20 ml. of $2M$ sodium hydroxide solution and the mixtures heated under reflux for 1–2 hr. The nitrobenzene phase was separated, washed with 10 ml. of water, which was joined with the aqueous phase. This was then acidified with 10 ml. of $6N$ hydrochloric acid and extracted with 25 ml. portions of ether. Each ether portion was washed with 10 ml. of water, which was added to the aqueous phase for the next extraction. The combined ether extracts were evaporated under reduced pressure at room temperature and the residue taken up in 50 ml. of 95% ethanol. This was then titrated with standard base. Blank determinations revealed that this procedure accounted for 98–99+% of the benzoyl chloride present in typical reaction mixtures.

A more convenient analytical procedure was developed subsequently.[16] This procedure involved the neutralization of the aluminum chloride and hydrogen chloride in the reaction mixture, followed by a direct titration of the benzoic acid and hydrochloric acid produced by the hydrolysis of the benzoyl chloride present. A detailed description of this procedure will be published shortly.[22]

Both procedures gave identical results.

Typical kinetic studies are reported in Table V.

LAFAYETTE, IND.

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[22] H. C. Brown, F. R. Jensen, and B. A. Bolto, paper in preparation.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Formation of Naphthalenes from Indenes. III.[1] Substituted Methanes as Carbene Precursors

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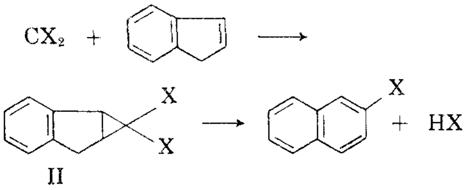
Seven substituted methanes have been examined as possible carbene precursors in reactions with potassium *t*-butoxide and indene. Dichlorobromomethane (III) gives principally the adduct of dichlorocarbene, and the apparent tendency for bromide ion to be eliminated from the anion of III is at least six times greater than for chloride ion. The thermally unstable adduct obtained from reactions employing dibromochloromethane (IV) was converted in high over-all yield to an approximately equimolar mixture of 2-chloro and 2-bromonaphthalene. Thus, there appears to be far less apparent selectivity of the halogen eliminated from the cyclopropane intermediates, than from the anions of the haloforms. Data obtained from reactions with dichlorofluoromethane (V) furnish direct evidence for the existence of chlorofluorocarbene, and indirect evidence to support the conclusion that the cyclopropane derived from this carbene and indene is more stable than other analogs studied. If carbene intermediates are involved in reactions of the substituted methanes VI–IX, they do not add appreciably to indene.

We have previously described a synthesis of 2-halonaphthalene[1,4] which involves the reaction of indene, or a substituted indene, with chloroform or bromoform and base.

$$\underset{}{CHX_3} + B^- \longrightarrow \underset{\text{I}}{CX_2} + X^- + HB$$



II

The principal product of this reaction is a dihalocyclopropyl compound (II), which loses hydrogen halide quantitatively, by a unimolecular process in polar solvents, to give 2-halonaphthalene. It is apparent[1,4] that dihalocarbenes (I) are intermediates in these reactions, and the existence of such intermediates has been more conclusively established by the work of Hine,[5] Doering,[6] Skell,[7] and their coworkers. The purpose of this study was to evaluate the substituted methanes III–IX as carbene precursors in the reaction of indene, substituted methane, and base.

$CHCl_2Br$ III

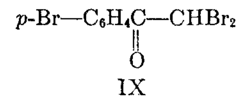
$CHClBr_2$ IV

$CHCl_2F$ V

$CHClF_2$ VI

$CHCl_2CO_2C_2H_5$ VII

$CHCl_2CO_2C(CH_3)_3$ VIII



$$p\text{-Br—}C_6H_4\underset{\underset{O}{\|}}{C}\text{—}CHBr_2$$

IX

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[1] Preceding paper, W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956).

[2] This work was supported in part by a grant (NSF-G2163) from the National Science Foundation.

[3] Parke, Davis and Co. fellow (1955–56), E. I. du Pont de Nemours fellow (summer 1955).

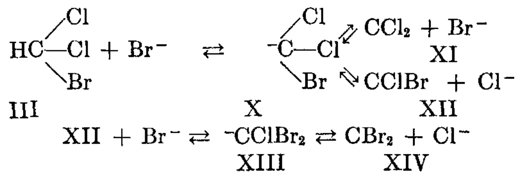
[4] W. E. Parham and H. E. Reiff, *J. Am. Chem. Soc.*, **77**, 1177 (1955).

[5] (a) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950); (b) J. Hine and A. M. Dowell, Jr., *J. Am. Chem. Soc.*, **76**, 2688 (1954); (c) J. Hine, P. C. Peek, Jr., and B. D. Oakes, *J. Am. Chem. Soc.*, **76**, 6162 (1954); (d) J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *J. Am. Chem. Soc.*, **78**, 479 (1956); (e) J. Hine and N. W. Burske, *J. Am. Chem. Soc.*, **78**, 3337 (1956).

[6] (a) W. von E. Doering and A. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954); (b) W. von E. Doering and P. LaFlamme, *J. Am. Chem. Soc.*, **78**, 5448 (1956).

[7] (a) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956); (b) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); (c) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

In the formation of a carbene from a haloform an S_N1 ionization occurs.[5b] When two different halogens are present, as in the haloform III, three different carbenes (XI, XII, XIV) are possible, provided equilibrium is attained.[5b] In the nonpolar solvent indene, in which potassium halide has limited solubility, it was considered unlikely that the equilibria involving XIII and XIV would be established; consequently, it was anticipated that only the two carbenes XI and XII would be formed and that the ratio of bromide ion to chloride ion formed in the first step (III → II) would serve to establish their relative concentrations.

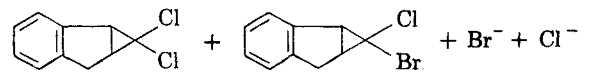


$$\underset{\text{III}}{\mathrm{HCCl_2Br}} + \mathrm{Br^-} \rightleftarrows \underset{\text{X}}{{}^-\mathrm{CCl_2Br}} \rightleftarrows \underset{\text{XI}}{\mathrm{CCl_2}} + \mathrm{Br^-};\quad \underset{\text{X}}{{}^-\mathrm{CCl_2Br}} \rightleftarrows \underset{\text{XII}}{\mathrm{CClBr}} + \mathrm{Cl^-}$$

$$\mathrm{XII} + \mathrm{Br^-} \rightleftarrows \underset{\text{XIII}}{{}^-\mathrm{CClBr_2}} \rightleftarrows \underset{\text{XIV}}{\mathrm{CBr_2}} + \mathrm{Cl^-}$$

The reaction product of dichlorobromomethane (III), indene, and potassium *t*-butoxide was processed in a manner[8] which allowed separation of the the inorganic salts that were formed, and isolation of the intermediate cyclopropyl compounds (XV and XVI).

III + indene ⟶

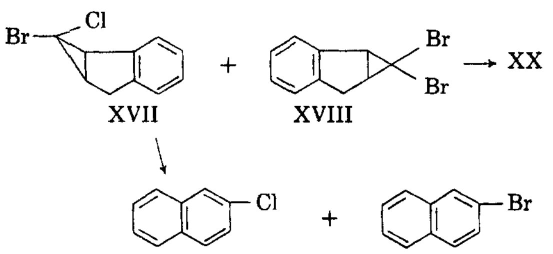


XV XVI

It was apparent, by examining the mixture of XV and XVI, that the reaction had followed the expected course[9,10] leading principally to XV. Essentially pure XV (60% of the crude product) was readily obtained merely by washing the crude product (56% yield) with cold petroleum ether. More quantitative data were obtained by determining the ratio of bromide ion to chloride ion formed, and this ratio proved to be about 3 to 1. Thus, the apparent tendency for bromide ion to be eliminated from the anion of III is at least six times greater than for chloride ion.

The results obtained with dichlorobromomethane suggested that the reaction of dibromochloromethane, indene, and base should lead preferentially to the formation of XVII (*exo-endo* isomers) rather than XVIII. Thus, a method was available for obtaining additional information concerning the elimination of hydrogen halide (conversion to naphthalenes) from the intermediate cyclopropyl derivatives. The crude cyclopropyl derivative, obtained from this reaction, proved to be thermally unstable, and attempts to isolate pure products have so far been unsuccessful. However, when the crude product was steam-distilled a high yield of a mixture of 2-bromo and 2-chloronaphthalene (70%, contaminated only by a small amount of indene) was obtained. The composition of the mixture was estimated, by elementary analysis both before and after further purification, to contain 50 ± 2% of each naphthalene. Although the method of sampling was not as good as the analytical method, there was no reason to assume that the composition of the mixture deviated markedly from the equimolar mixture. If the same relative order of halide elimination obtained for IV, as was observed for III, then the amount of XVII in the crude product should have exceeded that of XVIII by a factor of about 12 to 1. Thus, it would appear that the factors generally associated with hydrogen halide[9,10] elimination do not obtain for eliminations in this cyclopropyl series. We hope ultimately to decide whether the course of elimination is controlled stereochemically (*i.e.* from the two possible isomers of XVII, with chlorine being either *exo* or *endo* to the benzene ring), or whether the carbon-carbon bond is broken in the rate determining step.[11]

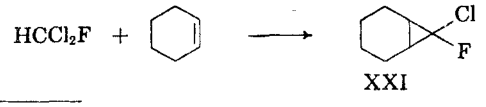
IV + indene ⟶



XVII XVIII XIX XX

Hine and Burske[12] have obtained kinetic evidence for the existence of chlorofluorocarbene. Our initial results, obtained with difluorochloromethane, indene, and base were rather discouraging, since only recovered indene, tars, and polymeric material were obtained. There were small amounts of volatile material obtained; however, the small yield, and our inability to separate them from indene, precluded their identification as possible products derived from difluorocarbene (F_2C).

We then directed our attention to dichlorofluoromethane (V), and the initial reactions were carried out with cyclohexene, instead of indene, to facilitate purification of the anticipated fluorochlorocyclopropane products. We have been unsuccessful in



XXI

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(8) We have previously shown (ref. 4) that halonaphthalene is not produced when the product is processed in nonpolar solvents at temperatures below 60°.

(9) (a) J. Hine and D. E. Lee, *J. Am. Chem. Soc.*, **74**, 3182 (1952); (b) J. Hine and D. E. Lee, *J. Am. Chem. Soc.*, **73**, 22 (1951).

(10) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., (1953) p. 339.

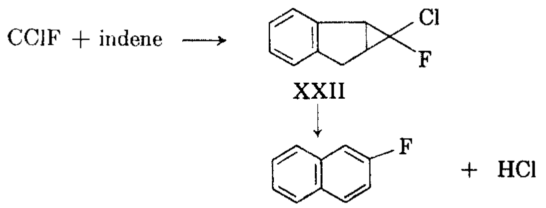
(11) An alternate possibility involves the rate-determining rupture of the carbon-carbon bond of the cyclopropane, with more random elimination of halogen.

(12) J. Hine and N. W. Burske, *J. Am. Chem. Soc.*, **78**, 3337 (1956).

elucidating the exact course of this reaction. The initial product was thermally unstable (eliminated hydrogen chloride); however, when the excess cyclohexene was removed slowly a thermally stable product was obtained in 24% yield. This product (b.p. 185–186°/736) contained a small amount of carbonyl impurity (infrared absorption at 1720 cm.$^{-1}$) which was readily removed, with little loss, by chromatography. The resulting product reacted slowly with bromine in carbon tetrachloride, and with potassium permanganate; the product had the empirical formula $C_7H_{10}ClF$, and showed the following absorption in the infrared region: C-F (1085 cm.$^{-1}$),[13a] cyclopropane ring (1020 cm.$^{-1}$),[13b] cyclohexene ring (1447,[14] 1042 and 975 cm.$^{-1}$),[13b] and absence of unsaturation (lack of absorption in the 1600–1700 cm.$^{-1}$ region).[13c] We feel that this product is XXI, which resulted by the direct addition of fluorochlorocarbene to cyclohexene; however, the thermal instability of the crude reaction product, together with the rather poor elementary analysis obtained, precluded positive identification with the available data.

More conclusive evidence for the addition of chlorofluorocarbene to an olefin was obtained by a study of the reaction of dichlorofluoromethane, indene and potassium *t*-butoxide. Analysis of the inorganic salt obtained from this reaction gave 91% of the theoretical value, calculated for carbene formation as shown in the above equation. A qualitative test for fluoride ion was weakly positive. The organic product was steam-distilled, and the residual aqueous solution was analyzed for halogen. Fluoride ion was absent, and the value obtained for chloride was 13.2% of theory. This low value for chloride ion was in sharp contrast to the results previously obtained when chloroform or bromoform were employed. In these latter cases, steam-distillation caused essentially quantitative loss of halogen acid to yield naphthalenes.[4] It was not, of course, assumed that all of the chloride ion produced in the initial reaction arose from the formation of fluorochlorocarbene, or that all of the fluorochlorocarbene produced reacted with indene; however, these results strongly suggested that the cyclopropane XXII was considerably more stable than analogous cyclopropanes containing chlorine or bromine. This conclusion is in accord with Hine's[9a] investigation of the effect of *alpha* fluorine atoms on S_N1 reactivity of other halogens. Further evidence that the steam-distillation had not completed the conversion of XXII to XXIII was obtained by examining the reaction product. This product (24% yield as XXIII) was an oil with strong odor of fluoronaphthalene; however, the material liberated hydrogen chloride upon attempted distillation. A thermally stable product was not obtained until the material was heated over a prolonged period in ethanol.[4] The yield of isolated pure 2-fluoronaphthalene was 7–9%.

$$B^- + Cl_2CHF \longrightarrow ClCF + Cl^- + BH$$

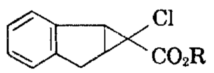


XXII

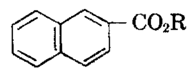
XXIII

The reaction of α,α-dibromoacetophenone (IX) with potassium *t*-butoxide in the presence of an olefin could yield a variety of products. If carbene intermediates are involved, then high dilution with olefin should favor the formation of the corresponding olefin-carbene adduct. The reaction of IX, potassium *t*-butoxide, and excess indene was examined; however, only recovered indene, tars and polymeric material were obtained. When a similar reaction was carried out in excess cyclohexene, some alcohol-soluble material was obtained. This product gave, by reaction with 2,4-dinitrophenylhydrazine, a substance considered to be the osazone of *p*-bromophenylglyoxal.[15] Though the above product was not positively identified, it was obviously not an adduct of *p*-bromobenzoyl bromocarbene and cyclohexene.

Finally, the reactions of ethyl dichloroacetate (VII) and of *t*-butyl dichloroacetate (VIII) with potassium *t*-butoxide and indene were examined. The reaction products were examined carefully for esters or acids of structures XXIV or XXV; however, only trace amounts of acidic products were obtained. In the reaction employing *t*-butyl dichloroacetate a small amount of acidic material was obtained in a rather pure state. The structure of this acid (m.p. 199–202° dec.) was not established; however, the product was not XXIV or XXVI. Hence, it can be concluded that if ethyl dichloroacetate and *t*-butyl dichloroacetate are converted into carbenes under these experimental conditions, these carbenes do not add appreciably to indene. On the other hand, studies now in progress involving these esters and other olefins indicate that carbenes are produced, but that these particular carbenes will add only to olefins more reactive than indene.



XXIV



XXV

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[13] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., 1954. (a) p. 270; (b) p. 28; (c) p. 31; (d) p. 37.

[14] A. Weissberger, *Technique of Organic Chemistry*, Vol. IX, Interscience Publishers, Inc., New York, N. Y., (1956), p. 564.

[15] E. Bayers and C. R. Hauser, *J. Am. Chem. Soc.*, **65**, 1095 (1943) have shown that the reaction of α,α-dibromoacetophenone with aqueous alkali gives phenylglyoxal.

EXPERIMENTAL

Reaction of dichlorobromomethane (III), *indene and potassium t-butoxide.* Freshly distilled dichlorobromomethane (0.172 mole, 28.2 g.) was added over a 20-min. period to a cold (0–10°) mixture of potassium *t*-butoxide (0.174 mole)[4,6a] and purified indene (1.72 mole, 200 g.). The resulting mixture was stirred for 75 min. (at 0–5°), and then allowed to stand (at 25°) for 12 hr. Petroleum ether B (200 ml.) was added to the reaction mixture, and the solids were removed by filtration. The flask and the solids (designated solid A) were washed with petroleum ether and the combined ether solution was concentrated to remove petroleum ether (aspirator) and excess indene (pressure 2–3 mm., pot temperature[4] less than 60°). The residue was chromatographed on Merck alumina (200 g.) using petroleum ether B as both developer and eluant. The yellow eluant (3–4 liters) was concentrated under reduced pressure (pot temperature less than 60°), and the resulting solid (19.1 g., 56% yield), which still contained some indene, was slurried with cold petroleum ether B (50 ml.) and filtered. The white solid (11.45 g., 33.5%) thus obtained, melted at 73–76° and was essentially pure 1,1-dichloro-1a,6a-dihydrocycloprop[*a*]indene (II, X = Cl) (reported m.p. 74.5–76°).[4] A sample of this material was recrystallized from 95% ethanol for analysis. The infrared spectrum of this product was identical with that of authentic material.[4]

Anal. Calcd. for $C_{10}H_8Cl_2$: C, 60.33; H, 4.05. Found: C, 60.07; H, 4.27.

The mixed solids (A) were analyzed for total halogen by precipitation as silver halide. The bromide ion was determined by modification[16] of the procedure reported by D'Ans and Höfer,[17] and the chloride ion was obtained by difference. The total halide ion obtained corresponded to 96.5 ± 1% of one mole, and the molar ratio of bromide to chloride ion was 2.81 ± 0.24. (The best data for this ratio is 3.04.)

Reaction of chlorodibromomethane (IV), *indene and potassium t-butoxide.* The reaction of chlorodibromomethane (35.8 g., 0.172 mole), potassium *t*-butoxide (0.174 mole), and indene (1.72 mole, 200 g.) was carried out as described above for the reaction with dichlorobromomethane; however, the reaction mixture was stirred at 0–10° for 5 hr. The reaction mixture was diluted with water (100 ml.), and then distilled with steam. The distillate was saturated with sodium chloride, and the organic phase was separated by extraction with petroleum ether F. The ether extract was dried (magnesium sulfate) and concentrated under reduced pressure (maximum pot temperature 60°). The residue (37.9 g.) was chromatographed on Merck alumina (200 g.) employing petroleum ether B as both developed and eluant. Evaporation of the eluant afforded 27.2 g. of waxy crystalline material, which was shown to be a mixture of 2-chloronaphthalene, 2-bromonaphthalene, and a small amount of residual indene. This material corresponded to an 84% yield of mixed naphthalenes. The solid was transferred (with some mechanical loss) to a desiccator, and was dried over paraffin. The product weighed 22.5 g. (70% yield) and melted at 41–48°. A sample (1 g.) of this material was sublimed at room temperature with little loss (0.05 g.). The white solid, thus obtained, melted at 51–55° (solid A), and probably contained a small amount of indene. The remaining product was separated into two fractions by crystallization from ethanol: solid B (6.67 g., m.p. 58–59°), total residue (14.1 g., m.p. 47–53°).

Anal. Calcd. for 50% 2-chloronaphthalene–50% 2-bromonaphthalene: C, 64.98; H, 3.81. Found: Solid A, C, 65.14; H, 4.19; Solid B, C, 65.14; H, 4.03.

The infrared spectrum of solid A showed only absorption found in the spectrum of 2-chloro- and 2-bromonaphthalene. Calculations of change in percent composition for C, H, Cl, and Br over the range 2-chloronaphthalene (38–62%)–2-bromonaphthalene (62–38%) revealed maximum change in % C (0.16% per 1% change of component) and minimum change in % H (0.007% per 1% change). Thus, the values obtained indicate that 2-chloro- and 2-bromonaphthalene were formed essentially in equal amounts (±2%).

Reaction of fluorodichloromethane (V), *indene, and potassium t-butoxide.* The reaction of fluorodichloromethane (*ca.* 16 g., 0.16 mole, b.p. 9°), indene (100 g., 0.86 mole), and potassium *t*-butoxide (0.087 mole) was carried out as described above for the reaction with dichloromethane, but with the following modifications: A total reflux condenser (dry-ice and acetone) was employed, the haloform was added over a 2-hr. period, a temperature of −10° was maintained, and the time of reaction at reduced temperature was 2 hr Petroleum ether B (100 ml.) was added, and the reaction mixture was filtered. Analysis of the solid for chloride ion by the Mohr method[18] indicated that 91% (0.79 mole/0.086 mole × 100) of the theoretical amount of chloride ion was produced. The organic filtrate was steam-distilled, and the distillate was saturated with sodium chloride. Analysis of the residual aqueous phase revealed that only 13.2% of an additional mole of chloride ion had been formed during steam distillation, and that no fluoride ion was produced. The organic phase was separated with ether, and the resulting solution was dried (magnesium sulfate) and concentrated (10-inch glass helices column, maximum pot temperature 60°, 1 mm. pressure). The residue was slurried with petroleum ether B and chromatographed on Merck alumina (50 g.), using petroleum ether B as developer and eluant. The combined eluant (*ca.* 1 l.) was concentrated under reduced pressure, and the yellow oil (3.03 g., 24% as 2-fluoronaphthalene), thus obtained, had the characteristic odor of halonaphthalene. Preliminary experiments indicated that this material still contained dihalocyclopropane, since attempted distillation at 1 mm. resulted in decomposition accompanied by the elimination of hydrogen chloride. The oil was dissolved in ethanol (20 ml.), containing potassium hydroxide (3 g.), and the resulting solution was heated at the reflux temperature for 45 min. Water was added to the cooled ethanol solution and the oil that separated was extracted with ether. The ether extract was dried (magnesium sulfate), and concentrated, and the residue was distilled. The product solidified in the column head, condenser, and in the receivers. There was obtained 0.96 g. (7.6% yield) of 2-fluoronaphthalene which melted at 58–59° (reported m.p. 61°).

Anal. Calcd. for $C_{10}H_7F$: C, 82.17; H, 4.83. Found: C, 82.36; H, 4.99.

A mixture melting point of this product with authentic 2-fluoronaphthalene showed no depression. The infrared spectrum of the product and that of authentic 2-fluoronaphthalene were essentially identical.

The above experiment was repeated; however, the product obtained from the steam distillate, subsequent to removal of indene, was treated with hot ethanol prior to chromatography in an attempt to complete the conversion of the cyclopropyl intermediate to fluoronaphthalene. This conversion was apparently not complete, however, since it was necessary to repeat the alcohol treatment before a thermally stable product resulted. The yield of pure 2-fluoronaphthalene in this experiment was 9.4%.

Reaction of fluorodichloromethane, cyclohexene and potassium t-butoxide. The reaction of fluorodichloromethane (7.60 g., 0.074 mole), potassium *t*-butoxide (0.097 mole) and cyclohexene (40 g., 0.486 mole) was carried out as described above for indene with the following modifications: The addition time was 1 hr., the reaction temperature was −15° to −20°, and the reaction time at reduced temperature (−10°) was 3 hr. Water (100 ml.) was added to the

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[16] H. C. Yutzy, Ph.D. thesis, University of Minnesota (1936), p. 78.

[17] J. D'Ans and P. Höfer, *Angew Chem.*, **47**, 73 (1934).

[18] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, The Macmillan Co., New York, N. Y. (1947).

reaction mixture, and the solids were dissolved by vigorous stirring. The organic solution was separated and the aqueous phase was extracted with ether. The combined organic solution was dried (magnesium sulfate), and ether and excess cyclohexene were removed by distillation at atmospheric pressure (4-inch Vigreux column). Near the end of the distillation the residue darkened and acidic vapors were evident. The residue was then distilled at reduced pressure and 2.72 g. (24.5% yield as XXI) of oil was obtained; b.p. 56–60°/20 mm., n_D^{25} 1.4567–1.4578. The material was washed with dilute sodium bicarbonate, and then redistilled to give 2.07 g. of product; b.p. 74°/40 mm., n_D^{25} 1.4554–1.4572. The infrared spectrum of this material showed absorption at 1720 cm.$^{-1}$, which suggested the presence of small amounts of carbonyl impurity. The carbonyl impurity was easily removed, with little loss of weight, by passing a solution of the product in petroleum ether over Merck alumina (100 g. of alumina for 8 g. of product in 160 ml. of ether). The product was then distilled; b.p. 158–159°/739 mm., n_D^{25} 1.4571–1.4577.

Anal. Calcd. for $C_7H_{10}ClF$: C, 56.57; H, 6.78; Cl, 23.86; F, 12.78; mol. wt., 148.6. Found: C, 57.10; H, 6.97; Cl, 22.87; F, 11.87; mol. wt. (ebullioscopic in benzene) 139.

The product reacted slowly with permanganate (2%) solution and with bromine (5% in carbon tetrachloride); the infrared spectrum showed absorption characteristic of C-F (1085 cm.$^{-1}$),[13a] cyclopropane[13b] (1020 cm.$^{-1}$), cyclohexane (1447 cm.$^{-1}$,[14] 1042 and 975 cm.$^{-1}$),[13b] and the absence of unsaturation (no absorption in the 1600–1700 cm.$^{-1}$ region).[13c]

The above reaction was repeated several times in an attempt to avoid the decomposition which occurred when the excess cyclohexane was removed. More rapid distillation of the excess cyclohexene, under reduced pressure, gave residues that foamed badly upon distillation (at 760 mm. or 20 mm.). The use of a photo-flood lamp as the sole heat source for distillation of these residues gave a clear distillate (n_D^{25} 1.4265) which liberated hydrogen chloride slowly at room temperature, and rapidly (with decomposition) at 120–125°.

Reaction of difluorochloromethane, indene, and potassium t-butoxide. (a) The reaction of difluorochloromethane (*ca.* 40 g., 0.46 mole, b.p. −41°), potassium *t*-butoxide (0.088 mole), indene (100 g., 0.86 mole), in olefin-free *n*-hexane (50 ml.) was carried out essentially as described above for the reaction of dichloromethane with indene. Water (100 ml.), containing sodium carbonate hydrate (12 g., 0.1 mole), was added, and the resulting mixture was steam-distilled. The residual aqueous solution gave a negative test for fluoride. The organic distillate was separated (petroleum ether F), dried (magnesium sulfate), and concentrated at 20 mm. to remove solvent and at 1 mm. (maximum pot temperature 60°) to remove indene. There was obtained a 92.8% recovery of indene and 2.35 g. of dark polymeric residue.

(b) The above reaction was repeated in an oxygen-free autoclave. The initial temperature was −10° and the contents were allowed to stand, with occasional stirring, for 84 hr. at 25°. The reaction mixture, and similar ones obtained by variations of reaction conditions, were processed by a variety of procedures similar to those previously described for related reactions; however, no isolable products were obtained. Analysis of inorganic material revealed 65.5% of the theoretical amount calculated for one mole of chloride ion; however, qualitative tests revealed that fluoride ion was also positive. The recovery of indene usually amounted to 70–80%; however, the latter fractions of indene contained some material of higher refractive index. Attempts to separate this component by careful fractionation (Podbielniak concentric tube column) were unsuccessful. Decomposition and polymerization of indene accompanied these distillations; some fractions of the indene distillate slowly polymerized (absorption at 1715 cm.$^{-1}$ in the infrared was observed). Other products were generally polymeric and tarry in nature.

Reaction of IX *with cyclohexene and potassium t-butoxide.* The procedure used was similar to that described for reactions employing haloform; the quantities of reactants were cyclohexene (1.49 mole), IX (0.087 mole), and base (0.087 mole). The crude oil, obtained after removal of solvent, was treated with hot ethanol, and the ethanol extract was concentrated. The amorphous solid (4.45 g.), thus obtained, was treated with 2,4-dinitrophenylhydrazine, and the product (5.0 g., m.p. ~300° dec., insoluble in most organic solvents) and recrystallized from dimethylformamide. Recovery from the recrystallization was poor, and decomposition was evident (solution turned black). The red solid that was obtained melted at 317–318° dec.

Anal. Calcd. for $C_{20}H_{13}N_8BrO_8$: C, 41.90; H, 2.28; N, 19.25. Found: C, 42.34; H, 3.03; N, 19–25%.

t-Butyl dichloroacetate. This ester was prepared from technical grade dichloroacetic acid (0.48 mole) by the procedure described in *Organic Syntheses*[19] for the preparation of *t*-butyl malonate. The yield of product (n_D^{25} 1.4316) was 42%.

Anal. Calcd. for $C_6H_{10}Cl_2O_2$: C, 38.94; H, 5.45; M.R., 41.3. Found: C, 39.19; H, 5.61; M.R., 41.1.

Reaction of ethyl dichloroacetate and reaction of t-butyl dichloroacetate with indene and potassium-t-butoxide. These reactions were carried out according to the same general directions previously described for reactions involving haloforms. The same quantities and ratio of reactants were observed. Fractions that could contain esters were hydrolyzed, both with alkali and with acid; however, only trace amounts of acidic materials were obtained. The crude acid (0.5 g.), obtained in the reaction employing the *t*-butyl ester, was purified by chromatography (alumina–petroleum ether B). The acid (0.25 g., m.p. 185–190°), thus obtained, melted at 199–202° after purification by recrystallization (petroleum ether C) and sublimation (120° at 0.02 mm.).

Anal. Found: C, 78.67; H, 5.62; Cl, 0; neut. equiv. 184. The identity of this acid, which appears to have the formula $C_{12}H_{10}O_2$, was not established.

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(19) A. L. McCloskey, G. S. Fonken, R. W. Kliuber, and W. S. Johnson, *Org. Syntheses*, **34**, 28 (1954).