Olefins are the principal products when iron is used as a heterogeneous catalyst for the gas-phase hydrogenation of acetylenes.[8] In our study of the reduction of tolane, the alkane was the principal product even before half of the tolane had reacted. This result indicates that stilbene is reduced to the alkane more rapidly than tolane is reduced to stilbene (see Table I). Strel'tsova and Shilov found the same order of reactivity when acidic protons were available (in the form of ethanol, for example) in the homogeneous reduction of tolane by potassium metal in liquid ammonia.[3] In fact, they obtained no stilbene as product. However, in the absence of a protonic acid, Strel'tsova and Shilov found the reverse order of reactivity. When half the stoichiometric amount of sodium for reduction of tolane to 1,2-diphenylethane was used, essentially pure stilbene was isolated as the reduction product. The highly basic, heterogeneous system of this study surprisingly yields the same kinetic results as the relatively acidic homogeneous system of Strel'tsova and Shilov.

Our experimental results can be explained in terms of a mechanism involving the following initial steps. (Here M denotes an active site on the catalyst surface.)

$$2M + H_2 \rightleftharpoons 2MH$$

$$MH + NH_2^- \rightleftharpoons M^- + NH_3$$

$$M^- \rightleftharpoons M + e^-_{am}$$
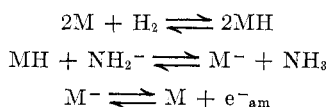
Subsequent steps are uncertain; they involve the substrate accepting either electrons (from M^- or e^-_{am}) or hydride ions (from MH^-). Although the details of the overall hydrogenation mechanism are uncertain, it seems very likely that the first two steps (the bonding of hydrogen atoms to the catalyst and the formation of a low oxidation state form of the catalyst) are involved.[9,10] The facts that these steps fit the data for *both* reaction 1 and the hydrogenations and that they are common features of hydrogenations[9] are strong support for their involvement.

When stilbene was treated at room temperature for several days with a potassium amide–ammonia solution, a product was obtained that had a melting point of 57–60° and a mass spectrum with a parent peak at m/e 195 (corresponding to the elemental composition $C_{14}H_{13}N$) and a fragmentation pattern suggesting either phenylbenzyl ketimine (1,2-diphenylethylidenimine) or 2,3-diphenylaziridine.[11] Because of the air sensitivity of the compound, only poor infrared spectra could be obtained. There definitely was no strong absorption in the 1100–1250-cm^{-1} region; therefore the compound cannot be 2,3-diphenylaziridine, which does have a very strong absorption at about 1200 cm^{-1}.[12] Phenylbenzyl ketimine (mp 57°) is known to decompose in air to produce deoxybenzoin.[13] When our product was allowed to come in contact with the atmosphere, a material was obtained which gave a mass spectrum identical with that obtained for a known sample of deoxybenzoin.

A similar analysis of the product obtained from the room temperature reaction of tolane with excess potassium amide in liquid ammonia again showed the product to be phenylbenzyl ketimine. When liquid ammonia solutions containing stilbene or tolane and potassium amide were allowed to stand for several weeks, high molecular weight species were produced in yields of a few per cent. These compounds were observed in the gas chromatogram of the product mixture, but were not identified.

The reaction of tolane with ammonia to form phenylbenzyl ketimine is a straightforward example of a well-known class of reactions: the reaction of acetylenes with amines and ammonia to form ketimines.[14] The reaction of stilbene with a potassium amide–ammonia solution to form phenylbenzyl ketimine probably involves the addition of ammonia to form 1,2-diphenyl-1-aminoethane followed by the amide-catalyzed conversion of the amine to the ketimine.[15] The high molecular weight products found when tolane and stilbene were in potassium amide–ammonia solutions for several weeks may be due to polymerization of the unstable phenylbenzyl ketimine or to the base-catalyzed polymerization of unreacted stilbene or tolane in a reaction similar to the polymerization of styrene in ammonia.[16]

(14) I. A. Chekulaeva and L. V. Kondrat'eva, *Russ. Chem. Rev.*, **34**, 669 (1965).

(15) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Amer. Chem. Soc.*, **78**, 1653 (1956).

(16) H. Smith, "Organic Reactions in Liquid Ammonia," Interscience, New York, N. Y., 1963, p 227.

(8) P. B. Wells, *Chem. Ind. (London)*, **1964**, 1742.

(9) R. K. Rideal, "Concepts in Catalysis," Academic Press, New York, N. Y., 1968, pp 27, 121, 161.

(10) J. Halpern, *Advan. Chem. Ser.*, **70**, 1 (1968); J. Halpern and J. B. Milne, "Actues du Deuxieme Congress International de Catalyse," Editions Technip, Paris, 1961, p 445.

(11) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967.

(12) M. J. Latch and D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 38 (1953).

(13) K. N. Campbell, *ibid.*, **59**, 2058 (1937).

Halogen Metathesis in Fluorocarbons

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The term metathesis is used in chemistry to describe reactions in which groups are transferred or exchanged. In organic chemistry the term has been used for the "scrambling" of olefins[1,2] and acetylenes[3] or the radical abstraction of an atom to produce another radical. The term can be extended to other reactions

$$R' \cdot + RX \longrightarrow R'X + R \cdot$$
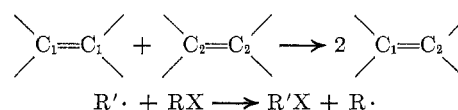
where there is a transfer of groups. For example, the transfer of chlorine in fluorocarbons fits within this defi-

(1) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

(2) Goodyear Tire and Rubber Co., British Patent 1,125,529 (Aug 28, 1968); *Chem. Abstr.*, **69**, 105851f (1968).

(3) F. Pennella, R. L. Banks, and G. C. Bailey, *Chem. Commun.*, 1548 (1968).

nition. We now describe this reaction and refer to it as *halogen metathesis*.
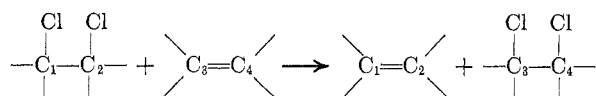
The reaction of chlorotrifluoroethylene with 1,1,2,2-tetrachloro-1,2-difluoroethane exemplifies this reaction.

$$CClF{=}CF_2 + CCl_2FCCl_2F \longrightarrow CCl_2FCClF_2 + CClF{:}CClF$$
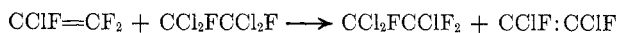
At 300° and a contact time of 60 sec over a carbon catalyst essentially all of the chlorotrifluoroethylene is reacted. The amount remaining was too small to measure by mass spectral analysis. The yield of 1,2-dichloro-1,2-difluoroethylene was 94.4%.

An estimation of the thermodynamic functions relating to this reaction indicates that (a) little or no change of entropy or heat capacity is involved and (b) the enthalpy of reaction is probably close to 8 kcal/mol (see later discussion and Table I). This would indicate an equilibrium constant, based on $\log_{10}K_{eq} = -\Delta F/RT$, of 2.8×10^6. It would be expected that the reaction would go essentially to completion.

A second example of this reaction is the preparation of hexafluorocyclobutene from the reaction of 1,2-dichlorohexafluorocyclobutane with chlorotrifluoroethylene. For this reaction the thermodynamic functions again predict an equilibrium constant which is near completion for the reaction. Under the conditions
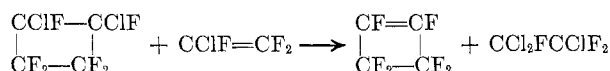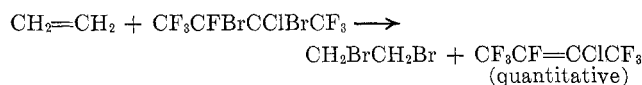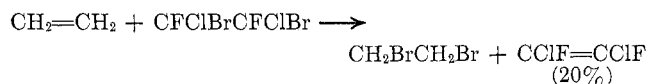

studied, however, this equilibrium has not been approached. The highest yield, based on the 1,2-dichlorohexafluorocyclobutane fed, was 18% (13% of the product).

This reaction is quite similar to the bromine transfer described by Tarrant and Tandon,[4] which was observed when free radical addition reactions were being studied.

$$CH_2{=}CH_2 + CFClBrCFClBr \longrightarrow$$
$$CH_2BrCH_2Br + CClF{=}CClF$$
$$(20\%)$$

$$CH_2{=}CH_2 + CF_3CFBrCClBrCF_3 \longrightarrow$$
$$CH_2BrCH_2Br + CF_3CF{=}CClCF_3$$
$$(quantitative)$$

Catalysis.—Chlorine metathesis is promoted by alumina and carbon with high surface areas and many small pores.

The preferred catalytic material appears to be activated carbon which has been treated with a chlorofluoroalkane at about 300° until the formation of acid has nearly ceased. This material was used for the reaction between 1,1,2,2-tetrachloro-1,2-difluoroethane and chlorotrifluoroethylene at 300°. The chlorine metathesis occurred readily and there was a minimum of by-product formation.

(4) P. Tarrant, *et al.*, "Research on Synthesis of Unsaturated Fluorocarbon Compounds," AD 662712, March 1967; *Chem. Abstr.*, **68**, 93047n (1967); *cf.* J. P. Tandon, Dissertation, University of Florida, Aug 1966.

The only other material which we examined with significant catalytic activity for chlorine metathesis was activated alumina,[5] but it required a temperature of 500° instead of the 300° used for activated carbon. Sodium fluoride on the alumina improves its activity. These results indicate that the decrease in acidic sites on alumina decreases side reactions with an apparent increase in chlorine metathesis.

It is possible that these materials provide a physical environment for this specific reaction, rather than actually participating in the reaction. Similar results by Tarrant and Tandon[5] in which bromine compounds undergo metathesis under radical conditions suggest that a radical mechanism may be functioning.

Additional work is needed to confirm these tentative conclusions.

Thermodynamics.—An indication of the thermodynamic differences is available from the heats of chlorination of various olefins which might be involved either as reactants or products.[6] The values for the heats of chlorination of several olefins are given in Table I. Those olefins with a large heat of chlorination

TABLE I

HEATS OF CHLORINATION OF HALOGENATED OLEFINS

Olefin	Heat of reaction	Ref
$CF_2{=}CF_2$	-57.32	a
$CClF{=}CF_2$	-48.83	a
$CF_3CF{=}CF_2$	-47.15	a
$C_2F_5CF{=}CF_2$	-44.95	b
$C_3F_7CF{=}CF_2$	-45.64	b
$(CF_3)_2C{=}CF_2$	-42.22	b
$CCl_2{=}CF_2$	-41.08	a
$CF{=}CFCF_2CF_2$	-37.38	c
$CH_2{=}CH_2$	-41.5	d
$CH{\equiv}CH$ (1 Cl$_2$)	-53.9	e

a J. R. Lacher, J. J. McKinley, C. M. Snow, L. Michel, G. Nelson, and J. D. Park, *J. Amer. Chem. Soc.*, **71**, 1330 (1949). *b* J. R. Lacher, A. Kianpour, and J. D. Park, *J. Phys. Chem.*, **61**, 584 (1957). *c* Reference 10. *d* C. R. Patrick, *Tetrahedron*, **4**, 26 (1958). *e* S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

should be good "chlorine sinks" and saturated dichloro compounds corresponding to olefins with smaller heats of chlorination should act as chlorine sources. Tetrafluoroethylene would serve as the best "chlorine sink," but chlorotrifluoroethylene should be useful for preparing any of the other olefins except tetrafluoroethylene and perhaps hexafluoropropylene.

(5) Alcoa F-1 alumina was used.

(6) There is a lack of some of the thermodynamic functions of the compounds involved in these reactions, and a range of values for others. For example, no thermodynamic values are available for 1,1,2,2-tetrachloro-1,2-difluoroethane and there is no data for the heat capacity of 1,2-dichloro-1,2-difluoroethylene above 300°K. On the other hand, care must be taken with reported values. The reported values for the heat of formation of chlorotrifluoroethylene range from -114[7] to -130.2[8] kcal/mol. Rodgers[9] in 1967 chose a "best value" of -117.5 ± 2 kcal/mol, which fits with a "best value" for the heat of formation of 1,1,2-trichloro-1,2,2-trifluoroethane, -166.1 kcal/mol, and the reported heat of chlorination.[10]

(7) P. G. Maslov and Yu. P. Maslov, *Khim. Tekhnol. Topl. Masel*, **3**, 50 (1958); *Chem. Abstr.*, **53**, 1910h (1959).

(8) V. P. Kolesov, I. D. Zenkov, and S. M. Skuratov, *Zh. Fiz. Khim.*, **37**, 224 (1963).

(9) A. S. Rodgers, *J. Phys. Chem.*, **71**, 1996 (1967).

(10) J. R. Lacher, J. J. McKinley, C. Walden, K. Lea, and J. D. Park, *J. Amer. Chem. Soc.*, **71**, 1334 (1949).

TABLE II
CHLORINE METATHESIS OF CHLOROTRIFLUOROETHYLENE WITH 1,2-DICHLOROHEXAFLUOROCYCLOBUTANE

Expt no.	Catalyst	Vol,[a] cc	Mole ratio, C_2ClF_3/ $C_4Cl_2F_6$	Temp, °C	Contact time, sec	Material balance, wt %	CClF=CF₂	CClF—CClF / CF₂——CF₂	CF=CF / CF₂—CF₂	CCl₂FCClF₂	CClF₂CF= CFCF₃[b]	CCl=CCl[b] / CF₂—CF₂
1	NaF on F-1 alumina	15	1.4	500	8.2	81.9	35.3	52.0	3.0	9.3		
2	Same	15	1.2	500	9.1	95.3	37.8	53.5	2.0	6.2		
3	Carbon	300	0.80	300	66.7	78.8	2.0	42.5	10.0	22.2	5.1	18.2

[a] The reaction was carried out in a Pyrex tube or a stainless steel 1-in. tube.   [b] The structure of these two compounds was assigned on the basis of their mass spectra.

The heats of chlorination are smaller for compounds with more chloro or perfluoroalkyl groups. One possibility of a less expensive "chlorine sink" than tetrafluoroethylene is acetylene.

By-Products.—The formation of by-products appears to be thermally induced. Although the amounts are small below 450°, there is a marked increase with temperature.

Previous studies of the thermal reactions of chlorotrifluoroethylene at 300–500° by Atkinson and Stedman[11] had shown that the first-formed 1,2-dichlorohexafluorocyclobutane appeared to open to form 1,4-dichlorohexafluorobutene-2. Miller[12] indicated that pyrolysis of chlorotrifluoroethylene at 560° seemed to give the products shown below. At 650° hexafluorocyclobutane was also observed.

$$CClF=CF_2 \xrightarrow{560°} \underset{\substack{| \quad | \\ CF_2\text{——}CF_2 \\ 34\%}}{CClF\text{—}CClF} + \underset{30\%}{CF_2\text{=}CFCClFCClF_2} +$$

$$\underset{10\%}{CF_2\text{=}CFCClF_2} + \underset{10\%}{CF_2\text{=}CFCCl_2F}$$

By-products which have been identified in the experiment utilizing chlorotrifluoroethylene and 1,2-dichlorohexafluorocyclobutane were 1-chloroheptafluoro-2-butene, 3,4-dichlorohexafluoro-1-butene, and 1,2-dichlorotetrafluorocyclobutene. Those identified from the reaction of chlorotrifluoroethylene with 1,1,2,2-tetrachloro-1,2-difluoroethane were 2-chloroheptafluoro-2-butene, 2,3-dichlorohexafluoro-2-butene, and 1,2-dichlorohexafluorocyclobutane.

Experimental Section

Reaction of Chlorotrifluoroethylene with 1,2-Dichlorohexafluorocyclobutane.—Three experiments were carried out to demonstrate the direct reaction of these two materials by chlorine metathesis. In the first two the catalyst was 15 cc of NaF-coated Alcoa F-1 Alumina in a 16-mm Pyrex tube. The third used Columbia CXA 6-8 mesh carbon in a 1-in. stainless steel tube. The conditions used and the results observed are presented in Table II.

Reaction of Chlorotrifluoroethylene with 1,1,2,2-Tetrachloro-1,2-difluoroethane.—The 1-in. stainless steel tube mentioned above was charged with Columbia CXA 6-8 mesh activated carbon. This had been used in the third experiment mentioned above, discharged, and allowed to stand for 3 weeks. The catalyst was recharged and heated to 300° in a nitrogen purge. 1,1,2,2-Tetrachloro-1,2-difluoroethane was fed over the catalyst for 5.5 hr to condition it. At first there was much acid in the condensate, but this decreased rapidly after 2 hr. A mixture of 47 g of chlorotrifluoroethylene and 77.5 g of 1,1,2,2-tetrachloro-1,2-difluoroethane was passed over the catalyst over a 2-hr period. The contact time was 60 sec at a temperature of 300°. Products were collected in Dry Ice cooled traps and analyzed by gas chromatography and mass spectroscopy.

(11) B. Atkinson and M. Stedman, *J. Chem. Soc.*, 512 (1962).
(12) W. T. Miller, U. S. Patent 2,733,277 (Jan 31, 1956).

The products included 47.7 g (94.4%) of 1,2-dichloro-1,2-difluoroethylene, 37.4 g of 1,1,2-trichloro-1,2,2-trifluoroethane, 4.5 g of recovered 1,1,2,2-tetrachloro-1,2-difluoroethane, a trace of chlorotrifluoroethylene, and 5.3 g of 1,2-dichlorohexafluorocyclobutane.

Registry No.—Chlorotrifluoroethylene, 79-38-9; 1,2-dichlorohexafluorocyclobutane, 356-18-3; 1,1,2,2-tetrachloro-1,2-difluoroethane, 76-12-0.

Facile Synthesis of Tricyclo[5.3.1.0³,⁸]undecane and Spiro[5.5]undecane Systems from a Common Intermediate

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Barton and his coworkers[1] and Johnson's group[2] reported that the cyclization of the unsaturated diketone of type I led stereoselectively to the *cis*-hydrindanone II.

In an attempt to investigate the stereochemical outcome of cyclization of the compound carrying the side chain with one more methylene unit in I, we have examined cyclization of 3-methyl-4-(4'-formylbutyl)-2-cyclohexenone (6) under a variety of conditions. The cyclohexenone aldehyde 6 employed in this study was prepared as follows. The Wolff–Kishner reduction of γ-(2-methyl-4-methoxybenzoyl)butyric acid[3] afforded δ-(2-methyl-4-methoxyphenyl)valeric acid (1). Lithium aluminum hydride reduction of the methyl ester of the acid 1 gave an alcohol 2, which, on Pfitzner–Moffatt oxidation yielded an aldehyde 3. The corresponding acetal 4 was submitted to the Birch reduction and the resulting enol ether was hydrolyzed with

(1) D. H. R. Barton, A. S. Campos-Neves, and A. I. Scott, *J. Chem. Soc.*, 2698 (1957).
(2) W. S. Johnson, S. Shulman, K. L. Williamson, and R. Pappo, *J. Org. Chem.*, **27**, 2015 (1962).
(3) D. Chakravarti and N. K. Roy, *J. Indian Chem. Soc.*, **42**, 607 (1965).