The conversion of V into III was reversed by using chlorobenzene in place of benzene. However, in this case the chief product was IV.

Di-(*o*-chlorobenzal)-acetone (VI).—This ketone was made from acetone and *o*-chlorobenzaldehyde by a modification of the method used in the synthesis of dibenzalacetone.[4] The principal difference was that in this case the reaction was much more rapid. The compound (from ethyl acetate) melted at 124–125°; yield, 90% of the theoretical amount.

Anal. Calcd. for $C_{17}H_{12}OCl_2$: C, 67.4; H, 4.0; Cl, 23.4. Found: C, 67.1; H, 4.2; Cl, 23.8.

o-Chlorobenzohydrylmethyl *o*-Chlorostyryl Ketone (VII)

(A) **By the Friedel–Crafts Method.**—To obtain VII the reaction between VI and benzene in the presence of aluminum chloride was interrupted when the mixture had become entirely liquid and the original bright red color had faded to a brown. The compound (from alcohol) melted at 144°.

Anal. Calcd. for $C_{23}H_{18}OCl_2$: C, 72.43; H, 4.76; Cl, 18.61. Found: C, 72.70; H, 4.73; Cl, 18.79.

(B) **By the Grignard Method.**—Phenylmagnesium bromide added to VI to give VII, which was identified with the product from (A) by the method of mixed melting points.

Sym-Dibenzohydrylacetone (VIII).—When the reaction described under (A) was continued for twelve hours VII was not isolated; under these conditions VIII was obtained. By similar methods VII, IX, X, XI and XII were in each case found to yield VIII.

The saturated ketone (VIII) was also prepared by the addition of phenylmagnesium bromide to XII; the latter compound was made in turn from XI by a similar procedure.

Summary

Benzalacetones (I), substituted benzohydrylacetones (II, IV, V), dibenzalacetones (VI, IX, X, XI) and benzohydrylmethyl styryl ketones (VII, XII) are transformed by the action of benzene in the presence of aluminum chloride into the corresponding unsubstituted benzohydryl compounds (III, VIII).

In the conversion of di-(*o*-chlorobenzal)-acetone (VI) into *sym*-dibenzohydrylacetone (VIII) the intermediate, VII, has been isolated. Similarly, in the conversion of benzalacetone and benzohydrylacetone into *p,p'*-dichlorobenzohydrylacetone, the intermediate, chlorobenzohydrylacetone (IV), has been obtained by interrupting the process.

URBANA, ILLINOIS RECEIVED JUNE 25, 1934

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[4] "Organic Syntheses," John Wiley and Sons, New York, 1932, Vol. XII, p 22.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF THE UNIVERSITY OF HEIDELBERG AND THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. IX. The Combination of Methyl Groups with Metallic Mercury

BY F. O. RICE AND B. L. EVERING

Fragments produced in the thermal decomposition of propane and butane[1] can be combined with metallic mercury to form mercury alkyls, which in turn react with alcoholic mercuric bromide to give crystalline alkyl mercuric bromides. Sublimation of these from the excess of mercuric bromide permitted the positive identification of the bulk of the material as methyl mercuric bromide. The remaining 5% was not identified although it seemed probable that it consisted mainly of the ethyl derivative.

In the past months we have attempted to make a complete analysis of the products formed in the above experiments. The work proved to be unexpectedly difficult, partly owing to the formation of a small quantity of an extremely unstable alkyl mercurous compound which decomposes in a few hours even at −80° (this may possibly be the compound $CH_3HgHgCH_3$), and partly because the presence of mercuric bromide catalyzes some change (which is not mentioned in the literature) in the alkyl mercuric bromides. However, we have proved that ethyl or higher derivatives are absent and that the material produced by the action of the fragments from propane or butane on metallic mercury is upward of 95% dimethyl mercury.

A method for the separation and estimation of methyl and ethyl groups has been developed by Willstätter and Utzinger;[2] this depends on the insolubility of tetramethylammonium iodide in such solvents as water, acetone, chloroform and absolute alcohol, in all of which trimethylethyl ammonium iodide dissolves easily. Accordingly

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(1) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932).

(2) Willstätter and Utzinger, *Ann.*, **382**, 148 (1911).

we warmed weighed samples of the alkyl mercuric bromides (formed by treating the fragments from the thermal decomposition of propane or butane as described above) with an excess of an aqueous solution of iodine and potassium iodide. The alkyl iodides formed were distilled off and an excess of alcoholic trimethylamine was added to the distillate; however, we obtained in this way only tetramethylammonium iodide and were unable to obtain any of the ethyl derivative.

We next considered the possibility of the presence of methylene groups which might have been produced either by simple decomposition of methyl radicals, $CH_3 \longrightarrow CH_2 + H$ or by the disproportionation reaction $CH_3 + CH_3 \longrightarrow CH_4 + CH_2$. These might be expected to combine with mercury to give compounds which would react with iodine to give either iodomethyl mercuric iodide or methylene iodide. Neither of these compounds was obtained. At this point we decided to verify the statement in the literature[3] that mercury dialkyls react quantitatively with mercuric halides to give the corresponding alkyl mercuric halide. A test with a synthetic sample of dimethyl mercury and an excess of mercuric bromide yielded only methyl mercuric bromide; the unreacted mercuric bromide dissolved completely in water and there was no trace of any mercurous salt.

We then analyzed the different fractions of the alkyl mercuric bromides for their halogen content, and obtained higher values than that for pure methyl mercuric bromide (27.04%), the values increasing with successive fractions from about 28 to 34% Br. A test with ammonium sulfide showed that only a part of this increase could be attributed to the presence of mercuric bromide, which sublimes to a slight extent with the methyl mercuric bromide. We also found that the residual mercuric bromide contained an appreciable amount of mercurous bromide.

These results appeared to us to be sufficiently interesting so that we decided to attempt to isolate and examine the mercury alkyls first formed by the action of the radicals on metallic mercury. We made a run of about eleven hours during which time we were decomposing butane at 1100°, and obtained several grams of the mercuric alkyls mixed, of course, with butane and its decomposition products. The contents of the liquid air trap were distilled through a small vacuum-jacketed still and after most of the butane was evaporated off a series of fractions was collected. We weighed these fractions and measured the pressure of the vapor at a known temperature so that we could calculate the molecular weight of each fraction;[4] after removal of the butane, the mol. wt. of 15 successive fractions increased from 220 to 242 (theoretical for $(CH_3)_2Hg$, 230). A few per cent. of a compound containing two mercury atoms such as $CH_3HgHgCH_3$ would account for this increase in density with successive fractions whereas a considerable amount of a higher dialkyl mercury compound would be required to produce the discrepancy.

We then mixed fractions 3–9 inclusive and distilled; the middle portion of the distillate was analyzed for carbon (10.04%) and hydrogen (2.41%); the theoretical values for dimethyl mercury are, respectively, 10.40 and 2.62%. Samples 10 to 15 were also mixed and distilled; three fractions were obtained and all were analyzed for carbon and hydrogen. The results were 11.14, 10.10, 9.60% C and 2.65, 2.47, 2.30% H, respectively.

It is clear from these results that practically the only product of the action of the fragments from butane on mercury is dimethyl mercury. In some of the samples, however, a small quantity of mercury separated; this behavior coupled with the increase in density and the diminution of the carbon–hydrogen percentage of successive fractions indicates the presence of small quantities of some other mercury compound, possibly $CH_3HgHgCH_3$. This compound would probably react with mercuric bromide to give methyl mercuric bromide and mercurous bromide which we found to be present in our product. However, all attempts to isolate this compound or to obtain any evidence as to its constitution have failed; it is formed only in small quantity and decomposes even at −80° in a day or two. Attempts to combine radicals with mercury at a hot surface very much diminished the yield of dimethyl mercury without increasing noticeably the amount of the other compound.

We also considered the possibility of the intermediate formation of mercury methyl CH_3Hg;[5] if this were formed at the mercury surface and evaporated off, we might have an explanation both of the formation of $CH_3HgHgCH_3$ and of the abnormal reactions with mercuric bromide.

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(3) Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, 1925.

(4) Dimethyl mercury vapor dissolved out the stopcock grease in the various joints in our apparatus to a considerable extent and we considered the possibility that a small amount of a volatile hydrocarbon might be given off from the grease. We tried to avoid this difficulty by using an inorganic lubricant but those mentioned in the literature do not seem to be suitable for vacuum work (Boughton, THIS JOURNAL, **52**, 242, 2813, 4335, 4858 (1930), and private communication). Finally we proved the absence of any volatile material by dissolving some of our stopcock grease (a commercial preparation) in dimethyl mercury and then evaporating off and analyzing the dimethyl mercury. Its carbon and hydrogen content were found to be unaffected.

(5) Kraus, *ibid.*, **35**, 1732 (1913).

Mercury methyl is prepared by electrolyzing a salt such as methyl mercuric chloride in liquid ammonia. Prepared in this way it is a black solid similar to any finely divided metal and is an excellent conductor of electricity. On allowing it to warm to near room temperature it decomposes suddenly according to the equation $2\,CH_3Hg \longrightarrow (CH_3)_2Hg + Hg$.

We prepared a few grams of mercury methyl in this way and tried to sublime it in a high vacuum keeping the sample at -10 to $-20°$ to prevent decomposition. However, its vapor pressure is so low that we obtained no detectable sublimate and we do not believe that any appreciable amount of mercury methyl evaporates from a mercury surface exposed to the action of free methyl groups. We found only dimethyl mercury in the colorless liquid obtained by decomposing mercury methyl.

It seems reasonably certain that the decomposition of propane and butane in the range 900–1100° yields only methyl radicals; ethyl or higher radicals are practically entirely decomposed at this temperature and no evidence for the presence of methylene radicals has yet been obtained. The abnormal results observed when alkyl mercuric bromides are used to identify the radicals may in all probability be ascribed in part to the formation of some alkyl mercurous compound such as $CH_3HgHgCH_3$, and in part to the presence of small amounts of mercuric bromide which sublimes with the alkyl mercuric bromide.

We wish to thank Professor K. Freudenberg for suggestions given to us during the course of this investigation and for facilities for carrying it out. We also wish to thank Mr. W. W. Davies for help in connection with the preparation and study of methyl mercury.

Summary

We have studied the reaction products resulting when the fragments formed during the thermal decomposition of propane or butane are brought into contact with metallic mercury. Analyses show that the mercury alkyls produced contain more than 95% of dimethyl mercury, indicating that methyl groups are the only alkyl radicals formed to any appreciable extent.

A small quantity of a very unstable organomercury compound occurs along with the dimethyl mercury. This is probably an alkyl mercurous compound, possibly $CH_3HgHgCH_3$.

Ethyl and higher radicals have been shown to be absent.

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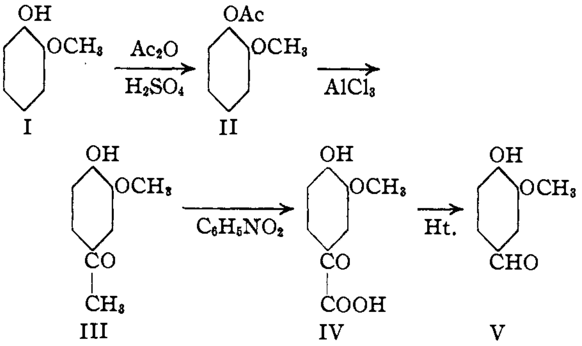
A New Vanillin Synthesis

BY HENRY O. MOTTERN

Syntheses of vanillin from guaiacol have depended largely upon a direct addition of a carbon atom to the 4-position in guaiacol. Guaiacol, possessing all the characteristics of a phenol, often produces large amounts of resin polymers when this type of reaction is used.[1]

In an attempt to eliminate the troublesome resin formation, the following synthesis of vanillin was devised. The synthesis depends upon the rearrangement of the acetyl group in guaiacol acetate to the 4-position, and subsequent oxidation of this group to form a substituted glyoxylic acid. The rearrangement follows the prediction of Fries and others.[2]



Guaiacol (I) is esterified with acetic anhydride in the presence of a trace of sulfuric acid to form guaiacol acetate (II). Guaiacol acetate treated with anhydrous aluminum chloride at low temperature rearranges to apocynin. The acyl group takes the position para to the hydroxy group rather than to the methoxy group. No 3-oxy-4-methoxyacetophenone seems to be formed.[3] If the addition of aluminum chloride is

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(1) Ullmann, "Enzyklopädie der technischen Chemie," Vol. VIII, p. 815, a review of existing methods of manufacture.

(2) Fries and Pfaffendorf, *Ber.*, **43**, 214 (1910); v. Auwers and Risse, *ibid.*, **64**, 2216 (1931); Cox, THIS JOURNAL, **52**, 352 (1930).

(3) Otto, *Ber.*, **24**, 2869 (1891).