[CONTRIBUTION FROM THE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# Studies on Acid Iodides. II. The Cleavage of Aliphatic Ethers by Acid Iodides

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It has long been known that aliphatic ethers may be cleaved by acid chlorides at elevated temperatures in the presence of catalysts.[1] Recently it has been shown that the reaction proceeds at ordinary temperatures, though very slowly.[2] With acid chlorides it has not been possible to dispense with a catalyst.[3] Acid bromides, however, cleave ethers without the use of catalysts, though high temperatures are required to accomplish this result.[4]

More than twenty years ago Kishner[5] observed that benzoyl iodide was able to cleave ethers readily at 100° without a catalyst, forming alkyl iodides and benzoates. Since this isolated observation has not received the further investigation which its suggestive character would indicate, we have undertaken a comprehensive study of the reaction between acid iodides and ethers with the hope not only of developing a useful method for the investigation of ethers, but also of adding to our knowledge of the mechanism of the reaction between acid halides and ethers.

Due to the sluggishness of the reaction between benzoyl iodide and ethers, requiring a temperature of 100° for several hours, we have directed our attention to aliphatic acid iodides[6] with the hope that they would prove more reactive and that transformations with them might be obtained at ordinary temperatures. Thus the detrimental effect of elevated temperatures on unstable substances would be eliminated. This expectation has been entirely fulfilled.

When an aliphatic ether is treated with acetyl iodide, the reaction mixture becomes warm after a short induction period of often less than a minute. This heat, which we believe is due to the formation of an oxonium complex, is soon dissipated. If the mixture is allowed to stand at room temperature for two to five days, it is found that the ether has been cleaved with the formation of an alkyl iodide and an alkyl acetate. This reaction was found to proceed much faster with di-secondary ethers than with di-primary.

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(1) For a review of the literature see Meerwein and Maier-Hüser, *J. prakt. Chem.*, **134**, 51 (1932).

(2) Norris and Rigby, THIS JOURNAL, **54**, 2093 (1932).

(3) Descudé, *Compt. rend.*, **132**, 1129 (1901).

(4) Lydén, *Finska Kemistsamfundets Medd.*, **35**, 19–36 (1926); **37**, 53–71 (1928); **38**, 19–46 (1929); **38**, 72–84 (1929). *Chem. Abstracts*, **22**, 3880 (1928); **23**, 1868 (1929); **24**, 335 (1930); **24**, 1628 (1930).

(5) Kishner, *J. Russ. Phys.-Chem. Soc.*, **41**, 651–659 (1909); *Chem. Zentr.*, **2**, 1132 (1909). Compare also Blaise, *Compt. rend.*, **139**, 1211 (1904); **140**, 661 (1905); Staudinger and Anthes, *Ber.*, **46**, 1423 (1913).

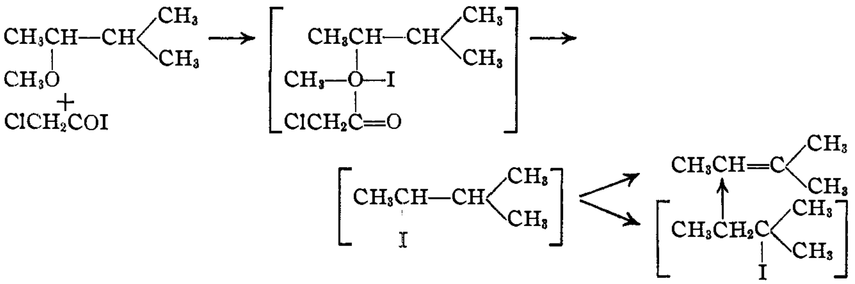
(6) Gustus and Stevens, THIS JOURNAL, **55**, 374 (1933).

After this work had been completed, a paper by Meerwein and Maier-Hüser[1] appeared in which these workers suggested the oxonium salt mechanism in the case of the acid iodides. Meerwein and Maier-Hüser, however, were not the first to use such a mechanism. Kishner,[5] the first to study ether cleavages by acid iodides, had already considered oxonium complex formation as a preliminary step to cleavage.

The molecular weight of primary ethers appears to influence slightly the ease with which they are cleaved. Thus the cleavage of di-*n*-propyl, di-*n*-butyl and diisoamyl ethers by acetyl iodide proceeds less readily as the molecular weight of the ether increases.

The introduction of chlorine into the ether molecule in the $\alpha$-position was found to affect greatly its stability toward acid iodides. Thus chloroacetyl iodide, which cleaves ordinary ethers readily, caused no cleavage of *sym*-dichlorodimethyl ether in twenty-five days at room temperature followed by six days at 100°. There was here no apparent evidence of oxonium complex formation. Possibly no oxonium complex formed, thus prohibiting cleavage.

The cleavage of unsymmetrical aliphatic ethers by acid iodides was also investigated. It was found with di-primary ethers that the greater proportion of iodine attached itself to the smaller alkyl group. This confirms Kishner's[5] observation with benzoyl iodide and is in accord with the work of Norris and Rigby[2] with acid chlorides. With mixed primary–secondary ethers about one-half of the iodine went to the smaller (in this case the primary) radical. In addition rearrangement products appeared. Thus the methyl ether of methylisopropylcarbinol with chloroacetyl iodide formed methyl iodide and trimethylethylene in about equal quantities. The latter substance may have come from methylisopropyliodomethane, or from tertiary-amyl iodide, a rearrangement product[7]



Norris and Rigby[2] have already shown that methyl isobutyl ether and acetyl chloride in the presence of zinc chloride form mainly isobutyl chloride with some tertiary-butyl chloride, a rearrangement product.

Acid iodides are practically always contaminated with dissolved iodine. It was thought that this substance might be acting as a catalyst in ether

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(7) Compare Wischnegradski, *Ann.*, **190**, 342 (1878).

cleavages. For this reason attempts were made to cleave ethers with acetyl chloride using iodine as a catalyst. After long standing at room temperature, no evidence of any reaction could be found.

The structure of the acid iodide in ether cleavage reactions is almost as important as the structure of the ether itself. The introduction of chlorine into the iodide has a marked effect. Thus chloroacetyl iodide was found to cleave ethers less readily than acetyl iodide, and dichloroacetyl iodide was very much less reactive. Definite evidence of a reaction between trichloroacetyl iodide and either primary or secondary ethers at room temperature could not be obtained. The same result was observed when zinc iodide was used as a catalyst. It is probable that an oxonium complex was first formed in each case, for heat was liberated when the iodide and ether were mixed. This was particularly noticeable with diisopropyl ether, but no cleavage took place. A very small amount of cleavage possibly occurred with diethyl ether at 100° after three hours. This failure of trichloroacetyl iodide to cleave ethers cannot be attributed to the lack of a hydrogen atom in the $\alpha$-position to the carbonyl group since benzoyl iodide, which has no $\alpha$-hydrogen atom, is able to cleave them.

Acid iodides not only cleave oxygen ethers, but thioethers as well. This was not unexpected for Cahours[8] had already reported the cleavage of thioethers by acid bromides at elevated temperatures, and had mentioned that acid iodides behaved similarly, though more vigorously. He failed, however, to report any experimental evidence. Owing to the criticism of his work by Obermeyer,[9] and the doubtful purity of the acid iodide available to him, this unsupported statement required further investigation.

While thioethers are cleaved by acid iodides, the rate of cleavage is very much slower than that of oxygen ethers. The cleavage products, in the case of diethyl sulfide, were ethyl iodide and ethyl thiolacetate. This slower cleavage may be due to the fact that the —S—C bond is in general stronger than the —O—R bond. Acetyl chloride without catalysts failed completely to cleave diethyl sulfide after seven days at 100°.

One of the most reactive ethers is ethylene oxide. Little work has been done on its reaction with acid halides.[10] Ethylene oxide reacts so vigorously with halogen acids that reactions with acid halides might be easily misinterpreted as true cleavages by the halide rather than as a chain reaction caused by small amounts of halogen acid present. Acetyl iodide reacts very vigorously with ethylene oxide even at −80°, and the reaction is so rapid that it seems quite reasonable to suppose true cleavage takes place. The product is $\beta$-iodoethyl acetate. The reaction with acetyl chloride was also tried, using acetyl chloride which had been freed from hydrogen chloride by distillation from dimethylaniline. Precautions were

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(8) Cahours, *Bull. soc. chim.*, [2] **25**, 563 (1876); *Compt. rend.*, **81**, 1163 (1876).

(9) Obermeyer, *Ber.*, **20**, 2921 (1887).

(10) Bodforss, *Ahrens Sammlung*, **26**, 221 (1920); Altwegg and Landrivon, U. S. Patent 1,393,191.

taken to exclude all moisture. There was no apparent reaction at −80° nor at room temperature. After forty-four days, the material was fractionated directly. The yield of β-chloroethyl acetate was about 90%.

A similar experiment was made with acetyl chloride and ethylene oxide in the presence of a small amount of iodine. Here considerable heat was evolved at the outset. After three and a half days at room temperature, the yield of β-chloroethyl acetate was about 30%. If instead of iodine one drop of concentrated hydrochloric acid was used, the yield of β-chloroethyl acetate after two and a half days was about 75%. From these experiments it appears as if acetyl chloride may slowly cleave this very reactive ether without a catalyst at room temperature. A further investigation of this reaction, however, is now in progress.

When equivalent quantities of ethylene oxide, acetyl chloride and iodine were mixed at −80°, at first no reaction occurred. The sealed tube containing the reaction mixture, now dark brown from dissolved iodine, was removed from the freezing mixture and shaken in the daylight. About fifteen seconds later, the tube exploded with great violence, although still at a low temperature. The formation of an iodo-hypoiodite at −80° reasonably accounts for the detonation.[11]

Although aromatic ethers, such as diphenyl ether and diphenylene oxide are unattacked by hydriodic acid even at 250°,[12] they were found to react vigorously with acetyl iodide at room temperature. This reaction will be made the subject of a future communication.

Though all acetyl iodides form oxonium complexes with ethers, the progressive introduction of chlorine decreases their ability to cleave ethers. The formation of a complex is, therefore, no criterion of subsequent cleavage. Halogen substitution apparently stabilizes the oxonium complex in some way not yet understood.

If the acid halides are compared with the hydrogen halides in regard to their reactivity toward ethers,[13] it will be seen that acid chlorides resemble hydrogen chloride. Since hydrogen halides, acid bromides[14] and iodides do form oxonium complexes with ethers, it is not unreasonable to suppose that acid chlorides may also do so, though to a very much less extent. The metal or non-metal halide used with acid chlorides as a catalyst for ether cleavage may greatly facilitate the formation of the oxonium complex, but it seems to us that the important role of the catalyst is rather the promotion of the decomposition of this complex.

We wish to express our thanks to Dean Frank C. Whitmore of the School of Chemistry and Physics of the Pennsylvania State College for laboratory

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(11) Compare Birckenbach and Goubeau, *Ber.*, **65B**, 397 (1932); Maass and Boomer, THIS JOURNAL, **44**, 1709–1721 (1922).

(12) Hoffmeister, *Ber.*, **3**, 747 (1870).

(13) Hantzsch, *ibid.*, **54B**, 1851 (1921).

(14) Based on the fact that acid bromides cleave ethers without catalysts at elevated temperatures.

facilities, to the Mallinckrodt Chemical Works for so generously donating the large quantities of iodine consumed in this research, and to E. I. du Pont de Nemours, Inc., for kindly contributing the dimethyl ether used in our experiments. Part of the funds required for this research were privately contributed.

## Experimental Part

**Acetyl Iodide and Di-*n*-propyl Ether.**—12.25 grams (0.12 mole) of di-*n*-propyl ether, b. p. 89–90.2° (from metallic sodium) was treated with 17 g. (0.10 mole) of acetyl iodide. The usual warming of the mixture was noticed, and the tube was allowed to stand protected from light at 25°. After eighty-nine hours, the reaction mixture was shaken with a saturated sodium carbonate solution, and 50 cc. of diisoamyl ether was added. After drying over anhydrous potassium carbonate, the solution was cooled, treated with 10 g. of anhydrous trimethylamine, and allowed to stand for twelve days at 25°, and then for six days at 65°. At the end of this time the solution was repeatedly washed with water, and the washings evaporated *in vacuo* over sulfuric acid; 10.5 g. of trimethyl-*n*-propylammonium iodide was obtained, which separated as platelets from absolute alcohol. The diisoamyl ether extract, after drying, was fractionated twice, finally yielding 0.45 g. of *n*-propyl acetate.

The following reactions were carried out in essentially the same way as described for *n*-propyl ether. Those marked with an asterisk are described in detail.

| Iodide | Ether | Ammonium iodide | M. p., °C. | Yield, % | Acetate | B. p., °C. (730 mm. ±) | $n^{20}_D$ | Hours |
|---|---|---|---|---|---|---|---|---|
| Acetyl | Dimethyl | Trimethylphenyl | 210–211 | 88.2 | Methyl | 55 - 56.6 | 1.3636 | 240 |
| | Di-*n*-propyl | Trimethyl-*n*-propyl | 185–186 | 45.8 | *n*-Propyl | 100 –102 | 1.3839 | 89 |
| | Di-*n*-butyl | Trimethyl-*n*-butyl | 230–231 | 45.2 | *n*-Butyl | 126 –130 | 1.3969 | 89 |
| | Diisoamyl | Trimethylisoamyl | 193–194 | 41.2 | Isoamyl | 139.2–141.2 | 1.4054 | 89 |
| | Diisopropyl | Trimethylisopropyl | 285–286 | 73.1 | Isopropyl | 87 - 88 | 1.3954 | 89 |
| | *Diethyl sulfide | Triethyl sulfonium cadmium iodide double salt | 154 | 13.2 | Ethyl thiol | See text | | 1296 |
| | *Ethylene oxide | | | 73.8 | β-Iodoethyl | 95 - 96 (43 mm.) | 1.5072 | 20 ± |
| Chloro-acetyl | *Diethyl | Dimethylethyl-phenyl | 135–136 | 90.9 | Ethyl chloro | 141.6–141.9 | 1.4217 | 120 |
| Dichloro-acetyl | Diethyl | Dimethylethyl-phenyl | 135–136 | 24.6 | Ethyl dichloro | 150 –152 | 1.4308 | 144 |
| Trichloro-acetyl | *Diisopropyl | No reaction | | | | | | 168 |

**Acetyl Iodide and Diethyl Sulfide.**—37.5 grams of acetyl iodide was treated with 70.5 g. of diethyl sulfide in the usual way. After twenty days, golden-yellow crystals of triethylsulfonium iodide began to separate. After fifty-four days the reaction mixture was shaken well with water, the aqueous layer separated, and the non-aqueous layer shaken for twenty-four hours with water to convert any ethyl iodide into the soluble triethylsulfonium iodide. This aqueous layer was separated, added to the previously obtained washings, and the whole neutralized with dilute sodium hydroxide. There was a large amount of acid, indicating much unreacted acetyl iodide. The neutralized solution was concentrated *in vacuo* to about 150 cc., filtered hot and treated with an excess of hot, filtered, half-saturated cadmium iodide solution. After twelve hours at 0°, the sparingly soluble crystalline double salt, $[(C_2H_5)_3SI]_2CdI_2$, was collected, washed with water and alcohol and air dried. It weighed 25 g., corresponding to 4.54 g. of ethyl iodide. It melted at 119–120° and showed no depression when mixed with a known sample which had been recrystallized from dilute cadmium iodide solution.

When recrystallized from alcohol, it melted at 154°[15] and showed no depression when mixed with a known sample, also from alcohol. It lost no weight in drying at 110° and 20 mm.

*Anal.* Calcd. for $C_{12}H_{30}S_2I_4Cd$: I, 59.13. Found: I, 58.95.

The non-aqueous portion consisted of excess diethyl sulfide and ethyl thiolacetate. As it was impossible to separate these two compounds by distillation, the diethyl sulfide was removed by diluting with diethyl ether, shaking up with water and excess methyl iodide until the aqueous extracts gave no precipitate of $[CH_3(C_2H_5)_2SI]_2CdI_2$ with cadmium iodide solution.[16] The ether extract, having the odor of ethyl thiolacetate, was dried and fractionated. The residue, boiling above 92°, was converted into ethyl mercaptochloride for identification according to the method of Sachs.[17] The ethyl mercaptochloride was recrystallized from a large volume of boiling xylene, separating in the form of characteristic hexagonal plates. It was dried at 110° and 20 mm.

*Anal.* (micro Carius). Calcd. for $C_2H_5SHgCl$: S, 10.79. Found: S, 10.70.

**Acetyl Iodide and Ethylene Oxide.**—Sixty-two grams of acetyl iodide, dissolved in an equal volume of carbon tetrachloride, was placed in a strong Pyrex tube, and the solution was frozen and cooled to −80°, carefully excluding moisture. An excess (20 cc.) of ethylene oxide was distilled in, and the tube sealed and shaken in the freezing bath. As soon as the reaction started, the frozen layer began to melt, and in a few moments complete mixing had occurred. The reaction proceeded with the liberation of much heat, as evidenced by the rapid vaporization of the carbon dioxide from the cooling bath. Within five minutes, the violence of the reaction had subsided, and the contents of the tube consisted of a dark, mobile liquid. After standing overnight at 25°, the tube was opened and the excess ethylene oxide allowed to evaporate. The reaction product, examined in the usual way, was fractionated *in vacuo.*

| | | | |
|---|---|---|---|
| 1st fraction | b. p. (43 mm.) 90–95° | 2.4 g. | |
| 2d fraction | b. p. (43 mm.) 95–96° | 46.7 g. | 73.8% yield |
| Residue | | 8.5 g. | |

The second fraction, β-iodoethyl acetate, had a sharp, fruity odor, and its vapor attacked the eyes. When colorless the refractive index was $n^{20}_{D}$ 1.5072.

*Anal.* ($PdI_2$). Calcd. for $C_4H_7O_2I$: I. 59.30. Found: I, 58.99.

**Acetyl Chloride and Ethylene Oxide.**—25.3 grams of acetyl chloride, freshly distilled from dimethylaniline, was treated with 18 g. of dry ethylene oxide. There was no obvious reaction at −80° nor at 25°. After standing for forty-four days at 25°, the excess of ethylene oxide (contaminated with acetaldehyde) and unreacted acetyl chloride were removed at 25° *in vacuo* and the residue fractionated, the second fraction being practically pure β-chloroethyl acetate.

| | | | | |
|---|---|---|---|---|
| 1st fraction | b. p. (733 mm.) up to 142.4° | $n^{20}_{D}$ 1.4215 | 2.5 g. | 95.7% yield |
| 2d fraction | b. p. (733 mm.) 142.4–143.8° | $n^{20}_{D}$ 1.4235 | 29.0 g. | |
| Residue | | $n^{20}_{D}$ 1.4333 | 6.3 g. | |

**Acetyl Chloride, Ethylene Oxide and Hydrochloric Acid.**—25.3 grams of the same pure acetyl chloride, 18 g. of dry ethylene oxide, and one drop of concentrated hydrochloric acid were treated exactly as in the preceding experiment but for only two and a half days.

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(15) Compare Ray. Adhikari and Banerjee. *J. Indian Chem. Soc.*, **8**, 739 (1931); *Chem. Abstracts*, **26**, 3199 (1932).

(16) Procedure suggested by Mr. J. M. Herndon of this Laboratory.

(17) Sachs, *Ber.*, **54B**, 1851 (1921).

| | | | |
|---|---|---|---|
| 1st fraction b. p. (732 mm.) 138–143° | $n_{\mathrm{D}}^{20}$ 1.4229 | 6.0 g. | 77.9% yield |
| 2d fraction b. p. (732 mm.) 143–144° | $n_{\mathrm{D}}^{20}$ 1.4240 | 18.8 g. | |
| Residue | $n_{\mathrm{D}}^{20}$ 1.4316 | 6.0 g. | |

**Acetyl Chloride, Ethylene Oxide and Iodine.**—"A," 25.3 g. of the same pure acetyl chloride was treated with 18 g. of dry ethylene oxide and 10 mg. of resublimed iodine. At −80° there was no apparent reaction but on warming to room temperature the iodine dissolved, giving the solution a brown color, which, however, soon disappeared. The tube became slightly warm and remained so for several minutes. After three and a half days at 25° the material was treated exactly as before.

| | | | |
|---|---|---|---|
| 1st fraction b. p. (723 mm.) 138–143° | $n_{\mathrm{D}}^{20}$ 1.4235 | 3.5 g. | 31.3% yield |
| 2d fraction b. p. (723 mm.) 143–144° | $n_{\mathrm{D}}^{20}$ 1.4242 | 3.5 g. | |
| Residue | $n_{\mathrm{D}}^{20}$ 1.4401 | 5.4 g. | |

"B," 26.5 g. of the same pure acetyl chloride was treated with 17.5 g. of dry ethylene oxide and 38.6 g. of dry, powdered, resublimed iodine. After sealing, the tube was removed from the cooling bath and shaken without protection from light. After fifteen seconds the tube exploded with great violence.

**Acetyl Chloride, Diisoamyl Ether and Iodine.**—Eighteen cc. of the same pure acetyl chloride was treated with 25 cc. of diisoamyl ether and 15 mg. of resublimed iodine. The iodine color slowly disappeared. After 44 days at 25°, the contents of the tube were examined in the usual way. The diisoamyl ether was recovered unchanged, and no evidence of cleavage of the ether could be found.

**Chloroacetyl Iodide and Diethyl Ether.**—Fifty-six grams of chloroacetyl iodide was treated with an excess (44 g.) of diethyl ether in the usual way. After five days, the products were carefully fractionated:

| | | |
|---|---|---|
| 1st fraction b. p. (736 mm.) 36–71.7° | $n_{\mathrm{D}}^{20}$ 1.4524 | 7.2 g. |
| 2d fraction b. p. (736 mm.) 71.7–72.2° | $n_{\mathrm{D}}^{20}$ 1.5077 | 28.5 g. |
| 3d fraction b. p. (736 mm.) 72.2–74° | $n_{\mathrm{D}}^{20}$ 1.5098 | 4.9 g. |
| 4th fraction b. p. (736 mm.) 74–141.6° | $n_{\mathrm{D}}^{20}$ 1.4292 | 8.0 g. |
| 5th fraction b. p. (736 mm.) 141.6–141.9° | $n_{\mathrm{D}}^{20}$ 1.4217 | 19.5 g. |
| Residue | $n_{\mathrm{D}}^{20}$ 1.4262 | 4.0 g. |

The second and third fractions were practically pure ethyl iodide, further identified by conversion into dimethylethylphenylammonium iodide. The fifth fraction, as shown by analysis and physical constants, was pure ethyl chloroacetate.

*Anal.* (micro). Calcd. for $C_4H_7O_2Cl$: C, 39.18; H, 5.76. Found: C, 39.30; H, 5.85.

The total yield of ethyl iodide was 90.9% and of ethyl chloroacetate 92.2%.

**Chloroacetyl Iodide and *n*-Butyl Methyl Ether.**—Forty-five grams of chloroacetyl iodide was treated with 22 g. of *n*-butyl methyl ether, b. p. (737 mm.) 69.8–70° (from metallic potassium). On mixing, the usual increase in temperature was noticed. After two weeks the contents of the bulb were partially fractionated to obtain the methyl iodide formed.

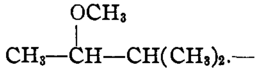
| | |
|---|---|
| 1st fraction b. p. (729 mm.) 42–43° | 22.6 g. |
| 2d fraction b. p. (729 mm.) 43–75° | 12.0 g. |

The residue was then treated to remove any acetyl iodide, dried and fractionated.

| | | |
|---|---|---|
| 3d fraction b. p. (727 mm.) 72–111° | $n_{\mathrm{D}}^{20}$ 1.4325 | 1.0 g. |
| 4th fraction b. p. (727 mm.) 111–135° | | 4.4 g. |
| 5th fraction b. p. (727 mm.) 135–178.2° | $n_{\mathrm{D}}^{20}$ 1.4522 | 4.9 g. |
| 6th fraction b. p. (727 mm.) 178.2–179° | $n_{\mathrm{D}}^{20}$ 1.4313 | 17.4 g. |
| Residue | | 4.8 g. |

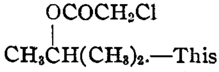
The first fraction, consisting of practically pure methyl iodide, and the second fraction were converted into trimethylphenylammonium iodide, giving 42.5 g. of the salt, m. p. 211–12°, 73.2% yield. The fourth fraction was *n*-butyl iodide. identified as trimethyl-*n*-butylammonium iodide, m. p. 230°, yield 13.3%. The sixth fraction was pure *n*-butyl chloroacetate.

**Chloroacetyl Iodide and Methylisopropylcarbinol Methyl Ether.**—Forty-five grams of chloroacetyl iodide was treated with 25 g. of methylisopropylcarbinol methyl ether. The usual increase in temperature was noticed on mixing. After sixteen days the tube was opened and the low boiling products were fractionated off directly: 36.5 g. of material, b. p. (731 mm.) 33–53°, was obtained. Floating on this distillate was about 0.5 g. of water. At present it is not possible to account definitely for the formation of water in this reaction. The distillate was diluted with benzyl alcohol, washed with dilute sodium carbonate, dried and treated with an excess of freshly distilled dimethylaniline. After standing for twenty-four hours the trimethylethylene was fractionated from this mixture; 13.9 g. of material, b. p. (730 mm.) 33–36°, was obtained which had the odor of trimethylethylene, reacted instantly with bromine in carbon tetrachloride without the formation of hydrogen bromide and gave a copious yellow precipitate with Denigès' reagent.[18] The trimethylphenylammonium iodide in the residue was precipitated with benzene, collected and washed with petrolic ether; wt. 20 g., m. p. 208°, 33.5% yield. The original residue from which the methyl iodide and trimethylethylene had been distilled was so decomposed that no homogeneous material could be isolated from it.



**Preparation of Methylisopropylcarbinol Methyl Ether,** $CH_3\text{—}\overset{\overset{OCH_3}{|}}{C}H\text{—}CH(CH_3)_2$.—132 grams of methylisopropylcarbinol, b. p. (734 mm.) 111–112°, dissolved in 800 cc. of pure *p*-cymene, was treated with a large excess (120 g.) of bright potassium shot. The material, after six hours on the steam-bath. was boiled for two hours. After cooling, 340 g. of redistilled dimethyl sulfate was slowly added. When the reaction had subsided, the reaction mixture was boiled for twelve hours and fractionated several times, yielding 86 g. of pure methylisopropylcarbinol methyl ether, b. p. (737 mm.) 81.2–81.5°, $d_{20}^{20}$ 0.7600, $d_4^{20}$ 0.7586, $n_D^{20}$ 1.3850.

*Anal.* (micro). Calcd. for $C_6H_{16}O$: C, 70.51; H, 13.82. Found: C, 70.45; H, 13.78.



**Preparation of Methylisopropylcarbinol Chloroacetate,** $CH_3\overset{\overset{OCOCH_2Cl}{|}}{C}H(CH_3)_2$.—This substance was an expected cleavage product from methylisopropylcarbinol methyl ether, but was not thus obtained. It was prepared from the carbinol with chloroacetyl chloride in benzene solution and potassium carbonate, b. p. (738 mm.) 180–181°, $d_{20}^{20}$ 1.0437, $d_4^{20}$ 1.0418, $n_D^{20}$ 1.4298.

*Anal.* (micro). Calcd. for $C_7H_{13}O_2Cl$: C, 51.05; H, 7.96. Found: C, 51.15: H, 8.20.

**Chloroacetyl Iodide and *Sym*-dichlorodimethyl Ether.**—Fifty grams of chloroacetyl iodide was treated with 31.25 g. of *sym*-dichlorodimethyl ether, b. p. (736 mm.) 101.2–101.5°. The usual increase in temperature on mixing was not noticed. After twenty-five days, a small sample was withdrawn. It reacted with water and dissolved completely, indicating that no reaction had occurred. The tube was re-sealed and heated to 100° for six days. On re-examination, large amounts of unchanged acid iodide and *sym*-dichlorodimethyl ether were found, and no material insoluble in water save a little separated iodine was observed. Since the products expected, chloroiodomethane which is insoluble in water. and chloromethyl chloroacetate which reacts slowly with water and

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[18] Denigès. *Compt. rend.*, **126**, 1145, 1277 (1898).

is sparingly soluble, were obviously absent, it was concluded that no reaction had taken place.

**Trichloroacetyl Iodide and Diethyl Ether.**—32.7 grams of trichloroacetyl iodide was treated with an excess (23.3 g.) of diethyl ether. There was a very slight increase in temperature on mixing. After one hundred and twelve hours, the reaction products were examined in the usual way, but only unchanged diethyl ether was recovered, and no evidence of any cleavage could be found. A similar result was obtained with one gram of zinc iodide dissolved in the reaction mixture.

**Trichloroacetyl Iodide and Diisopropyl Ether.**—Thirty grams of trichloroacetyl iodide was treated with 12 g. of diisopropyl ether. On mixing there was a very considerable increase in temperature. After seven days at 25°, the contents of the tube were examined in the usual way. Diisopropyl ether was recovered, and no evidence of any cleavage of the ether was observed. Another tube containing, in addition, 1 g. of zinc iodide gave a similar result. In this case, however, practically all of the zinc iodide remained undissolved.

**Trichloroacetyl Iodide and Diethyl Ether at 100°.**—Twelve grams of trichloroacetyl iodide was treated with 4 g. of diethyl ether and heated to 100° for three hours. On working up the material in the usual way, about 0.2 cc. of a heavy liquid with a fruity odor was obtained which gave qualitative tests for both chlorine and iodine. While too small in amount to permit separation and purification of the components, it probably consisted of ethyl trichloroacetate and ethyl iodide, contaminated with unchanged diethyl ether. It is possible that a slight amount of cleavage of the ether took place.

## Summary

1. The reactions between acetyl iodide and dimethyl ether, di-*n*-propyl ether, diisopropyl ether, di-*n*-butyl ether, diisoamyl ether, diethyl sulfide and ethylene oxide have been studied.

2. The reactions between chloroacetyl iodide and diethyl ether, *n*-butyl methyl ether and methylisopropylcarbinol methyl ether have been studied.

3. The introduction of chlorine into acetyl iodide has been found to diminish progressively its ability to cleave ethers, trichloroacetyl iodide being unable to cleave ethers at room temperature.

4. Di-secondary ethers react much more rapidly with acid iodides than di-primary ethers. Increasing the molecular weight of di-primary ethers decreases slightly the rate of cleavage.

5. *Sym*-dichlorodimethyl ether could not be cleaved by chloroacetyl iodide.

6. No reaction was observed at room temperature between primary ethers and acetyl chloride in the presence of dissolved iodine.

7. No reaction was observed between diethyl sulfide and acetyl chloride after one week at 100°.

8. The reaction between acetyl chloride and ethylene oxide has been studied.

9. The preparation and some physical constants of methylisopropylcarbinol methyl ether and methylisopropylcarbinol chloroacetate have been described.

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