products was approximately three to four times as great as the conversion to products boiling higher, showing that under the conditions used here, the principal reactions were cracking and isomerization.

Of the two butanes, only isobutane was found in the products of the reaction. This agrees with the results reported by Ipatieff and Grosse,[6] and Nenitzescu and Dragan.[4]

The formation of *n*-hexane and 3,3-dimethylpentane from the action of aluminum chloride on *n*-heptane has been reported.[8] Neither of these hydrocarbons was obtained in our work. Cycloparaffins have been reported among the products from the action of aluminum chloride on *n*-heptane.[4] In agreement with the results reported by Calingaert and Beatty,[8] we found no cycloparaffins in the reaction products.

The hydrocarbons present in the largest amount in the reaction products had a methyl group in the 2-position of the carbon chain. The prominence of this type of product must be accounted for in any mechanism which is proposed for this reaction.

Summary

The action of aluminum bromide on *n*-hexane at temperatures from −30° to room temperature and *n*-heptane at temperatures from 22 to 98° has been studied.

In the absence of a promoter no appreciable reaction occurs. In the presence of hydrogen bromide as a promoter, cracking, isomerization and alkylation occur with the formation chiefly of branched chain paraffins with methyl groups in the 2-position.

The results indicate that cracking is preceded by isomerization. Under mild conditions isomerization is the chief reaction.

No normal paraffin, cycloparaffin or aromatic hydrocarbons were found.

CLEVELAND, OHIO RECEIVED MAY 29, 1944

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Action of Aluminum Bromide on Paraffin Hydrocarbons. II. Branched Chain Hexanes

BY JOHN W. BISHOP, ROBERT E. BURK AND HERMAN P. LANKELMA

Introductory

Previous work done in this Laboratory has shown that the principal products from the action of aluminum bromide on *n*-hexane at low temperatures are isomeric hexanes.[1] The present investigation is an extension of this study to the four branched chain hexanes.

Experimental

Preparation of Materials.—The preparation and purification of the aluminum bromide was carried out as described by Winter and Cramer.[2] The hydrogen bromide was prepared by the action of bromine on tetrahydronaphthalene.[3] The isomeric hexanes were obtained as follows:

The 2-methylpentane and 3-methylpentane were prepared from the alcohols 4-methylpentanol-2 and 2-ethylbutanol-1, respectively. The alcohol was dehydrated to olefin by passing the vapor over activated alumina at 360–400°. The olefin was fractionated in Column C, described in the experimental section, and then hydrogenated to the hexane at 140–160° over Raney nickel catalyst. The product was treated with sulfuric acid, washed with water, and dried with "Drierite."

2,3-Dimethylbutane was prepared from pinacol. Pinacol was dehydrated to diene over activated alumina at 450–470°. The diene was hydrogenated over Raney nickel and the product purified as described above.

2,2-Dimethylbutane was obtained through the courtesy of the Phillips Petroleum Company. It was found to contain no unsaturated hydrocarbons and was distilled in Column C without further treatment. Oberfell[4] and Frey report that it contains about 2% cyclopentane. This could not be removed by distillation since the difference in boiling point between the two hydrocarbons is only 0.4°. This small amount of cyclopentane would not, however, interfere with the identification of the reaction products since 2,2-dimethylbutane is the only paraffin hydrocarbon which boils within 9° of it. A middle fraction of this material was taken.

The physical constants of the four hexanes used in this work were as follows

	Boiling point, °C. (760 mm.)	n^{20}_D	d^{20}_4
2-Methylpentane	60.2	1.3716	0.6528
3-Methylpentane	63.0–63.3	1.3765	.6639
2,3-Dimethylbutane	58.0–58.1	1.3749	.6613
2,2-Dimethylbutane	49.6–49.7	1.3697	.6508

Experimental Procedure.—The apparatus and the technique used for carrying out the reactions were essentially those described by Grummitt.[1] Dry hydrogen bromide was used as a promoter in all the reactions.

Analysis of Products.—Products of the reaction were separated by distillation. For this purpose, two fractionating columns were used. Column A was a concentric tube vertical surface type with three annular spaces.[5] The efficiency of this column using the formula of Calingaert and Beatty was 104 theoretical plates at total reflux.[6] Low boiling material, isobutane, and isopentane were collected in a Dry Ice trap at the head of this column and redistilled through a Podbielniak type column. Column C was 40 inches long and about 15 mm. in internal diameter. It was packed with 3-mm. stainless steel

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(1) Grummitt, Sensel, Smith, Burk and Lankelma, THIS JOURNAL, **67**, 910 (1945).

(2) Winter and Cramer, *Ind. Eng. Chem.*, **32**, 856 (1940).

(3) Duncan, "Inorganic Syntheses," McGraw-Hill Book Co., New York, N. Y., 1939, Vol. I, page 151.

(4) Oberfell and Frey, *Refiner Nat. Gasoline Mfg.*, **18**, 486 (1939).

(5) Selker, Burk and Lankelma, *Ind. Eng. Chem., Anal. Ed.*, **12**, 352 (1940).

(6) Calingaert and Beatty, *Ind. Eng. Chem.*, **26**, 504 (1934).

TABLE I

MATERIAL BALANCE

	Expt. number →	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Before reaction	C_6H_{14}, g.	121.5	94.6	110.7	88.0	26.7[b]	34.5[b]	31.5	263.5	20.9	23.8	31.9
	$AlBr_3$, g.	7.7	9.7	14.5	8.6			6.4	36.2	6.5	6.6	8.6
	Total	129.2	104.3	125.2	96.6			37.9	299.7	27.4	30.4	40.5
After reaction	Upper layer, g.	90.2[a]	91.1	104.8	81.3	23.4	22.4	29.1	257.6	14.1	18.8	27.7
	Dissolved $AlBr_3$, g.		6.0	2.9	1.0	1.4	0.3	3.3	16.8	2.0	1.8	1.8
	Lower layer, g.		3.4	16.8	11.9		9.1	5.0	24.0	6.7	7.1	9.6
	Loss, g.	19.0	3.8	0.7	2.4	1.9	2.7	0.5	1.3	4.6	2.7	1.4
	Total, g.		104.3	125.2	96.6	26.7	34.5	37.9	299.7	27.4	30.4	40.5

[a] Total contents of flask after 20 g. had been removed for testing. [b] 52.8 g. of hydrocarbon and 8.3 g. of $AlBr_3$ were employed. After 337 hours, 26.7 g. was taken for analysis (Expt. V), the remainder was allowed to react for 512 hours and then analyzed (Expt. VI).

TABLE II

SUMMARY OF EXPERIMENTS WITH THE FOUR BRANCHED CHAIN HEXANES

Experiment number →	I	II	III	IV	XI	VIII	V	VI	VII	IX	X
Starting material	2-Methylpentane			2,2-Dimethylbutane			3-Methylpentane		2,3-Dimethylbutane		
Temperature, °C.	−16	−11	0	0	0	−16	−11	−11	−11	0	0
Time, hours	192.7	217	136.5	149	130	453	337	512	313	52.75	24
Conversion, %	34	39.2	82.8	20.5	32.8	0.1	83	90.2	25	96	93.3
Products, % of upper layer											
Isobutane[b]	0.4	1.1	6.8	1.8	7.0	....	1.3	[e]	....	10.6	8.4
Isopentane	1.45	1.4	23.3	8.0	13.3	....	3.2	26.9	0.1	19.3	19.1
2,2-Dimethylbutane	2.2	1.4	11.5	79.5	67.2	99.9	4.6	14.5	6.8	18.7	15.6
2,3-Dimethylbutane	2.9	9.95	7.2	[c]	[d]	...	17.5	10.0	74.9	4.0	6.7
2-Methylpentane	66.0	60.8	17.2			....	50.3	18.7	12.3	6.9	12.8
3-Methylpentane	24.9	17.6	8.4			....	17.0	9.8	....	3.2	4.9
Heptanes			7.2								
Octanes			5.7								
Residue	2.1	7.7	12.7	6.1	10.5	....	6.2	20.1	6.0	37.4	32.4
Grams distilled	76.0	35.2	44.2	41.3	26.8	....	22.6	21.9	28.3	13.2	18.0
Distillation loss, g.[a]	.....	.....	...	2.1	4.0	....	....	....	0.4	0.7	..

[a] In expts. I, II, III, VIII, V, VI, X, negligible. [b] No *n*-butane was found in any of the experiments. [c] Unidentified hexanes 4.6%. [d] Unidentified hexanes 2.5%. [e] Total isobutane and isopentane.

helices. It had a maximum efficiency of 27 theoretical plates and a holdup of about 15 cc. This column was used chiefly for purifying the hexanes used as starting materials. The temperature in the head of Column A was measured with a 5-junction copper–constantan thermocouple and a Leeds and Northrup recording potentiometer sensitive to less than 0.3 millivolt. The temperature in the head of the Podbielniak type column was measured with a 2-junction copper–constantan thermocouple. Individual samples taken in the distillation of the reaction products averaged about 0.3 cc. The hydrocarbons separated from the reaction products were identified by means of physical constants: boiling point and refractive index. Boiling points recorded were column head temperatures when the sample was taken. They were corrected to 760 mm. Refractive index was measured with a Zeiss Abbe refractometer maintained at 20 ± 0.05°. Densities were also determined on many fractions. This was done with a pycnometer.

Results.—Eleven experiments were carried out. The material balances obtained are shown in Table I.

The results of these experiments are shown in Table II. Typical distillation curves are shown in Figs. 1, 2, and 3. In experiments IV and XI there is some doubt of the composition of the fraction called unidentified hexanes (c and d), since none of the hexanes of this fraction could be definitely identified. Probably some 2,2-dimethylbutane and some heptanes were present. In experiment VII, it is evident from the distillation curve of Fig. 3 that the column does not separate closely a small amount of 2-methylpentane from a large amount of 2,3-dimethylbutane.

Discussion of Results

The results of experiments I, II and V show that both 2-methylpentane and 3-methylpentane can isomerize with but a trace of cracking. The almost constant relation between the per cent. of 2-methylpentane and 3-methylpentane obtained suggests that equilibrium between them was reached. The relative amount of each isomer is in good agreement with the equilibrium value calculated by Rossini, Prosen and Pitzer.[7] The effect of reaction time on the conversion of 3-methylpentane in experiments V and VI shows two points of interest; the five-fold increase in cracking with the longer reaction time and the marked change in the relative concentration of the hexanes. In experiment VI, as a result of

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(7) Rossini, Prosen and Pitzer, *J. Research Natl. Bur. Standards*, **27**, 529 (1941).

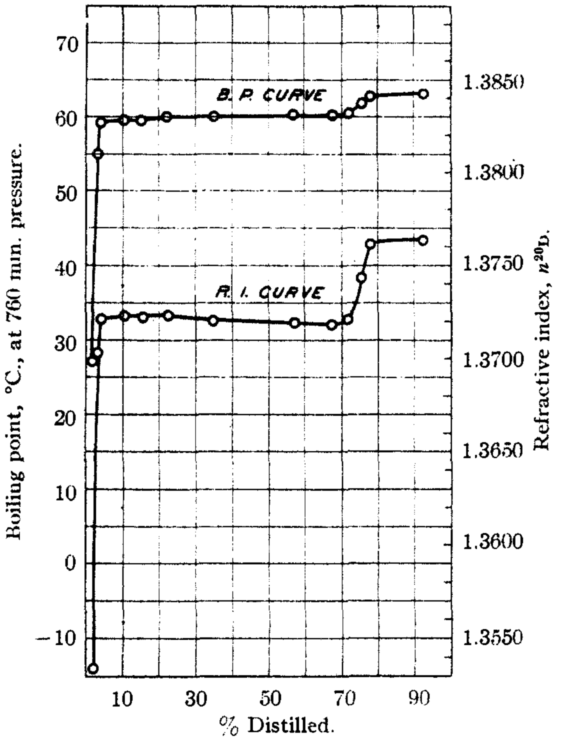

Fig. 1.—Distillation expt. II: 2-methylpentane–AlBr$_3$, 217 hours at −11°.

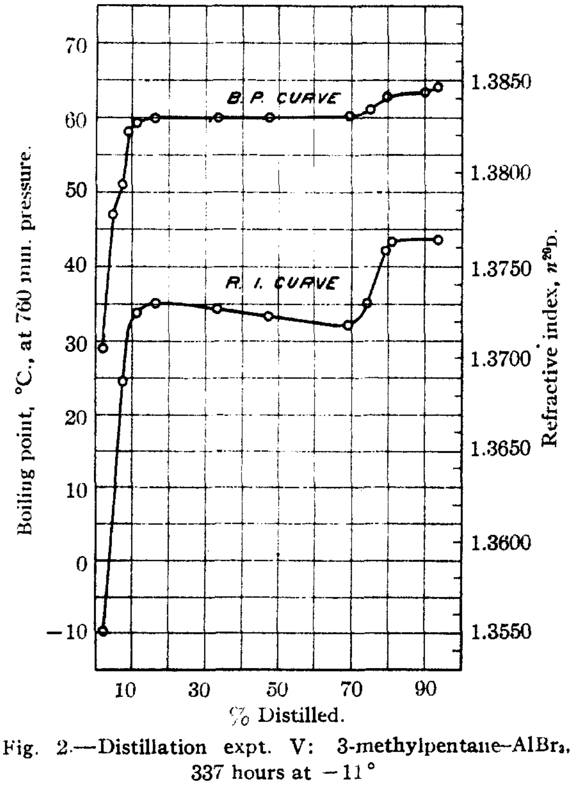

Fig. 2.—Distillation expt. V: 3-methylpentane–AlBr$_3$, 337 hours at −11°.

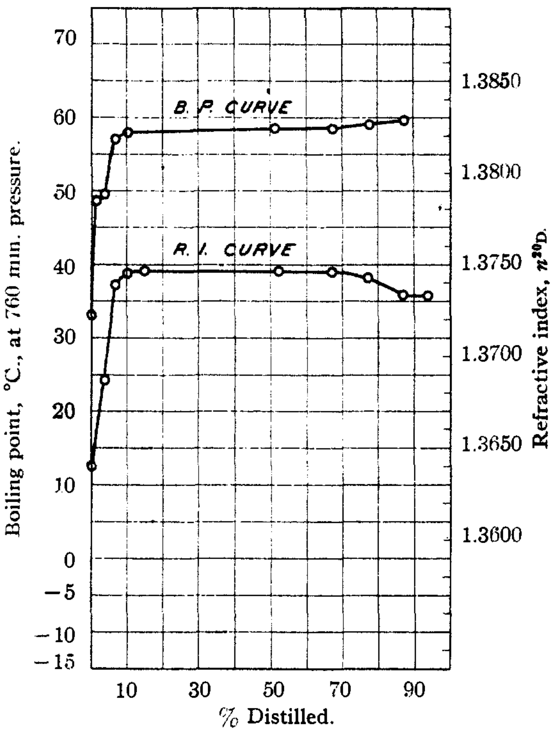

Fig. 3.—Distillation expt. VII: 2,3-dimethylbutane–AlBr$_3$, 313 hours at −11°.

the longer reaction time, the amount of 2-methylpentane diminished by about two-thirds and the amount of 2,3-dimethylbutane and 3-methylpentane by about one-half. On the other hand, the amount of 2,2-dimethylbutane formed more than tripled, probably as a result of cracking plus alkylation. The results of experiment VI compare quite closely with those of experiment III. It seems likely that since both experiments show a similar amount of cracking, this factor is responsible for the close agreement in results.

Experiment VIII shows that 2,2-dimethylbutane was not isomerized after 453 hours at −16°. The only reaction appeared to be a trace of cracking. At 0° also, no isomerization, only cracking, resulted, experiments IV and XI. This is in agreement with the results of Schuit, Hoog, and Verheus,[8] who were not able to isomerize it at 80°.

2,3-Dimethylbutane was isomerized but slowly at −11°, experiment VII. At 0° the chief reaction was cracking, experiments IX and X. The product in each of these experiments contained a large amount of material boiling higher than the hexanes indicating that the cracking was accompanied by considerable alkylation. 2,2-Dimethylbutane was a prominent product in both experiments.

The only low boiling hydrocarbons which we were able to identify from all of the reactions studied, were isobutane and isopentane. Straight

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(8) Schuit, Hoog and Verheus, *Rec. trav. chim.*, **59**, 793 (1940).

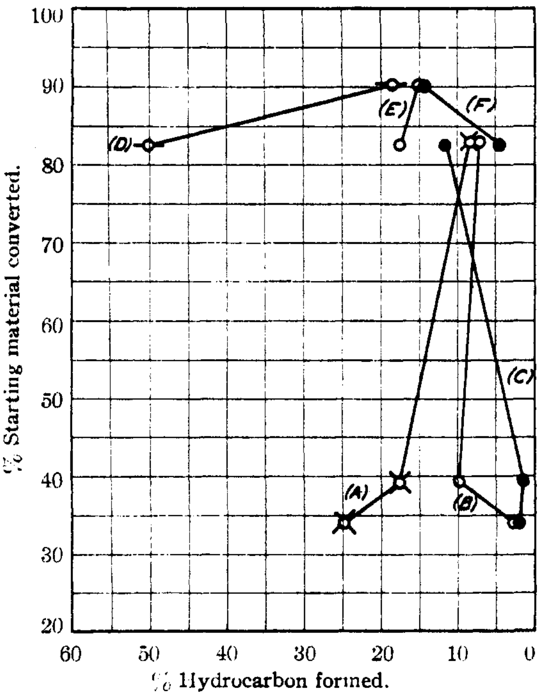

Fig. 4.—Relation of products formed to the amount of starting material converted: 2-methylpentane (reactant) *vs.* A, 3-methylpentane formed, -O-; B, 2,3-dimethylbutane formed, O; C, 2,2-dimethylbutane formed, ●; 3-methylpentane (reactant) *vs.* D, 2-methylpentane formed, -O-; E, 2,3-dimethylbutane formed, O; F, 2,2-dimethylbutane formed, ●

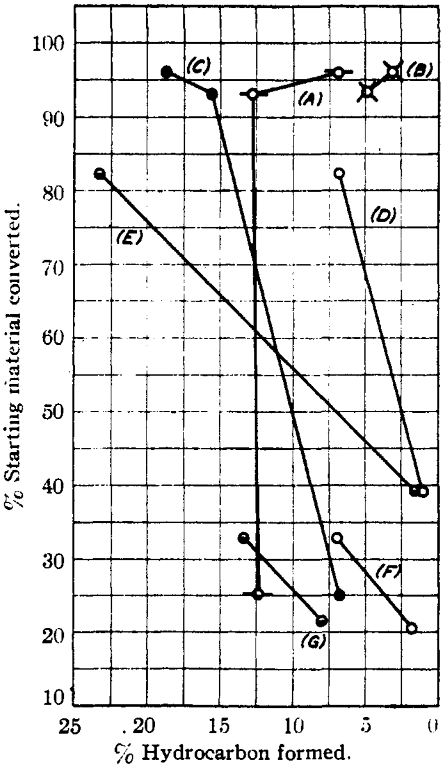

Fig. 5.—Relation of products formed to the amount of starting material converted: 2,3-dimethylbutane (reactant) *vs.* A, 2-methylpentane formed, -O-; B, 3-methylpentane formed, XX; C, 2,2-dimethylbutane formed, ●; 2-methylpentane (reactant) *vs.* D, isobutane formed, O; E, isopentane formed, ●; 2,2-dimethylbutane (reactant) *vs.* F, isobutane formed, O; G, isopentane formed, ●.

chain hydrocarbons were entirely absent. This is in agreement with the results reported by most previous workers.

Hydrocarbons boiling higher than the hexanes were formed in all experiments where appreciable cracking occurred. In one case, experiment III, the distillation was continued until a substantial portion of these higher hydrocarbons was distilled. The distillation curve showed the presence of branched chain heptanes and octanes with a considerable amount of higher boiling materials.

In all of the experiments there is a close correlation between the amount of cracking and the amount of 2,2-dimethylbutane obtained. It should be pointed out in comparing the results obtained at different temperatures that stable compounds formed by isomerization, cracking or alkylation at lower temperatures may not appear at higher temperatures due to further conversion. 2,2-Dimethylbutane is an example. Other workers have noted the almost complete absence of this hydrocarbon in the products of experiments made at room temperature and above, but the present work shows that at 0° and below all of the hexanes yield it in large amounts.

The relation between the amount of conversion and the amount of a given hydrocarbon obtained may give a clue to the mode of formation of the hydrocarbon. In Fig. 4, curves (a) and (b) show that the amounts of 3-methylpentane and 2,3-dimethylbutane decrease when a large amount of 2-methylpentane is decomposed. This indicates that cracking is not favorable to their formation. Curves (d) and (e) of Fig. 4 and curves (a) and (b) of Fig. 5 also show that the formation of 2-methylpentane, 3-methylpentane, or 2,3-dimethylbutane is not favored by cracking. Curves (c) and (f) of Fig. 4 and (c) of Fig. 5 show that the formation of 2,2-dimethylbutane is favored by cracking.

Any theory to account for the action of aluminum bromide on paraffin hydrocarbons must not only account for the various products obtained but must also show why certain hydrocarbons are conspicuously absent. The following results of the present work must be accounted for: 1. The ease with which the apparent equilibrium between 2-methylpentane and 3-methylpentane is attained. 2. 2,2-Dimethylbutane is not appreciably isomerized. 3. The absence among the reaction products of normal paraffins and of 2,2-dimethylpropane. 4. The amount of isobutane and isopentane formed is related to the amount of 2,2-dimethylbutane and high boiling material formed.

Summary

The action, at low temperatures, of anhydrous aluminum bromide promoted by hydrogen bromide upon the branched chain hexanes has been studied.

1. 2-Methylpentane and 3-methylpentane were isomerized with only traces of cracking yielding what was apparently an equilibrium mixture of the two.

2. Unlike its isomers, 2,2-dimethylbutane was not appreciably isomerized.

3. The formation of 2,2-dimethylbutane from the other hexanes has been correlated with cracking.

4. 2,2-Dimethylpropane and normal paraffin hydrocarbons were absent in all reaction products identified.

CLEVELAND, OHIO RECEIVED MAY 29, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Preparation of Polyfluorinated Acids*

BY ALBERT L. HENNE, THOMAS ALDERSON AND MELVIN S. NEWMAN

Fluorinated acids have been made by halogen substitution, but in poor yield due to extensive decomposition.[1] They have also been made by oxidation of fluorinated alcohols,[2] a procedure which is defeated by the difficulty of obtaining these alcohols. For trifluoroacetic acid, there is a practical preparation which consists in a lengthy heating of *m*-trifluorotoluidine with chromic acid, for a yield of 55 to 60%.[3] With trifluorotoluene now available commercially, this preparation could be made economically; it is, however, an individual case.

The method proposed here is the oxidation with alkaline permanganate of a judiciously fluorinated olefin. This method is made possible by the resistance of sufficiently fluorinated acids toward the haloform reaction. The oxidation is fast and almost quantitative. The limiting factors are that the fluorine atoms should be sufficient in number and should be properly placed. The method with its limitations is illustrated by the preparation of CF_3CO_2H from $CF_3CCl{=}CCl_2$, CHF_2CO_2H from $CHF_2CH{=}CCl_2$ and CF_2ClCO_2H from $CF_2ClCCl{=}CCl_2$ and by the failure to obtain $CFCl_2CO_2H$ from $CFCl_2CCl{=}CCl_2$. Its extension to the preparation of a number of acids with a CF_2 group in alpha position, and to ketones with a CF_2R or a $-CF_3$ group in alpha position is now under investigation. This method has been applied to preparations on a larger scale without further difficulties.

Experimental Details

Trifluoroacetic acid was prepared by oxidation of $CF_3CCl{=}CCl_2$,[4] in accordance with the equation: $3CF_3CCl{=}CCl_2 + 4KMnO_4 + 14KOH \rightarrow 3CF_3CO_2K + 4MnO_2 + 9KCl + 3K_2CO_3 + 7H_2O$. The apparatus consisted of a five-liter, three-neck flask fitted with an efficient reflux condenser, a sealed stirrer and a two-hole stopper bearing a thermometer dipping into the liquid and a separatory funnel. In the flask were placed 230 g. (calcd. 210 g.) of potassium permanganate, 260 g. (no excess)[5] of potassium hydroxide and 3 liters of water. The mixture was heated with continuous stirring to a temperature of 65–70°, which was then maintained throughout the oxidation. One mole (199 g.) of $CF_3CCl{=}CCl_2$ was added progressively, as fast as the refluxing caused by the reaction would permit The completion of the oxidation was detected by the disappearance of two-phase droplets in the reflux, usually after six to eight hours. At this stage a one-hour heating period at 100° may be resorted to, but is superfluous when the reaction has been conducted swiftly, with efficient stirring.

After cooling to 40°, the dropping funnel was replaced by an inlet tube reaching into the liquid, and a rapid stream of sulfur dioxide was passed until the purple color just disappeared. Sulfuric acid of 50% concentration was added through the reflux condenser until the carbon dioxide evolution ceased. The addition of sulfur dioxide was then resumed until the manganese dioxide just disappeared. This operation lasted about thirty minutes and required cooling to maintain the temperature below 60°; it should not be interrupted, lest the manganese dioxide should settle in a cake. The pink solution was neutralized until a permanent precipitate of manganese hydroxide just appeared, and then boiled down in the absence of air until crystals began to separate. After rapid cooling, one mole of 50% sulfuric acid was added; the crystals were allowed to settle and the supernatant liquid was decanted while cool. From the solution, trifluoroacetic acid was ether-extracted; with the ordinary glass devices for continuous extraction this took about thirty hours. Fractional distillation of the ether extract gave first ether which was used again in a subsequent operation, then a fraction boiling about 101° which was a mixture of 80% of trifluoroacetic acid with 20% of water. To isolate the pure acid, the sodium salt was formed by neutralization with a 20% solution of sodium carbonate, evaporation to dryness, extraction with absolute ethanol, and evaporation of the alcohol to leave anhydrous trifluoroacetate. A treatment of the salt with concentrated sulfuric acid yielded anhydrous trifluoroacetic acid. The net yield was 90%.

It is possible to avoid both the sulfur dioxide treatment and the ether extraction. After completion of the oxidation, the mixture is cooled, acidified with 50% sulfuric acid. The manganese dioxide is filtered off and extracted three times with 300-ml. portions of 25% sulfuric acid. The filtration and extraction are frequently inconvenient and this is the reason why the other procedure was preferred. The filtrate and washing are distilled until the

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* This manuscript, after acceptance for publication, was referred to the National Defense Research Committee, and at their request was withheld from publication until clearence was granted on May 5, 1945.

(1) Swarts, *Mém. Couronnés Acad. Roy. Belg.*, 51 (1895); 54 (1896); *Bull. Acad. Roy. Belg.*, [3] **31,** 675 (1896).

(2) Swarts, *Bull. classe sci., Acad. Roy. Belg.*, 757 (1902).

(3) Swarts, *ibid.*, 343–370 (1922).

(4) Prepared as shown in THIS JOURNAL, **63,** 3478 (1941); **64,** 1157 (1942).

(5) As much as 20% excess of caustic can be used but is not recommended. Larger excess, particularly in the case of higher concentrations, cause the formations of increasing amounts of fluoroform.