solution was seeded with the 89° form. (ii) A sample of commercial sucrose octaacetate had m. p. 72–74°. One crystallization from ether gave material of m. p. 86–87°. Crystallization from alcohol, acetic acid, water and chloroform gave in all cases products melting between 80° and 88°, and after further crystallization at 89°. (iii) In quantitative conversions, 7.4 g. of the octaacetate, m. p. 72–74°, yielded 7.1 g. of m. p. 88° after two crystallizations from ether. In another experiment 5.6 g. of the low melting octaacetate was dissolved in ether. The solution was filtered, seeded with the 89° octaacetate and the solvent removed; 5.6 g. of product was obtained, m. p. 87–88°. (iv) On one occasion a product melting at 72° was obtained by the use of the procedure employed in experiment 2. At the end of two days, the specimen had changed to the high melting compound (89°). Many attempts were made to repeat this experiment but the high melting compound was always obtained.

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COLUMBUS, OHIO
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Hydrogen Bonds Involving the C–H←F Link. XII[1]

BY C. S. MARVEL, M. J. COPLEY[2] AND E. GINSBERG

Although strong F–H←F bonds are present in the solid, liquid, and vapor phases of hydrogen fluoride, almost no evidence has been presented heretofore to indicate that a fluorine atom attached to a carbon atom is capable of acting as a donor atom for hydrogen bond formation. Zellhoefer, Copley, and Marvel[3] noted that the substitution of fluorine for chlorine in chloroform and in methylene chloride decreases the ratio of their observed to "ideal" (calculated from Raoult's law) solubilities at 3° in donor solvents. This effect is illustrated by the data[3] given in Table I when dimethyl ether of tetraethylene glycol is used as the solvent. The solubilities of the halogenated hydrocarbons were determined at partial pressures corresponding to their vapor pressure at 3°.

TABLE I

SOLUBILITY OF HALOGENATED HYDROCARBON IN TETRAETHYLENEGLYCOL DIMETHYL ETHER AT 3°

	Mole fraction Obsd.	Ideal	Ratio Obsd./Ideal
$CHCl_3$	0.625	0.283	2.20
$CHCl_2F$	.706	.381	1.85
$CHClF_2$	.740	.449	1.65
CH_2Cl_2	.600	.311	1.93
CH_2ClF	.647	.398	1.62

The decrease in the ratio may be explained by assuming that the smaller negative deviations observed with the fluorine derivatives are caused by weak C–H←F bonds between fluorinated hydrocarbon molecules. Unfortunately, fluoroform, for which the effect might be expected to be a maximum, is difficult to obtain and was not available.

It occurred to the authors that further evidence might be discovered by making a comparison of the heats of mixing with donor liquids of the vinylogs[4] $C_6H_5CF_3$ and $C_6H_5CCl_3$, respectively, of CHF_3 and $CHCl_3$. One would predict that the para hydrogens of the vinylogs are sufficiently activated to form hydrogen bonds with donor nitrogen or oxygen atoms. If the fluorine atoms have donor properties, some association through C–H←F bonds should be present in $C_6H_5CF_3$. The breaking of these bonds to form more stable C–H←N or O bonds on mixing with a donor liquid would lead to a smaller heat of mixing for $C_6H_5CF_3$ than for $C_6H_5CCl_3$. (This prediction contains the assumption that a chlorine atom does not bond or that at most it has a smaller donor capacity than a fluorine atom.)

The method followed in making these measurements has been described in a previous publication.[5] The data are tabulated in Table II.

TABLE II

HEATS OF MIXING IN CALORIES PER MOLE OF SOLUTION AT 3° FOR EQUIMOLAR MIXTURES

	Benzotrifluoride	Benzotrichloride
N,N-Dimethylacetamide	125	305
Dimethylcyclohexylamine	120	410
Ethyl phosphate	135	160
Ethyl ether	140	123
Acetone	40	40

The maxima in the heat of mixing curves occurred at approximately equimolar mixtures. A pronounced effect in the expected direction was observed with each of the nitrogen compounds but the results with the oxygen compounds are not conclusive. Apparently the para hydrogens of the ring are not sufficiently activated to form C–H←O bonds of any greater strength than the C–H←F bonds already present in the

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[1] For the eleventh communication in this series see Marvel, Copley and Ginsberg, THIS JOURNAL, **62**, 3109 (1940).

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[3] Zellhoefer, Copley and Marvel, THIS JOURNAL, **60**, 1337 (1938).

[4] Fuson, *Chem. Rev.*, **16**, 1 (1935).

[5] Zellhoefer and Copley, THIS JOURNAL, **60**, 1343 (1938).

benzotrifluoride. Previous results[6] have shown that a nitrogen atom is a considerably stronger donor than an oxygen atom. Further evidence of the existence of C–H←F bonds in benzotrifluoride or other fluorinated hydrocarbons should be obtainable from infrared absorption studies.

[6] Copley, Zellhoefer and Marvel, THIS JOURNAL, **60**, 2666 (1938).

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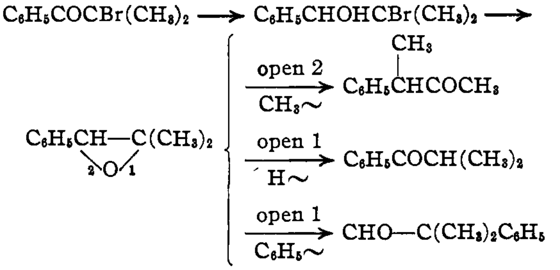
The Reduction of α-Bromo Ketones by Aluminum Isopropylate. II

BY PHILIP G. STEVENS[1] AND OWEN C. W. ALLENBY[2]

In our recent paper[3] we proposed a mechanism involving an intermediate oxide to explain the formation of methylbenzylcarbinol from α-bromopropiophenone and aluminum isopropylate. The carbinol mixture, which we obtained from α-bromoisobutyrophenone in a similar way, we have now identified, and the results lend further support to our proposed mechanism. Since no solid derivatives could be obtained, we oxidized with chromic acid, and then identified the resulting ketones or acids. In this way we obtained mainly isobutyrophenone, and a little dimethylphenylacetic acid. The other expected ketone, methylphenylacetone, was shown to be present solely by oxidation with sodium hypoiodide, whereby small amounts of iodoform were obtained. The formation of these substances can be attributed to isomerization of the intermediate oxide in three different ways, depending on the way the oxide opens, and on which group shifts.[4] The carbonyl compounds so formed are then reduced to carbinols



$$C_6H_5COCBr(CH_3)_2 \longrightarrow C_6H_5CHOHCBr(CH_3)_2 \longrightarrow$$

$$\underset{{}_2\diagdown O\diagup_1}{C_6H_5CH{-}C(CH_3)_2}\ \begin{cases} \xrightarrow[CH_3\sim]{\text{open 2}} C_6H_5\overset{CH_3}{\overset{|}{C}}HCOCH_3 \\ \xrightarrow[H\sim]{\text{open 1}} C_6H_5COCH(CH_3)_2 \\ \xrightarrow[C_6H_5\sim]{\text{open 1}} CHO{-}C(CH_3)_2C_6H_5 \end{cases}$$

In addition we isolated a somewhat higher boiling bromine-free substance, very likely a glycol ether, and large amounts of the low-boiling compound previously mentioned.[1] This was carefully purified by fractional distillation, and analysis again confirmed the composition as $C_{13}H_{20}O$. As cleavage with hydriodic acid yielded isopropyl iodide, this substance is undoubtedly an isopropyl ether of one or more of the above three carbinols.

Experimental Part

Reduction of α-Bromoisobutyrophenone.—318 grams of the bromo ketone was reduced with 4.2 moles of 1 molar aluminum isopropylate by boiling for twenty-one hours, the acetone, etc., being separated continuously by an effective column. An analysis of the distillate showed that 22% of the bromine appeared as isopropyl bromide. The product was then worked up as usual, and separated by repeated fractional distillation into three fractions. The ether fraction, b. p. (9 mm.) 84.8–85.0°, 33.5 g., $n^{25}D$ 1.4741, d^{25}_4 0.8881, was bromine-free, and did not reduce potassium permanganate: *MR* calcd., 60.28; found, 60.77. *Anal.* Calcd. for $C_{13}H_{20}O$: C, 81.2; H, 10.4. Found: C, 81.0; H, 10.5.

The alcohol fraction, b. p. 100.5–103° (9 mm.), weighed 65 g., $n^{25}D$ 1.5205. The third and smallest fraction, b. p. 113° (9 mm.), $n^{25}D$ 1.5175, was not further investigated. There was a considerable tarry residue.

Cleavage of the Low-boiling Ether.—Seven and one-half grams of the ether was heated to gentle boiling with 30 g. of constant-boiling hydriodic acid. A volatile halide was evolved, which was separated by distillation, and identified as isopropyl iodide by conversion with anhydrous trimethylamine to the quaternary iodide. This was recrystallized from alcohol, m. p. 290°, and showed no depression in melting point with an authentic sample.

Oxidation of the Carbinol Mixture. A.—Fifty grams of the carbinol fraction was dissolved in 325 ml. of acetic acid, and then treated with 100 g. of chromic acid likewise in 325 ml. of acetic acid. The temperature was kept below 23°, the addition with stirring taking five hours. Three liters of water was added, and the mixture extracted well with chloroform. This extract was neutralized with sodium carbonate solution, then made just faintly acid, washed well with water, and dried over anhydrous sodium sulfate. The solvent was partially evaporated, the residual liquor extracted with sodium carbonate solution, re-acidified and washed with water, dried over anhydrous potassium carbonate, and the remaining solvent evaporated *in vacuo*. The ketone mixture was investigated directly with 2,4-dinitrophenylhydrazine. Two such hydrazones were isolated after repeated recrystallizations from mixtures of alcohol and chloroform or dioxane. The main one, which constituted about 65% of the total, m. p. 159.5–160.5°, was quite soluble in hot alcohol, and was identified as a derivative of isobutyrophenone. The second was red, insoluble in hot alcohol, and melted at 241–242°.

The alkaline extract above was acidified with acetic acid and extracted with ether. The ether extract was

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[3] Stevens, Allenby and DuBois, THIS JOURNAL, **62**, 1424 (1940).

[4] Lévy and Tabart, *Bull. soc. chim.*, [4] **49**, 1776 (1940).