4. Oxidation of Acetopyruvic Acid with Permanganate in the Presence of Excess Alkali.—To a solution of 0.500 g. of acetopyruvic acid in 20 ml. of water was added 2.04 g. of potassium permanganate (5 atoms O) dissolved in 80 ml. of 0.485 *N* sodium hydroxide (7 equivalents). The permanganate was decolorized completely but no further decolorization of permanganate could be obtained with this amount of acid. The solution was filtered and made up to 200 ml. Analyses were then made on aliquots for acetic acid, oxalic acid, and carbon dioxide, the expected products. Found: 0.102 g. of acetic acid; 0.476 g. of oxalic acid; and 0.220 g. of carbon dioxide. These figures represent 97% recovery of the carbon. One mole of acid yielded 1.38 moles of oxalic acid, 0.45 mole of acetic acid, and 1.32 moles of carbon dioxide.

These results indicate that about half of the acetopyruvic acid used was oxidized by each of the two reactions

$$\mathrm{CH_3COCH_2COCOONa} \longrightarrow [\mathrm{CH_3COCOONa}] + (\mathrm{COONa})_2 \longrightarrow \mathrm{CH_3COONa} + \mathrm{Na_2CO_3} + (\mathrm{COONa})_2 \tag{5}$$

$$\mathrm{CH_3COCH_2COCOONa} \longrightarrow [\mathrm{CH_3COCOONa}] + (\mathrm{COONa})_2 \longrightarrow [\mathrm{CH_2{=}COHCOONa}] + (\mathrm{COONa})_2 \longrightarrow \mathrm{Na_2CO_3} + 2(\mathrm{COONa})_2 \tag{6}$$

Of these (5) accounts for the acetic acid found and (6) accounts for the excess over one mole of oxalic acid found.

Summary

1. A reliable procedure for the synthesis of acetopyruvic acid is given, and two derivatives of the compound are described.

2. Fundamental properties of this compound were determined and related to its synthesis and stability.

3. Acetopyruvic acid is stable in neutral and acid solutions. In strongly basic solutions it is hydrolyzed to acetone and oxalic acid, by a reaction of the first order, the velocity of which depends on the concentration of the base.

4. This acid is dibasic and the dissociation constants are $K_{\text{I}} = 2.6 \times 10^{-3}$ and $K_{\text{II}} = 3.2 \times 10^{-9}$, respectively.

5. Oxidation with potassium permanganate showed that acetopyruvic acid is attacked in two ways depending on the reaction conditions.

MADISON, WISCONSIN RECEIVED DECEMBER 31, 1941

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

The Study of the Action of an Aluminum–Aluminum Chloride Catalyst in Friedel–Crafts Reactions. Benzoylation

BY OLIVER GRUMMITT AND E. N. CASE[1]

It is now well known that highly purified aluminum chloride is catalytically inactive in the cracking and isomerizing of paraffin hydrocarbons.[2] Promoters for these reactions include a hydrogen halide or a substance such as water or an alkyl halide which is capable of forming the halide.[2] The powerful promoting action of a hydrogen halide in these reactions has suggested the possibility of moderating the catalytic activity of aluminum chloride by adding a substance which will react with the hydrogen halide. Hall and Nash[3] in studying the polymerization of ethylene by aluminum chloride found that added magnesium or aluminum inhibited cracking and retarded the formation of a catalyst–hydrocarbon complex without hindering the polymerization reactions. It was suggested that the metal reacted with any hydrogen chloride formed during the reaction and thus reduced the activity of the catalyst. Further evidence of the reduced activity of an aluminum–aluminum chloride catalyst was obtained by Smith,[4] who observed that the presence of aluminum inhibited the cracking of *n*-heptane by aluminum chloride at 98° almost completely.

In order to investigate more fully the nature of the action of aluminum in reactions catalyzed by aluminum chloride and possibly to improve certain of those reactions, a study of this catalyst combination in several typical Friedel–Crafts reactions has been undertaken. The present report covers the benzoylation of benzene by benzoyl chloride to form benzophenone.

For purposes of comparison the benzophenone synthesis was carried out in the usual way with a mole ratio of benzene: benzoyl chloride: aluminum chloride of 1.0/0.55/0.57. In carbon disulfide as a solvent, the average yield of benzophenone was 62%. Carefully duplicated experiments

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(1) Sherwin-Williams Research Fellow in Organic Chemistry, Western Reserve University.

(2) Ipatieff and Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936), and subsequent papers.

(3) Hall and Nash, *J. Inst. Petroleum Tech.*, **23**, 679 (1939).

(4) A. Smith, M.A. Thesis, Western Reserve University, 1939.

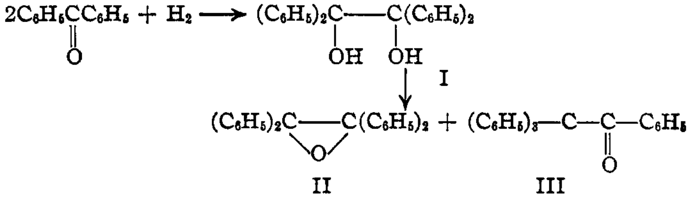
with 0.54 gram atom of added aluminum (50% by weight of the aluminum chloride) gave practically identical yields but the product was contaminated with a sulfur impurity which could not be removed readily. Using excess benzene as the solvent so that the mole ratio of benzene: benzoyl chloride: aluminum chloride was 1.0/0.179/0.182 the average yield of benzophenone was 90%. With the aluminum–aluminum chloride catalyst there was a marked decrease in the benzophenone yield accompanied by the formation of higher boiling by-products. As Table I shows, the reactions leading to these by-products were favored by higher temperatures.

TABLE I

Expt.	Reaction temp., °C.	Benzophenone yield,[a] g.	Yield, %	Volatile by-products,[b] g.	Non-volatile by-products, g.	Total products, g.
1	25–30	18.0	46	4.5	8.0	30.5
2	50	7.0	18	8.0	16.0	31.0
3	80	3.5	9	10.0	20.0	33.5

[a] Obtained by distillation at 125–130° at 1–2 mm.
[b] Obtained by distillation at 130–250° at 1–2 mm.

Examination of the volatile products showed the presence of tetraphenylethylene and *p*-benzoyltriphenylmethane. The non-volatile residue was a resinous solid of high molecular weight. Tetraphenylethylene and *p*-benzoyltriphenylmethane were among the products obtained by Delacre[5] from the thermal decomposition of alpha- (II) and beta-benzpinacolones (III). The pinacolones have been prepared by the reduction of benzophenone with zinc and sulfuric acid at elevated temperatures[6]



benzpinacol (I) being an intermediate compound.

These reactions and the conditions under which they occurred suggested that the benzophenone synthesis in the presence of aluminum–aluminum chloride catalyst involved a consecutive reaction wherein part of the benzophenone was reduced to the pinacol which underwent subsequent rearrangement to the pinacolones, and these compounds were thermally decomposed, with tetraphenylethylene and *p*-benzoyltriphenylmethane as identifiable products. The reduction was effected by the hydrogen displaced by aluminum from the hydrogen chloride, the hydrogen chloride having been formed in the benzoylation reaction.

Evidence in favor of this reaction scheme was gained from experiments which showed (1) hydrogen was evolved during the reaction; (2) benzophenone with aluminum–aluminum chloride under the conditions of the synthesis was recovered practically unchanged; (3) benzophenone with aluminum–aluminum chloride plus hydrogen chloride yielded by-products similar to those from the benzophenone synthesis.

The occurrence of reduction reactions in the presence of an aluminum–aluminum chloride catalyst and hydrogen chloride may explain in part the moderated catalyst activity observed by Hall and Nash.[3] The aluminum not only removed the hydrogen chloride promoter but also displaced hydrogen which reduced unsaturated hydrocarbons or free radicals *in situ*, thus retarding the formation of cracked products.

Experimental

Benzophenone Synthesis in Carbon Disulfide.—In a 500-cc. three-necked flask fitted with a mercury seal stirrer made of monel metal rod and nichrome wire paddles and a reflux condenser were placed 30 g. (0.385 mole) of benzene, 30 g. (0.214 mole) of benzoyl chloride, 100 cc. of carbon disulfide, and 29 g. (0.218 mole) of reagent grade anhydrous aluminum chloride. The mixture was stirred and heated on a water-bath at 45–50° for three hours. The condenser was set for distillation and the water-bath temperature raised to 65° to distill off the carbon disulfide. The warm residue was hydrolyzed by pouring into 400 cc. of ice water followed by the addition of 10 cc. of hydrochloric acid. This mixture was steam distilled for fifteen minutes and the residue extracted with 5 25-cc. portions of ether. The combined extracts were washed chloride free and dried with calcium chloride. Distillation gave 24.6 g. of benzophenone boiling at 290–305°, m. p. 46–48°; 63% yield. A duplicate experiment gave 62% yield.

To test the action of the aluminum–aluminum chloride catalyst the previous experiment was carried out in exactly the same manner except that 14.5 g. (0.54 g. atom) of aluminum turnings was present. Reagent grade aluminum turnings washed with soap and water, alcohol, and ether were used. This quantity of aluminum, which is 50% of the aluminum chloride used, is more than sufficient to react with the hydrogen chloride liberated from 0.214 mole of benzoyl chloride. After distilling off the carbon disulfide the reaction mixture was filtered through a glass wool plug to remove the residual aluminum before hydrolysis. Duplicate experiments with the modified catalyst gave benzophenone yields of 59 and 67%, m. p. 42–48°; but the products were yellow in color and had a strong mercap-

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(5) Delacre, *Bull. soc. chim.*, [4] **5**, 1149 (1909).

(6) Thorner and Zincke, *Ber.*, **11**, 1396 (1878).

tan-like odor which could not be removed by repeated distillations. Qualitative analysis gave a positive sulfur test. Several small-scale experiments were run with various combinations of the reactants to determine which substances form the sulfur impurities. Apparently the sulfur compound arises through an interaction of benzoyl chloride and carbon disulfide in the presence of aluminum–aluminum chloride; without the metal there is no reaction.

Benzophenone Synthesis in Excess Benzene.—The amount of benzene taken was increased to 93.0 g. (1.2 moles), the other starting quantities being the same. The procedure was the same as before except that the temperature of reaction was controlled by means of a water-bath and, at the end of the reaction, the excess benzene was removed by vacuum distillation. With aluminum chloride alone as the catalyst duplicate experiments at 50° gave 34.8 and 35.3 g. of benzophenone; 89 and 91% yields. The aluminum–aluminum chloride catalyst consisted, as before, of 14.5 g. of aluminum and 29.0 g. of aluminum chloride. Several experiments at various temperatures are summarized in Table I. Substantially similar results were obtained when "activated" aluminum, prepared by the action of alcoholic mercuric chloride on the metal, was used.

The products from an experiment at 50° (a duplicate of Expt. 2, Table I) were distilled at 1.5 mm.

TABLE II

Fraction	Boiling range, °C.	Wt., g.
1	to 110	2
2	110–125	5
3	125–180	2
4	180–200	2
5	200–240	5
6	240–260	5
	Non-volatile	12
Total		33

The first two fractions were mostly benzophenone (identified by the 2,4-dinitrophenylhydrazone), making the yield of benzophenone 7 g. (18%). Repeated crystallization of fraction 3 from petroleum ether (90–120°) yielded a small amount of colorless crystals, m. p. 215–218°. Chemical properties and molecular weight of this substance indicated that it was probably tetraphenylethylene; an authentic sample[7] melted at 215–217° and a mixed melting point with the unknown gave 215–218°. The tetra-(*p*-bromophenyl)-ethylene derivative[8] of both samples melted 245–248° and a mixed melting point showed no depression.

Several crystallizations of fraction 4 from petroleum ether (90–120°) yielded a slightly yellow solid, m. p. 161–162°. When this was further crystallized from alcohol, crystals were obtained which showed an incipient melting point at 148°, but on cooling and remelting the melting point was 160–162°. This property and the chemical behavior and molecular weight of this substance indicated that it was *p*-benzoyl-triphenylmethane. An authentic sample[9] melted at 162–163° and in a mixed melting with the unknown gave 162–163°. Each sample was converted into *p*-benzhydrol triphenylcarbinol[10]; the derivative from the unknown melted at 131–134°, that from the authentic sample at 134–137°; a mixed melting point gave 131–134°.

The non-volatile by-product (Table II) was a brown, hard, resinous solid, containing no halogen, with a molecular weight of about 700 (cryoscopically in benzene). This substance is probably a mixture of the resin formed in the thermal decomposition of benzpinacolones[5] and a polymer formed by the action of aluminum–aluminum chloride on benzoyl chloride. The latter reaction was observed in an experiment under the same conditions as the benzophenone synthesis except that ethylene chloride was used as an inert solvent to replace benzene. The product was 9.5 g. of resinous solid. Aluminum chloride alone under these conditions does not affect benzoyl chloride.

An experiment at 80° (a repetition of Expt. 3, Table I) with the aluminum–aluminum chloride catalyst was run so that the evolved gases were washed in water to remove hydrogen chloride and then in mineral oil to remove benzene vapor. The washed gas was collected over water and shown to be hydrogen by ignition.

Action of Aluminum–Aluminum Chloride on Benzophenone.—A mixture of 39.0 g. (0.214 mole) of benzophenone, 29.0 g. (0.218 mole) of aluminum chloride, 14.5 g. (0.54 g. atom) of aluminum, and 76 g. of benzene was allowed to react at 50° for three hours. Isolation of the products in the usual way gave 36.5 g. of benzophenone, 1.5 g. of volatile by-product and 0.5 g. of residue. Recovery of almost 94% of the benzophenone showed that it is stable with respect to aluminum–aluminum chloride under the conditions of synthesis. This experiment was repeated but with the addition of dry hydrogen chloride gas during the three-hour reaction period. The gas was bubbled into the reaction mixture at about one bubble per second. Isolation of the products gave only 21.0 g. of benzophenone (54%) recovery, 7.5 g. of volatile by-product and 3.0 g. of residue.

Summary

A study of the products formed when an aluminum–aluminum chloride catalyst is used in the benzoylation of benzene by benzoyl chloride has shown that reduction reactions occur simultaneously. Hydrogen, formed by the action of hydrogen chloride on aluminum, the hydrogen chloride being a product of the acylation, is the reducing agent. The diminished catalytic activity of aluminum chloride in the presence of aluminum which has been observed in hydrocarbon polymerization may be due in part to reduction of olefinic or free radical intermediates.

CLEVELAND, OHIO RECEIVED NOVEMBER 10, 1941

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[7] Finkelstein, *Ber.*, **43**, 1532 (1910).

[8] Biltz, *Ann.*, **296**, 231 (1897).

[9] Bourcet, *Bull. soc. chim.*, [3] **15**, 949 (1896).

[10] Tschitschibabin, *Ber.*, **41**, 2424 (1908), who also reported a crystalline modification of *p*-benzoyltriphenylmethane melting at 148°.