

### Discussion of Results

In view of these measurements, and of those previously reported for triphenylgermanium and triphenyllead, it may be concluded that no long-life organo-metallic free radical has yet been prepared. There remain, of course, the results of Midgley, Hochwalt and Calingaert on triethyllead. But the writers have no doubt that this compound too will prove to be diamagnetic, even in very dilute solution, and there seems little use in bothering to make measurements on it.

This work raises two questions. First, how can the low molecular weights of Krause, Kraus, Foster, Midgley, *et al.*, be explained? And, second, why do these compounds not exist in the free radical form, at least in the case of the triphenyl series, when the Ge-Ge, Sn-Sn, and Pb-Pb bond-energies are probably considerably less than the corresponding C-C bonds, as in hexaphenylethane?

A clue to the first problem may possibly be found in the reactions undergone by hexaarylethanes. Although no evidence is at hand on this point, yet it seems not improbable that a compound such as hexaphenyldiplumbane might slowly decompose to several fragments of relatively low molecular weight, especially at moderately elevated temperatures.

As regards the second problem: why are free radicals not found? the writers suggest that the explanation is to be found in the much greater atomic radius of the metal atoms as compared

with that of carbon. The covalent radius of lead is at least twice that of carbon,<sup>10</sup> hence the effect of three phenyl groups is more that of three protuberances on the surface of the lead, rather than of a tightly-fitting envelope, as in the case of carbon. Consequently the effective collision frequency leading to formation of the dimer must be far greater in the case of the metal radicals than of the carbon radicals. It is suggested that failure to observe an organo-metallic radical is principally a result of steric effects brought about by the large size of the metal atom. Failure to obtain trimethyltin as a monomer is then in no way surprising. In the failure to find tricyclohexyllead, the present work destroys a possible objection to the resonance theory of free radical stability. The probabilities are that if organo-metallic radicals are to be found they will be compounds such as tri-*o*-tolyltin or better tri-*o*-xenyln, in which both steric and resonance effects are strong. Experiments in this direction are being undertaken.

### Summary

Trimethyltin and tricyclohexyllead, in dilute benzene solution, do not exist as the monomer. It is suggested that the relatively large size of the tin and lead atoms greatly reduces the stability of organo-metallic free radicals as compared with carbon free radicals.

(10) Skinner and Sutton, *Trans. Faraday Soc.*, **36**, 1209 (1940).

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## Ketene in the Friedel-Crafts Reaction. II.<sup>1</sup> The Use of Mixed Acetic Anhydrides<sup>2</sup>

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A mixed acetic anhydride, the product of the reaction of ketene and a carboxylic acid,<sup>4</sup> may be used in the synthesis of a higher alkyl phenyl ketone in either of two ways. It may be used directly in a Friedel-Crafts reaction with an aromatic hydrocarbon, or it may be decomposed by heating or standing into acetic anhydride and a

(1) For the first paper in this series, see Williams and Osborn, *THIS JOURNAL*, **61**, 3438 (1939).

(2) Presented before the Organic Division of the American Chemical Society at the St. Louis meeting, April, 1941.

(3) Taken in part from the M.A. Thesis of Yancey J. Dickert.

(4) Hurd and Dull, *THIS JOURNAL*, **54**, 3427 (1932).

higher anhydride,<sup>4,5</sup> from which a ketone may easily be prepared.<sup>6</sup> The first of these two methods is described in this paper.

A study of the reactions of some unsymmetrical aromatic anhydrides with benzene in the presence of aluminum chloride has been made by Zeavin and Fisher.<sup>7</sup> They found that the ketone of lower molecular weight is obtained in the greater quan-

(5) Williams and Krynitsky, "Organic Syntheses," Vol. XXI, p. 13.

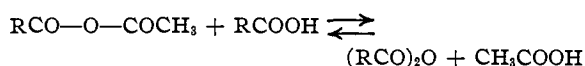
(6) Noller and Adams, *THIS JOURNAL*, **46**, 1889 (1924).

(7) Zeavin and Fisher, *ibid.*, **54**, 3738 (1932).

tity or as the sole product. In the present work, using aliphatic anhydrides, it has been found that the yield of the higher ketone is generally larger. This tendency is more pronounced when an excess of aluminum chloride is used.

The reaction provides a convenient method for the synthesis of higher alkyl phenyl ketones. Only one purification step is necessary, that is, the final fractionation of the two ketones.

In the preparation of anhydrides by the reaction of ketene with acids some acetic acid is always obtained. The amount of acetic acid is small when an excess of ketene is used, but is larger when an excess of organic acid is present. The acetic acid probably arises from the equilibrium



### Experimental

**Preparation of Mixed Acetic Anhydrides.**—The mixed acetic anhydrides were prepared by the reaction of ketene (prepared from acetone by means of the ketene lamp<sup>8</sup>) with carboxylic acid.<sup>4</sup> The pure acid (0.5 mole), freshly distilled, was placed in a gas-washing bottle, and ketene was passed through in slightly more than molar proportions (0.6 mole). In the case of the solid stearic and benzoic acids, a solution in a minimum amount of benzene was used, and more ketene, 0.9 and 0.7 mole, respectively, was added. The reaction mixture became quite warm, and cooling by means of an ice-bath was necessary to prevent loss by vaporization in the cases of propionic, butyric and isobutyric acids. A second gas-washing bottle containing 20% aqueous sodium hydroxide solution was connected in series with the bottle containing the acid. The heat of reaction of the ketene with the alkali was used as an indication of the completion of the reaction of the ketene with the carboxylic acid in the first bottle.

Mixed acetic anhydrides prepared in this way were contaminated by dissolved ketene and acetone carried over from the lamp by entrainment in the gas stream. Both of these impurities were easily removed by the application of reduced pressure (water pump) at room temperature. After such treatment, the residual anhydrides (or benzene solutions) were used directly in the Friedel-Crafts reaction.

**The Friedel-Crafts Reaction.**—The mixed acetic anhydride (0.5 mole) was added over a period of thirty to forty minutes from a dropping funnel to a stirred mixture of 3.37 moles (350 ml.) of anhydrous benzene and 1.6 moles (213 g.) of aluminum chloride contained in a 1-liter three-necked round-bottomed flask equipped with a mercury-sealed stirrer and a reflux condenser to which was attached a calcium chloride drying tube. After the reaction mixture began to cool, heat from a steam-bath was supplied for

four additional hours, the stirring being continued. The mixture was then cooled to room temperature and poured onto a mixture of 300 g. of ice and 100 ml. of concd. hydrochloric acid. To facilitate layer separation, 250 ml. of ether was added; the ether-benzene solution was separated and washed with 100 ml. of 25% aqueous sodium hydroxide solution. After drying over anhydrous sodium sulfate, the ether and benzene were removed by distillation and the remaining oil fractionated through a column containing glass helices and fitted with a heating jacket. Yields of acetophenone and the higher ketones are given in Table I. The percentage yields are based upon the mixed acetic anhydride used. The cases in which the yields of acetophenone and the higher ketone total more than 100% may be explained by the participation of the free acid liberated in the Friedel-Crafts reaction.

TABLE I

Mixed acetic anhydride	Acetophenone, % yield	Higher ketone % yield	B. p., °C.
Propionic	56.0	38.7	115–118 (32 mm.)
Butyric	33.8	66.2	220–230
Isobutyric	55.2	57.9	115–120 (30 mm.)
Valeric	42.2	67.8	240–246
Isovaleric	35.5	66.6	228–238
Trimethylacetic	35.8	25.3	250–255
Caproic	39.2	59.2	258–265
Stearic	33.5	10.7	M. p. 59
Benzoic	23.3	14.2	M. p. 69

**Effect of Conditions on Results.**—Better yields of ketones were obtained using a large excess of hydrocarbon as a solvent. Thus when one mole of benzene was allowed to react with 1.1 moles of acetic-butyric anhydride in the presence of 2.2 moles of aluminum chloride the yield of acetophenone was 8.3% and butyrophenone 8.1%.

To obtain a good yield of the higher ketone it was found advantageous to use aluminum chloride in about a 3:1 molar ratio to the anhydride rather than in the usual 2:1 proportion. Thus using 1.1 moles of aluminum chloride with 0.5 mole of acetic-caproic anhydride and 3.37 moles of benzene the yield of acetophenone was 44.0% and of caprophenone 44.6%.

Removal of acetone and ketene from the mixed anhydride was found to result in much better yields of both ketones. As an example, in a reaction using 1.6 moles of aluminum chloride, 3.37 moles of benzene and 0.5 mole of acetic-isovaleric anhydride from which the acetone and ketene had not been removed, the yield of acetophenone was 15.0% and of isovalerophenone 26.0%.

### Summary

The use of mixed acetic anhydrides in the Friedel-Crafts reaction has been investigated as another use for ketene. The procedure has been shown to provide a convenient method for preparation of higher alkyl phenyl ketones.

(8) Williams and Hurd, *J. Org. Chem.*, **5**, 122 (1940).