Summary

o-Allyltoluene and p-allyltoluene and their dibromides were synthesized. Study was made of the pyrolysis of the allyltoluenes. They provided a contrast to previously studied unsaturated hydrocarbons in possessing somewhat greater stability and in giving rise to more ethylene than propylene in the gas. The significance of these facts is discussed. Prolonged heating of 4-phenyl-1-butene failed to effect any rearrangement into o-allyltoluene.

EVANSTON, ILL. RECEIVED OCTOBER 2, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Reduction by Magnesium + Magnesium Iodide. XII. The Reduction of Benzopinacolone

BY W. E. BACHMANN

Aromatic ketones are reduced by a mixture of magnesium and magnesium iodide;[1] intermediate ketyl radicals R_2COMgI are formed which double up to form a pinacolate $R_2(OMgI)CC(OMgI)R_2$. We have now tried the action of the reducing mixture on the mixed aliphatic-aromatic ketone benzopinacolone. This compound was found to react readily with the binary mixture in ether and benzene with the formation of an orange-red to red color. If the reaction is carried out at 80–85° tetraphenylethylene is formed in yields as high as 92%; indeed, the reaction constitutes an excellent method for preparing tetraphenylethylene.[2] It is clear that the reducing action is accompanied by an intramolecular rearrangement; and the reaction may be formulated as follows

$$(C_6H_5)_3CCOC_6H_5 + Mg + MgI_2 \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + MgO + MgI_2$$

The quantity of magnesium that reacts corresponds to 90% of that required by the equation and is equivalent to nearly one gram atom of metal for one gram mole of pinacolone. That the tetraphenylethylene is formed in the mixture prior to hydrolysis was proved by isolation of the ethylene before addition of water. Since the magnesium iodide is regenerated in the reaction, it follows that small amounts of the halide should suffice for complete reduction. Such was found to be the case; however, the reaction is much slower and practically it was found desirable to use from 0.4 to 1.0 gram mole of magnesium iodide for each mole of pinacolone.

In addition to tetraphenylethylene there is produced a small amount (8–10%) of by-product in the form of an uncrystallizable yellow gum the composition of which is unknown. This gum is the principal product (70–80%) when the reaction is carried out at room temperature; the reactions leading to its formation require less magnesium, only 0.7 to 0.78 gram atom of magnesium per mole of pinacolone. It appears that the tetraphenylethylene and part of the gum come from the same intermediate reduction product since the yield of tetraphenylethylene is increased by continuing the reaction at 80° after interaction has been completed at room temperature. It is considered that reduction occurs through the addition of MgI groups to the carbonyl group but the actual nature of the intermediate reduction products is not known.

Experimental

Preparation of Tetraphenylethylene from Benzopinacolone.—A mixture of 3 g. of iodine (equivalent to 0.4 gram mole of halide per mole of pinacolone) and 3 g. of magnesium powder is heated in a mixture of 5 cc. of ether and 20 cc. of benzene until the mixture is nearly colorless; 10.5 g. of benzopinacolone and 70 cc. of benzene are added and the resulting mixture is refluxed for twenty hours. The orange-red mixture is filtered from the excess of magnesium and poured into water; dilute acid is added in order to dissolve the magnesium hydroxide which is produced. The ether–benzene solution is concentrated to a small volume and cooled. Total yield of tetraphenylethylene, 9.2 g. (92%).

Reaction under Various Conditions.—Numerous experiments were carried out on 3.48 g. (0.01 gram mole) samples in order to determine the effect of various factors. No reaction took place when benzopinacolone was heated with magnesium in the absence of magnesium halide.

When only one hour was allowed for the reaction using 0.4 gram mole of magnesium halide in 2 cc. of ether and 30 cc. of benzene, a considerable amount of pinacolone remained unchanged; by using a full mole of halide an 85% yield of tetraphenylethylene was obtained in the same length of time. By employing weighed amounts of

---

[1] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[2] Compare Steinkopf and Wolfram, *Ann.*, **430**, 114 (1922), who obtained tetraphenylethylene in 86% yield by reduction of benzopinacolone in alcohol solution by amalgamated zinc and hydrogen chloride.

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.

ANN ARBOR, MICH. RECEIVED OCTOBER 10, 1933

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 102]

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 nonmetal salts,[1] has been found to be sufficiently reactive to add to unsaturated hydrocarbons without the aid of catalysts.[2] 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[3] 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[4] substantiated the discovery of Kondakow (which had already been reinvestigated by Krapiwin[5] and Darzens)[6] 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 nonmetal salt. Both Kondakow and Wieland and Bettag were able to isolate the primary addition products, β-chloro ketones. With acetyl iodide, however, the primary addition products are the much more reactive β-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°.[7] Divinyl ether[8] 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.*, I, 1017 (1894).

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

(5) Krapiwin, *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.