Experimental studies on various acetals[41] indicate that E_A does not show any great change with temperature or with concentration of electrolytes, but the reactions are too sensitive to hydrogen ion to allow investigation over any wide range of concentration of acid. We plan to extend this study to a reaction of a less complicated substrate than sucrose, which can be studied over a similar range of hydrochloric acid concentration and temperature.

Summary

1. The velocity constant $k_{H_3O^+}$ for the inversion of sucrose has been measured from 0 to 40° over a wide range of hydrochloric acid concentration.

2. Equations for the effect of the electrolyte, hydrochloric acid, on $k_{H_3O^+}$ are given at 5° intervals between 10 and 40° and at $-0.01°$. The effect of electrolyte decreases with increasing temperature.

3. It has been shown that $k_{H_3O^+}$ increases with increasing sucrose concentration.

4. The energy of activation calculated from the Arrhenius equation shows that E_A and B decrease with increasing concentration of hydrochloric acid. This appears to be a general electrolyte effect.

5. The energy of activation also decreases with increasing sucrose concentration.

6. The decrease in E_A and B with increasing temperature has been confirmed.

7. An explanation of these results has been attempted on the basis of the transition state theory and the consideration of a preëquilibrium between reactants and the collision complex.

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[41] Unpublished results, Riesch and Kilpatrick.

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

The Action of *t*-Butylmagnesium Chloride with Acetyl Chloride

BY FRANK C. WHITMORE AND W. R. WHEELER

Researches in this Laboratory have shown that ketones of the type $RCOCR_3$ may be obtained by the action of tertiary alkylmagnesium halides and an acid halide.[1] In the present study *t*-butylmagnesium chloride was added to an excess of acetyl chloride in ether solution to determine the by-products.

Pinacolone, the normal product, was obtained in but 17% yield. $(CH_3)_3CMgCl + CH_3COCl \rightarrow (CH_3)_3CCOCH_3 + MgCl_2$. Other products were pinacolyl acetate, ethyl acetate, mesityl oxide, isobutylene, isobutane, carbon monoxide and hexamethylethane.

Pinacolyl alcohol, the product from the reducing action of the Grignard reagent on the ketone, appeared as its acetate in 8% yield.

Ethyl acetate, present to the extent of 9%, based on the acid chloride, was probably formed by interaction of acetyl chloride with the solvent ether rather than by direct reduction of the acid chloride to the primary alcohol.[2] This is confirmed by the formation of only 6.6% of isobutylene. Also, results from this Laboratory[3] have shown that ethyl esters are formed in the reaction of *n*-propyl, *n*-butyl and *n*-amyl Grignard reagents with *t*-butylacetyl chloride, in which cases formation of ethyl alcohol by reduction is excluded. Since acid halides are known to cleave ethers in the presence of anhydrous zinc chloride,[4] an experiment was undertaken which demonstrated that the anhydrous magnesium chloride, formed during the course of the reaction, may act in the same way as zinc chloride.

Several modes of formation are possible for the mesityl oxide, which occurred in 6.6% yield. Karasev[5] observed that *t*-butylmagnesium chloride reacts with ethyl acetate to produce acetone and its condensation products, mesityl oxide and phorone. Kondakow[6] prepared mesityl oxide from isobutylene and acetyl chloride in the presence of anhydrous zinc chloride. Recalling the similarity of zinc and magnesium chlorides in promoting the cleavage of ethers, the latter formation is also possible. In that case the small yield of isobutylene would be explained. Further studies on the mechanism of the forma-

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[1] Whitmore and Badertscher, THIS JOURNAL, **55**, 1559 (1933).

[2] *Cf.* Greenwood, Whitmore and Crooks, *ibid.*, **60**, 2028 (1938).

[3] Whitmore, Whitaker, Mattil and Popkin, *ibid.*, **60**, 2790 (1938).

[4] Norris and Rigby, *ibid.*, **54**, 2088 (1932); Gustus and Stevens, *ibid.*, **54**, 3461 (1932); **55**, 378 (1933).

[5] Karasev, *J. Gen. Chem.*, **7**, 179 (1937); *C. A.*, **31**, 4268 (1937).

[6] Kondakow, *J. Russ. Phys.-Chem. Soc.*, **26**, 12 (1894).

tion of ethyl acetate and of mesityl oxide are in progress.

The trace of hexamethylethane found is the coupling product ordinarily formed in the preparation of the Grignard reagent. A small amount of carbon monoxide was also produced; its formation has been noticed previously in analogous reactions.[7]

The evolution of so large an amount of isobutane as 23.6% was unexpected, and would seem to indicate that both pinacolone and mesityl oxide, totalling 24%, had reacted with the Grignard reagent to form isobutane and the —OMgCl compounds of their enol forms.

Experimental

Preparation of Materials.—The *t*-butylmagnesium chloride was prepared in the usual manner[1] from pure *t*-butyl chloride. The reagent evolved no gas when refluxed in a dry, nitrogen-filled fractionating column.

The acetyl chloride was obtained from Eastman practical grade by careful distillation from dimethylaniline in a 1.5 × 65 cm. fractionating column packed with 3.5 mm. glass helices (Column I).

Reaction of *t*-Butylmagnesium Chloride with Acetyl Chloride.—In a three-liter three-necked flask fitted with a dropping funnel, stirrer and condenser were placed 253 g. (3.2 moles) of acetyl chloride and 640 cc. of dry ether. To this was added, over a twelve-hour period, 2.46 moles of the clear, filtered Grignard reagent in 1010 cc. of solution. A yellow precipitate formed; gas was evolved and collected in carboys filled with salt solution and protected by calcium chloride tubes to prevent the diffusion of water vapor back into the reaction flask. When the addition was complete, the flask was immersed in a salt–ice bath and about one liter of water added with stirring, causing the mixture to become warm and evolve a small amount of gas. The ether layer was separated and the water extracted with three 300-cc. portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and distilled in column I. Some gas was evolved on warming, which was combined with the other gases. Distillation at 742–746 mm. gave the following fractions: nos. 1–7, ether; 8–10, 10.1 g., b. p. 36–61.5°, n^{20}D 1.3752–1.3868; 11–12, 18.6, 61.5–75.5°, 1.3815–1.3770; 13–14, 7.7, 75.5–85°, 1.3780–1.3827; 15–17, 15.2, 85–104.5°, 1.3920–1.3976; 18–21, 31.3, 104.5–109°, 1.3965–1.3943; 22–23, 15.9, 109–114°, 1.3952–1.3821; 24–26, 34.6, 114–122.5°, 1.3764–1.3852. The remainder of the distillation was carried out at 51 mm. pressure: 27–29, 15.9, 55–60°, 1.4210–1.4157; 30–33, 29.1, 60–64°, 1.4085–1.4040; residue, 46.3 g.

Identification of Products.—No. 9.—Identification of this material was not entirely satisfactory. It contained halogen, and its b. p. 45–50° and n^{20}D 1.3831 indicate that it was probably impure *t*-butyl chloride, b. p. 50°, n^{20}D 1.3850.

13.—The b. p. and n^{20}D corresponded to ethyl acetate. Hydrolysis gave acetic acid, identified by Duclaux numbers, and ethyl alcohol, 3,5-dinitrobenzoate, m. p. 91°.

14–16.—Repeated refraction of these cuts through a 0.55 × 43 cm. helix-packed column (column E) resulted only in the separation of ethyl acetate and pinacolone, and a small amount of hexamethylethane, boiling *ca.* 100°, m. p. 90–94° (sealed tube), insoluble in 93% sulfuric acid.

19.—Identified as pinacolone, 2,4-dinitrophenylhydrazone, m. p. 124.5°.

21–23.—These cuts, washed free of acetic acid using sodium bicarbonate, yielded only pinacolone on redistillation in column E.

25.—The b. p., n^{20}D and neutral equivalent corresponded to acetic acid.

27–29.—Redistillation through column E gave a fraction of b. p. 128° and n^{20}D 1.4377 which was identified as mesityl oxide, 2,4-dinitrophenylhydrazone, m. p. 199–200°. Semicarbazide reacted with it to form a solid, m. p. 130.5°, described as one of the possible products.[8]

32–33.—The b. p. and n^{20}D correspond to pinacolyl acetate. Hydrolysis gave an acid identified as acetic by its Duclaux numbers, and an alcohol boiling at 128°, phenylurethan m. p. 76°, corresponding to pinacolyl alcohol.

Residue.—The material could not be distilled without decomposition even at 5 mm. pressure. Decolorization in acetone solution yielded a reddish oil which could not be crystallized from the usual solvents. It was not investigated further.

Analysis of Gaseous Products.—Analysis was accomplished with the aid of a 0.55 × 36 cm. low temperature column, packed with a single nichrome spiral and the conventional Orsat apparatus. The following products were indicated: isobutane, 33.8 g.; isobutylene, 9.2 g.; carbon monoxide, 0.2 g.

Reaction of Acetyl Chloride with Ether.—One mole of redistilled acetyl chloride, 200 cc. of ether and 120 g. (1.26 moles) of anhydrous magnesium chloride, prepared by the method of Vanino[9] were stirred and refluxed for one hundred hours. The mixture became pasty but no gas was evolved. Water was added to remove the magnesium chloride, the ether layer washed again with a small amount of water and dried over magnesium sulfate. Distillation in a 0.9 × 45 cm. helix-packed column gave about 60 g. of material boiling at 22–31°, indicating that some ethyl chloride was present in ether solution, and four fractions, totaling 8.9 g., boiling 65–83°, n^{20}D 1.3712–1.3735, which proved to be mainly ethyl acetate; yield 8–10%.

Summary

1. Products formed in the reaction of *t*-butylmagnesium chloride with excess acetyl chloride are isobutane, isobutylene, carbon monoxide, ethyl acetate, pinacolone, pinacolyl acetate and mesityl oxide.

2. Acetyl chloride has been shown to react with diethyl ether in the presence of anhydrous magnesium chloride to form ethyl acetate.

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[7] Schmidlin. *Ber.*, **43**, 1139 (1910). Also unpublished work in this Laboratory by H. M. Crooks, Jr.

[8] Harries and Kaiser, *Ber.*, **32**, 1339 (1899).

[9] Vanino, "Präparative Chemie," 3rd ed., Stuttgart, 1925, p. 439.