[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE UNIVERSITY, MANHATTAN, KAN.]

Molecular Rearrangements. II. Chlorine Migration in the Epoxide–Carbonyl Rearrangement

BY RICHARD N. McDONALD AND PETER A. SCHWAB[2]

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Peracid epoxidation of *trans*-α-chlorostilbene has not yielded the α-chloroepoxide, but rather the α-chloroketone, desyl chloride. This result is explained by rearrangement of the intermediate α-chloroepoxide. Preferential chlorine migration is shown to occur by peracid epoxidations of *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene (Va) and *trans*-1-chloro-1-phenyl-2-(*p*-tolyl)-ethylene (Vb). The structures of the α-chloroketone products were determined by their ultraviolet absorption spectra and independent synthesis. Various mechanisms are considered for this novel chlorine migration in light of the results. It was also found that basic hydrolysis of desyl chloride to benzoin and reconversion to desyl chloride with thionyl chloride proceeds with no isomerization of the functional groups.

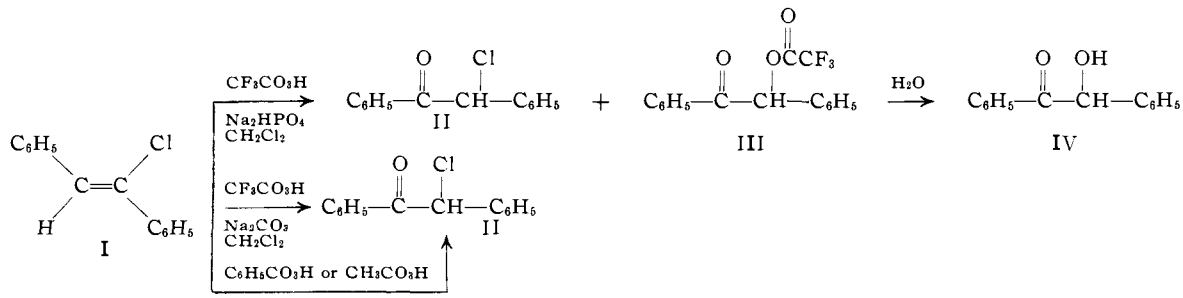
The literature contains a few reports of α-chloroepoxides and no reports of α-haloepoxides with the other halogens. The most frequently used and simplest method of preparation is the perbenzoic acid oxidation of vinyl chlorides.[3] More recently, Walling and Fredericks[4] were able to chlorinate photolytically ethylene and propylene oxides using *t*-butyl hypochlorite, and chlorine has been reported to effect the same process.[5] The Darzens condensation of methyl dichloroacetate and benzaldehyde has been reported to yield methyl 2-chloro-2,3-epoxy-3-phenylpropanoate,[6] while benzaldehyde and benzal chloride are reported to yield under Darzens conditions α-chlorostilbene oxide.[7]

The chemistry of these compounds has been studied even less. Hydrolysis leading to α-hydroxy ketones is mentioned in several of the above references. Prileschajew[3e] reported the Tollens and permanganate oxidations of 1-chloro-1-heptene oxide and 2-chloro-2-octene oxide. However, these conditions probably involved initial hydrolysis to the α-hydroxy ketone which then underwent oxidation. Russian workers[8] have studied the reactions of aliphatic α-chloroepoxides with various cyclic α-chloroepoxides, but made little mention of the meaning of the results.

trans-α-Chlorostilbene oxide[7] appeared to suit our needs to initiate a study of substitution and elimination reactions of α-haloepoxides. We attempted the Darzens reaction of benzaldehyde and benzal chloride under various conditions used normally for this condensation with no success, the majority of the starting materials being recovered in each case.

Our attention then turned to peracid oxidation of *trans*-α-chlorostilbene (I) as a method of obtaining the α-chloroepoxide. However, the isolation of this compound was not realized under any of the conditions used, but rather the only isolable product was the α-chloroketone, desyl chloride (II). This observation has led to the discovery of preferential chlorine migration in the epoxide–carbonyl rearrangement,[9] the details of which are the subject of this paper.

Treatment of *trans*-α-chlorostilbene[10] (I) with trifluoroperacetic acid in methylene chloride solution with disodium hydrogen phosphate as the insoluble base[11] gave a mixture of desyl chloride (II) and the trifluoroacetate of benzoin[12] (III). Upon standing exposed to the atmosphere for several days, or when hydrolyzed with water, this mixture was completely converted to benzoin (IV) (76% yield based on *trans*-α-chlorostilbene). Using sodium carbonate as the insoluble base,[11] trifluoroperacetic acid treatment gave desyl chloride (II) in 63% yield. Treatment of I with peracetic acid in methylene chloride solution gave a 67% yield of II, while perbenzoic acid in chloroform solution converted I to II in 74% yield. All of the yields thus far reported are of crystallized, sharp melting product.



To check these yield data and to determine the fate of the rest of the starting material the reaction product from a perbenzoic acid oxidation was shown by ultraviolet spectral analysis to contain some I as well as II. The α-chloroketone II was readily separated from α-chloroolefin I by column chromatography or careful

(1) For paper I in this series see R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, **85**, 820 (1963), a preliminary communication of some of these results.

(2) A portion of a dissertation to be presented by P. A. Schwab to the Graduate School of Kansas State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) (a) M. Mousseron, F. Winternitz, and R. Jacquier, *Compt. rend.*, **223**, 1014 (1946); (b) M. Mousseron, F. Winternitz, and R. Jacquier, *Bull. soc. chim. France*, 81 (1947); (c) M. Mousseron, F. Winternitz, and R. Jacquier, *ibid.*, 260 (1948); (d) M. Mousseron and R. Jacquier, *ibid.*, 698 (1950); (e) N. Prileschajew, *Ber.*, **59**, 194 (1926); (f) A. A. Durgaryan and S. A. Titanyan, *Izvest. Akad. Nauk Armyan. S.S.R., Khim. Nauki*, **13**, 263 (1960); *Chem. Abstr.*, **55**, 21084*b* (1961).

(4) C. Walling and P. S. Fredericks, *J. Am. Chem. Soc.*, **84**, 3326 (1962).

(5) H. Gross and A. Rieche, German Patent 1,084,707 (1960); *Chem. Abstr.*, **55**, 23562*c* (1961).

(6) V. F. Martynov and M. I. Titov, *Zh. Obshch. Khim.*, **32**, 319 (1962).

(7) F. Barrow, Inaugural Dissertation, Strasbourg, 1909; see M. S. Newman and B. J. Magerlein, "Darzens Glycidic Ester Condensation," *Org. Reactions*, **5**, 413 (1949), ref. 34b.

(8) A. A. Durgaryan, *Izvest. Akad. Nauk Armyan. S.S.R., Khim. Nauki*, **14**, 51 (1961); *Chem. Abstr.*, **56**, 465*f* (1962); and A. A. Durgaryan, S. A. Titanyan, and R. A. Kazaryan, *Izvest. Akad. Nauk Armyan. S.S.R., Khim. Nauki*, **14**, 165 (1961); *Chem. Abstr.*, **56**, 4741*d* (1962).

(9) Previous work on epoxide-carbonyl rearrangements has been reviewed by R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(10) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

(11) W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 89 (1955).

(12) Gas chromatographic and elemental analysis showed this mixture to consist of 24% of desyl chloride and 76% of the trifluoroacetate of benzoin.

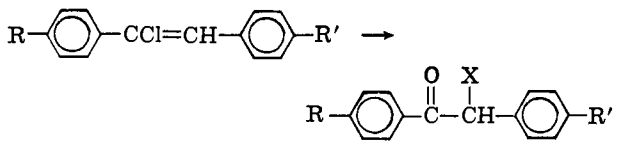
crystallization. The yield of II in this manner was 75% while compound I was recovered in 24.5%. This shows that the conversion to II is quantitative within experimental error.

The formation of the α-chloroketone, desyl chloride, can readily be explained in terms of the well known epoxide–carbonyl rearrangement[9] assuming the intermediacy of the α-chloroepoxide. This was considered reasonable in view of the nature of the reactants and the previous success in the isolation of α-chloroepoxides under similar conditions.[3]

The question remaining is which atom migrated, hydrogen or chlorine. Previous results on this and "related" molecular rearrangements[13] certainly show that hydrogen is frequently found to migrate. On the other hand, the migration of the acetoxy group in the epoxide–carbonyl rearrangement of enol ester epoxides has been demonstrated,[14] which lends support to the idea that chlorine might be the migrating group.[15]

To decide this question of which atom was migrating we chose to study the peracid oxidations of *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene (Va) and *trans*-1-chloro-1-phenyl-2-(*p*-tolyl)ethylene (Vb). With these two isomers we could distinguish between hydrogen and chlorine migration without significantly altering the path of rearrangement.

4-Methyl-α-phenylacetophenone[16] was prepared by the Friedel–Crafts reaction of phenylacetyl chloride with toluene and subsequently treated with phosphorus pentachloride in refluxing benzene to give the desired *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene (Va). When this vinyl chloride was treated with trifluoroperacetic acid in methylene chloride solution, using no insoluble base, a trifluoroacetate (VIb) was isolated and immediately hydrolyzed without purification to give a single product in 45% yield which was found to be methyl-α-hydroxy-α-phenylacetophenone[17] (VIc). Using sodium carbonate as the insoluble base, trifluoroperacetic acid gave a 58% yield of 4-methyl-α-chloro-α-phenylacetophenone (VIa).



Va, R = CH_3, R′ = H
b, R = H, R′ = CH_3

VI

a, R = CH_3, R′ = H, X = Cl
b, R = CH_3, R′ = H, X = $OCOCF_3$
c, R = CH_3, R′ = H, X = OH
d, R = H, R′ = CH_3, X = Cl
e, R = H, R′ = CH_3, X = $OCOCF_3$
f, R = H, R′ = CH_3, X = OH

Also, treatment of Va with peracetic acid in methylene chloride solution gave a 71% yield of the rearranged product VIa, and perbenzoic acid in chloroform solution give a 73% yield of VIa. Since the yield of α-chloroketone in this latter oxidation–rearrangement is comparable to the yield of desyl chloride using this same peracid, this demonstrates that only chlorine migration has occurred. The structure of the chloroketone VIa was established by independent synthesis by sulfuryl chloride chlorination of 4-methyl-α-phenylacetophenone.

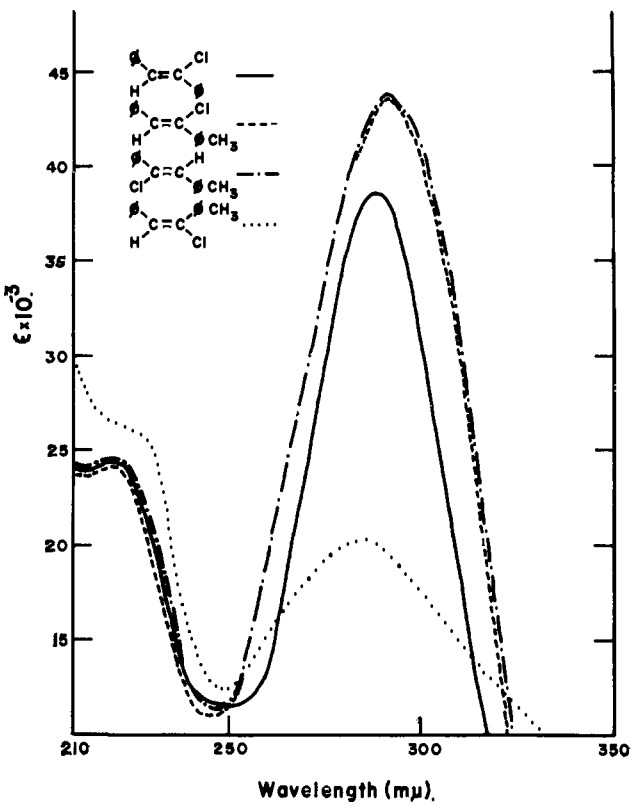


Figure 1.

trans-1-Chloro-1-phenyl-2-(*p*-tolyl)-ethylene (Vb) was prepared in the following manner. Photolytic bromination of *p*-xylene was carried out in carbon tetrachloride giving α-bromo-*p*-xylene.[16] This was then converted to α-cyano-*p*-xylene with sodium cyanide.[18] Hydrolysis of this nitrile gave *p*-tolylacetic acid[18] which was easily converted to its acid chloride with phosphorus trichloride. Friedel–Crafts reaction of this acid chloride with benzene gave the desired α-(*p*-tolyl)-acetophenone.[19] Subsequent treatment with phosphorus pentachloride in benzene and distillation gave the expected *trans*-vinyl chloride Vb.

As above, treatment of Vb with trifluoroperacetic acid, using no insoluble base, gave the trifluoroacetate VIe which was immediately hydrolyzed to the known α-hydroxy-α-(*p*-tolyl)-acetophenone[17] (VIf) in 42% yield; using sodium carbonate, α-chloro-α-(*p*-tolyl)-acetophenone (VId) was formed in 53% yield. Reaction of Vb with peracetic acid and perbenzoic acid gave the same α-chloroketone VId in yields of 67 and 71%, respectively. Sulfuryl chloride chlorination of α-(*p*-tolyl)-acetophenone likewise gave VId.

As evident from the above results, *in every instance only that α-chloroketone was isolated which necessarily involves chlorine migration.* Also, no acid chlorides or aldehydes were found which would be the result of aryl or hydrogen migration. These facts together with quantitative conversions from the perbenzoic acid reaction (assumed also in the other peracid reactions) demonstrate the high migratory ability of chlorine in these systems.

The assignment of the *trans* configuration to Va and Vb is based on the similarity of their ultraviolet spectra with that of known *trans*-α-chlorostilbene. These are shown in Fig. 1. The ultraviolet spectrum of *cis*-Va

(13) C. J. Collins, *Quart. Rev.* (London), **14**, 357 (1960), reviews the pinacol and certain related rearrangements.

(14) A. L. Draper, W. J. Heilman, W. E. Schaefer, H. J. Shine, and J. N. Shoolery, *J. Org. Chem.*, **27**, 2727 (1962), and references cited therein.

(15) The epoxide-carbonyl rearrangement is particularly well suited to study the migration of various groups, *e.g.*, the halogens and pseudo-halogens, due to the relative ease of synthesis of the necessary α-substituted epoxides. Such studies are presently underway in our laboratories.

(16) W. Mann, *Ber.*, **14**, 1645 (1881).

(17) R. T. Arnold and R. C. Fuson, *J. Am. Chem. Soc.*, **58**, 1295 (1936).

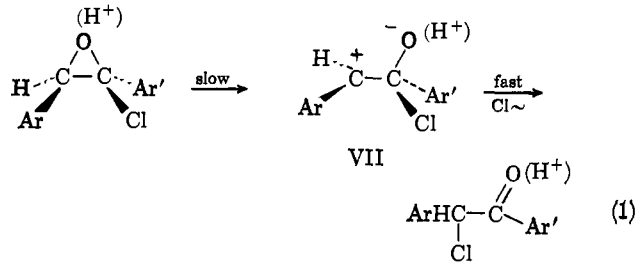
(18) E. F. J. Atkinson and J. F. Thorpe, *J. Chem. Soc.*, 1687 (1907).

(19) H. Strassmann, *Ber.*, **22**, 1229 (1889).

is also given.[20] The ultraviolet spectra of the product α-chloroketones are also in agreement with their assigned structures. 4-Methyl-α-chloro-α-phenylacetophenone (VIa) has its longer wave length absorption peak at 258 mμ (ε 26,200) illustrating the *p*-tolyl group conjugated with the carbonyl, while its isomer α-chloro-α-(*p*-tolyl)-acetophenone exhibits its longer wave length peak at 247 mμ (ε 24,500), very similar to that of desyl chloride.

We believe certain of our results are useful in attempting to describe the mechanism by which chlorine migrates in these examples. To simplify the mechanistic possibilities we will make the assumption that this rearrangement is intramolecular. Two pieces of evidence can be cited to support this assumption: (1) acetoxy (a "pseudo-halogen") has been shown to migrate intramolecularly in the thermal rearrangement of enol ester epoxides[14] and gives stereospecific α-acetoxy ketone product[21] and (2) our reactions with peracetic acid in acetic acid–methylene chloride solution containing added sodium acetate gave high yields of α-chloroketone and no evidence of benzoin acetates as products.

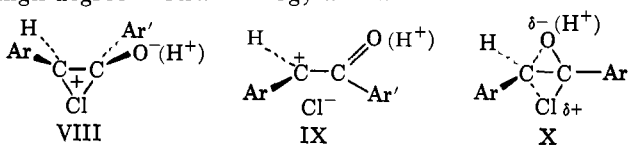
With this assumption there appear to be three reasonable mechanistic pathways which will account for chlorine migration.[22] The first that we might consider would be opening of the epoxide ring to give a carbonium ion followed by chlorine migration to yield the observed α-chloroketone product. The 1,2-shift of chlorine must be fast or we would have expected the carbonium ion



to be captured by acetate ion in the peracetic acid reactions.

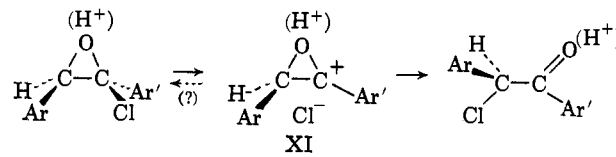
To maintain the intramolecular nature of the migration step, we may consider two methods of shifting the chlorine: (1) involvement of a chloronium ion, *e.g.*, VIII, following a rotation about the central carbon–carbon bond or (2) formation of an intimate ion pair, *e.g.*, IX, followed by bond formation leading to product. In either case there would appear to be little driving force for return to the carbonium ion VII.

A second mechanism that deserves mention would be a concerted process. However, this must involve considerably more C–O bond breaking than C–Cl bond making in the transition state, which may be crudely represented as X. Such a structure would involve a high degree of strain energy and would infer that chlorine migration is facilitating the C–O bond fission. This would then be similar to chlorine acting as a participating neighboring group in a modified solvolysis.[23] Since participation by neighboring chlorine has been shown to be very small in solvolyses[24] and the strain energy necessary to achieve X would be great, this mechanism can be discarded at present.

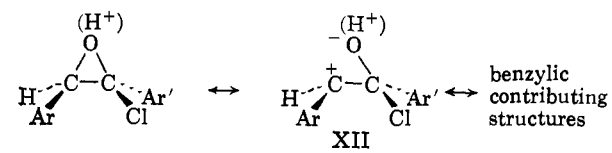


Another point regarding the use of the "concerted" mechanism in epoxide–carbonyl rearrangements is that there must be a rotation about the C–C single bond of the epoxide of approximately 76°[25] to bring the migrating group into a transoid position to the breaking C–O bond. In order to allow for this there must be considerable, if not complete, rupture of the epoxide ring and this pathway becomes the same as mechanism 1. This point does not appear to have been considered before.

The third mechanism worthy of consideration involves ion pair formation prior to epoxide ring opening, *e.g.*, XI. Here the strain problems inherent in the concerted mechanism are not involved and the group that will migrate will be that which forms anion most readily. This seems to be the only mechanism of the three considered that accounts for the preferential chlorine migration and lack of competition by hydrogen or aryl. Whether internal return of XI to the α-chloroepoxide (or its conjugate acid) takes place is unknown as is the extent, if any, of epoxide C–O bond fission in this process.



The breaking of the particular epoxide C–O bond in the discussion of the above listed mechanisms is explained by the following contributing structures to the possible hybrid of the α-chloroepoxide[26] (or its conjugate acid). Ion XII would be of greater stability than the isomeric one formed by breaking the alternate C–O bond due to destabilization of that carbonium ion by the attached chlorine. Allowing for the intermediacy of ion pairs the aryl group on the carbon bearing the chlorine would be expected to facilitate loss of chloride ion by resonance stabilization of the resulting carbonium ion. Such stabilization would explain why no α-chloroepoxide is isolated in these examples, whereas such compounds can be isolated when only alkyl substituents are present. In the latter examples only inductive and hyperconjugative stabilization can be involved in stabilizing intermediates so the free energy of activation for rearrangement is too high for it to proceed.



A result that also fits the idea of ion pairs is the apparent lack of stereospecificity of the rearrangement. House and Reif[27] showed that a pair of geometrical isomers, *cis*- and *trans*-α-benzoylstilbene oxides, rearrange to give different products. These results were rationalized in terms of concerted intermediate or

(20) The *cis* and *trans* isomers of Va were found to be readily separated by v.p.c. or by spinning-band distillation of the reaction product from 4-methyl-α-phenylacetophenone and phosphorus pentachloride.

(21) K. L. Williamson and W. S. Johnson, *J. Org. Chem.*, **26**, 4563 (1961).

(22) We will not attempt to differentiate between rearrangement of the α-chloroepoxide or its conjugate acid.

(23) The term "modified solvolysis" is employed in that the departing anion is part of the same molecule.

(24) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948); E. Grunwald, *ibid.*, **73**, 5458 (1951).

(25) Rotation of the full 76° would probably not be necessary to allow for participation of a neighboring group. However, it would appear from Dreiding models that a minimum rotation of about 50° is required.

(26) Similar structures of a hybrid have been proposed to explain the nature of the epoxide ring system (see ref. 9, pp. 739–740). Such structures should be of greater importance in the protonated epoxide to enable distribution of the charge.

(27) H. O. House and D. J. Reif, *J. Am. Chem. Soc.*, **77**, 6525 (1955).

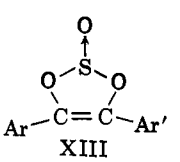
transition states involving phenonium ions. In our experiments, reaction of either *cis*- or *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene[20] with perbenzoic acid leads to the isolation of the same product α-chloroketone and in the same yield.

Our experiments using trifluoroperacetic acid (with or without added disodium hydrogen phosphate) resulting in formation of mixtures of the α-chloroketone and the trifluoroacetate of the benzoin can be explained by a secondary reaction of the α-chloroketone (primary product of rearrangement). A mixture of trifluoroacetic acid and trifluoroacetic anhydride in methylene chloride converts desyl chloride to benzoin trifluoroacetate in 75% yield. Neither reagent effects this conversion alone. In the peroxidations, trifluoroacetic acid is produced in the presence of anhydride (excess of anhydride used in making the peracid); before the acid is picked up by the insoluble disodium hydrogen phosphate, reaction with the α-chloroketone takes place. In the presence of the stronger base, sodium carbonate, removal of the trifluoroacetic acid by-product of the peroxidation would be expected to be faster and more complete[11] and such is realized in the good yields of the α-chloroketone.

In our discussion of possible mechanisms we have postulated that the first step in the rearrangement is that of epoxidation of the vinyl chloride to give the α-chloroepoxide. However, in the cases studied we were not able to isolate these compounds. Numerous attempts to synthesize these α-chloroepoxides by other methods have failed.[28] As we suggested above, the aryl groups apparently reduce the free energy of activation of the rearrangement sufficiently so that it proceeds under the conditions employed.

In repeating the work of Mousseron[3d] we have found that 1-chlorocyclohexene oxide was difficult to isolate and readily undergoes rearrangement at room temperature. However, it could be stored under nitrogen at −10° for several months. 1-Chloro-4-methylcyclohexene oxide is more stable than the unmethylated derivative, but readily undergoes thermal or acid-catalyzed rearrangement with chlorine migration.[29] Evidently even in the cases of the symmetrically substituted dialkyl α-chloroepoxides, these prove to be reactive materials and chlorine migration is observed.

We have also found that treatment of α-chloroketones with sodium hydroxide gives excellent yields of their respective benzoins by direct replacement of the chlorine by the hydroxyl group in 92–94% yield. It is interesting that no base-catalyzed isomerization of the benzoins is observed. Further, this process is reversed by allowing the benzoins to react with thionyl chloride in 74–76% yield. This latter result eliminates from consideration a mechanism involving chloride ion attack on the cyclic enediol sulfite XIII since this would give a statistical mixture of the two isomeric α-chloroketones. Compound XIII has been shown to be the intermediate in the formation of 25–30% of benzil in the reaction of benzoin and thionyl chloride.[30] The conversion to the α-chloroketone by thionyl chloride must then involve either an SN2 or an SNi mechanism.



XIII

(28) The chlorination of *trans*-stilbene oxide with various α-chlorinating agents has been attempted, but the α-chloroepoxide never isolated.

(29) Unpublished results with Theodore E. Tabor.

(30) L. F. Fieser and Y. Okumura, *J. Org. Chem.*, **27**, 2247 (1962); Y. Okumura, *ibid.*, **28**, 1075 (1963).

Our present results do not allow for a differentiation of the possible mechanisms operating in the migration of chlorine in this novel rearrangement. More questions have been raised than answered by this work and experiments designed to answer some of these, such as the intra- or intermolecularity, the apparent lack of steric requirements, and solvent effects of the chlorine migration in the rearrangement, are being carried out. Studies into the generality of halogen and pseudo-halogen migration and their migratory aptitudes in these and other systems are also presently under investigation.

Experimental

All melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin–Elmer Model 137 double beam recording spectrophotometer. Ultraviolet absorption spectra were determined on a Cary Model 11 recording spectrophotometer. Vapor phase chromatographic analyses were carried out on an F and M Model 500 linear programmed high temperature gas chromatograph. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials.—Trifluoroacetic anhydride was purchased from Fisher Scientific Co. and used without further purification. The 90% hydrogen peroxide was purchased from Becco Chemical Division of Food Machinery and Chemical Corp. as was the 40% peracetic acid. The perbenzoic acid was prepared according to Braun.[31]

***trans*-α-Chlorostilbene.**—To a stirred, refluxing mixture of 130 g. (0.63 mole) of PCl_5 and 250 ml. of dry benzene was added dropwise a solution of 120 g. (0.61 mole) of desoxybenzoin[32] in 400 ml. of dry benzene. Heating and stirring were continued for 2 hr. followed by stirring at room temperature overnight. This mixture was added dropwise to ice–water, separated, washed with cold water until free of chloride ion, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the liquid residue distilled. The fraction, b.p. 120–130° (0.05 mm.), was collected which solidified on standing. This was recrystallized twice from ethanol and once from Skelly B, giving 85 g. (65%) of *trans*-α-chlorostilbene, m.p. 51–52° (lit.[10] m.p. 53–54°, 39% yield), λ_{max} 288 mμ (ε 38,600) in cyclohexane.

Reaction of *trans*-α-Chlorostilbene with Organic Peracids. A. Trifluoroperacetic Acid. i. Using Na_2HPO_4 as Insoluble Base.—To a stirred mixture of 10 g. (0.047 mole) of *trans*-α-chlorostilbene and 30.0 g. (0.21 mole) of anhydrous Na_2HPO_4 (ground to a fine powder and dried *in vacuo* at 50° for 20 hr.) in 100 ml. of CH_2Cl_2 at reflux was added dropwise a solution of trifluoroacetic acid in CH_2Cl_2. (The solution of peracid was prepared by adding 2.0 ml. (0.072 mole) of 90% hydrogen peroxide to a chilled solution of 12 ml. (0.085 mole) of trifluoroacetic anhydride in 50 ml. of CH_2Cl_2 with stirring.) After addition the mixture was heated under reflux for an additional hour, cooled, and the insoluble salts filtered and washed with CH_2Cl_2. Evaporation of the solvent and distillation of the residual crude oil gave a colorless fraction, b.p. 110–112° (0.13 mm.), which would not crystallize. The infrared spectrum of this liquid showed it to be a mixture of benzoin trifluoroacetate and desyl chloride. Elemental analysis and vapor phase chromatography proved this mixture to contain approximately 76% of the benzoin trifluoroacetate and 24% of desyl chloride.

Anal. Calcd. for 76% $C_{16}H_{11}O_3F_3$ and 24% $C_{14}H_{11}OCl$: C, 64.95; H, 3.84; Cl, 3.70. Found: C, 63.89; H, 4.39; Cl, 3.70.

Upon standing exposed to the moist atmosphere for several days, or when treated with water, the mixture was completely converted to benzoin (7.5 g., 76% yield based on *trans*-α-chlorostilbene), m.p. 136–137°.

ii. **Using Na_2CO_3 as Insoluble Base.**—To a stirred mixture of 5.0 g. (0.024 mole) of *trans*-α-chlorostilbene and 20.0 g. (0.33 mole) of anhydrous Na_2CO_3 (ground to a fine powder and dried *in vacuo* at 50° for 20 hr.) in 100 ml. of CH_2Cl_2 under reflux was added dropwise a solution of trifluoroperacetic acid in CH_2Cl_2. (The latter solution was prepared by treating a chilled solution of 6.0 ml. (0.043 mole) of trifluoroacetic anhydride in 50 ml. of CH_2Cl_2 with 1 ml. (0.036 mole) of 90% hydrogen peroxide with stirring.) The reaction mixture was worked up as above. The crude product showed no trifluoroacetate carbonyl absorption in the infrared spectrum, only that of desyl chloride. This liquid could be distilled at 0.15 mm. and the fraction boiling at 118–124° collected. This fraction crystallized in the refrigerator and

(31) G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons Inc., New York, N. Y., 1941, p. 431.

(32) C. F. H. Allen and W. E. Barker, *ibid.*, Coll. Vol. II, 1943, p. 156.

was recrystallized twice from alcohol to yield 3.4 g. (63%) of desyl chloride, m.p. 62–63° (lit.[33] m.p. 66–67°).

B. **Perbenzoic Acid.**—Ten grams (0.047 mole) of *trans*-α-chlorostilbene was dissolved in 50 ml. of chloroform and cooled to 0°. To this solution was added 116 ml. (0.057 mole) of a 0.49 *M* chloroform solution of perbenzoic acid also cooled to 0° with stirring. The reaction mixture was allowed to come to room temperature and after 48 hr. was complete (negative starch–iodide paper test). The mixture was washed with three 50-ml. portions of 5% aqueous sodium hydroxide followed by 100 ml. of water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue crystallized in the cold. Ultraviolet spectral analysis of the crude reaction mixture showed a small amount of *trans*-α-chlorostilbene (λ_{max} 288 mμ) remaining with the desyl chloride (λ_{max} 248 mμ).

The solid was then fractionally crystallized from Skelly B, then recrystallized from alcohol to give 8.0 g. (75% yield, quantitative conversion) of desyl chloride, m.p. 62–63°, along with 2.5 g. of starting vinyl chloride, m.p. 50–53°.

The crude reaction product was dissolved in warm Skelly B and chromatographed on a 2 ft. × 1 cm. Woelm alumina column (basic, activity grade 1). Starting *trans*-α-chlorostilbene (2.5 g.) was eluted with Skelly B; desyl chloride (8.0 g.) was eluted with a mixture of Skelly B and CH_2Cl_2 (1:1).

C. **Peracetic Acid.**—A stirred solution of 5.0 g. (0.024 mole) of *trans*-α-chlorostilbene in 50 ml. of CH_2Cl_2 at 20° was treated dropwise with a mixture containing 5.2 ml. (0.034 mole) of a 6.55 *M* (40%) solution of peracetic acid in acetic acid and 0.5 g. of sodium acetate trihydrate in 20 ml. of CH_2Cl_2. Stirring was continued for 48 hr. The mixture was then poured into 50 ml. of water. The organic layer was separated and the aqueous layer extracted with 25 ml. of CH_2Cl_2. The CH_2Cl_2 extracts were combined, washed with two 20-ml. portions of 10% aqueous sodium carbonate, followed by 25 ml. of water, and dried over anhydrous sodium sulfate. Evaporation of the solvent left a liquid that crystallized in the refrigerator. This was recrystallized from Skelly B and then from alcohol to yield 3.6 g. (67%) of desyl chloride, m.p. 62–63°.

4-Methyl-α-phenylacetophenone.—The procedure for the preparation of deoxybenzoin[32] was used substituting dry toluene for anhydrous benzene. Recrystallization of the product three times from methanol gave 86.0 g. (82%) of 4-methyl-α-phenylacetophenone, m.p. 109–111° (lit.[16] m.p. 108–109°).

cis- and *trans*-**1-Chloro-1-(*p*-tolyl)-2-phenylethylene.**—To a stirred solution of 64.0 g. (0.31 mole) of phosphorus pentachloride in 100 ml. of dry benzene heated under reflux was added slowly a solution of 55.0 g. (0.26 mole) of 4-methyl-α-phenylacetophenone dissolved in 200 ml. of benzene. Heating was continued for an additional 2 hr. and the mixture stirred overnight at room temperature. The reaction mixture was hydrolyzed by pouring onto an ice–water mixture and the benzene layer separated. This was washed with 10% aqueous sodium hydroxide followed by water and dried over anhydrous sodium sulfate. After evaporation of the solvent the residual liquid was distilled and the fraction boiling at 118–120° (0.03 mm.) collected (34 g., 56%). This was an oil which would not crystallize. It was distilled through a micro-spinning-band column, collecting 11 g. of a fraction boiling at 82–84° (0.004 mm.) and 22 g. of a fraction boiling at 92–94° (0.02 mm.). The lower boiling fraction was the *cis*-1-chloro-1-(*p*-tolyl)-2-phenylethylene (m.p. 12–13°, λ_{max} 283 mμ (ε 20,000) in cyclohexane) and the higher boiling fraction the *trans* isomer. This latter isomer crystallized when placed in the refrigerator and after recrystallization once from Skelly B and twice from methanol had m.p. 36–38°, λ_{max} 292 mμ (ε 43,800) in cyclohexane.

Anal. Calcd. for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.75; H, 5.69; Cl, 15.62.

The *cis* and *trans* isomers could also be separated by v.p.c. on a 2-ft. silicone gum rubber column.

Reaction of *trans*-1-Chloro-1-(*p*-tolyl)-2-phenylethylene with Organic Peracids. A. Trifluoroperacetic Acid. i. Using No Added Base.—The reaction was run as before using 4.0 g. (0.018 mole) of *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene in 50 ml. of CH_2Cl_2. The peracid solution was prepared by mixing 1 ml. (0.036 mole) of 90% H_2O_2 with 6 ml. (0.043 mole) of trifluoroacetic anhydride in 15 ml. of CH_2Cl_2. After the reaction was complete, anhydrous sodium carbonate was added to the cooled solution. The insoluble salts were filtered, washed well with CH_2Cl_2, and the solvent was removed from the combined organic solutions under reduced pressure. Removal of the solvent yielded a liquid whose infrared spectrum showed two carbonyls—one a ketone, the second, that of a trifluoroacetate. None of the bands of the α-chloroketone was present.

This liquid was heated with water on a steam bath for 3 hr. and extracted with CH_2Cl_2. The organic layer was then dried and evaporation of the solvent under reduced pressure gave a red oil that crystallized from Skelly B after several days in the refrigerator. This was recrystallized once from alcohol and once from methanol to yield 1.8 g. (46%) of 4-methyl-α-hydroxy-α-phenylacetophenone, m.p. 108–109° (lit.[17] m.p. 109–110°).

ii. **Using Na_2CO_3 as Insoluble Base.**—The reaction was carried out as previously discussed using 3.0 g. (0.013 mole) of *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene and 10 g. (0.095 mole) of powdered, anhydrous Na_2CO_3 in 50 ml. of CH_2Cl_2. (The peracid solution was prepared by adding 0.55 ml. (0.02 mole) of 90% H_2O_2 to a solution of 3.3 ml. (0.023 mole) of trifluoroacetic anhydride in 15 ml. of CH_2Cl_2.) After the same work-up procedure the crude product crystallized from Skelly B in the refrigerator on standing. It was recrystallized once from methanol and twice from alcohol. The yield was 1.8 g. (58%) of 4-methyl-α-chloro-α-phenylacetophenone, m.p. 73–74°; λ_{max} 258 mμ (ε 26,200) in ethanol.

Anal. Calcd. for $C_{15}H_{13}OCl$: C, 73.65; H, 5.32; Cl, 14.50. Found: C, 73.43; H, 5.37; Cl, 14.39.

B. **Perbenzoic Acid.**—*trans*-1-Chloro-1-(*p*-tolyl)-2-phenylethylene (2.5 g., 0.01 mole) was added to 80 ml. (0.034 mole) of a 0.43 *M* chloroform solution of perbenzoic acid at 0°. After standing at room temperature for 48 hr., the product was worked up as mentioned previously to yield a yellow liquid which crystallized from Skelly B. Recrystallization twice from alcohol gave 2.0 g. (74%) of 4-methyl-α-chloro-α-phenylacetophenone, m.p. 73–74°.

C. **Peracetic Acid.**—This reaction was carried out in the usual manner using 2.5 g. (0.01 mole) of the olefin in 50 ml. of CH_2Cl_2 and treating this with 3 ml. (0.02 mole) of a 6.55 *M* solution of peracetic acid in acetic acid containing 0.25 g. of sodium acetate. The reaction time was 72 hr. The crude liquid product crystallized from Skelly B and after two recrystallizations from alcohol had m.p. 73–74° (1.9 g., 71%).

Reaction of 4-Methyl-α-chloro-α-phenylacetophenone with Sodium Hydroxide.—One gram (0.0041 mole) of the chloroketone in 50 ml. of ethanol was added to 6 ml. of a 5% sodium hydroxide solution. The color changed from initial yellow to red then back to yellow. After 4 hr. at room temperature the solution was poured into 100 ml. of 0.2 *N* hydrochloric acid with stirring. This gave a milky mixture and a colorless crystalline product resulted on cooling in an ice–salt bath. Recrystallization of this product from methyl and ethyl alcohols gave 0.85 g. (92%) of 4-methyl-α-hydroxy-α-phenylacetophenone, m.p. 108–110° (lit.[17] m.p. 109–110°).

Reaction of 4-Methyl-α-hydroxy-α-phenylacetophenone with Thionyl Chloride.—Two-tenths of a gram (0.0009 mole) of the benzoin was allowed to react with 2 ml. of $SOCl_2$ on a steam bath for 1 hr. The excess $SOCl_2$ was removed under reduced pressure and the crude yellow product crystallized from Skelly B. Recrystallization twice from alcohol gave 0.16 g. (74%) of 4-methyl-α-chloro-α-phenylacetophenone, m.p. 73–74°. Melting point, mixture melting point, and infrared spectra were used to identify this compound.

4-Methyl-α-chloro-α-phenylacetophenone (Independent Synthesis).—To a solution of 1.0 g. (0.0048 mole) of 4-methyl-α-phenylacetophenone in 50 ml. of CCl_4 stirred with a magnetic stirrer and heated in a water bath held at 45° was added dropwise a solution of 0.7 g. (0.005 mole) of SO_2Cl_2 in 10 ml. of CCl_4. After heating for 2 hr., the mixture was washed free of chloride ion with water and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a yellow liquid which crystallized from Skelly B. Recrystallization twice from alcohol yielded 0.97 g. (83%) of the product, m.p. 73–74°. Mixture melting points with the products obtained on peracid oxidation of *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene showed no depression. Their infrared spectra were identical. The ultraviolet absorption spectrum of this compound had λ_{max} 258 mμ (ε 26,200) in ethanol.

Reaction of *cis*-1-Chloro-1-(*p*-tolyl)-2-phenylethylene with Perbenzoic Acid.—The reaction was carried out in the manner described previously for the *trans* isomer using 5 g. (0.022 mole) of *cis*-1-chloro-1-(*p*-tolyl)-2-phenylethylene and 55 ml. (0.025 mole) of a 0.462 *M* chloroform solution of perbenzoic acid. Work-up gave 3.8 g. (71%) of the same α-chloroketone, m.p. 73–74°, which was isolated with the *trans* isomer.

α-Bromo-*p*-xylene.—The photolytic bromination of *p*-xylene was carried out using a GE-AH4 mercury lamp with the Pyrex glass envelope removed and the lamp placed in a quartz cell. This was jacketed by a second larger quartz tube so that cooling water could be passed through the jacket and the lamp container suspended in the reaction solution. This solution contained 250 g. (2.36 moles) of *p*-xylene in 250 ml. of chloroform which was stirred magnetically at room temperature. A solution of 300 g. (1.88 moles) of bromine was added at such a rate to maintain the color of the reaction mixture at a light red. After the addition was complete photolysis was continued until the color faded to yellow. The mixture was then washed free of bromide ion with water and dried over sodium sulfate. Distillation of the product after removing the solvent gave 53 g. of recovered *p*-xylene, b.p.

(33) A. M. Ward, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 159.

138–140°, and 190 g. (55%) of α-bromo-*p*-xylene, b.p. 94–96° (12 mm.) (lit.[18] b.p. 212° (760 mm.).

α-Cyano-*p*-xylene.—A solution of 190 g. (1.03 moles) of α-bromo-*p*-xylene in 200 ml. of 95% alcohol was added to one containing 65 g. (1.33 moles) of sodium cyanide dissolved in 60 ml. of water and the mixture heated on a steam bath for 4 hr. After cooling to room temperature the insoluble salts were filtered and washed thoroughly with alcohol. The alcohol and water were removed under reduced pressure and the product distilled. The product fraction, b.p. 94–96° (3 mm.), was collected and weighed 108 g. (81%) (lit.[18] b.p. 242–243° (760 mm.)).

***p*-Tolylacetic Acid.**—Hydrolysis of the above nitrile was carried out by heating under reflux a mixture of 156 ml. of water, 120 ml. of concentrated sulfuric acid, and 108 g. (0.825 mole) of the nitrile for 3 hr. It was then poured into 250 ml. of cold water with vigorous stirring and the product acid filtered off and washed with cold water. The acid was dried in a vacuum desiccator over phosphorus pentoxide for 36 hr. The weight of the product was 115 g. (92%), m.p. 91–92° (lit.[18] m.p. 91–92°).

α-(*p*-Tolyl)acetophenone.—The reaction was run in an analogous manner as described for the preparation of 4-methyl-α-phenylacetophenone. The amounts of the reactants were 114 g. (0.46 mole) of *p*-tolylacetic acid, 63 g. (0.59 mole) of PCl_3, 600 ml. of anhydrous benzene, and 135 g. (1.01 moles) of anhydrous $AlCl_3$. The crude product was recrystallized once from methanol and twice from ethanol to give 132 g. (83%) of the desired product, m.p. 93–95° (lit.[19] m.p. 94–95°).

***trans*-1-Chloro-1-phenyl-2-(*p*-tolyl)-ethylene** was prepared in the same manner as described for *trans*-1-chloro-1-(*p*-tolyl)-2-phenylethylene. The amounts of the reactants were 132 g. (0.63 mole) of α-(*p*-tolyl)-acetophenone in 250 ml. of anhydrous benzene, 135 g. (0.65 mole) of phosphorus pentachloride in 150 ml. of anhydrous benzene. The crude product was distilled and the fraction boiling at 121–125° (0.2 mm.) was collected. This fraction crystallized on standing and was recrystallized three times from alcohol and once from Skelly B giving 87.0 g. (61%) of the desired olefin, m.p. 47–48°, λ_{max} 292 mμ (ε 44,100) in cyclohexane.

Anal. Calcd. for $C_{15}H_{13}Cl$: C, 78.77; H, 5.73; Cl, 15.50. Found: C, 78.94; H, 5.69; Cl, 15.63.

Reaction of *trans*-1-Chloro-1-phenyl-2-(*p*-tolyl)-ethylene with Organic Peracids. A. Trifluoroperacetic Acid. i. Using No Added Base.—This reaction was carried out as mentioned previously by treating a solution of 6.0 g. (0.026 mole) of the α-chloroolefin in 50 ml. of CH_2Cl_2 with a solution prepared by adding 1.0 ml. (0.036 mole) of 90% H_2O_2 to 6.0 ml. (0.043 mole) of trifluoroacetic anhydride in 15 ml. of CH_2Cl_2. After hydrolysis this yielded 2.7 g. (42%) of α-hydroxy-α-(*p*-tolyl)-acetophenone, m.p. 116–117° (lit.[17] m.p. 116–118°).

ii. **Using Na_2CO_3 as Insoluble Base.**—This reaction was carried out as (i) above except in the presence of 20.0 g. (0.19 mole) of Na_2CO_3. The product was α-chloro-α-(*p*-tolyl)-acetophenone (3.4 g., 53%, m.p. 73–74°).

Anal. Calcd. for $C_{15}H_{13}OCl$: C, 73.65; H, 5.32; Cl, 14.50. Found: C, 73.30; H, 5.38; Cl, 14.63.

The mixture melting point of this compound and its isomer, 4-methyl-α-chloro-α-phenylacetophenone, was depressed to 35–45° and their infrared spectra were quite different.

B. **Perbenzoic Acid.**—The reaction was carried out in the manner described previously using these amounts of reactants: 5.0 g. (0.022 mole) of *trans*-1-chloro-1-phenyl-2-(*p*-tolyl)-ethylene and 60 ml. (0.025 mole) of a 0.43 *M* chloroform solution of perbenzoic acid. Work-up gave 3.8 g. (71%) of the desired α-chloroketone, m.p. 73–74°.

C. **Peracetic Acid.**—The reaction was carried out in the manner described previously with these amounts of reactants: 4.0 g. (0.0175 mole) of *trans*-1-chloro-1-phenyl-2-(*p*-tolyl)-ethylene in 50 ml. of CH_2Cl_2 and 8 ml. (0.052 mole) of a 6.55 *M* (40%) solution of peracetic acid containing 0.5 g. of sodium acetate trihydrate. Work-up gave 2.9 g. (67%) of the desired ketone, m.p. 73–74°.

Reaction of α-Chloro-α-(*p*-tolyl)-acetophenone with Sodium Hydroxide.—The reaction of 1 g. (0.004 mole) of the α-chloroketone in 50 ml. of alcohol with 5 ml. of a 5% solution of sodium hydroxide was carried out as given above for 4-methyl-α-chloro-α-phenylacetophenone. Recrystallization of the product from alcohol gave 0.87 g. (94%) of α-hydroxy-α-(*p*-tolyl)-acetophenone, m.p. 112–115° (lit.[17] m.p. 116–118°).

Reaction of α-Hydroxy-α-(*p*-tolyl)-acetophenone with Thionyl Chloride.—The reaction of 0.22 g. (0.001 mole) of the benzoin with 2 ml. of $SOCl_2$ was carried out as was the analogous conversion of 4-methyl-α-hydroxy-α-phenylacetophenone above. This likewise gave 0.18 g. (76%) of α-chloro-α-(*p*-tolyl)-acetophenone, m.p. 73–74°.

α-Chloro-α-(*p*-tolyl)-acetophenone (Independent Synthesis).—The preparation of this compound was carried out as previously described for 4-methyl-α-chloro-α-phenylacetophenone by treating 1.0 g. (0.0048 mole) of α-(*p*-tolyl)-acetophenone in 50 ml. of CCl_4 with a solution of 0.7 g. (0.005 mole) of SO_2Cl_2 in 10 ml. of CCl_4 for 24 hr. The desired product was obtained (0.97 g., 83%), m.p. 73–74°. Mixture melting point of this with the product from the peracid oxidation of *trans*-1-chloro-1-phenyl-2-(*p*-tolyl)-ethylene showed no depression and their infrared spectra were identical. The ultraviolet absorption spectrum of this compound had λ_{max} 247 mμ (ε 24,500) in ethanol.

1-Chlorocyclohexene Oxide.—1-Chlorocyclohexene (10.0 g.) was peroxidized with perbenzoic acid according to the published procedure.[3d] The crude product was fractionally distilled; collecting the fraction boiling at 64–65° (20 mm.) gave 5.2 g. (22%) of the α-chloroepoxide, $n^{20}D$ 1.4695 (lit.[3d] b.p. 62° (20 mm.), $n^{25}D$ 1.4699). This compound could be stored under dry nitrogen at −10° for 2 months; however, if exposed to the moist atmosphere it readily rearranged to a mixture of α-chlorocyclohexanone and adipoin.

A large amount of residue remained in the distillation pot which was found to consist mainly of α-chlorocyclohexanone and adipoin. During several attempts to prepare the α-chloroepoxide only the rearranged α-chloroketone could be isolated.

The Reaction of 1-Chlorocyclohexene with Trifluoroperacetic Acid.—To a stirring, refluxing mixture of 5.83 g. (0.05 mole) of 1-chlorocyclohexene and 30 g. (0.21 mole) of disodium hydrogen phosphate in 100 ml. of CH_2Cl_2 was added a solution of trifluoroperacetic acid made by slowly adding 2 ml. (0.07 mole) of 90% H_2O_2 to a cold solution of 10.6 ml. (0.076 mole) of trifluoroacetic anhydride in 25 ml. of CH_2Cl_2 with constant stirring. The reaction was run in the same manner as previously described. Work-up of the crude product gave a mixture whose infrared spectrum showed it to consist of 2-chlorocyclohexanone and the trifluoroacetate of adipoin. This is consistent with the results obtained from the same reaction with *trans*-α-chlorostilbene.

Reaction of Desyl Chloride with Trifluoroacetic Acid and Trifluoroacetic Anhydride.—A solution of 2.0 g. (0.0087 mole) of desyl chloride, 6 ml. of trifluoroacetic acid, and 6 ml. of trifluoroacetic anhydride in 25 ml. of CH_2Cl_2 was heated under reflux for 2 hr. Removal of the solvent and excess reagents under reduced pressure gave 2.0 g. (76%) of crude benzoin trifluoroacetate identified by its infrared spectrum. However, crystallization from alcohol yielded only benzoin (1.3 g., 72%), transesterification apparently taking place.

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