hydrolyzes with great ease in the presence of traces of moisture and loses ammonia readily, even at ordinary temperatures, with the formation of an imine and possibly some nitride.

Triphenyl germanium bromide is immediately and quantitatively ammonolyzed by potassium amide in liquid ammonia. In the presence of excess amide, the monopotassium salt, $(C_6H_5)_3GeNHK$, is formed. The amine is re-formed from the potassium salt on the addition of ammonium bromide.

Tritriphenyl germanium nitride was prepared by heating triphenyl germanium amine to 200° *in vacuo.* It crystallizes in the form of needles melting at 163–164°. It is soluble in petroleum ether and other common organic solvents and may be sublimed *in vacuo.*

Metallic sodium reacts with triphenyl germanium oxide in liquid ammonia with the formation of sodium triphenyl germanide and sodium triphenyl germanolate.

It is pointed out that the compounds of germanium are generally more reactive than are the analogous compounds of carbon.

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[Contribution from the Chemical Laboratory of the University of Illinois]

THE REACTION BETWEEN ALKALI METAL ALKYLS AND QUATERNARY ARSONIUM COMPOUNDS

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In some of the early work on organic arsenic compounds Cahours[1] reported the preparation of pentamethylarsine by the action of zinc dimethyl on tetramethylarsonium iodide. The evidence for the existence of this penta-alkylarsine was slight and the work has never been confirmed. Previous attempts in this Laboratory to prepare the analogous penta-alkyl nitrogen[2] and phosphorus[3] compounds by the action of alkali metal alkyls on the corresponding -onium salts have not been successful. In view of Cahour's claim for the existence of pentamethylarsine, the work has been extended to the arsonium salts.

The methods used in the study of the reactions of alkali metal alkyls and arsonium salts were very similar to those used in the earlier work on nitrogen and phosphorus compounds. Lithium ethyl and lithium *n*-butyl were used in most of the experiments.

The first reaction studied was that between lithium *n*-butyl and tetraethylarsonium bromide. Low-boiling petroleum ether was used as a sol-

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[1] Cahours, *Ann.*, **122**, 337 (1862).

[2] Hager with Marvel, This Journal, **48**, 2689 (1926).

[3] Coffman and Marvel, *ibid.*, **51**, 3496 (1929).

vent and the reaction mixture was carefully distilled out of contact with air or moisture in the hope of thus obtaining a high-boiling fraction that would prove to be the desired penta-alkyl arsenic compound. The only product that could be identified definitely was triethylarsine. Next an attempt was made to prepare a penta-alkyl arsenic compound from triethylarsine dibromide and lithium ethyl. Triethylarsine was the only product that was identified.

Since there seemed to be very little chance of isolating a pure stable penta-alkyl arsenic compound, it was decided to study some reactions that might lead to isomeric products of the type R_4AsR' and $R_3R'AsR$, as had been done before in the nitrogen series, and to determine whether or not their decomposition products would give any indication of the existence of penta-alkyl arsines in which the five valence bonds were equivalent. For this purpose the reactions between lithium *n*-butyl and tetra-ethylarsonium bromide and lithium ethyl and triethyl-*n*-butylarsonium bromide were investigated. The reaction products were worked up in such a manner as to make it possible to analyze the gaseous products. The reactions which occurred are shown by the following equations.

$$2LiC_4H_9 + 2(C_2H_5)_4AsBr \longrightarrow 2LiBr + 2(C_2H_5)_3As + C_2H_4 + C_2H_6 + C_4H_{10} + C_4H_2 \qquad (1)$$

$$LiC_2H_5 + (C_2H_5)_3C_4H_9AsBr \longrightarrow LiBr + (C_2H_5)_2C_4H_9As + C_2H_4 + C_2H_6 \qquad (2)$$

The fact that these two reactions give entirely different products shows that the arsenic atom did not at any stage of the reaction share five pairs of electrons with five hydrocarbon groups to give a penta-alkyl arsenic compound in which the alkyl groups were equivalent.

In working up these reaction mixtures it was found that the easiest way to identify the arsine was to allow it to undergo oxidation with air or oxygen. Instead of yielding the arsine oxides, it was found that triethylarsine gave diethylarsinic acid and diethyl-*n*-butylarsine gave ethyl-*n*-butylarsinic acid. These facts were checked by the use of the known arsines.

In analyzing the gaseous products of these reactions it was found that they were usually made up of less than 5% of unsaturated hydrocarbons and more than 95% of saturated hydrocarbons. This was the cause of considerable concern until it was found that ethylene was rather rapidly polymerized by a solution of a lithium alkyl to give non-gaseous products. Since the reaction mixtures containing in every case an excess of the lithium alkyl always stood for some two weeks under pressure it is not surprising that most of the olefins were polymerized before the tubes were opened.

One experiment was performed in which tetramethylarsonium iodide was treated with sodium triphenylmethyl in an attempt to isolate a compound analogous to the tetramethyltriphenylmethylammonium of Schlenk and Holtz.[4] There was some indication that a colored salt-like compound

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[4] Schlenk and Holtz, *Ber.*, **49**, 603 (1916).

was produced. However, the only product fully identified was triphenylmethane. The odor of trimethylarsine was apparent. No definite conclusion can be drawn from this experiment.

Experimental Part

Triethylarsine.—In a 5-liter two-necked flask fitted with a reflux condenser, a mechanical stirrer and a 1-liter separatory funnel were placed 168 g. of magnesium turnings and 3.8 liters of dry ether. The Grignard reagent was prepared by adding 720 g. of ethyl bromide in the usual manner. The air was swept out of the flask with a current of dry nitrogen and to the Grignard solution thus prepared was then added a solution of 300 g. of arsenic trichloride in 600 cc. of dry ether. During the addition of this solution stirring was maintained and the solution was kept at a temperature of about 20°. Stirring was then discontinued and the mixture was boiled under the reflux for about twenty-four hours. The reaction mixture was decomposed with ice water acidified with hydrochloric acid. The ether layer was separated and the water layer was extracted three times with more ether. The combined ether layers were dried over calcium chloride and distilled. After the ether was removed at ordinary pressures, the residue was distilled under reduced pressure in a current of dry nitrogen or carbon dioxide. The triethylarsine boiled at 65–70° at 25–30-mm. pressure. The yield was 150–173 g. (54–62% of the theoretical amount). Steinkopf and Müller[5] obtained yields of 40% of the theoretical amount of triethylarsine without refluxing the mixture.

Tetra-ethylarsonium Bromide.—A solution of 15 g. of triethylarsine and 21 cc. of ethyl bromide in 20 cc. of dry ether was heated at 98° in a sealed tube for about eight hours. The tube was cooled and opened. The salt was dissolved in absolute alcohol, then precipitated with dry ether and filtered with suction. The yield was 18 g. (75% of the theoretical amount). The product melted at 298–300° (uncorr.).

Anal. Subs., 0.5518: 19.62 cc. of 0.1043 *N* $AgNO_3$. Calcd. for $C_8H_{20}AsBr$: Br, 29.51. Found: Br, 29.45.

Triethyl-*n*-butylarsonium Bromide.—A solution of 15 g. of triethylarsine and 18 g. of *n*-butyl bromide in 20 cc. of dry ether was heated at about 98° in a sealed tube for about two days. The salt was purified by dissolving in absolute alcohol and precipitating with dry ether. The yield was 19 g. (75% of the theoretical amount). The product melted at 227° (uncorr.).

Anal. Subs., 0.1213: 4.59 cc. of 0.0893 *N* $AgNO_3$. Calcd. for $C_{10}H_{24}AsBr$: Br, 26.74. Found: Br, 26.99.

Diethyl-*n*-butylarsine.—To the Grignard reagent prepared from 24 g. of magnesium and 110 g. of ethyl bromide in 200 cc. of dry ether was added a solution of 60 g. of *n*-butyldichloro-arsine in 70 cc. of dry ether. The mixture was stirred and boiled under a reflux condenser for about eighteen hours. The reaction mixture was decomposed with ice water acidified with hydrochloric acid. The ether layer was separated, dried over calcium chloride and distilled. After the ether was removed, the residue was distilled under reduced pressure. The arsine boiled at 78° at 28 mm. The yield was 25 g. (44% of the theoretical amount); sp. gr. d^{20}_{20} 1.0306; n^{20}_{D} 1.4745.

The compound was not analyzed but a 5-cc. sample was heated in a sealed tube overnight with 5 cc. of ethyl bromide in 10 cc. of dry ether. The product was identical with the triethyl-*n*-butylarsonium bromide obtained from triethylarsine and *n*-butyl bromide.

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[5] Steinkopf and Müller, *Ber.*, **54B**, 844 (1921).

Tetramethylarsonium Iodide.—A solution of methylmagnesium chloride was prepared by passing dry methyl chloride into a well-stirred suspension of magnesium turnings in dry ether. The strength of this solution was determined by titrating a portion with acid according to the method of Gilman, Wilkinson, Fishel and Meyers.[6] To 2 liters of this ether solution containing 3.02 moles of methylmagnesium chloride was added 165 g. of arsenic trichloride. Considerable solid separated and stirring was impossible. After standing overnight the mixture was decomposed with ice water acidified with hydrochloric acid. The mixture was distilled directly until the ether was removed and the distillate containing ether and trimethylarsine was dried over calcium chloride. To this solution an excess of methyl iodide was added. After several weeks the precipitated tetramethylarsonium iodide was filtered off and recrystallized from ethyl alcohol. The product seemed to sublime at 320–328°.

Anal. Subs., 0.2413: 9.78 cc. of 0.0893 N $AgNO_3$. Calcd. for $C_4H_{12}AsI$: I, 48.49. Found: I, 48.55.

Diethylarsinic Acid.—A sample of triethylarsine was allowed to stand in a loosely stoppered test-tube. The crust which formed on the surface was broken from time to time and the material gradually solidified. This solid product was recrystallized from ethyl acetate several times and it then melted sharply at 136–137°.[7] Some reddish oil was formed during the oxidation. This was entirely removed in the crystallization. The acid was titrated with standard alkali. Subs., 0.1275: 6.4 cc. of 0.1199 N NaOH. Neutral equivalent, calcd. for $C_4H_{10}AsO_2H$: 165.9. Found: 165.1. The same material was obtained by bubbling dry oxygen through a solution of triethylarsine in dry ether.

Ethyl-*n*-butylarsinic Acid.—This was first prepared by oxidizing diethyl-*n*-butylarsine with air in oxygen exactly as described above. The product was recrystallized from a mixture of benzene and finally melted at 93–96°.

To prove the structure of this product a sample was prepared by the general method for the synthesis of arsinic acids devised by Quick and Adams.[8]

To a well-stirred mixture of 20 g. of ethyl bromide and 70 cc. of 10 N sodium hydroxide was slowly added 34 g. of *n*-butyl dichloro-arsine. The mixture was stirred for a few hours, then filtered and evaporated to dryness. The residue was extracted with hot benzene and the arsinic acid was precipitated with petroleum ether. After several recrystallizations from a mixture of benzene and petroleum ether this product melted at 93–96°. A mixed melting point with the product obtained from the oxidation of diethyl-*n*-butylarsine showed that the two were identical. The product was titrated. Subs., 0.1229: 5.3 cc. of 0.1199 N NaOH. Calcd. for $C_6H_{14}AsO_2H$, neutral equivalent, 193.9. Found: 193.3.

General Procedure Followed in Studying the Reactions of the Lithium Alkyls and Quaternary Arsonium Salts

Lithium ethyl and lithium *n*-butyl were prepared and used in both petroleum ether (b. p. 40–45°) and a high-boiling paraffin oil in the manner previously described by Hager with Marvel.[2] The petroleum ether solutions were analyzed but no analysis was made on the solutions in the high-boiling oil. The arsonium salts were dried in a vacuum desiccator over sulfuric acid before use. When petroleum ether was used as a solvent for the reaction, the lithium alkyl was prepared exactly as described before and the reaction with the arsonium salt was carried out in a flask such as is shown in Fig. 1. The

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[6] Gilman, Wilkinson, Fishel and Meyers, This Journal, **45**, 150 (1923).

[7] Wigren, *Ann.*, **437**, 288 (1924), gives the melting point as 133–134°.

[8] Quick and Adams, This Journal, **44**, 811 (1922).

dried salt was introduced into the small bulb (A), which was then sealed. The glass apparatus containing the lithium alkyl solution was sealed on at B and the apparatus was connected to a mercury vapor pump, all of the air exhausted and the apparatus was sealed. The valve on the reaction vessel containing the lithium alkyl was broken and the solution was allowed to flow into the large Bulb D. The reaction flask was then sealed at B. Some glass beads were placed in the large reaction flask so that shaking the flask prevented caking of the reaction mixture. The salt was introduced into the solution of the lithium alkyl by tilting the apparatus. Gas evolution was noted in all of the experiments. The reaction mixtures were allowed to stand for about two weeks with occasional shaking. After this time the flask was opened at C and the gas collected in an evacuated bulb of the type shown in Fig. 3.

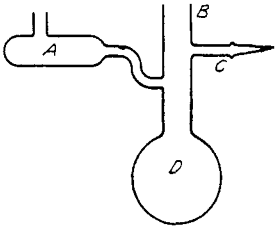

Fig. 1.

When the high-boiling paraffin oil was used as a solvent it was found more convenient to use the reaction vessel shown in Fig. 2. The dry salt was introduced in Bulb A (200 cc.). The solvent, mercury alkyl and lithium were placed in Bulb B (100 cc.). The system was evacuated with a mercury-vapor pump and sealed at C and D. E was a Gooch filter plate sealed into the apparatus. When the conversion of the mercury alkyl to the lithium alkyl was complete, as indicated by the settling of the lithium amalgam to the bottom of the solution, the oil solution was filtered over into the bulb containing the salt. These reaction mixtures were also allowed to stand for about two weeks and the gas was collected by opening at F.

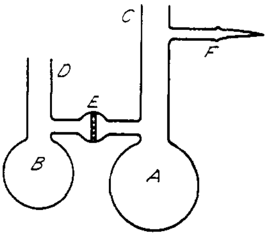

Fig. 2.

The gas was collected by attaching the evacuated gas pipet (Fig. 3) to the side-arm of the reaction flask by means of heavy-walled pressure tubing. One stopcock of the gas pipet was opened and the tip on the reaction flask was broken inside the heavy tubing. The reaction flasks were warmed to about 100° to insure driving out most of the gases when the high-boiling paraffin oil was used as a solvent. The gas in the pipet was brought to atmospheric pressure by introducing dry mercury until the pressure was equalized with atmospheric pressure.

The first gas analyses were made by absorption and combustion methods. However, it was found much more satisfactory to determine the unsaturated hydrocarbons by absorption in bromine water and to determine the density of the remaining saturated hydrocarbons after drying with anhydrous magnesium perchlorate by means of an Edwards gas density balance.[9] A sample of each gas was burned to be sure that it was not air.

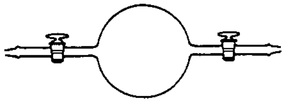

Fig. 3.

After removal of the gases in all of the later experiments, the flasks were opened. The odor of the arsine was always noticeable. From the high-boiling paraffin oil solutions it was impossible to isolate pure products of any sort. When petroleum ether was used as a solvent it was evaporated and the arsinic acids were obtained by allowing the residue to oxidize in the air.

Attempt to Prepare Tetra-ethyl-*n*-butylarsenic.—After a few preliminary trials the apparatus shown in Fig. 4 was used for this experiment. In Bulb A was placed 18 g. of carefully dried tetra-ethylarsonium bromide and some glass beads. The bulb was then

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[9] Directions for using this balance are given in Bureau of Standards Paper No. 89.

sealed. The reaction flask containing the lithium *n*-butyl solution was sealed on to the apparatus at C. The entire apparatus was evacuated with a mercury-vapor pump and carefully sealed. Then 0.048 mole of lithium *n*-butyl in 60 cc. of petroleum ether was introduced into Bulb B and the apparatus was sealed at C. The salt was slowly poured over into the lithium alkyl solution. Vigorous gas evolution was noted. The petroleum ether solution was poured back and forth from Bulb A in order that all of the salt would come into contact with the lithium *n*-butyl. After about two days the reaction mixture was filtered through the filter sealed into the apparatus at D into Flask E. The petroleum ether was then partially distilled back into B to wash the salt and again filtered. The gas was then removed from the apparatus by opening the side-arm on Flask B and the apparatus was evacuated to a pressure of 30 mm. The apparatus was then sealed at F. The solid left in Flask B was found to be lithium bromide and some unchanged tetra-ethylarsonium bromide.

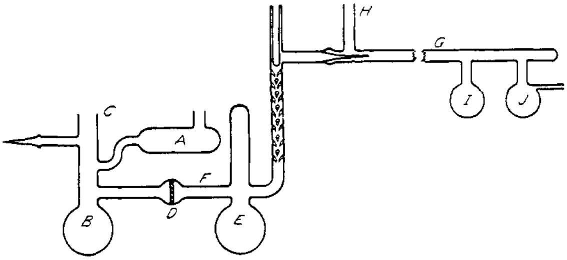


Fig. 4.

The petroleum ether solution in Flask E was then distilled. The two-bulb receiver was sealed onto the side-arm, evacuated and sealed. The valve at H was broken. The distillation flask was placed in an oil-bath and the receiver I was placed in an ice-bath. A first fraction was obtained up to about 54°. The bulb I was sealed off and a second fraction boiling up to 77° was collected in Bulb J. This bulb was sealed and about a half gram of liquid which boiled at 100–110° was collected in the tip of G. This was obtained by directly heating the bulb with a flame and the high-boiling temperature was undoubtedly due in part to superheating.

The first fraction was redistilled under atmospheric pressure and boiled at 40–65°. It did not have the characteristic arsine odor. The second fraction on redistillation in the air boiled at 65 to 140°. Most of the material came over at 139–140°, which indicated that it was nearly pure triethylarsine. A sample on standing in the air was oxidized to diethylarsinic acid. Another sample gave triethylarsine dibromide when treated with bromine. The small amount of high-boiling liquid was again distilled under atmospheric pressure and distilled below 150°. It gave all of the tests for triethylarsine.

Lithium Ethyl and Tetraethylarsonium Bromide.—A solution of 0.095 mole of lithium ethyl in petroleum ether (b. p. 40–45°) was added to 25 g. (0.092 mole) of tetraethylarsonium bromide. A vigorous evolution of gas was noted but no color was produced. After two weeks the flask was cooled in an ice-bath, opened and the gas collected. It contained 1.4% of ethylene as shown by absorption in bromine water. The remaining gas was analyzed by combustion.

Anal. 60 cc. gas: 90 cc. of O_2. Vol. after combustion, 99.2 cc. Contraction, 50.8 cc. Vol. after absorption of CO_2 in alkali, 55.5 cc. CO_2, 43.7 cc. 48.7 cc. gas 89.9 cc. of O_2. Vol. after combustion, 94.5 cc. Contraction, 44.1 cc. Vol. after absorption of CO_2 in alkali, 58.3 cc. CO_2, 36.2 cc. (The gases were measured at the same temperatures and pressures.) Calcd. for ethane: contraction, CO_2: 1.25. Found: 1.17, 1.22.

After the gas was collected, the reaction flask was opened, the reaction mixture filtered and the petroleum ether allowed to evaporate in the air. Diethylarsinic acid crystallized and after recrystallization melted at 136–137°.

For more accurate analysis of the gas the reaction was run in high-boiling paraffin oil. The reagents used were 2 g. of lithium, 20 g. of diethyl mercury and 23 g. of tetraethylarsonium bromide. The gas collected was analyzed by determining the density as mentioned in the general discussion.

Anal. (Gas density) bar. pressure, 742.00 mm.; gage readings with air, 705.9 mm.; 98.9 mm. Pressure, 607.0 mm. Total pressure, 135 mm. Gage readings with gas, 705.9 mm.; 98.9 mm. Pressure, 607.0 mm. Total pressure, 135 mm. Calcd. for C_2H_6: sp. gr., 1.049. Calcd. for C_2H_4; sp. gr., 0.978. Found: sp. gr., 1.00. (Absorption) 88.2 cc. of gas, 4.7 cc. lost by absorption in bromine water: 5.3% of unsaturated hydrocarbons.

The odor of the arsine was apparent in the paraffin oil solution but no arsinic acid was isolated.

Lithium *n*-Butyl and Tetraethylarsonium Bromide.—A solution of 0.04 mole of lithium *n*-butyl in petroleum ether was added to 11.11 g. (0.041 mole) of tetraethylarsonium bromide. A vigorous reaction occurred and gas evolution was noted. No attempt was made to collect this gas. The reaction flask was opened and the contents were filtered. On allowing the solution to stand in the air the petroleum ether evaporated and the arsine was oxidized to diethylarsinic acid, m. p. 136°.

A second reaction was carried out in high-boiling paraffin oil solution. The reagents used were 2 g. of lithium, 25 g. of di-*n*-butyl mercury and 23 g. of tetraethylarsonium bromide. After two weeks the reaction flask was opened and the gas collected.

Anal. (Gas density) bar. pressure, 742.3 mm.; gage readings with air, 713.5 mm.; 90.0 mm.; pressure, 623.5 mm.; total pressure, 118.8 mm. Gage readings with gas, 735.0 mm.; 66.1 mm.; pressure, 668.9 mm.; total pressure, 73.4 mm.; sp. gr. of gas, 1.62. (Absorption) 99.5 cc. of gas: 1.0 cc. lost by absorption in bromine water. 1.0% of unsaturated hydrocarbons. The density figures indicate that the gas is approximately 45% ethane and 55% butane. Such a mixture would have a specific gravity of 1.60.

Lithium Ethyl and Triethyl-*n*-butylarsonium Bromide.—A solution of 0.058 mole of lithium ethyl in petroleum ether was added to 175 g. (0.058 mole) of triethyl-*n*-butylarsonium bromide. After three weeks the mixture was cooled in ice, the reaction flask was opened and the gas collected. The gas density reported was determined after removal of the unsaturated hydrocarbons. Gas density: bar. pressure, 746.0 mm.; gage readings with air, 721.9 mm., 80.0 mm.; pressure, 641.9 mm.; total pressure, 104.1. Gage reading with gas: 725.8 mm., 76.1 mm.; pressure, 649.7 mm.; total pressure, 96.3: sp. gr., 1.08.

The specific gravity of this gas indicated that it was nearly pure ethane. It undoubtedly was contaminated with some petroleum ether vapors. After removal of the gas the reaction mixture was worked up as described before and ethyl-*n*-butylarsinic acid melting at 92° was obtained.

This reaction was run in paraffin oil using 2 g. of lithium, 20 g. of diethyl mercury and 25 g. of triethyl-*n*-butylarsonium bromide. The gas was collected and analyzed.

Anal. (Gas density) bar. pressure, 744 mm.; gage readings with air, 707.2 mm., 96.1 mm.; pressure, 611.1 mm.; total pressure, 132.9 mm.; gage reading with gas, 711.3 mm., 92.0 mm.; pressure, 619.3 mm.; total pressure, 124.7 mm.: sp. gr., 1.065. (Absorption) 96.5 cc. of gas: 2.4 cc. lost by absorption in bromine water: 2.5% of unsaturated hydrocarbons. These results indicated that the gas was nearly pure ethane with some ethylene and possibly a small amount of butane.

Lithium *n*-Butyl and Triethyl-*n*-butylarsonium Bromide.—A solution of 0.048 mole of lithium *n*-butyl in petroleum ether was added to 5 g. of triethyl-*n*-butylarsonium bromide. From the reaction mixture ethyl-*n*-butylarsinic acid, m. p. 87–89°, was isolated.

The reaction was repeated in paraffin oil using 2 g. of lithium, 25 g. of di-*n*-butyl mercury and 25 g. of triethyl-*n*-butylarsonium bromide. The gas was collected and analyzed. The unsaturated gases were removed after the density was taken on the original gas.

Anal. (absorption) 91.7 cc. of gas: 5.2 cc. lost by absorption in bromine water: 5.6% of unsaturated hydrocarbons. Gas density: bar. pressure, 743.4 mm.; gage readings with air, 715.0 mm., 88.5 mm.; pressure, 626.5 mm.; total pressure, 116.9 mm.; gage readings with gas, 735.0 mm., 66.0 mm.; pressure, 669.0 mm.; total pressure, 74.4 mm.; sp. gr., 1.57. This specific gravity indicated a mixture of about 47% of ethane and 53% of butane.

Lithium-*n*-Butyl and Triethylarsine Dibromide.—A solution of 0.047 mole of lithium *n*-butyl in petroleum ether was added to 7.8 g. (0.024 mole) of triethylarsine dibromide. A vigorous reaction occurred and gas was evolved. This gas was collected and by a gas density determination the specific gravity was found to be 1.801. Since petroleum ether vapors were present, this value was not very significant. However, not much ethane could have been present. The odor of an arsine was apparent when the flask was opened but not enough arsinic acid was isolated for positive identification.

Lithium Ethyl and Triethylarsine Dibromide.—A solution of 0.06 mole of lithium ethyl in petroleum ether was added to 9.5 g. of triethylarsine dibromide. No attempt was made to collect the gas. From the petroleum ether solution diethylarsinic acid, m. p. 136–137°, was isolated in the usual way.

Sodium Triphenylmethyl and Tetramethylarsonium Iodide.—A solution of 0.012 mole of sodium triphenylmethyl in dry ether was added with shaking to 5 g. of tetramethylarsonium iodide. The color of the solution faded and a solid of dull brick-red color remained in the flask. This solid was washed with anhydrous ether a few times. The red solid was not affected by dry carbon dioxide. When an attempt was made to recrystallize the solid from pyridine it appeared to decompose. The pyridine solution turned pale green. Triphenylmethane was isolated from the pyridine solution. If a compound related to the penta-alkyl ammonium of Schlenk and Holtz[4] had formed, it should have reacted with dry carbon dioxide to give tetramethylarsonium triphenylacetate.

Effect of Heat on Solutions of Lithium Alkyls in High-Boiling Paraffin Oil.—A solution of lithium ethyl in high-boiling paraffin oil did not give off gas when heated to 100°. Above this temperature gas was evolved. When such a solution was heated to 250° the gas obtained was about 75% unsaturated hydrocarbons. Gas density measurements indicated about 3% of hydrogen and 22% of ethane as the remaining constituents of the gas.

Lithium *n*-butyl in high-boiling paraffin oil solution did not liberate much gas until heated to about 173°. Gas evolution then became very marked. The gas collected was 94% unsaturated hydrocarbons. Gas density measurements indicated that the original gas was about 94% butylene, 3% butane and 3% hydrogen.

Effect of Lithium Alkyl Solutions on Ethylene.—A solution of lithium *n*-butyl was prepared from 1 g. of lithium and 10 g. of di-*n*-butyl mercury in 100 cc. of high-boiling paraffin oil. Ethylene from a tank of the commercial product was admitted under pressure. The pressure soon dropped and then more ethylene was introduced. In about two weeks 620 cc. of ethylene had been introduced. When an attempt was made to recover the ethylene, only 120 cc. of gas could be recovered on heating the solution to 100°. This gas was not pure ethylene but contained some inert material, probably air, which must have been present in the commercial gas. The ethylene did not remain in the oil as such because a similar experiment without the lithium alkyl showed that all of the gas could be recovered.

A similar experiment was tried with lithium ethyl instead of lithium *n*-butyl. The results were essentially the same. Only a small amount of gaseous hydrocarbons could be recovered by heating the paraffin oil solution.

Another experiment was made using a solution of 0.031 mole of lithium *n*-butyl in 50 cc. of petroleum ether (40–45°). Ethylene was absorbed readily and within two weeks a white solid began to appear on the surface of the solution. This solid has not been studied further.

The authors desire to express their thanks to Dr. G. F. Smith for help in some of the analytical problems met in this work.

Summary

1. Lithium alkyls have been found to react readily with tetra-alkyl arsonium bromides to give trialkylarsines and hydrocarbons which come from disproportionation of the alkyl groups. No evidence of the formation of a stable penta-alkyl arsenic compound was obtained.
2. Lithium alkyls have been found to cause polymerization of ethylene to give non-gaseous products.
3. It has been observed that trialkylarsines are oxidized by air to give dialkylarsinic acids.
4. Improved methods for the preparation of some trialkylarsines and tetra-alkyl arsonium salts have been reported.

URBANA, ILLINOIS

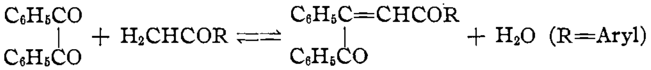
[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

DIACYLSTYRENES. II

BY CHARLES F. H. ALLEN AND J. ROCKWELL HUBBARD

RECEIVED AUGUST 12, 1929 PUBLISHED JANUARY 8, 1930

In an earlier paper[1] it was shown that benzil easily condensed with acetophenones that did not have a substituent in the position ortho to the carbonyl group.



$$\begin{array}{l} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + H_2CHCOR \rightleftharpoons \begin{array}{l} C_6H_5C{=}CHCOR \\ | \\ C_6H_5CO \end{array} + H_2O \quad (R{=}Aryl)$$

We have extended this investigation to include methyl ketones having different types of rings and found that diacylstyrenes are always formed under the conditions previously described. Methyl α-thienyl (I) and methyl α-furyl (II) ketones were selected as examples of heterocyclic compounds.

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[1] Allen and Rosener, THIS JOURNAL, **49**, 2110 (1927).