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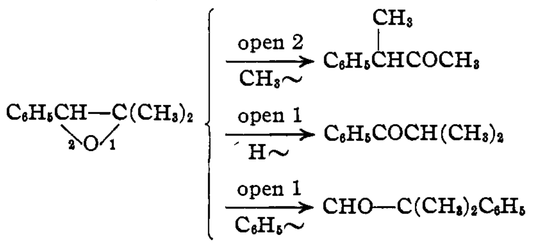
The Reduction of α-Bromo Ketones by Aluminum Isopropylate. II

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

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



$$C_6H_5CH\text{—}C(CH_3)_2 \left\{ \begin{array}{l} \xrightarrow[CH_3\sim]{\text{open 2}} C_6H_5\overset{CH_3}{\overset{|}{C}}HCOCH_3 \\ \xrightarrow[H\sim]{\text{open 1}} C_6H_5COCH(CH_3)_2 \\ \xrightarrow[C_6H_5\sim]{\text{open 1}} CHO\text{—}C(CH_3)_2C_6H_5 \end{array} \right.$$

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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[2] Graduate student, McGill University, holding a Canadian National Research Council Bursary, for which grateful acknowledgment is hereby made.

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

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

dried over anhydrous sodium sulfate and evaporated. After some manipulation, 0.3 g. of a solid acid was obtained, which crystallized from aqueous alcohol, m. p. 77–78°.[5] The amide, prepared in the usual way, melted at 158–158.5°,[3] and so the acid was judged to be dimethylphenylacetic acid.

B.—Ten grams of the carbinol mixture was treated with sodium hypoiodide solution (prepared using 30 g. iodine, 60 g. potassium iodide, 240 ml. water and excess 10% sodium hydroxide solution). Only a few tenths of a gram of iodoform was obtained. The reaction was continued using 90 g. of bromine and excess sodium hydroxide solution. Some benzoic acid and a little oily acid with the odor of methylphenylacetic acid were obtained. The amount of the latter however was too small for further identification.

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(5) Wallach, *Chem. Zentr.*, **70**, 11, 1047 (1899).

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The Heat of Dilution of Aqueous Hydrochloric Acid at 25°

BY JULIAN M. STURTEVANT

Subsequent to the publication of data on the heats of dilution of hydrochloric acid solutions by the author,[1] Gucker and Pickard[2] pointed out the necessity for correcting such data for the heat effects resulting from differences in the vapor pressures of the concentrated and diluent solutions. The required corrections have now been made.

TABLE I

INTEGRAL HEATS OF DILUTION OF HYDROCHLORIC ACID SOLUTIONS AT 25°

Square root of concentration (moles per 1000 g. $H_2O)^{1/2}$			Heat of dilution from initial to final concentration $-\Delta H$, joules (int.) per mole
Initial	Final	Diluent	
1.2513	0.3541	0	1617
1.4840	.4229	0	2069
1.7214	.4757	0	2666
1.7783	.4528	0	2891
1.8267	.0678	0	3798
1.8267	.0943	0	3706
1.8267	.1132	0	3621
1.8267	.1339	0	3574
1.8267	.1919	0	3466
1.8267	.2230	0	3412
1.8267	.2332	0	3381
1.8267	.2676	0	3325
1.8267	.3349	0	3233
1.8267	.3367	0	3217
1.8267	.3454	0	3198
1.8267	.3836	0	3143
1.8267	.4463	0	3041
1.8267	.4748	0	2999
1.8267	.5377	0.3050	2903
1.8267	.5434	0	2883
1.8267	.6128	0.4214	2782
1.8267	.7604	.6264	2532
1.8267	.8623	.7651	2361
1.8267	.9628	.8345	2176
1.8267	.9695	.8917	2164
1.8267	1.0647	.9800	1979
1.8267	1.2179	1.1470	1651

TABLE II

APPARENT AND PARTIAL RELATIVE MOLAL HEAT CONTENT OF SOLUTE AND PARTIAL RELATIVE MOLAL HEAT CONTENT OF SOLVENT IN HYDROCHLORIC ACID SOLUTIONS AT 25°

Square root of molality of hydrochloric acid	Heat content, joules (int.) per mole		
	$\Phi_H - \Phi_H^0$	$\overline{L}_2$	$\overline{L}_1$
0.0000	0	0	0
.0500	100		
.1000	199	297	− 0.0177
.1500	295		
.2000	388	570	− .131
.2500	475		
.3000	560	810	− .405
.3500	642		
.4000	722	1039	− .914
.4500	801		
.5000	880	1271	− 1.76
.5500	959		
.6000	1039	1519	− 3.11
.6500	1120		
.7000	1202	1784	− 5.14
.7500	1285		
.8000	1369	2060	− 7.97
.8500	1455		
.9000	1544	2360	− 11.9
.9500	1636		
1.0000	1731	2699	− 17.4
1.0500	1830		
1.1000	1932	3064	− 24.7
1.1500	2038		
1.2000	2147	3467	− 34.2
1.2500	2259		
1.3000	2374	3891	− 46.2
1.3500	2492		
1.4000	2613	4348	− 61.3
1.4500	2739		
1.5000	2870	4857	− 80.5
1.5500	3005		
1.6000	3146	5436	−106
1.6500	3293		
1.7000	3443	6027	−135
1.7500	3596		
1.8000	3752	(6628)	(−168)
1.8267	3838		

The vapor pressure and density data have been taken from the "International Critical Tables." The vapor pressure of hydrogen chloride over the solutions used is small enough so that no correction for vaporization or condensation of hydrogen chloride need be applied. Both the correction for distillation of water into the air space over the more concentrated solution, and that for the con-

(1) Sturtevant, THIS JOURNAL, **62**, 584 (1940).

(2) Gucker and Pickard, *ibid.*, **62**, 1464 (1940).