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.

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 compounds[1] 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 $C_{23}H_{17}N$: 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 recently[2] with compounds like benzylsodium, 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
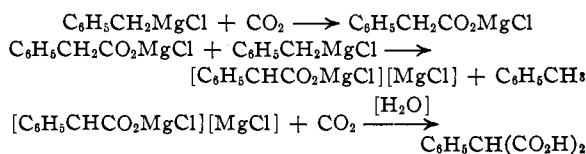
(1) Gilman and Spatz, THIS JOURNAL, **62**, 446 (1940).

(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).

carbon dioxide gives, in addition to the expected carboxylic acids, significant quantities of the malonic acids. The malonic acids probably owe their formation largely to a secondary metalation reaction of the active methylene group by the unused RM compound present in slow carbonation. The typical transformations may be illustrated by the studies of Ivanoff and Spassoff[3] with benzylmagnesium chloride.

$$C_6H_5CH_2MgCl + CO_2 \longrightarrow C_6H_5CH_2CO_2MgCl$$
$$C_6H_5CH_2CO_2MgCl + C_6H_5CH_2MgCl \longrightarrow$$
$$[C_6H_5CHCO_2MgCl][MgCl] + C_6H_5CH_3$$
$$[C_6H_5CHCO_2MgCl][MgCl] + CO_2 \xrightarrow{[H_2O]} C_6H_5CH(CO_2H)_2$$

Our carbonation experiments with benzylalkali types[2] raise a question concerning benzylidene-dialkali compounds like $C_6H_5CHM_2$. If such compounds are formed in one way or another incidental to the several procedures[2] for the preparation of benzylalkali compounds, then it is possible, but somewhat unlikely, that they are not carbonated by solid carbon dioxide. We are at present of the opinion that they are either not formed or are formed to a subordinate extent, incidental to the preparation of benzylalkali types.

Of more immediate interest are the aliphatic types, $RCHM_2$, like amylidene-disodium.[4] From the experiments now reported, we find that the organosodium compound or compounds formed by interaction of n-amyl chloride and sodium give largely caproic acid with very little n-butylmalonic acid when carbonation is effected by solid carbon dioxide; and a mixture of caproic acid with large amounts of n-butylmalonic acid when gaseous carbon dioxide is used. Additional experiments may provide an answer to the question as to whether secondary metalations or other transformations, some of which have been reported,[4] are responsible for the reactions of compounds of benzylidene-dimetallic and amylidene-dimetallic types.

Calomel electrode	Satd. KCl	Outside solution: dilute HCl

Experimental Part

In a typical experiment, a solution of 16.5 g. (0.155 mole) of freshly distilled n-amyl chloride (b. p., 107–108°) in 15 cc. of petroleum ether (b. p. 85–100°) was added dropwise over a one-hour period to 8.75 g. (0.38 g. atom) of sodium sand in 75 cc. of petroleum ether. The mixture was stirred at room temperature for four hours, after which it was carbonated by pouring jet-wise on solid carbon dioxide, the addition being completed within ten seconds. The products obtained (by isolation and weighing) were 6.9 g. or 38.5% of caproic acid and less than 1% of impure n-butylmalonic acid. In a check experiment on this carbonation by solid carbon dioxide the yield of n-caproic acid was 7.3 g. or 40.8%; and the yield of impure n-butylmalonic acid was again less than 1%. In a parallel experiment in which carbonation was effected by admitting gaseous carbon dioxide to the surface of the reaction mixture over a five-hour period at 27–28° and with stirring, the yield of n-caproic acid was 2.72 g. or 15.2%; and the yield of n-butylmalonic acid was 2.1 g. or 16.9%.

Again using the same quantities of reagents, two parallel experiments were carried out by first stirring at 27–28° for one hour and then at 42° for two hours. Rapid carbonation (solid carbon dioxide, ten seconds) yielded 6.52 g. or 36.4% of n-caproic acid, and less than 1% of impure n-butylmalonic acid. Slow carbonation (gaseous carbon dioxide, five hours) yielded 3.53 g. or 19.5% of n-caproic acid, and 1.83 g. or 14.8% of n-butylmalonic acid.

Acting on the suggestion that low boiling petroleum ether might give different results, parallel experiments were carried out with purified petroleum ether distilling over the range 28–38°. Rapid carbonation (solid carbon dioxide, five to ten seconds) yielded 51.5% of caproic acid and less than 2% of n-butylmalonic acid. Slow carbonation (gaseous carbon dioxide, four hours) yielded 17.3% of caproic acid and 31.4% of n-butylmalonic acid.

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Agaric Acid and the Donnan Theory of Membrane Equilibrium

BY R. J. HARTMAN, E. W. KANNING AND J. E. WEBER[1]

The electromotive force of the following cell was measured at 25°.

"Parlodion" membrane	Inside solution: agaric acid, 1.25%; Ca(OH)₂ or HCl, in varying quantities	Satd. KCl	Calomel electrode

The agaric acid was prepared by electrodialyzing "Noble Difco" agar agar for twenty-four hours under a potential of 110 volts according to the procedure of Hoffman and Gortner.[2] The procedure followed in making the electromotive force measurements was essentially the same as that used by Loeb.[3] After about twenty-four hours a true membrane equilibrium was established as

(3) Ivanoff and Spassoff, *Bull. soc. chim.*, **49**, 19 (1931). See, also, Morton, Fallwell and Palmer, THIS JOURNAL, **60**, 1426 (1938), for the carbonation of benzylsodium.

(4) Morton and Richardson, *ibid.*, **62**, 129 (1940). Earlier references are to be had from this most recent article.

(1) This paper is constructed from a dissertation presented by Joseph Elliott Weber to the Faculty of the Graduate School of Indiana University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Hoffman and Gortner, *J. Biol. Chem.*, **65**, 371 (1925).

(3) J. Loeb, "Proteins and the Theory of Colloidal Behavior," Chapter XI, McGraw-Hill Book Co., New York, N. Y., 1924, p. 177.