

organic layer was separated, washed with water and sodium bicarbonate solution and dried. *p*-Chloro- ω -fluoroacetophenone distilled at 115–119° (8 mm.) and crystallized immediately as plates, m.p. 54–55° (from aqueous ethanol), yield 72 g. (52%). This ketone also has been described by Bergmann, Kalmus and Breuer,¹¹ who also have carried out the reduction with lithium aluminum hydride, described below; ultraviolet spectrum: 255 m μ (log ϵ 4.25); infrared spectrum (KBr pellet): $\nu_{C=O}$ 1700 cm.⁻¹.

Anal. Calcd. for C₈H₆ClFO: C, 55.8; H, 3.5. Found: C, 55.7; H, 4.5.

1-(*p*-Chlorophenyl)-2-fluoroethanol.—To an ice-cold solution of lithium aluminum hydride (1.5 g.) in anhydrous ether (80 ml.), a solution of *p*-chloro- ω -fluoroacetophenone (12 g.) in ether (50 ml.) was added during 90 minutes. After 10 minutes, the mixture was decomposed with a solution of sulfuric acid (1 ml.) in 30 ml. of ice-water, and the ethereal layer separated, washed and dried. 1-(*p*-Chlorophenyl)-2-fluoroethanol distilled at 124–134° (8 mm.) as a colorless oil; yield 11 g. (90%), n_D^{20} 1.5398; infrared spectrum: 3400, 1500, 1100, 1010, 900, 830 and 750 cm.⁻¹.

Anal. Calcd. for C₈H₈OCIF: C, 55.2; H, 4.6. Found: C, 55.5; H, 4.7.

1,1-Di-(*p*-chlorophenyl)-2-fluoroethane (XIII).—To an ice-cold mixture of 1-(*p*-chlorophenyl)-2-fluoroethanol (2 g.) and chlorobenzene (5 g.), a mixture of concentrated sulfuric acid (20 ml.) and fuming sulfuric acid (4 ml.) was added dropwise. The reaction mixture was shaken mechanically for 2 hr., then poured onto ice and extracted with ether. The ethereal solution was washed, dried, evaporated and the product distilled *in vacuo*. It boiled at 155–165° (2 mm.) and solidified spontaneously; from methanol, m.p. 54–55°, yield 1 g. (32%).

Anal. Calcd. for C₁₄H₁₁Cl₂F: Cl, 26.3. Found: Cl, 26.0.

Reaction with Alkali.—The compound XIII (0.3 g.) was refluxed with 1 *N* methanolic potassium hydroxide solution (5 ml.) for 1 hr., hydrochloric acid (2 ml.) and water (30 ml.) added and the product extracted with ether. The ether residue was recrystallized from methanol (0.2 g.) and melted at 84–85°. It was identified as 1,1-di-(*p*-chlorophenyl)-ethylene by comparison with an authentic sample; infrared spectrum: 3400, 1600, 1500, 1420, 1190, 1120, 1085, 1018, 970, 855, 825, 790, 725 cm.⁻¹.

Difluorochloromethyl-*p*-chlorophenylcarbinol.—A solution of the ketone VI (11.3 g.) in ether (30 ml.) was added, dropwise, to a well-stirred ice-cold suspension of lithium aluminum hydride (1.5 g.) in ether (50 ml.). An ice-cold mixture of sulfuric acid (10 ml.) and water (50 ml.) was added cautiously, the ethereal layer separated, washed with water and concentrated and the residue distilled *in vacuo*; b.p. 115–120° (10 mm.), colorless liquid, n_D^{20} 1.5144, yield 9 g. (80%).

Anal. Calcd. for C₈H₆Cl₂F₂O: C, 42.3; H, 2.7. Found: C, 42.4; H, 2.8.

Dichlorofluoromethyl-*p*-chlorophenylcarbinol.—The ketone VII (4 g.) in ether (15 ml.) was reduced with lithium aluminum hydride (0.5 g.) in ether (20 ml.). The product distilled at 120–125° (2 mm.) as a colorless liquid, n_D^{20} 1.543, yield 3.5 g. (87%); infrared spectrum: 3500, 1600, 1400, 1200, 1085, 1010, 950, 870–880, 820, 795, 771, 715 cm.⁻¹.

Anal. Calcd. for C₈H₆Cl₂FO: Cl, 43.7. Found: Cl, 43.4.

1,1-Di-(*p*-chlorophenyl)-2,2-difluoro-2-chloroethane (XI).—To a well-stirred mixture of chlorobenzene (4.5 g.), concentrated sulfuric acid (10 ml.) and 20% fuming sulfuric acid (3 ml.), was added, slowly and with cooling, *p*-chlorophenyldifluorochloromethylcarbinol (5 g.). The mixture was then shaken for 5 hr., added to crushed ice and extracted with ether. After removal of the ether and excess chlorobenzene by distillation, the ethane XI distilled at 160–165° (2 mm.), yield 6 g. (85%). The product solidified; after recrystallization from methanol, it melted at 54–55°; ultraviolet spectrum: 228 m μ (4.20); 260 m μ (2.60); 267 m μ (2.62); infrared spectrum (KBr pellet): 1500, 1400, 1210, 1170, 1090, 1015, 962, 765 cm.⁻¹.

Anal. Calcd. for C₁₄H₉Cl₃F₂: C, 52.3; H, 2.8. Found: C, 52.1; H, 2.9.

Reaction with Alkali.—The compound XI (1 g.) was refluxed for 1 hr. with 1 *N* methanolic potassium hydroxide (20 ml.). Water was added and the mixture extracted with ether. After removal of the solvent, 1,1-di-(*p*-chlorophenyl)-2,2-difluoroethylene (XIV) distilled at 165–169° (2 mm.), yield 0.7 g. (79%), n_D^{20} 1.5732. The substance was so unstable that only approximate analyses could be obtained. However, the spectrum indicated (see above) that the compound had structure XIV; ultraviolet spectrum (isooctane): 228 m μ (4.46); 255 m μ (4.06).

1,1-Di-(*p*-chlorophenyl)-2,2-dichloro-2-fluoroethane (XII).—Condensation of *p*-chlorophenyldichlorofluoromethylcarbinol (2.5 g.) and chlorobenzene (2 g.) in the presence of concentrated sulfuric acid (5 ml.) and 20% fuming sulfuric acid (1.5 ml.) gave XII (2 g., 57%); b.p. 180–185° (2 mm.), m.p. after recrystallization from methanol 78–79°; ultraviolet spectrum (log ϵ): 232 m μ (4.26), 260 m μ (2.74), 267 m μ (2.76); infrared spectrum (KBr pellet): 1500, 1400, 1120, 1090, 1015, 940, 810, 780 cm.⁻¹.

Anal. Calcd. for C₁₄H₉Cl₃F: C, 49.8; H, 2.7. Found: C, 50.4; H, 2.8.

Reaction with Alkali.—Upon alkaline hydrolysis of the ethane XII (0.75 g.) as described above, 1,1-di-(*p*-chlorophenyl)-2-chloro-2-fluoroethylene (XV) (0.55 g., 85%) was very probably obtained. It distilled at 165–166° (3 mm.) as a colorless but unstable oil, of n_D^{20} 1.6059.

TEL-AVIV, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF THE HEBREW UNIVERSITY-HADASSAH MEDICAL SCHOOL]

ω -Fluoroacetophenone. III. Reaction of Fluoroacetyl Chloride with Halobenzenes. On the Mechanism of Side-chain Chlorination by Sulfuryl Chloride

BY FELIX BERGMANN, ABRAHAM KALMUS AND ELI BREUER¹

RECEIVED FEBRUARY 8, 1957

The synthesis of ω -fluoroacetophenone has been extended to halobenzenes. The mechanism of side-chain chlorination of these ketones by sulfuryl chloride has been studied and a reaction scheme proposed.

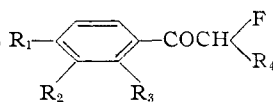
The synthesis of ω -fluoroacetophenone (I), which was described previously,² was based on the observation that prolonged contact of I with aluminum chloride is responsible for halogen exchange, pro-

ducing ω -chloroacetophenone (II). Short reaction periods are required to secure sizable yields of I. It remained undecided, however, whether the same type of exchange proceeds with fluoroacetyl chloride, prior to condensation. This possibility was tested by treating the latter with the Friedel-Crafts catalyst in methylene chloride at room tem-

(1) Part of a M.Sc. thesis, submitted to the Faculty of Science, The Hebrew University, Jerusalem, 1957.

(2) F. Bergmann and A. Kalmus, *THIS JOURNAL*, **76**, 4137 (1954).

TABLE I

PROPERTIES AND ANALYSES OF KETONES 

R ₁	R ₂	R ₃	R ₄	M. p. or b. p. (mm.), °C.	Recrystallized from	Analyses, %			
						Carbon, Calcd.	Carbon, Found	Hydrogen, Calcd.	Hydrogen, Found
Cl	H	H	H	53-54	Petr. eth.	55.8	55.6	3.5	3.6
F	H	H	H	50-51	Petr. eth.	61.5	61.4	3.8	3.9
F	H	F	H	62-63	Ligroin	55.2	55.6	2.9	3.1
H	NO ₂	H	H	95-96	Ethanol	52.5	52.7	3.3 ^a	3.3
F	H	H	Cl	33, 84-88 (10)	50.5	50.6	2.6	2.9
F	H	H	Br	120-130 (14)	40.9	42.5	2.1	2.8
F	H	H	I	42-45	Unstable			

^a Calcd.: N, 7.7. Found: N, 7.8.

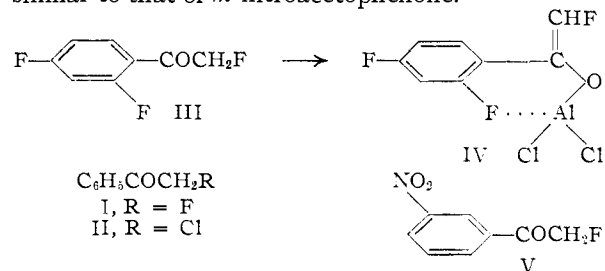
perature for six hours, then cooling the solution to 0°, adding benzene and carrying out the reaction exactly as described previously. The product (50% yield), consisted of about equal parts of I and its chloro analog II. The pretreatment thus decreased the yield of I considerably. However, halogen exchange with fluoroacetyl chloride proceeds at a much lower rate than with the ketone I. The latter, when incubated under similar conditions, is converted almost quantitatively into chloroacetophenone.

When substituted benzenes were submitted to the same reaction, only the halogeno derivatives gave positive results, albeit yields were much inferior to benzene itself (see Table I). Chlorobenzene produced, in addition to 24% of the ω -fluoro ketone, also about 3% of p,ω -dichloroacetophenone.³ With fluorobenzene, the yield of ketones was nil when standard conditions were applied. A highly viscous oil was isolated instead, indicating the occurrence of secondary condensation reactions. However, when the reaction was carried out at 0° and interrupted after 10 minutes, a 55% yield of p,ω -difluoroacetophenone was obtained. The structure of this compound was established in the way described below. Bromobenzene did not react with fluoroacetyl chloride at 0°. At room temperature, some debromination took place also, in addition to condensation, and no defined product was isolated from the mixture. Anisole gave, even after very short reaction times, a resinous product, which decomposed at about 180° when vacuum distillation was attempted.

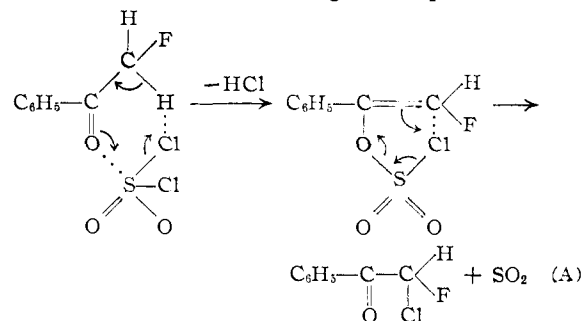
In contrast to fluorobenzene, m -difluorobenzene had to be exposed to much more drastic conditions in order to promote condensation with fluoroacetyl chloride (30 minutes at 0° and 30 minutes at room temperature). The reaction product is assumed to be III. Although in this case the yield was only 10%, no trace of the ω -chloro derivative accompanied III. The ketone III proved to be rather stable toward halogen exchange, presumably because of competition of the o -fluorine with the ω -halogen in complexing the metal atom (as *e.g.* in IV). On this basis it was expected that during a Grignard reaction the intermediate would similarly be protected against rearrangement to a desoxybenzoin² by complexing of the metal atom with o -fluorine. Therefore, a mixture of phenylmag-

nesium bromide and 2,4, ω -trifluoroacetophenone (III) in ether was refluxed for four hours. The product, however, was identified as a desoxybenzoin and no trace of its precursor, the tertiary carbinol, was detected.

Nitration of I in acetic acid gave the m -nitro derivative V, the point of substitution being proved by oxidation to m -nitrobenzoic acid. Likewise, the ultraviolet absorption spectrum of V is quite similar to that of m -nitroacetophenone.



The p -fluoro- and p -chloro derivatives of I can be halogenated by the methods available for ω -fluoroacetophenone itself.⁴ The chlorination with sulfuryl chloride was studied in more detail. Acetophenone reacts instantaneously at room temperature, and chlorination is completed within 2 hours, giving a practically quantitative yield of II. With ω -fluoroacetophenone—as described previously—reaction starts at room temperature with a marked delay (about 0.5 hour) and requires 16 hours for its completion. With p,ω -difluoroacetophenone and p -chloro- ω -fluoroacetophenone substitution can be effected only with refluxing sulfuryl chloride. The ketones III and V were not attacked even under these conditions. No trial was made at still higher temperatures.



(3) D. Woodcock, *J. Chem. Soc.*, 203 (1949); Gautier, *Ann. chim.*, 14, 395 (1888).

(4) F. Bergmann, A. Kalmus and S. Vromen, *THIS JOURNAL*, 77, 2494 (1955).

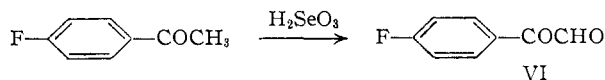
TABLE II

2,4-DINITROPHENYLHYDRAZONES OF THE KETONES OF TABLE I, R_1 $-C(=O)-R_2$

R ₁	R ₂	M.p., °C.	Recrystd. from	Analyses, %							
				Carbon, %		Hydrogen, %		Nitrogen, %		Fluorine, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Cl	H	218-219	Butyl acetate	47.7	47.7	2.8	3.1	5.4	5.3
F	H	210-211	Acetic anhyd.	50.0	50.0	3.0	3.2	16.7	16.9
F	F	182-183	<i>n</i> -Butyl alc.	47.3	47.8	2.5	2.7	15.8	15.3

The outstanding capacity of sulfuryl chloride to chlorinate methyl as well as fluoromethyl, in α -position to the carbonyl, may be interpreted by way of a cyclic mechanism, indicated in scheme A. Here, the reagent is assumed first to polarize the carbonyl group strongly, forming an enol ester and eliminating HCl. In the second phase of the reaction, the electronic cycle swings back and introduces positive chlorine into the α -position.⁵

In order to test this hypothesis, other acid chlorides, capable of forming similar enol esters and carrying out the corresponding electronic cycles, were tried. Oxalyl chloride was found unreactive. Phosphorus pentachloride attacked the carbonyl group, but the expected ω -chloro- ω -fluoro ketone was not formed. The structure of the reaction products was not elucidated, but differs from the known possible products (*i.e.*, the dichloride or the corresponding chloroethylene). Sulfuryl chloride thus occupies a unique position in that it can split off the stable molecule SO₂, after having released first a negative then a positive chlorine.



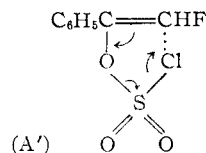
In an attempt to establish the point of substitution in the ketone, obtained by fluoroacetylation of fluorobenzene, the usual methods of oxidation of the side chain did not give the expected aromatic acids, suitable for identification. Therefore, the following method was adopted: *p*-Fluoroacetophenone^{6a, b} was converted by selenious acid into the glyoxal VI. The bis-dinitrophenylhydrazone of VI decomposes at about 296°. In order to identify unequivocally this compound with the corresponding derivative, obtained from *p*, ω -fluoro- ω -chloroacetophenone (Table II), the X-ray powder diagrams were compared. They were found to be identical, as did also the infrared spectra of the hydrazones from the two sources.

Experimental

All melting points are uncorrected.

p-Chloro- ω -fluoroacetophenone.—Condensation of chlorobenzene (35 g.) with fluoroacetyl chloride (29 g.) was carried out in ethylene chloride (100 ml.), with aluminum chloride (65 g.) as catalyst, exactly under the conditions described previously.² The product was fractionated *in vacuo*: (a) b.p. 73-75° (0.4 mm.), yellow oil, which crystallizes

(5) It should be noted that this is not the only possible way of representation. An alternate possibility is shown in scheme A' as nucleophilic substitution at the methylene carbon.



(6) (a) R. E. Lutz and co-workers, *J. Org. Chem.*, **12**, 617 (1947); (b) Ng. Ph. Buu-Hoi, Ng. Hoán and Pierre Jacquignon, *Rec. trav. chim.*, **68**, 781 (1949).

spontaneously. From petroleum ether needles of m.p. 53-54°; 13 g. (24%) yield of *p*-chloro- ω -fluoroacetophenone; (b) b.p. 90° (0.4 mm.), yield, 2 g. (3%) of *p*, ω -dichloroacetophenone; from ethanol needles of m.p. 100-101°³; oxime m.p. 101°.⁷

p-Chloro- ω -fluoroacetophenone (1 g.) was dissolved in sulfuryl chloride (5 ml.). No evolution of gas occurred at room temperature (26°) during 12 hours, and the starting material could be recovered. Upon refluxing the solution, hydrogen chloride and sulfur dioxide escaped slowly. After 5 hours' heating, the reaction mixture was decomposed with ice and extracted with ether. The ether residue was strongly lachrymatory and tended to decompose during vacuum distillation. It was, therefore, converted directly into a bis-2,4-dinitrophenylhydrazone, which decomposed at about 280° but was so difficultly soluble that no suitable medium for recrystallization could be found.

p, ω -Difluoroacetophenone.—Aluminum chloride (80 g.) was stirred with ethylene dichloride (300 ml.) for 20 minutes and the solution decanted and cooled to 0°. Fluoroacetyl chloride (18 g.) in ethylene dichloride (60 ml.) was added and immediately thereafter fluorobenzene (25 g.) in the same solvent (60 ml.) during 10 minutes. Stirring at 0° was continued for another 10 minutes, and the mixture poured at once into concentrated hydrochloric acid and ice. The ketone was isolated in the usual way and purified by distillation, b.p. 85-90° (4 mm.). The substance crystallized immediately, and after recrystallization from petroleum ether formed sharp-edged plates of m.p. 50-51°. Its 2,4-dinitrophenylhydrazone crystallized from acetic anhydride in deep-red columns.

p, ω -Difluoroacetophenone (15 g.) was dissolved in sulfuryl chloride (35 ml.). No reaction occurred at room temperature, but evolution of hydrogen chloride was observed when refluxing the solution. After 5 hours, the mixture was decomposed with ice and extracted with ether. The ether residue distilled smoothly *in vacuo*, b.p. 84-88° (10 mm.). The yellow oil solidified when kept in a refrigerator. The lachrymatory product, *p*, ω -difluoro- ω -chloroacetophenone, melted at 33°, yield, 12.5 g. (68%). The ketone formed a bis-2,4-dinitrophenylhydrazone which crystallized from pyridine-*n*-butyl acetate in red needles of m.p. 295-296°. *Anal.* Calcd. for C₂₀H₁₃O₃N₂F: C, 46.8; H, 2.5. Found: C, 46.7; H, 2.4.

Bromination was effected at room temperature by the method described for ω -fluoroacetophenone.² *p*, ω -Difluoro- ω -bromoacetophenone was purified by distillation *in vacuo*, b.p. 120-130° (14 mm.), but did not crystallize; yield 65%. The substance is a strongly irritating tear gas. When the ω -bromo ketone was dissolved in ethanol containing an equivalent of sodium iodide, reaction proceeded at room temperature within half an hour. *p*, ω -Difluoro- ω -iodoacetophenone could not be purified, since it is unstable even at room temperature and easily soluble even in petroleum ether. It is a very powerful lachrymator.

2,4- ω -Trifluoroacetophenone (III).—*m*-Difluorobenzene⁸ was added to a mixture of fluoroacetyl chloride and aluminum chloride in methylene chloride at 0°. The mixture was stirred for 30 minutes at 0° and an additional half-hour at room temperature. The product was isolated as usual and crystallized immediately after evaporation of the solvent. From ligroin, plates of m.p. 62-63° were obtained. The 2,4-dinitrophenylhydrazone crystallized from *n*-butyl alcohol in rods of m.p. 182-183°.

m-Nitro- ω -fluoroacetophenone (V).— ω -Fluoroacetophenone (10 g.) in concentrated sulfuric acid (22 ml.) was cooled

(7) A. Collet, *Bull. soc. chim.*, [3] **27**, 539 (1902).

(8) The authors wish to thank Dr. G. C. Finger of the State Geological Survey Division, Urbana, Illinois, for the generous supply of this product.

o -15° . A mixture of nitric acid (d. 1.42) (10 ml.) and sulfuric acid (10 ml.) was added dropwise, the temperature being kept below -5° . Stirring was continued for 30 minutes and the mixture poured on ice. The solid material was filtered, washed with water and twice with ethanol and recrystallized from methanol or ethanol; yellow rods of m.p. $95-96^{\circ}$, yield 8.8 g. (66%).

***p*-Fluorophenyglyoxal (VI).**—To a solution of selenious acid (43 g.) in dioxane (200 ml.), warmed to 60° , *p*-fluoroacetophenone^{6a,b} (46 g.) was added slowly. After 5 minutes, a red precipitate formed. The solution was refluxed for 4 hours and left overnight. It was then decanted from the red precipitate and fractionated. At $105-115^{\circ}$ (30–35 mm.) a thick, yellow oil went over which showed no tendency to crystallize; yield 35 g. (78%). The oil was dissolved in benzene and a few drops of water added. This resulted in the formation of a white powder. Recrystallization from water gave the hydrate of VI as glistening, white leaflets, m.p. 80° .

Anal. Calcd. for $C_8H_6O_2F \cdot H_2O$: C, 56.5; H, 4.1. Found: C, 56.9; H, 4.3.

The bis-2,4-dinitrophenylhydrazone crystallized from pyridine-*n*-butyl acetate, decomposition point 296° .

Grignard Reaction with 2,4, ω -Trifluoroacetophenone (III).—To a Grignard solution, prepared from bromobenzene (4.7 g.) and magnesium (0.7 g.) in ether, was added slowly an ethereal solution of 2,4, ω -trifluoroacetophenone (4.5 g.) during 15 minutes. The mixture was refluxed for 2 hours and then left overnight. It was decomposed with ammonium chloride and worked up in the usual way. Fractional distillation gave 5.2 g. of a yellow oil of b.p. $135-138^{\circ}$ (4 mm.).

Anal. Calcd. for $C_{14}H_{10}OF_2$: C, 72.4; H, 4.3. Found: C, 72.0; H, 4.7.

The 2,4-dinitrophenylhydrazone crystallized from isopropyl alcohol in pointed plates of m.p. $165-167^{\circ}$.

Anal. Calcd. for $C_{20}H_{14}O_4N_4F_2$: N, 13.6. Found: N, 13.4.

The authors wish to thank Prof. E. Alexander, Department of Physics, for the X-ray spectra and Mrs. Hanna Feilchenfeld, Department of Organic Chemistry, for the infrared measurements used for identification of *p*, ω -difluoroacetophenone.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

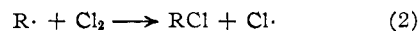
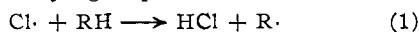
The Relative Reactivities of Substituted Toluenes toward Chlorine Atoms¹

BY CHEVES WALLING AND BERNARD MILLER²

RECEIVED JANUARY 23, 1957

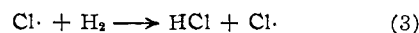
Competitive halogenations of a series of substituted toluenes have been carried out and relative reactivities determined by the precise deuterium tracer technique of Russell and Brown.⁷ For photochlorination the results yield a ρ value for attack of chlorine atoms of -0.76 , appreciably smaller than the value of -1.5 reported by Kooyman.¹⁶ Identical relative reactivities and k_H/k_D ratios are observed in photochlorination and in reaction with SO_2Cl_2 , giving no evidence for different chain carriers in this system. However, some variation in relative reactivity is observed for reactions run in primarily aromatic media and in carbon tetrachloride. Data on photobromination are also presented, together with a discussion of the importance of polar effects in free radical halogenation.

The reaction of chlorine with aliphatic hydrocarbons and the side-chains of alkyl-aromatics is well established³ as a radical chain process involving the chain carrying steps.



With hydrocarbons containing more than one type of C–H bond (or in mixtures of hydrocarbons) the products formed evidently will depend upon the relative rates of reactions of type (1) of chlorine atoms with the different sorts of C–H bond available. The work of Hass, McBee and Weber⁴ has shown clearly that, with aliphatic hydrocarbons, the case of hydrogen displacement lies in the order primary < secondary < tertiary, the selectivity being somewhat greater in the vapor than in the liquid phase and decreasing with increasing temperature. Recently Pritchard, Pyke and Trotman-Dickenson⁵ have studied the competitive chlorina-

tion of a number of simple hydrocarbons with results leading to similar conclusions, and have actually determined rate constants for hydrogen abstraction by carrying out competitions with the process



for which the rate constant is known over a wide temperature range.⁶ Since C–H bond dissociation energies lie in the order primary > secondary > tertiary, decreasing approximately 4 kcal. with each substitution, this weakening, presumably due to resonance stabilization of the resulting radicals, has commonly been given as the explanation of the observed order of chlorine atom substitution.

Unfortunately for this simple picture, more complex molecules do not yield results which indicate a simple parallel between C–H bond strength and ease of attack by chlorine atoms. Competitive chlorination of toluene and *t*-butylbenzene shows⁷ that the C–H bonds of the former are only slightly more reactive in spite of the great resonance stabilization (~ 25 kcal.) of the benzyl radical. More strikingly, the C–H bonds of cyclohexane prove to be more reactive than those of toluene by a factor of 2.7.^{7,8} Still more anomalous results are observed in the chlorination of molecules containing other

(1) Taken from a portion of a dissertation submitted by Bernard Miller in 1955 to the Graduate Faculty of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy; a preliminary report of this work was made at the 126th meeting of the American Chemical Society, New York, September, 1954.

(2) University Fellow, Columbia University, 1954–1955.

(3) Extensive experimental evidence is reviewed by E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1954, Chapter X.

(4) H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

(5) H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *THIS JOURNAL*, **77**, 2629 (1955).

(6) P. G. Ashmore and J. Chanmugam, *Trans. Faraday Soc.*, **49**, 254 (1953).

(7) G. A. Russell and H. C. Brown, *THIS JOURNAL*, **77**, 4578 (1955).

(8) H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952).