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The Trifluoroacetic Acid Catalyzed Reaction of Iodobenzene Dichloride with Ethylenic Compounds

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The kinetics of the trifluoroacetic acid catalyzed reactions of both *trans*-stilbene and cyclohexene with iodobenzene dichloride in carbon tetrachloride have been studied. If the concentration of the unsaturate is sufficiently high, essentially all of the products are formed through direct attack of the dichloride on the double bond, rather than by the alternate path in which free chlorine formed by dissociation of the dichloride initiates the addition reaction. Under conditions known to favor the direct reaction, the products formed from *trans*-stilbene are a mixture of the *dl*- and *meso*-stilbene dichlorides and 1,2-diphenyl-1-acetoxy-2-chloroethane. Both *trans*-1,2-dichlorocyclohexane and *trans*-1-acetoxy-2-chlorocyclohexane, but not their *cis* isomers, have been identified in the cyclohexene reaction product. The mechanistic implications of these results are discussed.

Several groups of investigators[1-3] have reported that the steric result of chlorine addition to a carbon–carbon double bond changes when molecular chlorine is replaced by iodobenzene dichloride as the halogen source. The possibility that iodobenzene dichloride may under certain circumstances react by making a direct attack on the unsaturated system[1] rather than by prior dissociation to free halogen, therefore, has seemed worthy of serious consideration.

It has been demonstrated previously that in polar media iodobenzene dichloride functions as a chlorinating agent for aromatic hydrocarbons.[4,5] With acetic acid as the solvent the reaction is preceded by breakdown of the dichloride to free chlorine, which then attacks the aromatic ring.[4] If, however, the reaction takes place in carbon tetrachloride in the presence of trifluoroacetic acid as a catalyst, the iodide dichloride itself is the actual chlorinating agent. It has seemed reasonable to expect that similar reaction conditions might be used successfully to induce a direct attack of iodobenzene dichloride on an alkene. It has now been demonstrated by a study of the reaction kinetics that both cyclohexene and *trans*-stilbene can react in this way to form the corresponding dichlorides. The stereochemistry of the products of these direct reactions has also been investigated and compared with that of the adducts formed in the reaction of the unsaturates with free chlorine in dilute solutions of trifluoroacetic acid in carbon tetrachloride.

Experimental

Materials.—Eastman Organic Chemicals spectro grade carbon tetrachloride was stored for at least 48 hours over freshly ignited Drierite (calcium sulfate) and was then distilled, b.p. 78°, using a 4-foot column packed with glass helices. The cyclohexene, *trans*-stilbene, trifluoroacetic acid and trifluoroacetic anhydride were also furnished by Eastman Organic Chemicals. The cyclohexene was dried with Drierite, refluxed for 1 hour over sodium wire to remove peroxides and then fractionated, b.p. 83°. The stilbene was recrystallized from ethanol, m.p. 124–125°. The acid was distilled, b.p. 71.5–72°, before use.

A number of compounds of interest in connection with the product studies were prepared. A sample of 3-chlorocyclohexene, b.p. 55° (32 mm.), n^{24}D 1.4890, was synthesized from 1,3-cyclohexadiene[6] by the method of Courtout and Pierron.[7] The 1-chlorocyclohexene was prepared from 1,1-dichlorocyclohexane which was obtained from the reaction of cyclohexanone with phosphorus pentachloride.[8] The *trans*-1,2-dichlorocyclohexane was produced by direct addition of chlorine to cyclohexene,[9] b.p. 188.5–189.5° (768 mm.), n^{24}D 1.4900. The *cis* isomer, b.p. 85° (13 mm.), was prepared from *trans*-2-chlorocyclohexanol[10] and thionyl chloride.[11]

To prepare *cis*-1-trifluoroacetoxy-2-chlorocyclohexane, 10 g. of *cis*-2-chlorocyclohexanol[12] was refluxed for 2 hours with an excess of trifluoroacetic anhydride. The product was separated by distillation, b.p. 75–77° (5 mm.), $n^{24.5}$D 1.4102, yield 13.7 g. (87%).

Anal. Calcd. for $C_8H_{10}O_2F_3Cl$: C, 41.60; H, 4.35; Cl, 15.4. Found: C, 41.37; H, 4.45; Cl, 15.9.

It was established by gas chromatographic analysis (see below) that this product was contaminated with about 20% of the *trans* isomer. A sample of *trans*-1-trifluoroacetoxy-2-chlorocyclohexane [b.p. 89° (24 mm.), n^{24}D 1.4142] was produced in similar fashion from *trans*-2-chlorocyclohexanol.[10]

Anal. Calcd. for $C_8H_{10}O_2F_3Cl$: C, 41.60; H, 4.35; Cl, 15.4. Found: C, 42.51; H, 5.05; Cl, 15.0.

The infrared spectra of the *cis* and *trans* isomers in carbon disulfide both showed strong bands at 5.6 and 8.2 μ, characteristic, respectively, of the carbonyl and trifluoromethyl groups.

A mixture of *dl*- and *meso*-stilbene dichlorides was prepared from *trans*-stilbene and chlorine in 1,2-dichloroethane.[13] The solvent was evaporated, and the product was redissolved in hot ethanol. The *meso*-dichloride, which crystallized when the solution was cooled, was recrystallized from benzene, m.p. 189°. The crude *dl*-isomer, obtained by concentration of the ethanolic mother liquor, was recrystallized from ethanol; m.p. 91°.

A sample of 1,2-diphenyl-1-trifluoroacetoxy-2-chloroethane (presumably the *erythro* isomer) was prepared by refluxing *erythro*-stilbene chlorohydrin[14] for 1 hour with trifluoroacetic anhydride. The product distilled at 115° (3 mm.).

Anal. Calcd. for $C_{16}H_{12}O_2F_3Cl$: C, 58.50; H, 3.66. Found: C, 58.05; H, 3.95.

Like the corresponding cyclohexane derivatives this material in carbon disulfide solution has strong infrared absorption bands at 5.6 and 8.2 μ.

Iodobenzene dichloride was freshly prepared as needed by a procedure described previously.[15]

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The Rate Runs.—Stock solutions of trifluoroacetic acid, iodobenzene dichloride and the unsaturated substance (cyclohexene or stilbene) in carbon tetrachloride were prepared at the temperature of the rate measurements. The rate samples were prepared by mixing measured volumes of these solutions of the reactants and the catalyst in 1-cm. absorption cells. The cells were transferred to a temperature controlled (±0.1°) housing of a Beckman spectrophotometer, and the consumption of iodobenzene dichloride in the reaction mixtures was followed to completion by measuring the optical densities, *d*, of the solutions at 380 mμ against a carbon tetrachloride blank. In nearly all runs there was a small residual optical density reading at infinite time. The values of d_{380} mμ recorded during the runs were corrected to account for this final reading before rate constants were calculated. The concentrations of both the catalyst and the unsaturate were in most instances in substantial excess of that of the iodobenzene dichloride. Rate constants for individual runs (see eq. 1 in which the subscripts i and t refer to initial time and time *t*) were evaluated from the slopes of the lines obtained by plotting log d_{380} mμ *versus* time. In those cases in which the concentration of the unsaturate changed significantly during the runs, the

$$kt = 2.303 \log [C_6H_5ICl_2]_i/[C_6H_5ICl_2] = 2.303 \log d_i/d_t \quad (1)$$

rate constants reported were based on the early phases of the reactions. Other details concerning the rate measurements and the preparation and handling of iodobenzene dichloride, chlorine and hydrogen chloride solutions have been discussed elsewhere.[4,5,15]

Isolation and Identification of the Reaction Products.—The products of the reactions of the unsaturated substances with iodobenzene dichloride, as formed in solutions in which the initial reactant and catalyst concentrations were similar to those of the rate runs, were investigated. A solution of 1.10 g. (0.0061 mole) of stilbene, 0.321 g. (0.00117 mole) of iodobenzene dichloride and 3.0 ml. (0.0401 mole) of trifluoroacetic acid in 100 ml. of carbon tetrachloride was stored in one arm of a two-limbed vessel, which was closed to the atmosphere while reaction took place. The second limb contained 15 ml. of distilled water. When reaction was complete, as established by spectrophotometric study of a separate sample of the same composition as the reaction mixture, the contents of the two limbs were shaken together. The aqueous layer was separated and the carbon tetrachloride phase was extracted with an additional 25 ml. of water. It was found by analysis by the Volhard procedure that the combined aqueous phases contained 3.4 × 10^{-4} mole of hydrogen chloride (29% yield based on iodobenzene dichloride). This figure is presumed to correspond to the yield of 1,2-diphenyl-1-trifluoroacetoxy-2-chloroethane (see below). It is assumed with some uncertainty that no hydrogen chloride was produced by substitution processes. However no substitution products were found in chromatographing the mixture of organic substances which were formed.

The carbon tetrachloride solution of the products was then dried with magnesium sulfate and concentrated to a small volume under reduced pressure. The concentrate was chromatographed on a 28 × 5 cm. silicic acid column. A 1% benzene in pentane mixture was used as developer and eluant. The various fractions which were collected were stripped of solvent using a rotary evaporator. Iodobenzene, identified only by its characteristic odor, was eluted first. The excess stilbene, eluted next, was identified by its infrared spectrum and by mixed melting point determination. The material thus recovered (0.82 g.) was 89% of that to be expected if the dichloride were quantitatively consumed in a reaction with an equimolar amount of stilbene. Next 0.107 g. (37% yield based on iodobenzene dichloride) of *dl*-stilbene dichloride, also identified by its infrared spectrum and by its mixed melting point with an authentic sample, was eluted. After this a solid (0.069 g.) of broad melting range, and presumably a mixture, was recovered. This generally had the characteristic infrared absorption spectrum of *meso*-stilbene dichloride (with a band at 13.3 μ). In addition small absorption bands at 5.6 and 8.2 μ, which are present in the spectrum of 1,2-diphenyl-1-trifluoroacetoxy-2-chloroethane (*vide supra*), were observed in this spectrum. Finally uncontaminated *meso*-stilbene dichloride (0.030 g.) identified by its mixed melting point with an authentic sample, was recovered. No other substances were eluted from the column. The over-all yield of product was only of the order of 67%, probably because of handling losses sustained in the recovery of solids from over 60 chromatographic fractions.

No satisfactory procedure for quantitative separation of the fraction containing both the *meso*-dichloride and the trifluoroacetate of stilbene chlorohydrin was found. Several modifications of this procedure for analysis of the stilbene reaction products were tried, though none was more successful than that described. In one of these the products of reaction of a mixture originally containing 1.08 g. (0.0059 mole) of stilbene, 0.53 g. (0.0019 mole) of iodobenzene dichloride and 5.0 ml. (0.055 mole) of trifluoroacetic acid in 105 ml. of carbon tetrachloride were freed of acid and transferred to a silicic acid column. After elution of the unreacted stilbene (0.68 g., 93.2% recovery) with 10% benzene in hexane, the column was washed with benzene to remove other products. The benzene solution was evaporated to dryness and the residue recrystallized from 95% ethanol to provide 0.105 g. (20.8% yield based on iodobenzene dichloride) of *meso*-stilbene dichloride, which was identified by its infrared spectrum and a mixed melting point determination. By evaporation of the mother liquor a solid of melting range 70–85° was obtained. It was concluded on the basis of an examination of its infrared spectrum that this material was a mixture of *dl*-stilbene dichloride and the trifluoroacetate of stilbene chlorohydrin. Analysis of the original product mixture, as described above, revealed that it contained 3.4 × 10^{-4} mole (18% based on iodobenzene dichloride) of hydrogen chloride. Had it not been necessary to use a large excess of stilbene to ensure that the dichloride actually disappeared in a direct bimolecular reaction with the unsaturate (rather than by dissociation to iodobenzene and chlorine), more satisfactory analytical methods might have been devised.

In a procedure similar to that used in studying the reaction of stilbene and iodobenzene dichloride, free chlorine was substituted for the dichloride. To 1.19 g. (0.0065 mole) of stilbene and 20 ml. (0.27 mole) of trifluoroacetic acid in 30 ml. of carbon tetrachloride a dilute solution of chlorine in carbon tetrachloride was added until the first permanent green color appeared. The acids were removed by washing with sodium bicarbonate solution after the very rapid addition reaction was complete. The dried organic phase was then evaporated. The residual solid was recrystallized from petroleum ether. A white solid, 0.32 g., m.p. 192°, which did not depress the melting point of a pure sample of *meso*-stilbene dichloride, was obtained. The mother liquor was evaporated to dryness and the residue recrystallized from ethanol to yield 0.062 g. of a solid, m.p. 173–185°, which was characterized by its infrared spectrum as a mixture of the *meso*-dichloride and 1,2-diphenyl-1-trifluoroacetoxy-2-chloroethane. The mother liquor from this second recrystallization was evaporated to yield 0.84 g. of a solid, m.p. 83–84°, the infrared spectrum of which was identical with that of *dl*-stilbene dichloride. One recrystallization from petroleum ether raised the melting point to 89–91°.

To establish that the stilbene dichlorides did not isomerize or react with the catalyst under the conditions of the trifluoroacetic acid chlorination reaction, 0.5-g. samples of each pure isomer were dissolved in solutions of 10 ml. of trifluoroacetic acid and 30 ml. of carbon tetrachloride. The mixtures were allowed to stand for 12 hours. The actual reaction mixtures containing iodobenzene dichloride stood only about 1 hour before product recovery was begun. The acid was then washed from the carbon tetrachloride solutions, and these were evaporated to dryness. The *meso*- and *dl*-isomers were recovered in unisomerized form (respectively, 89 and 88%) from the solutions into which they were originally introduced.

It has been reported that trichloroacetic acid adds to the carbon–carbon double bond[16] and that trifluoroacetic acid is a powerful catalyst for the cationic polymerization of styrene.[17] That such reactions between unsaturate and catalyst do not accompany the reactions involving iodobenzene dichloride was shown by recovering stilbene in 91.4% yield from a carbon tetrachloride solution of stilbene (0.161 *M*) and trifluoroacetic acid which had stood at room tem-

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[16] C. P. Brown and A. R. Mathieson, *J. Chem. Soc.*, 3608 (1957).

[17] J. J. Throssel, S. P. Sood, M. Szwarc and V. Stannett, *J. Am. Chem. Soc.*, **78**, 1122 (1956).

perature for 20 hours. Stilbene was also recovered essentially quantitatively from a hydrogen chloride saturated solution of stilbene (0.11 mole) and trifluoroacetic acid (0.81 mole) in carbon tetrachloride which had stood at room temperature for 3 hours. That is, hydrogen chloride does not add to stilbene under the conditions of the iodobenzene dichloride reactions.

In a typical mixture of reagents, as prepared to study the products of reaction of cyclohexene and iodobenzene dichloride, there were 0.401 g. (0.0049 mole) of the cycloolefin, 0.462 g. (0.00168 mole) of the dichloride and 3.07 g. (0.027 mole) of trifluoroacetic acid in 100 ml. of carbon tetrachloride. When reaction was complete, as was established spectrophotometrically, the acids were washed out of the solution. This was dried over magnesium sulfate and its components were determined qualitatively by gas–liquid chromatography at 140° on a Loe Engineering Co. fractometer equipped with an 18-ft. copper column containing diethylene glycol succinate impregnated on firebrick with helium as the carrier gas. A thermal conductivity cell was used in the detection system. Under these conditions the retention times of authentic samples of substances considered as possible components of the product were, as referred to the air peak, 3-chlorocyclohexene, 3 min.; 1-chlorocyclohexene, 12 min.; *trans*-1-trifluoroacetoxy-2-chlorocyclohexane, 16 min.; *cis*-1-trifluoroacetoxy-2-chlorocyclohexane, 20 min.; *trans*-1,2-dichlorocyclohexane, 24 min.; iodobenzene, 28 min.; *cis*-1,2-dichlorocyclohexane, 50 min. On chromatographing 100-μl. samples of the solution of reaction products, peaks only at 28, 24, 16 and 3 min. were obtained. The last, an intense peak, encompassed carbon tetrachloride and unreacted cyclohexene. In an attempt to determine whether this peak also included 3-chlorocyclohexene, a second sample of the product mixture was chromatographed on the same column at a temperature of 80°, at which the substances in question are separated. The 3-chlorocyclohexene peak (37.5 min.) was absent. A number of unsuccessful attempts were made to estimate semi-quantitatively (by chromatography) the relative amounts of the two cyclohexane derivatives in the reaction product, but the results with simulated product mixtures were not reliable, except in the qualitative sense. It was established with certainty that were 1-chlorocyclohexene, *cis*-1,2-dichlorocyclohexane or *cis*-1-trifluoroacetoxy-2-chlorocyclohexane present in significant quantity in the products, they would have been detected. The case for 3-chlorocyclohexene is less certain since the thermal conductivity cell response to this substance as it emerges from the column is relatively feeble both at 80° and 140°. Clearly this chloro compound was not a major product, although a significant quantity of it may have escaped detection.

Analyses for hydrogen chloride formed during the reactions were conducted in the same way as has been described for workup of the stilbene reaction products. The ratio of *trans*-1,2-dichlorocyclohexene to *trans*-1-trifluoroacetoxy-2-chlorocyclohexane can be calculated by making an assumption of questionable validity that all of the hydrogen chloride was produced in the reaction to form the latter substance. Presumably the iodobenzene dichloride which did not react to form hydrogen chloride produced the dichlorocyclohexane. As seems reasonable, this ratio was found to increase with increases in the trifluoroacetic acid concentration of the reaction mixtures. A ratio of 3.6/1 was found for the products of reaction of a solution initially 0.0129 *M* in iodobenzene dichloride, 0.0329 *M* in cyclohexene and 0.224 *M* in trifluoroacetic acid. It must be emphasized, however, that this figure is not reliable because of the uncertainty concerning the origin of the hydrogen chloride.

The products formed when chlorine rather than iodobenzene dichloride was added to solutions of cyclohexene and trifluoroacetic acid in carbon tetrachloride also were investigated by gas–liquid chromatography. Again the only products which could be detected in this way were *trans*-1,2-dichlorocyclohexane and *trans*-1-trifluoroacetoxy-2-chlorocyclohexane. It was found by analysis of the products for hydrogen chloride that at least when there was no trifluoroacetic acid in the medium an appreciable fraction of the halogen was consumed in reactions leading to substitution rather than addition of chlorine. It is therefore possible that some of the hydrogen chloride formed in reactions in which trifluoroacetic acid was also in the medium was produced in substitution processes. Certainly no quantitative estimate, based on available data, of the product composition in the reactions with free chlorine can be made.

Neither hydrogen chloride nor trifluoroacetic acid add to cyclohexene under the conditions of the halogen addition reactions. A solution of cyclohexene (1.97 *M*) and the fluoro acid (1.00 *M*) in carbon tetrachloride was extracted with water after it had stood 3 hours. It was shown by titration with standard base that the aqueous phase contained 95% of the original acid. A carbon tetrachloride solution of cyclohexene (0.39 *M*), trifluoroacetic acid (0.54 *M*) and hydrogen chloride (0.041 *M*) was extracted with water 1 hour after it was prepared. By Volhard analysis it was shown that the aqueous phase contained 95.5% of the original hydrogen chloride.

In an experiment designed to test whether or not *trans*-1,2-dichlorocyclohexane was stable under the conditions of the addition reactions, a 0.56-g. sample of this substance was dissolved in a solution of 6 ml. of trifluoroacetic acid in 25 ml. of carbon tetrachloride. After 4.5 hr. the solution was extracted to remove acid and subjected to gas–liquid chromatography by the procedure described previously for separation of the cyclohexene reaction products. A single peak (other than the solvent peak) at 24 min. was observed. In a similar experiment in which *cis*-1,2-dichlorocyclohexane was used as starting material, the gas chromatogram of the product had only a single peak (other than the solvent peak) at 50 min.

Since only the *trans* isomer of 1-trifluoroacetoxy-2-chlorocyclohexane was found in the cyclohexene reaction product, it seemed of interest to check the stability of its *cis* isomer under the conditions of the addition reactions. A solution of 2.5 g. of the *cis* compound, known to contain about 20% of the *trans* isomer, and 11 ml. of trifluoroacetic acid in 50 ml. of carbon tetrachloride was allowed to stand at room temperature for 2.5 hr. The solution was then freed of acids and subjected to gas chromatography in the usual way. In addition to the solvent peak only peaks for the *cis*- and *trans*-trifluoroacetoxychlorocyclohexanes were observed. The peak heights were in the same ratio as those in the chromatogram of the impure *cis* isomer used as the starting material.

Results

The Kinetic Studies.—In Table I rate constants *k* (eq. 1) for the trifluoroacetic acid catalyzed reaction of iodobenzene dichloride with stilbene and with cyclohexene are listed. As they should be, the constants are essentially independent of the concentration of the dichloride. They are approximately proportional both to the concentration of the unsaturate and to the square of the catalyst concentration. The rate constants calculated on the assumption that the reaction is fourth order (first order with respect to both the dichloride and the unsaturate and second order with respect to the catalyst) are subject to an appreciable variation, as indicated in the right-hand column of Table I, but no other assumed simple integral order serves as satisfactorily for the correlation of the results of the kinetic studies. The tabulated *k*-values for reaction at a particular catalyst concentration are very much greater than the rate constants k_1 for dissociation of the dichloride (at the same catalyst concentration) to iodobenzene and free

$$C_6H_5ICl_2 \xrightarrow{k_1} C_6H_5I + Cl_2 \qquad (2)$$

chlorine in carbon tetrachloride. This latter process is also approximately second order dependent in rate with respect to the catalyst. When the unsaturate concentration is as high as in the run summarized in Table I, the dichloride must be consumed almost entirely in a process in which it makes a direct attack on the unsaturate. The alternate path, in which free chlorine produced by reaction 2 adds to the double bond, can make a

TABLE I

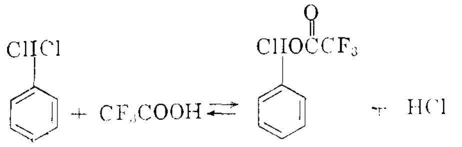
RATE CONSTANTS FOR REACTION OF $C_6H_5ICl_2$ WITH STILBENE AND CYCLOHEXENE (CCl_4, 25.2°)

10^2[Unsaturate], moles l.$^{-1}$	10^3[$C_6H_5ICl_2$], moles l.$^{-1}$	[CF_3COOH], mole l.$^{-1}$	$10^4 k$, sec.$^{-1}$	$\frac{10^2 k}{[\text{Unsaturate}][CF_3COOH]^2}$, mole^{-3} l.^{3} sec.$^{-1}$
		Stilbene[a]		
6.61	5.03	0.162	0.62	3.6
6.61	5.03	.215	1.52	5.0
6.61	5.03	.324	2.69	3.9
5.51	4.43	.161	0.55	3.8
5.51	4.43	.403	3.77	4.2
5.51	4.43	.644	14.0	6.1
3.05	6.80	.269	0.81	3.7
9.15	6.80	.269	2.76	4.2
10.3	3.42	.269	4.37	5.8
10.3	5.14	.269	4.83	6.5
10.3	6.84	.269	3.95	5.3
11.0	2.88	.162	1.68	5.8
11.0	4.32	.162	1.75	6.1
11.0	5.76	.162	1.68	5.8
3.29	4.60	.673	5.75[b]	..
3.29	4.60	.673	12.4	8.3
3.29	4.60	.673	46.0[c]	..
5.1	4.74	.359	3.54	5.3
5.1[d]	4.74	.359	3.08	4.6
		Cyclohexene[a]		
3.29	4.86	0.090	0.69	26
3.29	4.90	.446	13.6	21
3.29	4.86	.896	78.6	30
3.29	4.90	.269	4.97	21
3.29	4.90	.628	36.1	28
16.4	4.90	.269	26.2	22
6.56	4.90	.269	8.93	19
3.29	4.90	.446	5.98[b]	..
3.29	4.90	.446	36.8[e]	..

[a] The k_1-values at 25.0° for the trifluoroacetic acid catalyzed dissociation of $C_6H_5ICl_2$ to Cl_2 and C_6H_5I are 0.15 × 10^{-4} sec.$^{-1}$ at 0.539 *M* catalyst and 0.73 × 10^{-4} sec.$^{-1}$ at 1.08 *M* catalyst (see ref. 5). [b] Temperature of the run was 10.0°. [c] Temperature of the run was 44.8°. [d] Hydrogen chloride (1.8 × 10^{-2} *M*) was also present. [e] Temperature of the run was 45.2°.

significant contribution to the over-all reaction only when the concentration level of the stilbene and cyclohexene is much less than in these runs. It should be noted that the addition of free chlorine to these unsaturates in carbon tetrachloride at trifluoroacetic acids concentrations comparable to those recorded in Table I occurs at an immeasurably fast rate. Under the conditions of the rate runs, the dichloride does not react with the unsaturates in the absence of the catalyst.

The trifluoroacetic acid induced chlorination (direct) of durene in solutions of iodobenzene dichloride in carbon tetrachloride is strongly inhibited by hydrogen chloride.[5] This inhibition is explained on the assumption that an equilibrium (eq. 3) is established in the reaction mixture with respect to the formation of $C_6H_5ICl(OCOCF_3)$.



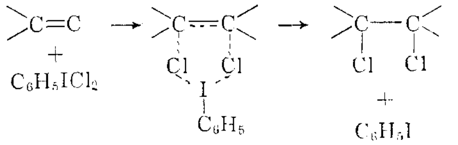
(3)

The concentration of the latter, which is presumably a much more reactive chlorinating agent than is iodobenzene dichloride, must diminish with increasing hydrogen halide content of the medium with a corresponding diminution of the over-all reaction rate. A few runs were made to check the hydrogen chloride effect on the rate of the trifluoroacetic acid catalyzed reaction of the dichloride with the unsaturates. The effect, if any, was very small (see, for example, the last two entries under the heading "Stilbene" in Table I). It should not, however, necessarily be inferred that $C_6H_5ICl(OCOCF_3)$ does not readily attack the carbon–carbon double bond. Rather, it seems more probable that at the relatively low concentrations of the catalyst used to promote the addition reactions, the concentration of the iodobenzene chloride trifluoroacetate is low enough so that this substance does not compete effectively with the dichloride as a reactant.

The effect of substituting acetic acid (with no catalyst present) for carbon tetrachloride as the solvent in the reaction of stilbene was tested. A rate constant, k = 2.02 × 10^{-4} sec.$^{-1}$ (25.2°), was obtained for a run in which the initial concentrations of stilbene and the dichloride were 0.064 and 0.010 *M*, respectively. This is essentially identical with the first-order rate constant k_1 (eq. 2) for formation of free chlorine from the dichloride. Under these conditions, as is also the case for chlorination of alkylbenzenes by the dichloride in acetic acid,[4,5] the free halogen is a true reaction intermediate.

Activation energies for the reactions with stilbene and cyclohexene were estimated using the rate constants for a series of runs at 10°, 25° and 45° (Table I) in which the initial reactant and catalyst concentrations were identical. The E_a-values, as calculated from the slopes of plots of log k *vs.* $1/T$, were approximately 9 and 11 kcal./mole, respectively, for cyclohexene and stilbene. These figures are not reported more precisely since they are calculated on the assumption (which may not be exactly correct[18]) that the order of the reactions with respect to the catalyst is temperature independent.

The Reaction Products.—Barton and Miller[1] have suggested one mechanism for reaction of iodobenzene dichloride with an ethylenic compound in which the double bond is subject to *cis* addition through direct attack by the dichloride, as in eq. 4.



(4)

The interesting possibility has been considered that the trifluoroacetic acid catalyzed reaction under investigation takes place by such a *cis* addition process when the experimental conditions are properly controlled to provide for participation of both the dichloride and the unsaturate in the rate-determining step.

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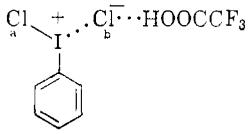
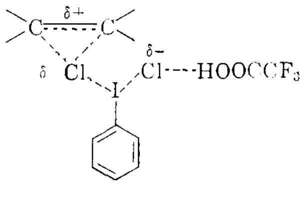
[18] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **82**, 3059 (1960).

As described in the Experimental section, the products of reaction of the dichloride with both stilbene and cyclohexene, as formed by reaction at concentration levels of the catalyst and the reactants similar to those used in the rate studies, have been investigated qualitatively. In neither case have exclusively *cis* addition products been found. Stilbene (the *trans* isomer) reacts to form substantial quantities of *meso* as well as of *dl*-stilbene dichloride and also an appreciable amount of chlorotrifluoroacetate, $C_6H_5CHClCH(OCOCF_3)$-C_6H_5. The product from cyclohexene is completely free of *cis* adducts. The only identifiable organic substances which it has been found to contain are *trans*-1,2-dichlorocyclohexane and *trans*-1-trifluoroacetoxy-2-chlorocyclohexane. It has been demonstrated that the isomeric dichlorides of stilbene and of cyclohexane are stable under the conditions of the addition reactions.

Qualitatively these reactions products are similar in composition to those formed when free chlorine is substituted for iodobenzene dichloride as the halogen source. The procedures devised for analysis of the reaction products are not sufficiently precise so that even a semi-quantitative comparison of the relative amounts of the various adducts formed from the dichloride and from free chlorine can be made. It is probable, however, that the product composition is subject to some change with the change in halogen source. Very likely it also varies appreciably with changes in the concentrations of the reactants and the catalyst, although no very reliable supporting data have been collected.

The catalytic action of trifluoroacetic acid in promoting the direct reaction of an ethylenic compound with iodobenzene dichloride must be attributed to the capacity of the acid to promote the electrophilic character of one of the halogen atoms of the dichloride molecule (chlorine a) through hydrogen bonding to the other halogen (chlorine b).[5] For the sake of simplicity the acid is represented as the monomer in the formulas accompanying this discussion, although very likely it is dimeric in character. In the activation process for the slow step of the addition reaction, in which positive halogen must be transferred to the double bond, polarization of the reactants must occur as shown below. At least one more catalyst molecule, in addition to that shown, must be included in the solvation sphere of this aggregate since the reaction order with respect to the catalyst is second or larger. The intermediate formed in the slow step of the reaction of cyclohexene is presumed to be akin to a cyclic chloronium ion in character, since the products which are formed on further reaction, the dichloride and the trifluoroacetoxy chloride, are exclusively *trans* in character. In the case of the reaction of stilbene the electrophilic chlorine atom apparently provides much less neighboring group protection. There is other evidence[19] that the effectiveness of a neighboring chlorine atom in stabilizing an electron-deficient carbon atom is by no means at a maximum when that carbon bears a phenyl substituent.





Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research. They wish to thank Professor R. E. Kepner and Mr. J. D. Davis for their assistance with the chromatographic phases of this work.

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[19] S. Winstein and D. Seymour, *J. Am. Chem. Soc.*, **68**, 119 (1946).

[CONTRIBUTION FROM THE JAMES BRYANT CONANT LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

The Reduction of Olefinic Double Bonds with Dihydropyridines

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Two dihydropyridines reduce the olefinic double bond of 1-phenyl-4,4,4-trifluoro-2-buten-1-one in good yield under mild conditions. Tracer experiments show that hydrogen is transferred directly from the 4-position of the pyridine ring to the carbon atom beta to the carbonyl group. The reaction thus roughly parallels the enzymatic reduction of androstenedione achieved by McGuire and Tompkins. The model reaction is restricted to activated double bonds, and (among the seven N-alkyl dihydropyridines tried) has succeeded only with 1,3,5-trimethyl-3,5-dicarboethoxy-1,4-dihydropyridine. Specific examples of the reduction of carbon–carbon double bonds by dihydropyridines are presented and discussed.

Diphosphopyridine nucleotide (DPN) and triphosphopyridine nucleotide (TPN) are among the principal coenzymes for biochemical oxidation–reduction reactions. Recently, McGuire and Tompkins[1] have reduced the olefinic double bond of androstenedione with TPNH (reduced triphosphopyridine nucleotide) and an enzyme from rat-liver mitochondria. In this paper, a non-enzymatic model for the reduction of the carbon–carbon double bond of an α,β-unsaturated ketone is presented and discussed.

The enzymatic reduction of various carbonyl compounds with DPNH (reduced diphosphopyri-

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[1] J. S. McGuire and G. M. Tompkins, *Fed. Proc.*, **19**, A29 (1960).