparated cyclo adduct mixture gave an isomer composition of 44% *trans* and 56% *cis*.

Cycloadditions and Thermal Stability.—All reactions were carried out using chlorotrifluoroethylene (Allied Chemical) which was shown by gas chromatography to be at least 99% pure.

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[1] J. R. Lacher, G. W. Tompkin, and J. D. Park, *J. Am. Chem. Soc.*, **74**, 1693 (1952).

[2] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 14 (1962).

[3] A. Wilson and D. Goldhammer, *J. Chem. Ed.*, **40**, 599 (1963).

[4] Lacher, Tomkin, and Park report that the *cis* isomer predominates about 5 to 1 over *trans* in cycloaddition.[1] Roberts and Sharts[2] reiterate that compound I is the major constituent, while Wilson and Goldhammer[3] indicate that the reaction results in a 50:50 mixture of compounds I and II. Park and co-workers have recently stated that cycloaddition provides equal amounts *cis* and *trans*.[5]

[5] J. D. Park, H. V. Haller, J. H. Lacher, *J. Org. Chem.*, **25**, 990 (1960).

[6] Compound II was available from other studies for comparison of spectra.

[7] A complete n.m.r. interpretation of this case is presented in No. 86 of the "N.M.R. at Work Series," Varian Associates, Palo Alto, Calif.

[8] Unpublished results of these laboratories.

[9] S. Proskow, H. E. Simmons, and T. L. Cairns, *J. Am. Chem. Soc.*, **85**, 2341 (1963).

[10] A referee has pointed out that the studies of Proskow and co-workers,[9] in which a diradical transition state is not expected, may not bear close resemblance to the present case. Indeed, these workers studied reactions in which one reagent is relatively electron rich; in contrast, the present case concerns cycloaddition between reactants which are both substituted with electronegative groups.

[11] J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

[12] P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

[13] It is important that this column be conditioned by passage of helium at 100° for 24 hr. prior to use.

The procedure of Rapp and co-workers was normally followed for preparative-scale reactions, and yields of better than 95% were generally noted.[14] In one case, the stainless steel bomb containing chlorotrifluoroethylene was brought rapidly to 300° (whereupon a pressure of 990 p.s.i. was noted). As soon as the pressure fell to 900 p.s.i., the reaction was quenched by immersing the pressure bomb in an ice bath. A yield of only 3% was obtained for this reaction, and gas chromatography was used to measure the product ratio. Pure *cis* adduct was placed in a stainless steel vessel and heated to 350–400° for 3 hr. An infrared spectrum of material which had been treated in this fashion indicated that the starting cyclobutane was at least 95% unchanged. This same experiment was carried out on the pure *trans* adduct with an identical result.

Chlorotrifluoroethylene (5 ml. of liquid) was vacuum transferred into a heavy wall glass tube (12 ml.) which had been cooled to −195°. The tube was sealed under vacuum and heated at 200° for 24 hr. The crude reaction mixture was analyzed by gas chromatography. A second reaction was carried out in a sealed glass ampoule at lower pressures (590 mm.) and higher temperature (340° for 24 hr.). In the latter case, 300 mm. of chlorotrifluoroethylene was admitted to an evacuated ampoule which was then sealed off under vacuum. Upon completion of the reaction, starting material was removed by cooling the mixture to −78° and evacuating (1 mm.) the sample tube for 20 min. The infrared spectrum of the remaining liquid was taken. In both of the preceeding experiments, the *cis–trans* ratio appeared to be the same as was obtained in stainless steel apparatus.

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[14] K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. A. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3642 (1950).

The Isomerization of 7,14-Diketo-1,2,3,4,6,6a,7a,8,8a,9,10,11,13,13a,14a,14b-hexadecahydrodibenz[*a,h*]anthracene

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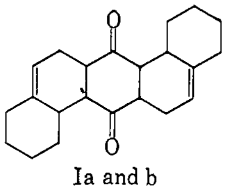
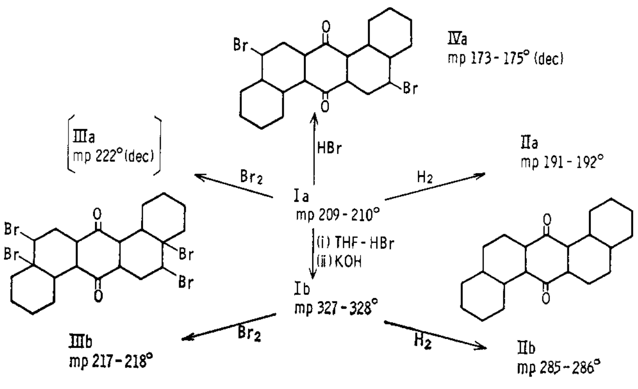
In the course of the development of a new general synthetic scheme for the preparation of various substituted dibenz[*a,h*]anthracenes, the title compound, Ia, was prepared by condensation of 2 moles of 1-vinylcyclohexene-1 with 1 mole of *p*-benzoquinone, and also, in higher yield, from the monoadduct of *p*-benzoquinone and 1-vinylcyclohexene-1.[1,2] Ia readily isomerized to a new high-melting diketone (Ib) labeled the "isobisadduct," m.p. 327–328°, by treatment of a solution of Ia in tetrahydrofuran with dry hydrobromic acid gas. The bisadduct Ia can also be converted to Ib by refluxing with methanolic potassium hydroxide. However, it is recovered unchanged when refluxed with acetic anhydride.



Ia and b

CHART I



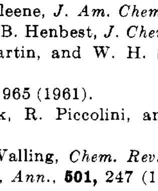
The isomerization of Ia to Ib also does not occur when Ia is heated with aqueous hydrobromic acid or with tetrahydrofuran alone or when it is refluxed with 1,4-dibromobutane, which is the product of the reaction between tetrahydrofuran and hydrobromic acid.[3]

In view of the recent interest in the stereochemistry of the bisadducts of butadiene[4–6] and cyclopentadiene[7] with *p*-benzoquinone, the isomerization observed with the bisadduct of 1-vinylcyclohexene-1 and *p*-benzoquinone are recorded here. The reactions carried out on the two isomers Ia and Ib are summarized in Chart I.

Both Ia and Ib gave the hydrocarbon dibenz[*a,h*]-anthracene on dehydrogenation with palladium. The isomeric dibenz[*a,j*]anthracene could not be detected by paper and thin layer chromatography, thus confirming the structure of the bisadduct as Ia, previously assigned to it.[1,2]

Both isomers Ia and Ib could be catalytically hydrogenated to two different saturated compounds IIa and IIb. The isobisadduct Ib and its catalytic hydrogenation product IIb had notably higher melting points than their isomers Ia and IIa. Bromination of Ia in dioxane gave an unstable bromide. The tetrabromide of the isobisadduct IIIb, on the other hand, was stable. Ia could be converted to a saturated dibromide (IVa) by treatment with hydrobromic acid in chloroform.

Since the hydrobromination was carried out in the presence of a small amount of benzoyl peroxide, the bromide is probably IVa rather than the isomer in which bromine becomes attached to the more highly substituted carbon atom.[8] The monoadduct of 1-vinylcyclohexene-1 and *p*-benzoquinone would be expected, according to the Alder and Stein[9] rule, *i.e.*, *endo* addition in the Diels–Alder reaction, to have the *cis–syn* structure V, since mild conditions are used in the preparation of this monoadduct. The formation of adducts with *cis–anti* configurations under strenuous



V

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[1] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

[2] H. J. Backer and J. R. van der Bij, *Rec. trav. chim.*, **62**, 561 (1943).

[3] R. Fried and R. D. Kleene, *J. Am. Chem. Soc.*, **62**, 3258 (1940).

[4] N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960).

[5] R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Am. Chem. Soc.*, **83**, 4006 (1961).

[6] R. L. Clarke, *ibid.*, **83**, 965 (1961).

[7] L. de Vries, R. Heck, R. Piccolini, and S. Winstein, *Chem. Ind.* (London), 1416 (1959).

[8] F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).

[9] K. Alder and G. Stein, *Ann.*, **501**, 247 (1933).