

These results indicate that the ratio of Al_2Br_6 to C_6H_6 is 1:6 and that the complex contains some hydrogen bromide.

When the oil was shaken with petroleum ether it decreased in volume. The residual oil gave on analysis the ratios Al 1, Br 2.9, C_6H_6 0.63. It appeared that the product contained Al_2Br_6 and C_6H_6 in the ratio 1:1.

The vessel containing a sample of the original oil was evacuated at 12 mm. Crystals soon appeared. This behavior is different from that of the complexes formed from the other hydrocarbons which gave no crystals but left a product containing the bromide and the hydrocarbon. The crystals appeared to be aluminum bromide. When 18.2 g. of the complex was held under diminished pressure, in about three hours the residue weighed 8.8 g., which is very close to the weight of the aluminum bromide in the complex.

In a second experiment the complex was held at 12 mm.

for four hours and then at 0.002 mm. The loss at the latter pressure was 0.01 g. The residue was slightly impure aluminum bromide. The sum of the percentages of aluminum and bromine was 94.4%.

Summary

1. The ethyldimethylbenzene prepared by the Friedel and Crafts reaction from ethyl bromide and *m*-xylene has been restudied and evidence given that the hydrocarbon has the symmetrical structure.

2. The preparation and properties of complexes of certain aromatic hydrocarbons and aluminum bromide or aluminum chloride are described.

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NOTES

Reaction between a Highly-Substituted Bromopyridine and Lithium

By C. F. H. ALLEN AND G. F. FRAME

In view of the increasing interest in organometallic heterocyclic compounds¹ it seems advisable to record that lithium reacts slowly with the highly-substituted 2-bromo-3,4,6-triphenylpyridine. The resulting suspension does not seem to react with carbon dioxide, aldehydes, or ketones. Upon decomposition by acids, a 20–25% yield of 2,4,5-triphenylpyridine can be secured by distilling in a high vacuum. No conditions were found under which the highly-substituted 2,3,5-triphenyl-4-bromofuran would react with lithium. Neither of these substances reacts with magnesium.²

In the usual apparatus, swept by nitrogen, a mixture of 50 cc. of dry ether, 0.5 g. of lithium, and 13.8 g. of 2-bromo-3,4,6-triphenylpyridine was refluxed with stirring for four hours. A slow reaction was noted and the solution became a deep reddish-brown. After standing for several days practically all the metal had disappeared. The ether layer, which separated after adding iced hydrochloric acid, was removed, washed, dried, and the solvent evaporated. After efforts to induce crystallization had failed, the thick oil (1.2 g.) was distilled at 1.2–2 microns; a black tarry residue remained. The clear distillate (1.8 g.) crystallized when rubbed with alcohol. 2,4,5-Triphenyl-

pyridine crystallizes in glistening, slightly iridescent rods, m. p. 112°, readily soluble in alcohol, ether and benzene.

Anal. Calcd. for $\text{C}_{23}\text{H}_{17}\text{N}$: N, 4.6. Found: N, 4.5.

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The Carbonation of Organoalkali Compounds

By HENRY GILMAN AND H. A. PACEVITZ

The kind and ratio of products obtained by carbonation of organometallic compounds are influenced markedly by the rate and temperature of carbonation. With organolithium compounds,¹ in particular, low temperature together with a large excess of carbon dioxide (conditions realized by pouring RM compounds jet-wise on crushed solid carbon dioxide) give predominantly the acid and little of the ketone or tertiary alcohol. Furthermore, carbonation by solid carbon dioxide depresses markedly the formation of malonic acids from benzylmetallic types. This is strikingly illustrated in studies submitted recently² with compounds like benzylium, benzylpotassium and 3,5-dimethylbenzylpotassium. These RM compounds when carbonated by solid carbon dioxide give almost exclusively the corresponding carboxylic acids; however, carbonation by gaseous

(1) Gilman and Spatz, *THIS JOURNAL*, **62**, 446 (1940).

(2) Allen and Rosener, *ibid.*, **49**, 2113 (1927).

(1) Gilman and Van Ess, *THIS JOURNAL*, **55**, 1258 (1933). See, also, Gilman and Parker, *ibid.*, **46**, 2816 (1924).

(2) Gilman, Pacevitz and Baine, *ibid.*, **62**, June (1940).