which can be converted into the known 1′,9-methylene-1,2-benzanthracene. γ-(4,5-Methylene-2-phenanthryl)-butyric acid is obtained in good yield by dehydrogenating the dihydro intermediate as the ester and it cyclizes exclusively at position 1, affording a very satisfactory route to 4,5-methylenechrysene in which the over-all yield from 4,5-methylenephenanthrene is 30%.

The structures of the different products are fully established by the transformations indicated.

In all of the inter- and intramolecular acylations observed in the 4,5-methylenephenanthrene series a strong para directive influence of the 4-methylene group is discerned.

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Certain Trialkylated Benzenes and their Compounds with Aluminum Chloride and with Aluminum Bromide

BY JAMES F. NORRIS AND JOHN N. INGRAHAM[1]

In a recent paper[2] methods were described for the preparation, with high yields, of mesitylene and *s*-triethylbenzene by the Friedel–Crafts reaction. By the use of similar conditions toluene and *m*-xylene were ethylated and methyldiethyl- and dimethylethylbenzene were prepared. It seemed highly probable that these hydrocarbons had the symmetrical structure, although the properties of some of their derivatives were not in accord with those recorded in the literature for the symmetrical hydrocarbons.[3]

The ethyldimethylbenzene has been restudied and additional evidence is presented in favor of the symmetrical structure of the hydrocarbon.

In the paper by Norris and Rubinstein results were given of the study of the product formed from toluene, aluminum bromide and hydrogen bromide. Since Gustavson[4] has reported that the compound containing *s*-triethylbenzene and aluminum bromide is a crystalline solid, the investigation of this substance was undertaken. It was formed by passing hydrogen bromide into a solution of aluminum bromide in the hydrocarbon. Heat was generated and a light red oil separated from the excess of hydrocarbon. When cooled the compound formed yellow crystals which melted at 64–66°. Analyses of the crystals gave results which checked with the formula proposed by Gustavson: $Al_2Br_6 \cdot 2C_6H_5(C_2H_5)_3 \cdot HBr$. The complex was held at 0.002 mm. pressure at room temperature. When it came to constant weight the residue was shown by analysis to contain the Al_2Br_6 and hydrocarbon in the ratio of 1 to 1.

When the crystalline complex was treated with acetyl chloride, the yield of methyltriethylphenyl ketone was 67%.

An attempt was made to prepare a compound having the formula $Al_2Br_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HCl$ by passing hydrogen chloride into a solution of the bromide in the hydrocarbon. Analyses of the product from time to time showed that the bromine in aluminum bromide was being replaced by chlorine. When aluminum chloride and the hydrocarbon were treated with hydrogen bromide, the chlorine was replaced and the complex containing aluminum bromide was formed.

A crystalline complex having the formula $Al_2Cl_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HCl$ was isolated. The complex prepared from mesitylene had the formula $Al_2Br_6 \cdot 3C_6H_3(CH_3)_3 \cdot HBr$ (m. p. 47–48°). When held at 0.002 mm. to constant weight the residue contained Al_2Br_6 and $C_6H_3(CH_3)_3$ in the molecular ratio 1:1.

The complex with pseudocumene contained three moles of hydrocarbon. The complex with benzene and aluminum bromide was very unstable. When held at 12 mm. pressure, nearly all the benzene was lost.

The complex prepared from toluene and aluminum bromide when held at 12 mm. to constant weight left a residue which contained one mole of the hydrocarbon to one of Al_2Br_6. When held at 0.002 mm., it lost nearly all the hydrocarbon. The compounds containing trimethyl and triethyl benzene (ratio to Al_2Br_6 1:1) were stable at this

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[1] From a part of the thesis of John N. Ingraham submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1938.

[2] Norris and Rubinstein, THIS JOURNAL, **61**, 1163 (1939).

[3] Jacobson, *Ber.*, **7**, 1430 (1874); Tohl and Geyger, *ibid.*, **25**, 1533 (1895).

[4] Gustavson, *Compt. rend.*, **140**, 940 (1905).

pressure. The results show that the stability of the complexes increases as the number of alkyl groups present increases.

Details of Experiments

Dimethylethylbenzene.—The hydrocarbon was prepared by the method of Norris and Rubinstein except that *m*-xylene, furnished by the du Pont Company, which contained less than 1% of isomers was used instead of commercial "metaxylene." The product, after fractionation only, boiled at 184–184.6°. The crude tribromo derivative melted at 86.5–88°, and after repeated recrystallization at 87–89°. Distillation in a molecular still did not change the melting point. The trinitro compound melted at 114–116° (uncor.). Oxidation of the hydrocarbon gave a mixture of acids from which the monobasic acid was recovered by steam distillation; it melted at 161–162° (uncor.). The melting point of 3,5-dimethylbenzoic acid is 165° (cor.) and that of the 2,4-isomer is 124°.

A sample of the crude hydrocarbon was sulfonated, hydrolyzed and distilled. There were obtained 6 cc. at 182–184°, 21 cc. at 184.0°, and 6 cc. at 184–185.6°. The fraction boiling at 184.0° (total immersion thermometer, pressure, 752 mm.) was redistilled without change in boiling point. The index of refraction taken of the distillate, from time to time, remained constant. The tribromo derivative melted at 89–89.5° and the trinitro derivative at 117–117.6°. The hydrocarbon was analyzed. Calcd.: C, 89.55; H, 10.45. Found: C, 90.35, 90.18, 89.66; H, 10.47, 10.46, 10.23.

A sample of the hydrocarbon was converted into the sulfonamide, which was crystallized; it melted at 123.0–123.6° (literature 126°). The hydrocarbon was recovered from the sulfonamide by hydrolysis and converted into the tribromo derivative, which melted at 88.0–88.5°, and the trinitro derivative which melted at 115–116°.

1,3-Dimethyl-4-ethylbenzene.—This compound has been prepared by a number of investigators, but the constants of its derivatives are not in good agreement. We prepared it by condensing pure *m*-xylene with acetyl chloride at 0° with aluminum chloride in the presence of carbon disulfide, and subsequent reduction of the ketone formed.

The hydrocarbon boiled at 187.8° (total immersion thermometer) and gave a tribromide derivative (m. p. 81–82°) and a trinitro derivative (m. p. 119–120°). The monobasic acid formed by oxidation melted at 123.5–124.0° (uncor.), the melting point of 2,4-dimethylbenzoic acid. The boiling points given in the literature for the hydrocarbon vary from 183 to 187°; the melting points of the tribromo derivative from an oil to 135° and of the trinitro derivatives from 119–127°. The sulfonamide was found by four investigators to melt at 148°. It was evident that our hydrocarbon was not 1,3-dimethyl-4-ethylbenzene.

Complexes Containing Aluminum Halides and *s*-Triethylbenzene.—In the preparation and manipulation of the complexes precautions were taken to exclude moisture. The aluminum bromide used was distilled in an all glass vessel into the tube in which the complex was made. The tube was then sealed off from the distilling apparatus. The compounds were manipulated, when necessary, in a stream of dry nitrogen.

Analyses of a complex were made by melting the latter, and drawing up a sample into a pipet. The liquid was run into a small flask of known weight, which was weighed again. The weight of complex used was about 1.5 g. Water and ice were added and the flask stoppered. During the decomposition of the complex the flask was kept in cold water. The aqueous solution was diluted to a definite volume, a part of which was titrated with standard alkali, using phenolphthalein as indicator, for the determination of acid. It was shown that the bromine in aluminum bromide could be accurately determined in this way. The solution was next treated with a slight excess of ammonia and heated. The aluminum hydroxide was separated and ignited. The amount of hydrocarbon in the complex was determined by decomposing it in a small Babcock bottle. Enough water was added to bring the hydrocarbon into the graduated neck of the bottle, which was then placed in a centrifuge to ensure complete separation of the two liquids. The volume of the hydrocarbon measured on the standardized scale gave results from which could be calculated the weight. In most of the analyses the complex was decomposed in the Babcock bottle and the same sample used for the determination of aluminum, halogen, and hydrocarbon. The total of the percentages obtained served as a check on the accuracy of the analysis. With the samples that contained both chlorine and bromine the halogens were determined, in separate portions of the solution, by precipitation with silver nitrate and by neutralization with an alkali.

The Complex $Al_2Br_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HBr$. Preparation and Analysis.—About 25 cc. of the complex was made by passing hydrogen bromide into a solution of aluminum bromide in *s*-triethylbenzene. Heat was generated and a red oil began to separate at once. When precipitation was complete the product changed to a mass of yellow crystals which melted at 64–66°. Without further treatment two samples were analyzed (Sample 1). The complex was washed with petroleum ether, the excess of the latter removed and the product held under diminished pressure (15 mm.) for five minutes (Sample II). A complex was made by forming it from a mixture of equal volumes of petroleum ether and the hydrocarbon. It separated as a fluffy precipitate, from which the liquid was poured off. It was washed with petroleum ether, dried by evacuation and analyzed (Sample III). The results are given in Table I. The duplicate analyses of each sample were made on different samples.

TABLE I

Sample	Al, %	Br, %	Hydrocarbon, %	Molecular ratios Al	Br	Hydrocarbon
I	5.94	61.23	32.13	1	3.46	0.9
	5.99	61.23	32.48			
II	5.97	61.23	32.64	1	3.45	.9
	6.03	61.28	32.52			
III	5.54	59.23	34.01	1	3.56	1.0
	5.75	59.60	34.55			
Calculated for $Al_2Br_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HBr$				1	3.5	1

Behavior under Reduced Pressure.—A sample of the complex which weighed 7.547 g. was held at room temperature and 0.002 mm. pressure of mercury, and weighed at intervals. At the end of two hours the loss in weight was 0.273 g. Constant weight was reached in forty-five hours, when the loss was 1.775 g. The theoretical loss in weight should have been 1.823 if the residue had the compostion $Al_2Br_6 \cdot C_6H_3(C_2H_5)_3$. The residue was analyzed. The molecular ratio found was Al, 1, Br, 3.06, $C_6H_3(C_2H_5)_3$, 0.48.

Reaction of the Complex with Acetyl Chloride.—A mixture of 19.6 g. of complex and 6 cc. of acetyl chloride (molecular ratio 1 to 2) was allowed to stand in an ice-bath for two hours. After decomposition with water the oil was dried and distilled. The product solidified when cooled and melted at −17°. The yield of the mono-acetyl derivative of *s*-triethylbenzene was 5.5 g. (67%).

Reaction of the Complex with Ethyl Bromide.—A cold saturated solution of the complex in ethyl bromide was treated with petroleum ether; an oil was formed which crystallized when cooled with dry-ice. The oil was separated, held at 15 mm. pressure to remove solvent and analyzed. The sample used melted at about −20°. Bromine and aluminum were determined in the usual way. The liquid formed by decomposition with water was a mixture of triethylbenzene and ethyl bromide. To determine the amount of ethyl bromide present, the index of refraction of the mixture was determined and compared with a plot of the indexes of known mixtures of ethyl bromide and the hydrocarbon. The molecular ratios found were Al 1, Br 3.7, triethylbenzene 1.17, ethyl bromide 0.46. These results have led to further study. If the complex containing ethyl bromide is heated slightly above room temperature it decomposes with the evolution of hydrogen bromide.

Reaction of the Complex with Hydrogen Chloride.—An attempt was made to prepare a complex with the formula $Al_2Br_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HCl$ by passing hydrogen chloride into a solution of aluminum bromide in the hydrocarbon. At the end of ten minutes, when the reaction appeared to be complete, the product was washed and the vessel containing it was evacuated. The molecular ratios found were Al 1, Br 2.4, Cl 1.25, $C_6H_5(C_2H_5)_3$ 1.01. The result showed that bromine was being replaced by chlorine. The preparation was repeated and hydrogen chloride passed through the mixture for five hours. The product melted at 48–49° and an analysis gave the ratios: Al 1, Br 0.4, Cl 3.3, $C_6H_5(C_2H_5)_3$ 0.99. Repeated efforts failed to obtain a product free from bromine. It appears probable that the bromine of the aluminum bromide alone is replaced and not that in the hydrogen bromide in the complex. The molecular ratios in such a compound are: Al 1, Br. 0.5, Cl 3, $C_6H_5(C_2H_5)_3$ 1.

The product obtained as above was treated with hydrogen bromide. The mole ratios found were Al 1, Br 3.6, Cl 0, $C_6H_5(C_2H_5)_3$ 0.9. All the chlorine that had replaced bromine was removed from the compound.

Purity of the Triethylbenzene Recovered from Complexes.—It was found that the hydrocarbon recovered from complexes which had stood for not longer than two days had the correct index of refraction. In the case of the evacuation experiments which continued for several days, the index was about 0.0050 too high. Samples of the hydrocarbon from these experiments were combined and fractionated (180 cc.). A small amount of low- and high-boiling hydrocarbons was obtained along with 145 cc. of *s*-triethylbenzene which boiled at 215.4°.

The Complex $Al_2Cl_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HCl$.—Freshly sublimed aluminum chloride was covered with the hydrocarbon and hydrogen chloride was passed into the mixture. An oil was formed rapidly and on cooling changed to crystals that melted at 48–49°. The compound on analysis gave the following results: Al 8.66, 8.55%; Cl 40.33, 39.78%; $C_6H_5(C_2H_5)_3$ 52.85, 52.78. Calcd.: Al 8.60, Cl 39.66, $C_6H_5(C_2H_5)_3$ 51.69. The mole ratios found were Al 1, Cl 3.54, $C_6H_5(C_2H_5)_3$ 1.01.

The Complex Containing Mesitylene.—Experiments showed that apparently more than one complex was formed from mesitylene. Products were obtained in which the molecular ratios of the constituents changed when varying amounts of aluminum bromide and the hydrocarbon were used. When a large excess of the hydrocarbon was used the crystalline material obtained after cooling the reaction product was washed with petroleum ether and the vessel containing it was evacuated. The molecular ratios found were Al 1, bromine 3.6, $C_6H_3(CH_3)_3$ 1.6. These results are in fair agreement with the formula $Al_2Br_6 \cdot 3C_6H_3(CH_3)_3 \cdot HBr$. There was evidence of the formation of a complex which contained less of the hydrocarbon. The problem will be considered in a later paper.

The complex was treated with hydrogen chloride; a large percentage of the bromine was replaced by chlorine. The vessel containing a sample of the complex (10.22 g.) was evacuated to constant weight at 0.002 mm. in one hundred thirty-six hours. The loss in weight was 50%. If the residual compound had the composition $Al_2Br_6 \cdot C_6H_3(CH_3)_3$ the loss in weight would have been 52%. The hydrocarbon recovered from the complex after evacuation had the index of refraction $n^{14.7}\text{D}$ 1.5059 (literature for mesitylene at this temperature 1.4966 and for pseudocumene 1.5072). It was evident that on long standing the hydrocarbon had undergone a change.

Complex Containing Pseudocumene.—This was prepared in the usual way from the pure hydrocarbon. It separated as a red oil, which lost about one-fourth of its volume when washed with petroleum ether. When cooled in running water crystals were formed. The analysis gave the ratios Al 1, Br 3.44, $C_6H_3(CH_3)_3$ 1.5, which is in good agreement with the formula $Al_2Br_6 \cdot 3C_6H_3(CH_3)_3 \cdot HBr$.

Complex Containing Toluene.—The amounts of hydrogen bromide required to precipitate the complex containing aluminum bromide and toluene were determined. When the amounts of hydrogen bromide and aluminum bromide (Al_2Br_6) were in the ratio 1:1, precipitation was complete. With smaller amounts of hydrogen bromide the amount of precipitated oil decreased as the hydrogen bromide decreased. In these cases the addition of more hydrogen bromide brought about complete precipitation. The experiments confirm the view that the toluene complex contains aluminum bromide (Al_2Br_6) and hydrogen bromide in the ratio 1:1.

Complex Containing Benzene.—The complex was evidently very unstable and the analyses made did not fit accurately any definite molecular ratios. The precipitated oil gave the molecular ratios Al 1, Br 3.2, C_6H_6 3.05. An analysis of a second preparation gave 1:3.2:3.15.

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 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-Triphenylpyridine 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.

EASTMAN KODAK COMPANY
ROCHESTER, N. Y.
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[1] Gilman and Spatz, THIS JOURNAL, **62**, 446 (1940).

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

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

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[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).