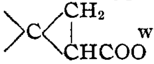
resulting mixture was poured into cold 1 *N* hydrochloric acid and the aqueous solution extracted with ether. The combined organic layers were washed successively with dilute sodium carbonate and water, dried over sodium sulfate and evaporated to a small volume. The concentrate was vapor-phase chromatographed at 108°. A single peak appeared after 25 minutes. The infrared and ultraviolet spectra of the chromatographed product were identical to those of an authentic sample of methyl β-cyclopropylacrylate (XVI) prepared from the previously reported β-cyclopropylacrylic acid[16] with diazomethane; b.p. 76° (19 mm.), $n^{24}D$ 1.4777, λ_{max} 230.5 mμ (ε 16,600).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 67.05; H, 8.29.

Attempted Ring Cleavage of Methyl Spiropentaneacetate (III).—In contrast to the two preceding experiments, when methyl spiropentaneacetate (III) was refluxed with sodium hydride in cyclohexane or with sodium methoxide in methanol no ultraviolet chromophore appeared. Vapor-phase chromatography showed the compound to be largely unchanged.

Ethyl Spiropentanecarboxylate (XVII).—A stirred mixture of 10.5 g. (0.16 mole) of zinc-copper couple, 42.9 g. (0.16 mole) of methylene iodide, several crystals of iodine and 75 ml. of ether was heated at reflux for 30 minutes and 2.0 g. (0.016 mole) of ethyl 2-methylenecyclopropanecarboxylate in 5 ml. of ether was then added over a 5-minute period. After 24 hours the mixture was cooled, filtered and washed successively with several portions each of dilute hydrochloric acid, dilute ammonium hydroxide and water. The solution was then dried over sodium sulfate, concentrated to a small volume, and vapor-phase chromatographed. Two major peaks were obtained at 13 minutes (starting material) and 24 minutes (ethyl spiropentanecarboxylate, XIX), respectively. The structure of the latter was confirmed by its n.m.r. spectrum[10] which showed a typical 12 line ABX pattern[19] from the grouping



$>C<(CH_2)(CHCOO)$

with the α-proton quartet centered at 7.98 and the eight lines from the methylene protons centered at 8.63. The protons of the unsubstituted ring showed a single peak at 9.05.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.96; H, 8.68.

A total yield of 0.42 g. (19%) of the chromotographed spiropentane was obtained. However, substantial losses occurred during chromatography (*vide supra*).

Acknowledgments.—We wish to thank Dr. S. R. Safir for helpful discussions during the course of this work and Dr. J. E. Lancaster for the determination and aid in interpretation of the n.m.r. spectra.

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[19] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 138.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, PENNSALT CHEMICALS CORP., PHILADELPHIA 18, PA.]

Addition of Iodine Halides to Fluorinated Olefins. II. The Addition of Iodine Monofluoride to Halogenated Olefins

BY MURRAY HAUPTSCHEIN AND MILTON BRAID

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An excellent method for the addition of iodine monofluoride (considered to be formed "*in situ*") to perfluoro- and perfluorochloroölefins is described. The most effective source of iodine monofluoride was the system iodine and iodine pentafluoride ($2I_2 + IF_6 \rightarrow 5IF$) in the presence of a catalyst. The novel iodides CF_3CFICF_3, CF_3CFClI, CF_3CCl_2I, CF_3CHClI and CF_3CHFI were formed by the addition of iodine monofluoride to $CF_2{=}CFCF_3$, $CF_2{=}CFCl$, $CF_2{=}CCl_2$, $CF_2{=}CHCl$ and $CF_2{=}CHF$, respectively. The addition of iodine monofluoride to tetrafluoroethylene, preferably in the presence of a small amount of the "inhibitor" CF_2ClCCl_2I, to give a high yield of CF_3CF_2I is described. The iodides $CF_2ClCFClI$ and CF_3CH_2I were formed in the reactions of iodine and iodine pentafluoride with $CFCl{=}CFCl$ and $CF_2{=}CH_2$, respectively.

This paper relates to a novel and excellent method for adding iodine monofluoride to halogenated olefins.[1] A mixture of iodine and iodine pentafluoride in a molar ratio of 2:1 or slightly greater (preferably preheated usually to temperatures of 100–175° and in the presence of a catalyst) has been found to be an effective source of iodine monofluoride.

$$2I_2 + IF_5 \longrightarrow 5IF$$

It has been demonstrated that if perhaloölefins containing a terminal $=CF_2$ group are allowed to react with the above mixture high yields of the corresponding iodine fluoride adducts are obtained. Examples of such olefins include the perfluoroolefins $CF_2{=}CF_2$, $CF_2{=}CFCF_3$ and the perfluorochloroölefins $CF_2{=}CFCl$ and $CF_2{=}CCl_2$. Other olefins including $CFCl{=}CFCl$, $CF_2{=}CHCl$, $CF_2{=}CHF$ and $CH_2{=}CF_2$ have given low to moderate yields of the IF adduct.

The addition of iodine monofluoride to $CF_2{=}CCl_2$ was studied most extensively. This reaction represents the best route to the reactive iodide CF_3CCl_2I previously isolated as a rearrangement product from the reaction of ICl with $CF_2{=}CFCl$ in the presence of aluminum chloride.[2]

The initial reactions which were carried out at 20–25° using undistilled iodine pentafluoride (poured directly from a storage cylinder) gave conversions of 24 to 48% to mixtures of isomers containing about 90% of CF_3CCl_2I[2] and 10% of $CFCl_2CF_2I$.[2] The results were unsatisfactory when carefully distilled iodine pentafluoride was used and a search for catalysts for this reaction was then made. Aluminum iodide, aluminum chloride and aluminum fluoride were not effective catalysts when used alone. When aluminum wire containing 0.1% iron was used as the catalyst only a 6% conversion to a mixture of isomers containing 70% CF_3CCl_2I and 30% $CFCl_2CF_2I$ was obtained. Thus iron appeared to be detrimental not only in lowering the isomer content of

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[1] It should be noted that very recently A. Bowers, L. C. Ibanez, E. Denot and R. Becerra, *J. Am. Chem. Soc.*, **82**, 4001 (1960), reported the addition of an iodine and a fluorine atom across the double bonds of cyclohexene and unsaturated steroids by use of N-iodosuccinimide (a source of electrophilic iodine) and hydrogen fluoride in the presence of ether or tetrahydrofuran.

[2] Paper I, this series M. Hauptschein, M. Braid and A. H. Fainberg, *ibid.* **83**, June 5, (1961).

CF_3CCl_2I[3] but in reducing the total conversion to isomers. Under identical conditions (preheating at 130°, reaction temperature 0°) except that the aluminum wire was replaced with iron-free high purity aluminum shavings, 60% conversions to CF_3CCl_2I of 98 to 100% isomeric purity were obtained.

The preferred catalyst system from the standpoint of conversions and reproducibility was a mixture of iron-free aluminum metal and aluminum iodide. When this combination of catalysts was preheated with the iodine-iodine pentafluoride mixture prior to the addition of $CF_2{=}CCl_2$, and when the addition reaction was carried out at 0°, reproducible conversions of the order of 80% to CF_3CCl_2I of 95-98% isomeric purity were obtained. When the addition was conducted at 20-25° the conversion remained about the same, *i.e.*, 81%, but the CF_3CCl_2I:$CFCl_2CF_2I$ isomer ratio was 77:23 showing that the reaction was temperature dependent.[2]

The addition of iodine monofluoride to chlorotrifluoroethylene at 20-25° gave a 95% conversion to a nearly equimolar mixture of the two possible adducts, CF_2ClCF_2I and the new isomer CF_3CFClI.

The addition of IF to tetrafluoroethylene[4] using the Al-AlI_3 catalyst system proceeded so vigorously at 20-25° that the main products of the reaction were carbon tetrafluoride and carbon apparently produced by a disproportionation reaction. In the presence of about 2 mole % (based on tetrafluorethylene) of CF_2ClCCl_2I,[2] a very efficient chain transfer agent which presumably acted to inhibit any run-away polymerizations, a 78% conversion to CF_3CF_2I resulted at room temperature.

Iodine monofluoride was added to perfluoropropene to give the new isomer 2-iodoheptafluoropropane, CF_3CFICF_3. This iodide was the exclusive isomer in the aluminum-aluminum iodide-catalyzed reaction of perfluoropropene with iodine and iodine pentafluoride and was obtained in 34, 52 and 77% conversions at the respective temperatures of 25°, 62-75° and 125°. The striking similarities in the vapor infrared spectra of the secondary haloperfluoropropanes, CF_3CFXCF_3, where X = I, Br and Cl, is attributed to the presence of the $(CF_3)_2CF$- group in all cases.

In a single experiment carried out at 25° the aluminum-catalyzed reaction of iodine and iodine pentafluoride with $CFCl{=}CFCl$ gave the iodide $CF_2ClCFClI$[2] in 23% conversion.

The new compound CF_3CHClI was obtained as substantially the single isomeric iodide in 48% conversion at room temperature from the reaction of $CF_2{=}CHCl$ with iodine and iodine pentafluoride in the presence of the aluminum-aluminum iodide catalyst system.

Similarly, the novel CF_3CHFI was obtained as the exclusive isomer from the reaction of $CF_2{=}CHF$ with iodine and iodine pentafluoride, while a low yield of CF_3CH_2I resulted from reaction of $CH_2{=}CF_2$ with the iodine-iodine pentafluoride mixture.

A detailed investigation of the catalyzed formation and isolation of the interhalogen compound, IF,[5] was outside the scope of the present work. The provocative observation that a distillate fraction from the reaction at 130-140° of iodine with iodine pentafluoride in the presence of catalytic amounts of aluminum-aluminum iodide reacted at 20° with the olefin $CF_2{=}CCl_2$ to produce some IF adduct, CF_3CCl_2I, is nevertheless worthy of mention. Iodine monofluoride was not isolated and characterized as a pure chemical individual, however, from this single attempt.

Experimental

Reactions of 1,1-Dichloro-2,2-difluoroethylene with Iodine and Iodine Pentafluoride. General Procedure.—Under a high-purity dry nitrogen atmosphere, a 300-cc. Monel or nickel autoclave was charged with iodine, iodine pentafluoride and a catalyst, and was preheated while shaking at temperatures of 100-150°. After cooling to room temperature, the autoclave was further cooled in solid carbon dioxide and evacuated. When an aluminum-aluminum iodide catalyst system was used, it was found best to load the aluminum metal first and cover it with the iodine and iodine pentafluoride to avoid ignition of the aluminum by the flame reaction which occurred when aluminum iodide was contacted with iodine pentafluoride. Moreover, the aluminum iodide was always ground finely under a nitrogen atmosphere and added carefully in small portions to the reaction mixture (*caution*). The 1,1-dichloro-2,2-difluoroethylene was admitted to the autoclave by vacuum gaseous transfer. The vessel was then sealed and shaken for the period of reaction. The cooled autoclave was then opened and the reaction mixture was poured while stirring into an iced saturated solution of sodium bisulfite made basic with sodium hydroxide. The resulting mixture was then neutralized with additional sodium hydroxide. The lower organic layer was separated, dried with Drierite, and distilled and analyzed by vapor liquid partition chromatography (v.-l.p.c.)[2] to determine the composition and ratio of the two possible isomeric products, CF_3CCl_2I[2] and $CFCl_2CF_2I$,[2] of the addition of IF to $CF_2{=}CCl_2$.

In a typical run, a mixture of 56 g. (0.442 g. at.) of crystalline resublimed iodine, 24 g. (0.108 mole) of distilled iodine pentafluoride (0.540 mole of theoretical IF), 2 g. (0.074 g. at.) of aluminum shavings of 99.99% purity (kindly supplied by Aluminum Co. of America) and 2 g. (0.0049 mole) of aluminum iodide was preheated in a 300-cc. Monel autoclave while shaking for 2.5 hr. at 130-135°. The autoclave was cooled in Dry Ice, evacuated, and charged with 110 g. (0.828 mole) of 1,1-difluoro-2,2-dichloroethylene. The autoclave was shaken in an ice-bath for 17 hr. and worked up as described above. There was finally obtained 155 g. of reaction products shown by v.l.p.c. to consist of 125 g. (83% conversion based on maximum theoretical IF)[6] of

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[3] See ref. 2 for the catalytic effect of iron in reversing the direction of addition of ICl to $CF_2{=}CFCl$ to produce over 60% of the isomer $CFCl_2CF_2I$.

[4] The reaction of iodine pentafluoride with tetrafluoroethylene to give C_2F_5I in undisclosed yield was reported by J. H. Simons and T. J. Brice, U. S. Patent 2,614,131 (1952); the maximum theoretical yield is, of course, quite low since four of the five fluorine atoms in IF_5 are either wasted or cause further fluorination of C_2F_5I to C_2F_6. It is interesting to note that using IF_5 alone, these investigators reported that no reaction was detected below a reaction tube temperature of about 175°.

[5] Iodine monofluoride is the only diatomic interhalogen compound that has not been isolated as a chemical individual, although R. A. Durie and A. G. Gaydon, *J. Phys. Chem.*, **56**, 316 (1952), detected a band system due to IF from the emission spectrum of the flame produced when fluorine reacted with iodine. From theoretical calculations these investigators concluded that the dissociation energy of IF was less than those of BrF and ClF. L. Slutsky and S. H. Bauer, *J. Am. Chem. Soc.*, **76**, 270 (1954), however, noted an arithmetical error in Durie's and Gaydon's work, and suggested that IF should be somewhat more stable than BrF and ClF.

Vapor pressure measurements by O. Ruff and A. Braida, *Z. anorg. Chem.*, **220**, 43 (1934), on iodine penta- and heptafluorides mixed with iodine led them to conclude that it was unlikely that any lower compound of iodine and fluorine existed.

a mixture of the isomers $CFCl_2CF_2I$ and CF_3CCl_2I, the latter isomer comprising 95% of the mixture, and 30 g. of unreacted $CF_2{=}CCl_2$.

Another experiment carried out at 0° under the same conditions afforded the iodide CF_3CCl_2I of 98% isomeric purity in 77% conversion.

Using the same conditions except that the reaction was conducted at 20–25° rather than at 0° gave an 81% conversion to a mixture of isomers consisting of 77% CF_3CCl_2I and 23% $CFCl_2CF_2I$.

Several preliminary runs carried out at 20–25°, with and without preheating at 100°, using undistilled iodine pentafluoride directly from the cylinder and in the absence of any added catalysts gave conversions of 24 to 48% based on theoretical IF to mixtures of isomers containing about 90% CF_3CCl_2I.

In a number of runs carried out at 0° after a 3-hr. preheating period at 130° (brief exotherms to 190°) and using as an added catalyst only iron-free high-purity (99.99%) aluminum shavings, there were obtained about 60% conversions to CF_3CCl_2I of 98 to 100% isomeric purity. When aluminum wire containing 0.1% iron was used as the catalyst only a 6% conversion to CF_3CCl_2I of only 70% purity was obtained.

Aluminum iodide, aluminum chloride and aluminum fluoride were not effective catalysts when used alone.

In addition to iron, other metals appear to exert a detrimental effect. Thus, for example, in a single experiment conducted in the presence of brass, a 31% conversion to a mixture of isomers consisting of 14% CF_3CCl_2I and 86% $CFCl_2CF_2I$ resulted.

Reaction of 1,2-Dichloro-1,2-difluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 56 g. (0.442 g. at.) of iodine, 24 g. (0.108 mole) of distilled iodine pentafluoride and 2 g. of aluminum shavings of 99.99% purity was heated while shaking in a nitrogen atmosphere in a 300-cc. Monel autoclave at 130° for 1.5 hr. The reactor was cooled in Dry Ice, evacuated, and charged by vacuum gaseous transfer with 95 g. (0.714 mole) of $CFCl{=}CFCl$. The vessel was sealed and shaken at 25° for about 17 hr. After cooling in ice, the autoclave was opened and the contents were poured while stirring into iced saturated sodium bisulfite solution. The resulting mixture was neutralized with sodium hydroxide solution and the lower organic layer was separated and dried with Drierite. Analysis by v.l.p.c. of the 79 g. of product thus obtained showed it to consist essentially of 73 mole % of $CFCl{=}CFCl$ and 27 mole% $CF_2ClCFClI$ (23% conversion based on maximum theoretical iodine monofluoride). The infrared spectrum of this iodide matched that of a sample previously prepared by the addition of iodine monochloride to chlorotrifluoroethylene at 0° in the absence of iron.[2]

Reactions of Chlorotrifluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 126.9 g. (0.999 g. at.) of iodine and 45 g. (0.203 mole) of undistilled iodine pentafluoride (poured directly from a metal cylinder) was heated in a 300-cc. Monel autoclave while shaking at 100° for 2 hr. After cooling to room temperature, the reactor was further cooled in liquid nitrogen and evacuated. Two hundred grams (1.72 moles) of chlorotrifluoroethylene was admitted to the autoclave by gaseous vacuum transfer, and the reaction mixture was shaken for 2 hr. at 0–10°. The temperature was then allowed to rise and shaking was continued at 20–25° for two additional days. Upon venting the autoclave, there was recovered 61 g. of unreacted olefin. The remaining liquid products in the reactor were washed with cold saturated aqueous sodium bisulfite solution made basic with sodium hydroxide, and then washed with water. The organic layer was separated and then dried. There was thus obtained 253 g. (95% conversion based on maximum theoretical IF) of a liquid product, b.p. mainly 54–56°, shown by v.l.p.c. to consist almost entirely of a mixture of 55% CF_2ClCF_2I[7a] and 45% of CF_3CFClI.[7b] Pure samples of each isomer were obtained by preparative chromatography using a Perkin–Elmer 2-meter "B" column at 50° under a pressure of helium of 30 p.s.i.g.

The infrared vapor spectrum of CF_2ClCF_2I matched that of a sample prepared by addition of iodine monochloride to tetrafluoroethylene, and had characteristic bands at 8.03s, 8.47vs, 8.86vs, 9.76vs, 11.46s, 12.8vvs μ (vvs = very, very strong; vs = very strong; s = strong). The absorption maximum in the ultraviolet spectrum in isoöctane was at 271 mμ.

Characteristic absorption bands in the infrared vapor spectrum of CF_3CFClI were at 7.85vs, 8.12vvs, 8.22vs, 9.16vs, 10.89vs, 11.88vs, 13.9s μ. The absorption maximum in the ultraviolet spectrum in isoöctane was at 282 mμ.

Anal. Calcd. for C_2ClF_4I: C, 9.15; Cl, 13.51. Found: C, 9.44; Cl, 13.53.

When the above reaction was carried out at 0° for 17 hr. there was obtained a 52% conversion to the same mixture of isomers, shown by v.l.p.c. to contain 51% of the isomer CF_3CFClI.

Reactions of Perfluoropropene with Iodine and Iodine Pentafluoride.—A 300-cc. Monel autoclave was charged with a mixture of 56 g. (0.442 g. at.) of iodine, 24 g. (0.108 mole) of distilled iodine pentafluoride, 2 g. of aluminum shavings of 99.99% purity and 2 g. of aluminum iodide under a high purity nitrogen atmosphere. The autoclave and contents were heated while shaking at 140 to 150° for 1.75 hr. The autoclave was cooled to room temperature, further cooled in solid carbon dioxide, evacuated, and charged by vacuum gaseous transfer with 114 g. (0.76 mole) of perfluoropropene. The reactor was sealed and heated while shaking at 125° for a total of 7 hr. On venting the autoclave, 40 g. of unreacted perfluoropropene was recovered by condensation in a refrigerated receiver. The remaining reaction product was worked up by hydrolysis in iced saturated sodium bisulfite solution made basic with sodium hydroxide followed by neutralization with additional sodium hydroxide. The lower organic layer was separated, dried with Drierite, and analyzed by v.l.p.c. On distillation there was obtained 122 g. (77% conversion based on maximum theoretical iodine monofluoride) of 2-iodoheptafluoropropane, CF_3CFICF_3, b.p. 40°, n^{20}D 1.327, as the exclusive isomeric product.[8] The infrared spectrum of CF_3CFICF_3 taken of the vapor had the principal absorption bands at 7.78vvs, 8.05vvs, 8.50s, 8.92vs, 10.45vs, 11.08vs, 13.3s and 14.1s μ. This spectrum was in marked contrast to the vapor spectrum of $CF_3CF_2CF_2I$[9] which has the principal bands at 7.53vs, 7.87s, 8.04vvs, 8.17vs, 8.65s, 8.83vs, 9.34s, 9.63s, 11.33s, 12.20vs, 13.3s, 13.6vs, 14.95s; only the 8.05 and 13.3 μ bands are common to both isomers. The infrared spectrum of CF_3CFICF_3 was strikingly similar to the vapor infrared spectra of $CF_3CFBrCF_3$[10] and $CF_3CFClCF_3$.[11] The spectrum of the secondary perfluoropropyl bromide had bands at 7.72vs, 8.02vvs, 8.44s, 8.82vs, 10.45vs, 10.71 vs, 13.2s and 14.0s μ, while that of the secondary perfluoropropyl chloride had bands at 7.68vs, 7.97vvs, 8.40s, 8.80vs, 10.29vs, 13.1m, and 13.9s μ. As in the case of the iodide isomers, the spectra of the normal perfluoropropyl bromides[12] and chlorides[12] were in marked contrast to the corresponding secondary bromides and chlorides. The marked similarities in infrared spectra of the three secondary halo-perfluoropropanes are undoubtedly due to the presence of the $(CF_3)_2CF{-}$ group in all cases.

Anal. Calcd. for C_3F_7I: C, 12.2; I, 42.9. Found: C, 12.0; I, 42.4.

The absorption maximum of CF_3CFICF_3 in the ultraviolet spectrum taken in isoöctane was at 276 mμ.

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(6) In this and subsequent reactions any consumption of iodine fluorides by reaction with metals or metal halides present as catalysts was neglected in calculating the maximum theoretical IF based on the reaction $2I_2 + IF_5 \rightarrow 5IF$. The conversions given are therefore usually artificially low since the available IF present was less than the theoretical maximum.

(7) (a) R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953). (b) See ref. 2 for characteristic v.l.p.c. elution time ratios of the isomeric chloroiodotetrafluoroethanes.

(8) See ref. 2 for characteristic v.l.p.c. elution time ratios of the isomeric iodoheptafluoropropanes.

(9) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 2461 (1951).

(10) Prepared from the reaction of an excess of perfluoropene with equimolar quantities of bromine and bromine trifluoride (M. Hauptschein and M. Braid, unpublished work).

(11) Prepared by the reaction of CF_3CFICF_3 with chlorosulfonic acid at 142°; see M. Hauptschein and M. Braid, *ibid.*, **83**, June 5, (1961).

(12) M. Hauptschein, E. A. Nodiff and A. V. Grosse, *ibid.*, **74**, 1347 (1952).

In similar experiments carried out at reaction temperatures of 25° for 17 hr. and at 62–75° for 20 hr., there were obtained respective conversions of 34 and 52%. In both cases the secondary iodide was the exclusive isomer formed.

Reactions of Tetrafluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 47.5 g. (0.374 g. at.) of iodine, 18.4 g. (0.083 mole) of undistilled iodine pentafluoride, 1 g. of aluminum shavings and 1 g. of aluminum iodide was heated in a nitrogen atmosphere in a 300-cc. Monel autoclave while shaking for 2 hr. at 130–140°. The autoclave was cooled, opened, and charged with 3 g. (0.0102 mole) of 1,1,2-trichloro-2,2-difluoro-1-iodoethane.[2] The reactor was sealed, cooled in liquid nitrogen, evacuated, and charged by vacuum gaseous transfer with 55 g. (0.55 mole) of tetrafluoroethylene. The reaction mixture was shaken at room temperature overnight and then heated while shaking at 50° for 7 hr. On venting the autoclave, there was recovered by condensation in refrigerated receivers 11 g. of unreacted olefin. By distillation of the remaining products there was collected a total of 80 g. (78% conversion based on maximum theoretical iodine monofluoride) of C_2F_5I[9] shown by v.l.p.c. and by its infrared spectrum to exceed 99% purity.

In a similar run carried out in the absence of CF_2ClCCl_2I at 20–25° there was obtained only a very small yield of C_2F_5I, the principal products being CF_4 and carbon (*caution*). From two other runs in the absence of CF_2ClCCl_2I carried out mainly at 0°, 90% of the olefin was recovered unreacted in one case with a small amount of C_2F_5I formed, while in the other case there was once again almost complete conversion of the tetrafluoroethylene to carbon and carbon tetrafluoride with only a small quantity of C_2F_5I detected.

Reaction of 1-Chloro-2,2-difluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 56 g. (0.442 g. at.) of iodine, 24 g. (0.108 mole) of undistilled iodine pentafluoride, 2 g. of aluminum shavings and 2 g. of aluminum iodide was heated in a nitrogen atmosphere in a 300-cc. Monel autoclave while shaking for 2 hr. at 135–140°. The reactor was cooled in Dry Ice, evacuated, and 64 g. (0.649 mole) of 1-chloro-2,2-difluoroethylene was admitted to the autoclave by vacuum gaseous transfer. The autoclave was sealed and shaken overnight at room temperature. On venting the autoclave at atmospheric pressure, there was recovered 31 g. of unreacted olefin. The remaining liquid products from the autoclave were hydrolyzed in cold aqueous saturated sodium bisulfite solution made basic with potassium hydroxide. The resulting mixture was neutralized with additional potassium hydroxide solution. The lower organic layer was separated and dried with Drierite. There was thus obtained 65 g. of liquid product, b.p. 60–80° (mostly 79–80°), shown by v.l.p.c. to contain 90 mole % (48% conversion based on maximum theoretical IF) of substantially a single isomeric iodide b.p. (middlecut) 80°, $n^{25}D$ 1.4304. From the similarity of its vapor infrared spectrum to those of $CF_3CHClBr$, CF_3CHClF and CF_3CHFI as well as the position of the absorption maximum in the ultraviolet spectrum taken in isoöctane which was at 275 mμ, the iodide was assigned the structure CF_3CHClI. Characteristic absorption bands in the infrared vapor spectrum of CF_3CHClI are at 7.66vs, 7.89vvs, 8.39vs, 8.61vs, 9.03vs, 11.6s, 12.5vs and 15.0s μ.

Anal. Calcd. for C_2HClF_3I: C, 9.84; H, 0.44; F, 23.39; I, 52.01. Found: C, 10.04; H, 0.31; F, 23.12; I, 52.17.

Reaction of Trifluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 56 g. (0.442 g. at.) of iodine, 24 g. (0.108 mole) of distilled iodine pentafluoride, 2 g. of aluminum shavings and 2 g. of aluminum iodide was heated for 2 hours at 130° while shaking in a 300-cc. Monel autoclave. The reactor was cooled in liquid nitrogen, evacuated, and 62 g. (0.757 mole) of trifluoroethylene was admitted to the autoclave by vacuum gaseous transfer. The autoclave was shaken at room temperature for 16 hr. and at 70–83° for 15 hr.

By the isolation procedures previously described there was obtained from this reaction 15 g. of CF_3CHFI as the exclusive isomer. A pure sample of this iodide was obtained by preparative chromatography using a 2-meter Perkin–Elmer "B" column. The characteristic v.l.p.c. elution time ratio t_c/t_{CCl_4}[2] at 50°, for this column was 0.57. The iodide CF_3CHFI, a colorless liquid, $n^{25}D$ 1.3665, has the characteristic absorption bands in the infrared (vapor) spectrum at 7.35vs, 7.82vs, 8.09s, 8.30vvs, 8.85vs, 9.22vs, 11.60s and 14.4vs μ. The maximum in the ultraviolet spectrum of CF_3CHFI taken in isoöctane was at 262 mμ.

Anal. Calcd. for C_2HF_4I: C, 10.54; H, 0.44; F, 33.34; I, 55.68. Found: C, 10.20; H, 0.68; F, 33.19; I, 55.65.

It should be noted that the other possible IF adduct of trifluoroethylene, *i.e.*, CHF_2CF_2I, has been reported to have an ultraviolet maximum in light petroleum at 266 mμ.[13]

Reaction of 1,1-Difluoroethylene with Iodine and Iodine Pentafluoride.—A mixture of 56 g. (0.442 g. at.) of iodine, 24 g. (0.108 mole) of distilled iodine pentafluoride, 2 g. of aluminum shavings and 2 g. of aluminum iodide was heated at 130–140° for 2 hours while shaking in a 300-cc. Monel autoclave. After cooling in liquid nitrogen, the autoclave was evacuated and 50.5 g. (0.790 mole) of 1,1-difluoroethylene was introduced by vacuum transfer. The autoclave was shaken at 0–12° for 18.5 hr. and at 50° for 3 hr. There was obtained from this reaction among other products a low yield of CF_3CH_2I which was separated by v.l.p.c. using a 2-meter Perkin–Elmer "B" column. The characteristic elution time ratio t_c/t_{CCl_4} at 75° was 0.67. The infrared spectrum of this iodide matched the spectra of samples of CF_3CH_2I prepared previously by iodide displacement on 2,2,2-trifluoroethyl tosylate[14] and by the thermal reaction of 1,1-difluoroethylene with iodine.[15]

Acknowledgment.—We wish to thank Dr. Arnold H. Fainberg for the chromatographic and infrared data, Mr. Fred P. Curtis for technical assistance and Mr. Howard Francis and co-workers for elemental analyses and ultraviolet spectra.

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[13] R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953).

[14] G. V. D. Tiers, H. A. Brown and T. S. Reid, *J. Am. Chem. Soc.*, **75**, 5978 (1953).

[15] M. Hauptschein, A. H. Fainberg and M. Braid, *J. Org. Chem.*, **23**, 322 (1958); the principal infrared bands for CF_3CH_2I are given therein.

COMMUNICATIONS TO THE EDITOR

THE RACEMIZATION OF L(+)-2α-TROPANOL

Sir:

When L(+)-2α-tropanol (I)[1] was treated at room temperature with acetic anhydride containing a drop of perchloric acid the acetate II, isolated as the hydrochloride,[2] was formed ($[\alpha]^{25}D$ + 39.5° (2.5% H_2O)). When I was refluxed overnight with acetic anhydride the acetate III was obtained (hydrochloride, m.p. 195–197° $[\alpha]^{25}D$ +0.0° (2.5% H_2O)). After three hours a mixture of II and III was formed from which a substantial amount of pure III·HCl was isolated. The infrared spectra

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[1] M. R. Bell and S. Archer, *J. Am. Chem. Soc.*, **82**, 4642 (1960).

[2] Elementary analyses of all new compounds are satisfactory. Analyses and optical rotations were carried out under the supervision of M. E. Auerbach and F. C. Nachod, respectively.