

magnesium ribbon and a filtered colorless solution of magnesium iodide it was found that 0.22 g. (theoretical, 0.24 g.) of metal had reacted in eighteen hours and an 84% yield of tetraphenylethylene was obtained. In one experiment after interaction of the pinacolone with the hot reducing mixture, the solution was filtered and concentrated without addition of water; 1.3 g. of tetraphenylethylene crystallized on cooling.

By shaking a mixture of 3.48 g. of pinacolone with magnesium and magnesium iodide from 2.6 g. of iodine in 2 cc. of ether and 30 cc. of benzene for two days at room temperature a 27% yield of tetraphenylethylene and a 73% yield of yellow gum was obtained; when a similar mixture was heated for one hour after being shaken for two days a 57% yield of tetraphenylethylene was produced.

When a larger proportion of ethyl ether was used (15 cc. of ether and 30 cc. of benzene) the yield of tetraphenylethylene was decreased to 55-60% because of the lower boiling point of the mixture. By using propyl ether the yield was increased. When the reaction was carried out in ether alone the reaction began instantly and an intense scarlet

color developed; as reduction took place the magnesium became coated with a sticky precipitate; hydrolysis after nineteen hours gave a 40% yield of tetraphenylethylene.

When the reaction was carried out at room temperature the yield of tetraphenylethylene varied from 20-30%, the remaining product being a gum; this was true whether small or large amounts of ether were used. By using the magnesium ribbon it was found that 0.17 g. (0.7 gram atom) of magnesium reacted in two days at room temperature; in two months 0.19 g. of metal reacted; the yield of tetraphenylethylene in both cases was 20%.

It was found that a mixture of magnesium and magnesium bromide likewise reduces benzopinacolone to tetraphenylethylene.

### Summary

Benzopinacolone is reduced by a mixture of magnesium and magnesium iodide at 80° to tetraphenylethylene.

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## Studies on Acid Iodides. III. The Addition of Acetyl Iodide to Unsaturated Hydrocarbons

BY PHILIP G. STEVENS

Acetyl iodide, unlike acid or alkyl chlorides which require catalysts such as metal or non-metal salts,<sup>1</sup> has been found to be sufficiently reactive to add to unsaturated hydrocarbons without the aid of catalysts.<sup>2</sup> The hydrocarbons investigated were butene-2, isobutene, stilbene, benzene, trimethylethylene and cyclohexene. All reacted with acetyl iodide at 25° but only the last two gave unsaturated ketones which were identified. Trimethylethylene and cyclohexene formed dimethylpentenone, and tetrahydroacetophenone and cyclohexyl iodide, respectively.

Kondakow<sup>3</sup> was the first to show that acid chlorides react with unsaturated aliphatic hydrocarbons with the aid of catalysts. He described the mechanism of the reaction as involving the addition of the acid chloride to the double linkage followed by a loss of halogen acid to form an unsaturated ketone. Later Wieland and Bettag<sup>4</sup> substantiated the discovery of

Kondakow (which had already been reinvestigated by Krapiwinski<sup>5</sup> and Darzens)<sup>6</sup> and showed in all probability that this mechanism could be used to explain the Friedel-Crafts reaction. This same mechanism can also be used equally well with acetyl iodide, especially as there is no complication due to the presence of a metal or non-metal salt. Both Kondakow and Wieland and Bettag were able to isolate the primary addition products,  $\beta$ -chloro ketones. With acetyl iodide, however, the primary addition products are the much more reactive  $\beta$ -iodo ketones, the isolation of which was not attempted.

Other unsaturated substances were treated with acetyl iodide, *e. g.*, *sym*-dichloroethylene, divinyl ether, furan and thiophene. The first named failed to react even after 150 days at 25°.<sup>7</sup> Divinyl ether<sup>8</sup> and acetyl iodide apparently did not react during the first six hours; but later the mixture exploded. Furan reacted vigorously

(1) Some exceptions to this rule do exist: Michler, *Ber.*, **9**, 400 (1876); Döbner, *Ann.*, **217**, 223 (1883); Staudinger, *Ber.*, **41**, 3558 (1908); Liebermann and Zsuffa, *ibid.*, **44**, 202 (1911).

(2) This recalls the great reactivity of acid iodides (in contrast to acid chlorides) toward ethers: Gustus and Stevens, *THIS JOURNAL*, **55**, 378 (1933).

(3) Kondakow, *Chem. Zentr.*, **1**, 1017 (1894).

(4) Wieland and Bettag, *Ber.*, **55**, 2246 (1922).

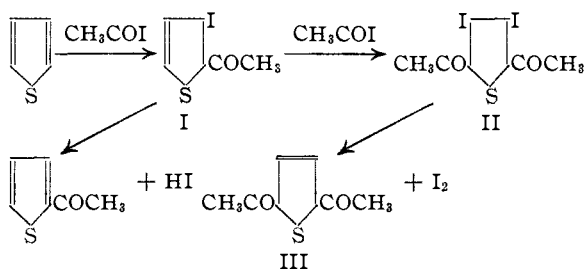
(5) Krapiwinski, *Bull. Soc. Imp. des Naturalistes de Moscou*, **22**, 1 (1908).

(6) Darzens, *Compt. rend.*, **150**, 707 (1910).

(7) This was however not altogether unexpected, as Prins, *Rec. trav. chim.*, **51**, 1065 (1932), reported that *sym*-dichloroethylene is not attacked by aluminum chloride, although it reacts readily enough with dichloroethanes in the presence of aluminum chloride.

(8) I am indebted to Dr. N. A. Milas for the specimen of this ether.

at 25° with the formation of iodine and a tar. Thiophene<sup>9</sup> likewise reacted readily at 25°, liberating considerable heat. At -15° the reaction took place in two distinct steps, first the precipitation of iodine and second the formation of a black tar. After some manipulation a small quantity of acetothienone was obtained. The precipitation of iodine would lead to the conclusion that both double linkages in thiophene add acetyl iodide. The diiodide II would then lose iodine most easily, followed by a polymerization of the diketodihydrothiophene III. The primary addition product I and acetothienone may also polymerize.



I am indebted to Professor James F. Norris for the facilities of this Laboratory, and to the Mallinckrodt Chemical Works for so generously donating the large quantities of iodine necessary for this work. Part of the funds required for this research were privately contributed.

### Experimental

**Trimethylethylene and Acetyl Iodide.**—Twenty-five cc. of trimethylethylene<sup>10</sup> of b. p. (760 mm.) 38.3–38.4° corrected (from sodium) was treated with 17 cc. of acetyl iodide. There was no apparent heat of reaction. After twenty-six days at 25° in the dark, the mixture was shaken with water and cold sodium bicarbonate, yielding a heavy dark-colored oil. This was dried over sodium sulfate and the excess trimethylethylene removed *in vacuo*. Considerable material was then distilled at 1 mm. at 25°. The residue was dark red and contained 40.4% iodine (instead of 52.9% for the expected iodo ketone). Since it was not possible to purify the material further, it was taken up in ether, treated with 30 cc. of dimethylaniline, dried over potassium carbonate, and distilled at 30 mm. The material boiling below 100° and the residue were separately washed with dilute sulfuric acid, dried over sodium sulfate and then combined and distilled. After several fractionations, about 1 g. of an unsaturated ketone was obtained, which was identified as dimethylpentenone by conversion into the semicarbazone. After four recrystallizations from benzene, the diamond plates melted at 182.5–184°, sintering at 181°. A mixed melting

point with the semicarbazone of dimethylpentenone from trimethylethylene, acetyl chloride and stannic chloride was 183–184.5°, sintering at 181°; with the semicarbazone of dimethylpentenone from butanone and acetone, 182–184°, sintering at 181°.

**Cyclohexene and Acetyl Iodide.**—Sixty cc. of cyclohexene, b. p. (763 mm.) 83.0–83.1° (from sodium), was treated with 25 cc. of acetyl iodide. There was no apparent heat of reaction. After ten days, as much tar had formed, 2 cc. was pipetted out and titrated, using 9.3 cc. of 0.305 *N* sodium hydroxide. This indicated that about 80% of the acetyl iodide had been consumed. The entire material was shaken with water and sodium bicarbonate, extracted with ether, and dried over sodium sulfate. The ether was removed *in vacuo*, leaving a dark-colored viscous liquid (65 g.). If this material is vacuum distilled, only cyclohexyl iodide contaminated with a little tetrahydroacetophenone is obtained: b. p. (0.015 mm.) 40–42°; b. p. (20 mm.) 80.5–81.0°;  $n_D^{20}$  1.5383; 52.9% I.<sup>11</sup> In order to isolate the unsaturated ketone, it was necessary to heat the crude material with dimethylaniline for three hours at 170–185°. The product from this treatment was extracted with ether and water. The ether was then washed with dilute sulfuric acid, dried and evaporated. The residue was distilled at 18 mm. Most of the material remained behind as a tar; only a small amount distilled at 75–130°. This was redistilled, yielding 3.1 g. of tetrahydroacetophenone: b. p. (20 mm.) 89–93°,<sup>12</sup> yield 8.3%, identified by conversion into the semicarbazone. This melted after two recrystallizations from ethyl alcohol at 217–218° with decomposition. A mixed melting point with an authentic specimen (m. p. 217–218° with decomposition) was the same.

**Thiophene and Acetyl Iodide.**—Twenty-seven grams of thiophene, b. p. 84° (from sodium), was added to 27 g. of acetyl iodide chilled to -15°. At first there was no apparent reaction but after two hours large quantities of iodine had crystallized out. After five hours the temperature had risen to 0° and a heavy tar had formed. After three days at 0° the reaction mixture was decomposed with water and ether. The tar, insoluble in ether, was dissolved in chloroform. Both ether and chloroform solutions were washed with sodium hydroxide, and then were combined and steam distilled. Three grams of a liquid with the odor of acetothienone was obtained which, when distilled, yielded about 0.5 g. of red liquid, b. p. 205–220°. This was taken up again in ether, washed with sodium hydroxide, dried over calcium chloride, and the ether evaporated. The remaining liquid was identified as acetothienone by conversion into the semicarbazone, which after four recrystallizations from benzene melted at 186–187°. A mixed melting point with an authentic specimen<sup>13</sup> (m. p. 188°) was 186–187.5°.

**Preparation of Dimethylpentenone (CH<sub>3</sub>)<sub>2</sub>C=CCH<sub>3</sub>—COCH<sub>3</sub>.**—(A). Two hundred and fifty grams of stannic chloride<sup>7</sup> was added to a chilled mixture of 78 g. of acetyl chloride, 71 g. of trimethylethylene, b. p. (760 mm.)

(9) This reaction can be regarded as support for Wieland and Bettag's mechanism of the Friedel-Crafts reaction.

(10) I am indebted to Dr. George Thomson for this specially pure sample.

(11) Authentic cyclohexyl iodide: b. p. (20 mm.) 81.0°;  $n_D^{20}$  1.5470; 60.5% I.

(12) Authentic tetrahydroacetophenone: (Darzens, *loc. cit.*) b. p. (20 mm.) 89.5–92°.

(13) Stadnikoff and Rakowsky, *Ber.*, **61**, 268 (1928).

38.4–39.0° corrected, and 600 g. of carbon disulfide. After stirring all day, the reaction mixture was allowed to stand overnight at 25°. The material was then worked up in the usual way. Before fractionating off the solvent, 121 g. of dimethylaniline was added. After removal of the solvent, the residue was heated to 175–185° for three hours, and then distilled. The fraction of b. p. 60–190° was taken up in ether, shaken with dilute sulfuric acid, dried over sodium sulfate and distilled. After several fractionations 2.2 g. of the ketone was obtained of b. p. (751 mm.) 145–148°,  $n_D^{18}$  1.4460.<sup>14</sup>

This material possessed a pleasant odor, reduced potassium permanganate and added bromine in glacial acetic acid instantly; 0.5 g. of the ketone gave 0.5 g. of a semicarbazone, which formed diamond plates from benzene, and after three recrystallizations sintered at 183° and melted at 184–185°.<sup>15</sup>

*Anal.* (micro) Calcd. for  $C_8H_{16}ON_2$ : N, 24.9. Found: N, 24.0.

(B). A mixture of 221 g. of butanone, b. p. 78–79°, and 61 g. of acetone was saturated in a freezing mixture with dry hydrochloric acid gas, and then allowed to stand forty-two hours at 0°. The yellow solution was decomposed as usual, steam distilled, dried over calcium chloride and fractionated. Since large quantities of hydrochloric acid were liberated at this point, the material, b. p. (755 mm.) 136–153°, 50.5 g., was boiled with 40 cc. of dimethylaniline for two hours, then washed with dilute sulfuric acid,

(14) Krapiwín (Ref. 5) reported b. p. (743 mm.) 144–145°,  $n_D^{18}$  1.4378.

(15) Krapiwín (Ref. 5) reported 178–180°.

extracted with ether, dried and distilled. The fraction of b. p. (750 mm.) 144–148°,  $n_D^{18}$  1.4410, 4.5 g. reduced potassium permanganate and absorbed bromine in glacial acetic acid instantly. One gram of the ketone gave 0.65 g. of a semicarbazone which consisted of two individuals, needles and diamond plates. The latter were finally obtained fairly pure after six recrystallizations from benzene melting at 181.5–183.5°, sintering at 180°.

**Cyclohexane and Acetyl Iodide.**—Cyclohexane when treated with acetyl iodide was recovered unchanged even after 290 days at 25°.

### Summary

1. The reactions between acetyl iodide and butene-2, isobutene, trimethylethylene, cyclohexene, stilbene, benzene, divinyl ether, furan, thiophene, *sym*-dichloroethylene and cyclohexane have been studied.

2. Trimethylethylene, cyclohexene and thiophene alone formed the expected unsaturated ketones.

3. *sym*-Dichloroethylene and cyclohexane failed to react with acetyl iodide.

4. Acetone and butanone condense in the presence of hydrochloric acid to form a mixture of isomeric unsaturated ketones, one of which is dimethylpentenone.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, SCHOOL OF MEDICINE, UNIVERSITY OF ARKANSAS]

## The Extractability of Vitamin G ( $B_2$ ) from Yeast by Various Acetone–Water and Methyl Alcohol–Water Mixtures

BY PAUL L. DAY<sup>1</sup>

In a series of quantitative experiments, Sherman and Sandels<sup>2</sup> found that vitamin G was not appreciably extracted from dried baker's yeast by neutral 95% ethyl alcohol. Alcohol 80% by weight extracted about one-quarter of the vitamin, and 60% alcohol extracted about one-half of the vitamin in the yeast. It thus appears that with ethyl alcohol–water mixtures, the extractability of vitamin G from yeast increases with increased proportion of water in the solvent mixture. In order to find out whether vitamin G would exhibit similar properties toward other solvents miscible with water, experiments have been made on the extractability of the vitamin from dried yeast by 99.5, 80 and 60% (by

weight) acetone; absolute, 80 and 60% (by weight) methyl alcohol. The author wishes to report here the results of these quantitative experiments.

### Experimental

The highest purity acetone and methyl alcohol obtainable were used in the preparation of the extracts. For the acetone–water and methyl alcohol–water mixtures, dilutions were made by weighing suitable portions of the solvents and distilled water. Air-dried baker's yeast was treated with the various solvents, using essentially the same technique as was used by Sherman and Sandels<sup>2</sup> with ethyl alcohol. The procedure was as follows: 400 g. of yeast was treated with 1500 cc. of the solvent, stirred and allowed to stand at room temperature for twenty-four hours, again stirred and filtered with suction, and the residue washed with 750 cc. of the solvent in several successive small portions; the residue was treated with another 1500-cc. portion of the solvent, allowed to stand

(1) With the technical assistance of William J. Darby.

(2) Sherman and Sandels, *Proc. Soc. Exptl. Biol. Med.*, **26**, 536 (1929). *J. Nutrition*, **3**, 395 (1931).