Experimental

Formation of Triphenylmethyl.—To a mixture of 2 g. of sodium powder in 80 cc. of anhydrous ether (or 40 cc. of ether and 40 cc. of benzene) in an Erlenmeyer flask was added 5 g. of triphenylchloromethane. Frequently the sodium immediately became colored with red triphenylmethyl-sodium and the solution became yellow. The flask was fitted with a stopper bearing a movable glass rod flattened at one end. By pressing the sodium against the bottom of the flask a rapid reaction was initiated and the solution became orange-yellow as the radical was formed. After ten minutes the color began to change to the red color of triphenylmethyl-sodium, an indication that all of the triphenylchloromethane had reacted. Oxidation of the triphenylmethyl gave an 80% yield of triphenylmethyl peroxide, m. p. 185–186°. A similar result was obtained by vigorously shaking a mixture of the metal and triphenylchloromethane in ether with sharp particles of glass for twenty minutes.

p-Benzohydryltetraphenylmethane is formed to a slight extent when the complete reaction between the sodium and triphenylchloromethane is slow. This is the case when only the theoretical amount of sodium (1 atom) is employed and the mixture is shaken for a day or two in order to allow time for the last traces of sodium to react. When the reaction proceeds rapidly as is the case when the sodium is pressed with a glass rod, the formation of the dimer is practically entirely suppressed.

Preparation of Triphenylmethyl-sodium.—After pressing the sodium (2 g.) contained in a solution of 5 g. of triphenylchloromethane in 40 cc. of anhydrous ether and 40 cc. of benzene with a glass rod for ten minutes, the rod was removed and the mixture was shaken for two hours. Hydrolysis of the deep-red triphenylmethyl-sodium solution gave a 96% yield of triphenylmethane and only a trace of *p*-benzohydryltetraphenylmethane. The excellent yield of triphenylmethane is an indication of the completeness of the two reactions: the reaction of sodium with triphenylchloromethane and the addition of sodium to triphenylmethyl. Even after one-half hour of shaking the solution contained only 2% of triphenylmethyl that had not been converted to triphenylmethyl-sodium. Similar results were obtained by simply shaking a mixture of triphenylchloromethane and sodium powder in ether–benzene with sharp particles of glass for several hours. In addition to hydrolysis the triphenylmethyl-sodium was also treated with benzyl chloride to give *unsym*-tetraphenylethane and with carbon dioxide to form triphenylacetic acid in excellent yields.

By shaking a mixture of 2.78 g. of triphenylchloromethane, 2 g. of sodium powder and two dozen glass beads in 40 cc. of benzene for one month, triphenylmethyl-sodium was formed as a red precipitate. Hydrolysis gave a 70% yield of triphenylmethane.

Oxidation of Triphenylmethyl-sodium.—Dry air was passed through a solution of triphenylmethyl-sodium that had been prepared from 5 g. of triphenylchloromethane for one hour. From the products of hydrolysis there were isolated 3.15 g. (67%) of triphenylcarbinol and 0.2 g. (4%) of triphenylmethyl peroxide. Although the oily residue liberated iodine from hydrogen iodide, a search for triphenylmethyl hydrogen peroxide was unsuccessful.

Summary

Sodium reacts rapidly with triphenylchloromethane in ether provided fresh surfaces of the metal are exposed throughout the reaction.

Sodium adds to triphenylmethyl in ether and in benzene to form triphenylmethyl-sodium.

Triphenylcarbinol is the principal product of the oxidation of triphenylmethyl-sodium.

ANN ARBOR, MICHIGAN RECEIVED JULY 6, 1936

[CONTRIBUTION FROM THE GENERAL MOTORS CORPORATION, RESEARCH LABORATORIES SECTION]

The Action of Aluminum Halides on *n*-Pentane

BY A. L. GLASEBROOK, N. E. PHILLIPS AND W. G. LOVELL

Recently, Nenitzescu[1] investigated the reactions of *n*-hexane and *n*-heptane in the presence of aluminum chloride and found isomerization to the 2- or 3-methyl isomer to be the main reaction. Dehydrogenation, condensation to higher paraffins, cyclization to mono and bicyclic cycloparaffins, hydrogenation and splitting of the chain to lower paraffins also occurred. Calingaert[2] repeated the work of Nenitzescu and found that only about 6% of the reacting *n*-heptane was isomerized.

We attempted to study the reported isomerization of *n*-heptane; however, preliminary experiments gave reaction products which were very difficult to analyze and we decided to use *n*-pentane as the starting material. The use of this hydrocarbon was expected substantially to reduce the number and complexity of reaction products, and, since Nenitzescu[3] had shown the reaction between *n*-pentane, acetyl chloride and aluminum chloride to lead to the formation of *unsym*-methyl isopropyl acetone, a result which can best be explained by the preliminary isomerization of *n*-

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[1] Nenitzescu and Dragan, *Ber.*, **66**, 1892 (1933).

[2] Calingaert and Beatty, THIS JOURNAL, **58**, 51 (1936).

[3] Nenitzescu and Chicos, *Ber.*, **68**, 1584 (1935).

pentane to isopentane, we did not expect the isomerization reaction to be affected by the change in starting materials.

Using freshly sublimed aluminum chloride and dry pentane no reaction occurred even after refluxing for several days. When small amounts of water, alkyl chlorides (but not aromatic chlorides), or hydrated aluminum chloride were added to the reaction mixture, the pentane commenced to undergo decomposition almost immediately. The products did not appear to vary, regardless of the method used to start the reaction, and only the butanes and isopentane could be identified, the latter being the chief product. During the reaction, the aluminum chloride surface became coated with a layer of brown tar, which, after hydrolysis of the aluminum chloride residue, was found to consist of a mixture of highly unsaturated, halogen-containing compounds. Substances boiling higher than *n*-pentane and soluble in the reaction mixture were also formed, but, owing to the small amounts present, could not be identified.

Since water and hydrated aluminum chloride react with aluminum chloride to give aluminum oxide and hydrochloric acid, these substances were investigated for their ability to induce the decomposition of pentane in the presence of aluminum chloride. Anhydrous aluminum oxide had no effect, but when dry hydrogen chloride was bubbled through the reaction mixture, the usual reaction commenced, and, apparently, this is the substance which is responsible for the increased activity of the aluminum chloride. This fact was also observed by Ipatieff and Grosse.[4] The same explanation can also be used in the case of the alkyl chlorides, since these substances react with aluminum chloride to give hydrogen chloride.[5] In addition, we found anhydrous hydrogen bromide to be exceptionally effective in activating aluminum chloride.

Aluminum bromide was next investigated. This compound is quite soluble in *n*-pentane. The bromide proved much more effective in causing the decomposition of pentane, and it was unnecessary knowingly to add other substances to the reaction mixture to induce reaction. In one day a reaction mixture containing only 1.52 mole % aluminum bromide undergoes as much change as a reaction mixture containing 17.4 mole % aluminum chloride, and, promoted by 0.2 mole of water per mole of aluminum chloride, undergoes in two days' reaction time. Qualitatively the products obtained using the bromide catalyst were the same as those obtained using the chloride. The amount of pentane reacting increased with the reaction time and the aluminum bromide concentration. Table I gives the results obtained in a study of these variables. The amount of butanes formed is shown to increase practically linearly with the extent of the reaction, whereas the amount of isopentane formed reaches a maximum from which it slowly declines as the extent of the reaction is further increased.

The addition of such substances as anhydrous hydrobromic acid or water increases the reaction velocity. The effects caused by the addition of these substances to the reaction mixture are shown in Table II.

When gaseous *n*-pentane carried by a stream of dry nitrogen was passed over aluminum chloride at temperatures from 40 to 133°, no reaction could be detected outside of a slight discoloration of the aluminum chloride. The addition of promoter substances to the gas stream readily caused the decomposition of *n*-pentane, and it was unnecessary to use temperatures higher than 40°. Anhydrous hydrobromic acid was the most effective substance investigated for activating the aluminum chloride. Using gaseous *n*-pentane the amount of butanes formed was greatly increased and only insignificant amounts of isopentane formed. Traces of hydrogen were also formed in these experiments. Most of the higher boiling substances remained behind on the aluminum chloride and caused the latter to slowly liquefy with continued use.

The aluminum chloride became decreasingly active when the addition of hydrogen halides or halogen halide forming substances was discontinued. Aluminum chloride which had been activated by mixing anhydrous hydrobromic acid to the gas stream lost its activity more slowly than the other substances investigated, and it was also possible to activate the aluminum chloride by treatment with anhydrous hydrobromic acid prior to the introduction of the *n*-pentane vapor. This procedure was ineffective with water vapor and anhydrous hydrochloric acid. Using aluminum chloride which had been activated by treatment with anhydrous hydrobromic acid before use, we were able to test the gases leaving the

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[4] Ipatieff and Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936).

[5] See, for example, Mouneyrat, *Compt. rend.*, **127**, 109 (1898).

TABLE I

THE EFFECT OF REACTION TIME AND CATALYST CONCENTRATION ON THE DECOMPOSITION OF *n*-PENTANE IN THE PRESENCE OF ALUMINUM BROMIDE

n-Pentane used, g.	105	105	105	105	110	110	110	110
Aluminum bromide used, g.	11.3	11.3	11.3	11.3	6.2	21.5	36.4	57.2[b]
Mole % aluminum bromide	2.82	2.82	2.82	2.82	1.52	5.28	8.94	14.05
Reaction time, hrs.	22	51	95	169	26.2	26.2	26.2	26.2
Reaction loss, % by wt.	1.0	1.4	1.0	4.3[a]	1.5	0.9	3.2[c]	6.8[c]
Butanes, % by vol.	1.5	2.8	5.0	8.8	1.5	6.1	10.2	14.1
Isopentane, % by vol.	40.8	51.0	55.9	44.2	27.2	53.5	46.8	40.4
Material boiling higher than *n*-pentane, % by vol.	2.5	3.4	3.4	5.9	2.8	3.1	5.4	5.9
Insoluble tar, % by wt.	Neg.	Neg.	0.5	1.0	Neg.	Neg.		

[a] The capacity of the gas receiver was exceeded in this experiment, and some of the gas is known to have escaped [b] All of the aluminum bromide did not dissolve in this experiment. [c] These figures include the insoluble tar.

TABLE II

THE EFFECT OF PROMOTERS IN THE REACTION OF *n*-PENTANE IN THE PRESENCE OF ALUMINUM BROMIDE

	Reaction with 2 cc. water added	Reaction without water	Reaction in presence of HBr	Reaction in absence of HBr
n-Pentane used, g.	200	200	202	202
Aluminum bromide used, g.	27	29	18	18
Mole % aluminum bromide	3.52	3.77	2.36	2.36
Reaction time	about 3 days		about 38 hours	
Reaction loss and tar, % by wt.	3.0	1.5	2.5	neg.
Butanes, % by vol.	10.7	5.9	7.0	3.0
Isopentane, % by vol.	58.6	51.0	51.5	42.8
Material boiling higher than *n*-pentane, % by vol.	6.0	2.7	2.5	3.6

aluminum chloride for bromine content, and found that the amount of decomposition decreased as the bromine content of the exit gases dropped.

Experimental

Reagents.—The *n*-pentane used was a commercial product derived from petroleum. Before use the material was shaken with concentrated sulfuric acid until the acid remained colorless on further treatment, then washed, dried and distilled from sodium. The distilled material had a practically constant boiling point and the constants: n^{20}_{D} 1.3579; d^{20}_{4} 0.6264. The anhydrous aluminum chloride was a C. P. grade and was resublimed in a current of dry nitrogen at 200 to 230° before use. The aluminum bromide was prepared by the action of bromine on the hot metal and purified by distillation. Before use the aluminum bromide was redistilled over aluminum.

Aluminum Bromide Dissolved in *n*-Pentane.—*n*-Pentane (usually between 100 to 200 g.) was placed in a round-bottomed flask and aluminum bromide added. The flask was fitted with a reflux condenser cooled with refrigerated water at 5 to 10°. The top of the condenser was attached to a drying tube filled with dehydrite. The drying tube in turn, connected to a gas receiver. At all times the system was kept under a slight vacuum. The aluminum bromide did not dissolve immediately, and, after the closed system had been established, the flask was shaken and heated to hasten the process of solution.[6] After solution of the aluminum bromide had occurred, the heat was removed and the flask allowed to stand undisturbed at room temperature.

Before stopping the experiment, the flask containing the reaction mixture was cooled with ice water. In practically every case, this cooling sufficed to condense all the gas (usually 200–400 cc.) which had formed during the experiment. The flask was then disconnected and the flask contents slowly poured into a cooled separatory funnel containing crushed ice which hydrolyzed the dissolved aluminum bromide. The aluminum bromide–tar compounds which formed were separately hydrolyzed and extracted with ether because after hydrolysis they were slightly soluble in *n*-pentane and readily so in higher hydrocarbons.

Identification of the Reaction Products.—The analyses were obtained by distillation of 100 cc. of the reaction product. The column used for isobutane was a 91-cm., 5 mm. inside diameter Podbielniak-type column with a partial condensation head, which was cooled with a dry-ice–acetone bath. The isopentane was separated from *n*-pentane in a 28-plate vacuum jacketted column with a partial condensation head. The holdup of this column was 6 cc. A number of known mixtures were analyzed in these columns and excellent results obtained. The total distillation loss from the two distillations was usually between 0.5 and 1.5 cc. Figure 1 shows a typical distillation curve obtained.

Although the distillation curve shows only the presence of isobutane, a small amount of *n*-butane could probably

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(6) If the pentane contains even traces of olefins the process of solution will be characterized by the formation of a yellow cloudiness in the solution. This gradually clears, and, after an hour or so, the solution becomes entirely clear and colorless. The clearing of the solution is accompanied by the precipitation of small droplets of brown polymer on the sides of the flask. These coalesce on further standing and sink to the bottom of the flask. When pure pentane is used, usually two days elapse before any tar precipitates. Outside of this, however, no differences could be detected.

be found by a redistillation of the break material between isobutane and isopentane. The isopentane fractions were always checked by their critical solution temperatures[7] and frequently the refractive index and density were measured. The average values for the refractive index and density of the isopentane fractions reported in Table I were n^{20}_D 1.3548 and d^{20}_4 0.6203.

The substances boiling higher than *n*-pentane were not present in sufficient quantities to allow purification and identification.[8] By distilling the residues from several experiments a single plateau occurred in the distillation curve at 58 to 60°, but insufficient material was obtained to allow its identification. The fractions were all saturated and measurement of the refractive index suggested the material to be largely paraffinic. Usually the analysis for the higher boiling material was obtained by measurement of the critical solution temperature of the residue from the isopentane distillation.

Likewise, the insoluble tars which formed were not present in sufficient quantities to be identified. The tars from a series of experiments were saved and distilled. The material distilled over the range 100 to 240° without the appearance of a constant boiling substance. All of the fractions were strongly unsaturated and gave tests for halogens. The tars gave an intense purple color when bromine and *m*-cresol were added to their dilute solutions in *n*-heptane or other higher paraffins. The same color reaction is also given by the tars obtained from the reactions of other hydrocarbons with aluminum halides.

Aluminum Chloride and Liquid *n*-Pentane.—In general, the same experimental procedure was used as with aluminum bromide. However, the aluminum chloride reaction mixtures were always kept at the boiling point instead of room temperature. Usually 30 to 40 g. of aluminum chloride was used for each 100 g. of pentane and 0.2 mole of water (or its equivalent when other substances were used) added per mole of aluminum chloride used. With aluminum chloride the reaction velocities were slower, and even after five to ten days' reaction only 30 to 40% of the pentane could be decomposed. In several experiments a large butane fraction was obtained by starting with quantities of *n*-pentane as much as 1000 g. In these cases up to 10% *n*-butane was found in the butane fraction.

Experiments with Gaseous *n*-Pentane.—In the usual experiment a charge of 250 to 300 g. of aluminum chloride was placed in the middle of a 91-cm. long Pyrex tube of 3.8-cm. inside diameter. The reaction tube was heated in a horizontal electric furnace. The mixture of *n*-pentane vapor and nitrogen was produced by bubbling a stream of dry nitrogen through a wash bottle containing the hydrocarbon. The amount of pentane introduced was controlled by regulation of the temperature of the liquid pentane. In experiments in which water was added to the vapor entering the reaction tube, an additional wash bottle containing water was placed in the line just previous to entrance into the reaction tube. In certain experiments anhydrous hydrogen bromide or chloride replaced nitrogen as the carrier gas. A carrier gas flow of 50 cc. per min. was used to introduce 0.2 g. per minute of *n*-pentane into the reaction tube. When water vapor was used, it was added to the gas stream at the rate of 0.005 g. per minute. Varying the rate of flow of the pentane changed only the amount of decomposition. The gases leaving the reaction tube passed through a trap cooled to −60 to −70°. The gas which did not condense in this trap was collected in a gas receiver.

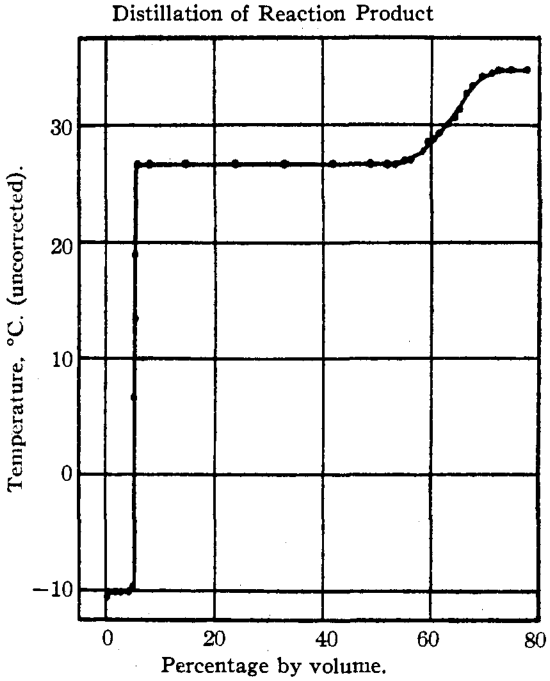

Fig. 1.—Sample used, 100.0 cc.; isobutane distillation loss, 0.4 cc.; isopentane distillation loss, 1.0 cc.

When nitrogen was used as the carrier, 85 to 95% of the pentane sent through was recovered as liquid, the tarry deposit on the aluminum chloride and the gas accounting for the balance. When the gas collected in the gas receiver was slowly passed through a trap at −30 to −40° practically the entire hydrocarbon content was condensed. Traces of hydrogen were found in the gas remaining, and its hydrocarbon content had carbon numbers between 3.9 and 4.6. When the halogen acids were used as carriers, they were removed, after leaving the reaction tube, by treatment with dilute caustic solution, and in these cases the gas loss was negligible.

In a typical experiment a product was obtained containing 33.7% butanes and 13.4% isopentane. Reducing the amount of decomposition did not materially change the relative amounts of products formed. Redistillation of the butane fractions in a Podbielniak low temperature column showed these fractions to contain from 4 to 11% *n*-butane, the balance being isobutane.

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(7) In order to avoid the use of sealed tubes, Eastman Kodak practical *m*-cresol was used instead of aniline for the critical solution temperature measurements. This material lowered the critical solution temperature of isopentane to about 12° depending upon the water content of the cresol. The solution temperature of *n*-pentane was 10° lower. The cresol was kept protected from the atmosphere and was measured out with a mercury sealed buret. The solution temperatures so determined remained constant as long as a given sample of cresol was in use.

(8) Insoluble tars and substances boiling higher than the starting material are produced in greater abundance with *n*-heptane and are being more thoroughly investigated in the study of this substance.

Summary

1. Dry n-pentane, either in the form of vapor or liquid, undergoes little, if any, decomposition in the presence of freshly sublimed aluminum chloride. If, however, anhydrous hydrogen bromide or chloride, water, hydrated aluminum chloride, or alkyl chlorides are added, reaction immediately commences. In the liquid phase reaction, the butanes and isopentane have been identified as reaction products. The latter is the chief product. Undefined saturated higher boiling products and an insoluble unsaturated polymer are also produced. In the vapor phase reaction the amount of isobutane formed is greatly increased and with extensive reaction becomes the chief product. For the vapor phase reaction aluminum chloride and anhydrous hydrobromic acid provide the most active catalyst.

2. In moderate concentration, aluminum bromide is soluble in n-pentane. It is a much more active substance than aluminum chloride and does not require the addition of other substances to cause the decomposition of n-pentane. The extent of reaction has been found to depend on the aluminum bromide concentration as well as the reaction time. The reaction products were the same, qualitatively, as those obtained with the chloride catalyst. As the extent of reaction was increased, the amount of butanes formed increased linearly, whereas the amount of isopentane formed reached a maximum value and then slowly declined. As much as 55.9% isopentane was obtained from n-pentane. When water is added to the reaction mixture, or anhydrous hydrogen bromide bubbled through it, the reaction velocity is increased.

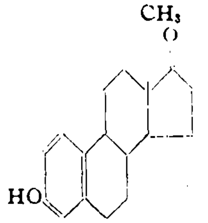
DETROIT, MICHIGAN RECEIVED JULY 21, 1936

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE, AND THE PARKE, DAVIS AND CO. RESEARCH LABORATORIES]

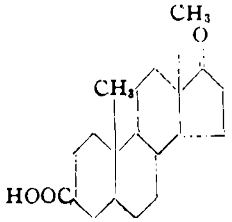
Sterols. VII. *Cis* and *Trans* 3-Carboxyandrostanone, An Oestrus-Producing Male Hormone Derivative, and *epi*-Cholesterol

BY RUSSELL E. MARKER, OLIVER KAMM, THOMAS S. OAKWOOD AND JOSEPH F. LAUCIUS

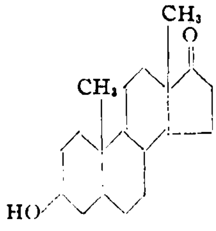
Because of the acidic nature of theelin, we prepared an androsterone derivative having a carboxyl group in the 3-position to see whether this compound would have female hormone properties in addition to male activity. The product was the mixture of *cis*- and *trans*-3-carboxyandrostanone. We made no attempt to separate the two stereoisomers. We found that the ethyl ester of this compound gave an oestrus response in rats when given in quantities of from 5–10 γ. The ethyl ester is much more active than the free acid. These compounds, however, were inactive when tested for male hormone properties by the cock's comb test in doses of 2 mg. Thus it is not necessary to have unsaturation in the molecule to have an oestrus-producing compound.



Theelin



Cis and Trans-3-Carboxyandrostanone



Androsterone

Because of the importance of obtaining *epi*-cholesterol in large quantities for research purposes avoiding the expensive digitonin process for the separation of the *cis* and *trans* isomers, we have looked for other means of separating these isomers, and found that by crystallizing the acetates from ethyl alcohol, a partial separation can be accomplished giving a product containing 80–90% of *epi*-cholesterol. The remaining cholesterol can then be removed completely by recrystallizing the benzoates from ethyl alcohol. We previously separated the two isomers by digitonin.[1]

We found that *epi*-cholesterol behaves very similarly in instability to *epi*-allocholesterol pre-

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[1] Marker, Oakwood and Crooks, THIS JOURNAL, **58**, 481 (1936).