pany for the perfluorinated acids used in this work. Thanks are also due to the Office of Naval Research which partially supported this research.

BOULDER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

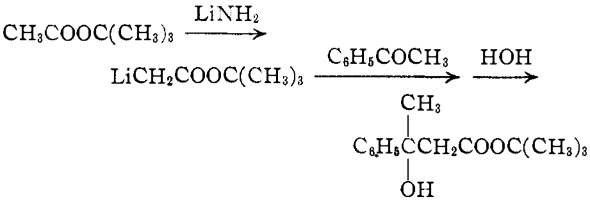
Role of Metallic Cation in Aldol Condensation of Metallo Esters with Acetophenone to Form β-Hydroxy Esters. Reversal to Claisen Acylation or Self-condensation of the Ketone[1]

BY CHARLES R. HAUSER AND W. H. PUTERBAUGH[2]

RECEIVED MAY 18, 1953

The metallic cation plays an important role in the aldol type condensation of metallo acetic esters with acetophenone to form β-hydroxy esters, since the reaction may be realized satisfactorily with lithio, zinchalo and magnesiumhalo esters but not with sodio esters. The aldol condensation was realized with a sodio ester under special conditions but, under usual conditions, metal–hydrogen exchange between the sodio ester and the α-hydrogen of the ketone occurred to form a β-diketone. Moreover, sodio β-hydroxy esters were found to be relatively unstable; they underwent the reverse aldol condensation even in refluxing ether. The reverse aldol condensation was realized also with lithio- and zinchalo-β-hydroxy esters, but much more drastic conditions were required. The success of the aldol condensation of lithio, zinchalo and magnesiumhalo esters with acetophenone is ascribed to the coördinating capacities of the metallic cations.

The aldol type of condensation of certain esters having α-hydrogen with the carbonyl group of ketones or aldehydes to form β-hydroxy esters, such as that of *t*-butyl acetate with acetophenone to form β-hydroxy ester I, have been realized through the intermediate formation of the lithio ester,[3,4] zincchloro ester[3] and magnesiumbromo ester,[5] but not with the sodio ester.[3] The reaction is illustrated below with lithium amide. These condensations, particularly that with the zincchloro ester, are related to the well-known Reformatsky reaction in which an intermediate zinchalo ester is formed by the action of zinc on an α-halo ester.

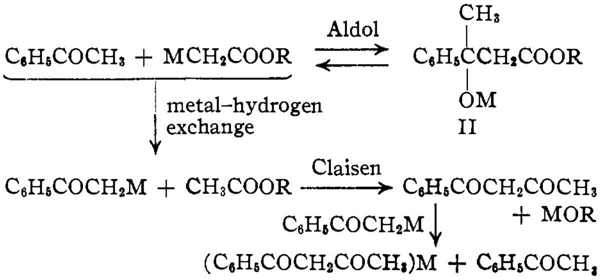


$$CH_3COOC(CH_3)_3 \xrightarrow{LiNH_2} LiCH_2COOC(CH_3)_3 \xrightarrow{C_6H_5COCH_3} \xrightarrow{HOH} C_6H_5\overset{CH_3}{\underset{OH}{C}}CH_2COOC(CH_3)_3$$

I

It has now been found that, whereas β-hydroxy ester I is obtained in 76% yield on refluxing acetophenone with lithio-*t*-butyl acetate for two hours in ether, a different product, benzoylacetone, is produced by a similar treatment of this ketone with sodio-*t*-butyl acetate or with sodio-ethyl acetate (prepared by means of sodium triphenylmethide). The β-diketone evidently arises from metal–hydrogen exchange between the sodio ester and α-hydrogen of the ketone, followed by Claisen acylation of the resulting sodio ketone with the regenerated ester as represented in scheme A in which M stands for the metal. The yield of benzoylacetone was only 6%[6] with sodio-*t*-butyl acetate (much of the original ester and ketone being recovered) but was 94%[6] with sodio-ethyl acetate from which was generated the relatively good acylating agent, ethyl acetate. However, since a 30% yield of β-hydroxy ester I was isolated from sodio-*t*-butyl acetate and acetophenone on stopping the reaction after only 15 minutes, some of the aldol condensation must first have occurred and then reversed completely during the usual two-hour treatment in accordance with scheme A (when M is sodium).[7]

SCHEME A



$$\begin{array}{l} \underbrace{C_6H_5COCH_3 + MCH_2COOR} \overset{\text{Aldol}}{\rightleftarrows} C_6H_5\overset{CH_3}{\underset{OM}{C}}CH_2COOR \quad \text{II} \\ \downarrow \text{metal–hydrogen exchange} \\ C_6H_5COCH_2M + CH_3COOR \xrightarrow{\text{Claisen}} C_6H_5COCH_2COCH_3 + MOR \\ \quad C_6H_5COCH_2M \downarrow \\ (C_6H_5COCH_2COCH_3)M + C_6H_5COCH_3 \end{array}$$

These results indicated that the metallo-β-hydroxy ester (II), the form in which the β-hydroxy ester is present in the reaction mixture before acidification, is much less stable when the metallic cation (M) is sodium than when it is lithium. This was confirmed with sodio- and lithio-β-hydroxy esters prepared from the β-hydroxy esters and sodium amide and lithium amide, respectively (Table I). Thus, on refluxing two hours in ether, sodio salt II (R = ethyl) was converted completely to benzoylacetone and acetophenone in accordance with scheme A, whereas the corresponding lithio salt was only slightly decomposed, 75% of the orig-

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(1) Paper LI on Condensations; supported in part by a grant from the Duke University Research Council.

(2) Carbide and Carbon Chemicals Company Fellow, 1950–1952.

(3) C. R. Hauser and W. H. Puterbaugh, THIS JOURNAL, **73**, 2972 (1951).

(4) C. R. Hauser and W. H. Puterbaugh, *ibid.*, **75**, 1068 (1953).

(5) K. Sisido, H. Nozaki and O. Kurihara, *ibid.*, **74**, 6254 (1952).

(6) The yield of β-diketone is calculated on the basis that only half of the sodio ketone from the metal–hydrogen exchange is available for the Claisen acylation, the other half being used to convert the β-diketone to its metallo salt or chelate as represented in scheme A. See J. T. Adams and C. R. Hauser, THIS JOURNAL, **66**, 1220 (1944).

(7) It seems likely that, in certain of the reported Claisen acylations of ketones with esters by sodium reagents to form β-diketones, some of the aldol condensation to form the β-hydroxy ester also first occurred and then reversed. Of course, only the aldol condensation may occur between ethyl acetate and a ketone or an aldehyde having no α-hydrogen; for example, this ester undergoes with benzaldehyde, in the presence of sodium ethoxide, an aldol condensation accompanied by dehydration to form ethyl cinnamate.

TABLE I

CONVERSION OF METALLO-β-HYDROXY ESTERS (II) TO ACETOPHENONE, BENZOYL ACETONE AND DYPNONE

Metallo-β-hydroxy ester (II)		Refluxing solvent	Time, hours	Benzoyl-acetone, yield, %	Aceto-phenone, yield, %	Dypnone, yield, %	β-Hydroxy ester recovered, %
M	R						
Sodium	Ethyl	Ethyl ether	2	81	17	..	0
Lithium	Ethyl	Ethyl ether	2	8[a]	8	..	75
Lithium	*t*-Butyl	Ethyl ether	22	..[b]	9	..	75
Lithium	Isopropyl	Liq. ammonia[c]	4	12[d]	7	..	76
Lithium	Ethyl	Toluene[e]	8[f]	49	5	29	0
Lithium	Isopropyl	Dibutyl ether[g]	5	25	8	35	0

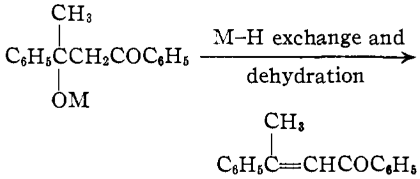
[a] This yield estimated from material, b.p. 138–143° (15 mm.), which gave a positive enol test. [b] A small amount of product, b.p. 130–136° (10 mm.), was obtained which gave a weak enol test. [c] After stirring for 4 hours in this medium, the ammonia was driven off and replaced by 100 ml. of stock ether and then worked up as described in the general procedure. [d] This yield was estimated from material, b.p. 130–134° (10 mm.), which gave a positive enol test. [e] Brown gummy residue (6.0 g.) was also obtained from this reaction. [f] The reaction mixture was stirred an additional 2 hours at 80°. [g] Gummy residue (1.7 g.) also was obtained from this reaction.

inal β-hydroxyl ester being recovered. In addition, certain β-hydroxy esters were largely recovered from their lithio salts even after 22 hours of refluxing in ether or several hours in liquid ammonia (Table I).

However, the lithio-β-hydroxy esters also were found to be convertible to benzoylacetone and acetophenone in accordance with scheme A under sufficiently drastic conditions. Even in refluxing ethyl ether, the lithio salts were converted partly to these reversion products, and the complete conversion to these products and dypnone, which resulted from self-condensation of the ketone,[8] was realized in refluxing toluene or dibutyl ether (Table I). Some self-condensation of the ester might also have occurred, but none of the product was isolated. As in the Claisen acylation represented in scheme A, the sodio ketone is presumably the reactive intermediate in the formation of the dypnone.

$C_6H_5COCH_3 + MCH_2COC_6H_5 \longrightarrow$

(Intermediates in scheme A)



$$C_6H_5\overset{\displaystyle CH_3}{\underset{\displaystyle OM}{C}}CH_2COC_6H_5 \xrightarrow[\text{dehydration}]{\text{M-H exchange and}} C_6H_5\overset{\displaystyle CH_3}{C}{=}CHCOC_6H_5$$

Similarly, zinchalo-β-hydroxy esters (II, M = ZnX), formed in the Reformatsky reaction, evidently undergo reversion on prolonged heating.[9] Thus, whereas a 60% yield of the β-hydroxy ester was obtained from ethyl α-bromoacetate, acetophenone and zinc on refluxing in a mixture of benzene and toluene under the usual Reformatsky conditions, only a 1% yield of this product could be isolated after 29 hours of refluxing. The main products obtained under the latter conditions were dypnone (49%) and benzoylacetone (6%). Evidently the intermediate zinchalo ketone (resulting from metal–hydrogen exchange as shown in scheme A, M = ZnBr) condenses preferentially with the ketone rather than with the ester; but this is not surprising since, under the usual Reformatsky conditions, the zinchalo ester undergoes the aldol type condensation preferentially to a Claisen acylation.[10]

From these results it may be concluded that the aldol condensation of metallo-acetic esters with acetophenone to form metallo-β-hydroxy esters (II) tends to reverse in favor of the Claisen acylation (scheme A) or self-condensation of the ketone not only when the metallic cation is sodium but also when it is lithio or zinc, although the rate of this reversion is much slower in the latter cases. The crucial step in this relationship is presumably the metal–hydrogen exchange between the metallo ester and the ketone. This exchange involves an acid–base reaction between an α-hydrogen of the ketone and the ester anion to form the more weakly basic ketone anion and more weakly acidic molecule of the ester. Actually the acid–base reaction functions as if it were irreversible and independent of subsequent condensations. This was demonstrated with acetophenone and sodio-*t*-butyl acetate with which the acid–base reaction to form sodio-acetophenone and *t*-butyl acetate was essentially complete within two hours in refluxing ether. Thus, carbonation of the reaction mixture after this time produced benzoylacetic acid (30%) but no *t*-butyl hydrogen malonate,[11] and the addition of ethyl acetate to the reaction mixture (in another experiment) followed by two more hours of refluxing gave benzoylacetone (84%)[6] but no *t*-butyl acetoacetate.[11] Of course, some of this β-diketone resulted from acylation of the sodio ketone by the *t*-butyl acetate, but a blank experiment indicated that relatively little (9%)[6] of it was formed in this manner. Presumably also with acetophenone and lithio or zinchalo esters, the acid–base reaction between the ketone and the potential ester anion, which occurs relatively slowly, is essentially irreversible and independent of subsequent condensations.

The fact that, in spite of the unfavorable equilibrium, the aldol condensation may be realized

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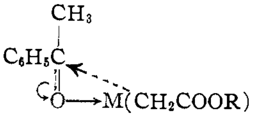
(8) The considerable self-condensation of the acetophenone even when the regenerated ester was ethyl acetate may be attributed at least partly to the relatively high boiling solvents employed since lithio ketones may usually be acylated satisfactorily with esters in refluxing ethyl ether. See G. R. Zellars and R. Levine, *J. Org. Chem.*, **13**, 160 (1948).

(9) Prolonged heating in the Reformatsky reaction has been reported to lower the yield of β-hydroxy ester but apparently the products formed were not previously established; see R. L. Shriner, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, Chapter 1.

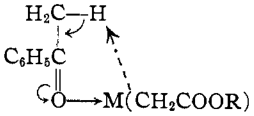
(10) See R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 167.

(11) This experiment was performed by Mr. W. J. Chambers.

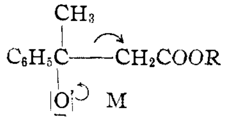
satisfactorily with lithio, zinchalo or magnesiumhalo esters, but not with sodio esters, may be ascribed to the relatively greater coördinating tendencies of the lithium, zinc and magnesium cations. This tendency may be exhibited, first, in favoring reaction of the metallo esters at the carbonyl carbon of the ketone (III)[12] over that at the α-hydrogen (IV)[13] and, second, in retarding the reverse aldol condensation (V). Coördination of an organometallic reagent through the metallic cation such as that shown in III must, in general, favor reaction at the carbonyl carbon since, whereas sodium phenyl mainly ionizes the α-hydrogen of acetophenone,[14] lithium phenyl and phenylmagnesium bromide are known to add largely to the carbonyl group of this ketone. The retarding of the reverse aldol condensation is evidently due to a greater association (more covalency) of the alcoholate anion in V with the lithium, zinc or magnesium cation than with the sodium cation, since the reverse aldol condensation indicated would be favored by the greater freedom of movement of the electrons in the sodio salt. The greater tendency for reverse aldol condensation with the sodio salt than with the lithio salt cannot be ascribed to a solubility factor, since the more stable lithio salt was found to be more soluble in the medium (ether) than the sodio salt (see Experimental).



III, M = Li, ZnX or MgX > M = Na



IV, M = Na > M = Li ZnX or MgX



V, M = Na > M = Li, ZnX or MgX

Experimental

Lithio- and Sodio-*t*-butyl Acetates with Acetophenone.—The general procedure described previously for the condensation of lithio-*t*-butyl acetate with acetophenone was adapted to the present cases.[4]

To 0.21 mole of lithium amide suspended in 250 ml. of liquid ammonia was added 23.2 g. (0.2 mole) of *t*-butyl acetate[15] in 50 ml. of ether, and the ammonia replaced by 100 ml. of ether. To the resulting lithio ester was added 24.0 g. (0.2 mole) of acetophenone in 50 ml. of ether. After stirring and refluxing 2 hours, the reaction mixture was decomposed with cold, dilute hydrochloric acid, and the ether layer dried over drierite. The solvent was removed and the residue distilled *in vacuo* to yield 4.1 g. (17%) of recovered acetophenone, b.p. 88–95° (16 mm.), and 36.0 g. (76%, 92% based upon the acetophenone consumed) of *t*-butyl β-hydroxy-β-phenylbutyrate, b.p. 111–112.5° (2 mm.).

In a similar manner, sodio-*t*-butyl acetate was prepared from 0.2 mole of the ester and 0.21 mole of sodium amide and treated with 0.2 mole of acetophenone under the same conditions. There was obtained 8.9 g. (39%) of recovered *t*-butyl acetate, b.p. 34–37° (pressure of water-pump), 20.5 g. (86%) of recovered acetophenone, b.p. 90–92° (16 mm.), and 1.1 g. (6%)[6] of benzoylacetone, b.p. 106–109° (2 mm.), which gave a positive (red) enol test with ferric chloride. None of the β-hydroxy ester was found.

However, when 0.2 mole of acetophenone in 50 ml. of ether was added during 10 minutes to sodio-*t*-butyl acetate in 150 ml. of ether (prepared from 0.21 mole of sodium amide and 0.2 mole of *t*-butyl acetate), and the reaction mixture decomposed after stirring 5 minutes longer, there was obtained 6.6 g. (28%) of recovered *t*-butyl acetate, b.p. 44–48° (90 mm.), 15.0 g. (63%) of recovered acetophenone, b.p. 80–84° (10 mm.), and 14.0 g. (30%) of *t*-butyl β-hydroxy-β-phenylbutyrate, b.p. 138–139° (10 mm.). The β-hydroxy ester, which was uncontaminated with benzoylacetone (as indicated by a negative enol test with ferric chloride), was identified by conversion to β-methylcinnamic acid, m.p. 97–97.5° (reported m.p. 97–98.8°).[16]

Sodio-ethyl Acetate with Acetophenone.—To an ice-cold solution of 0.18 mole of sodio-ethyl acetate (prepared from 0.18 mole each of ethyl acetate and sodium triphenylmethide) in 350 ml. of ether was added during 10 seconds 21.6 g. (0.18 mole) of acetophenone in 50 ml. of ether. After standing 8 hours at room temperature, the reaction mixture was decomposed with glacial acetic acid. Water was added, and, after shaking, the ether layer was washed with saturated sodium bicarbonate solution and then with water. The ether solution was dried over drierite and the solvent removed. The residue was distilled *in vacuo* to give recovered acetophenone (5.3 g., 25%), b.p. 83–88° (11 mm.), and benzoylacetone, b.p. 137–143° (11 mm.), which after one recrystallization from ethanol–water melted at 60–61° (reported m.p. 60°)[17]; yield 13.6 g. (94%).[6] Also there was obtained 50 g. of residue which consisted mostly of triphenylmethane. The β-diketone was further identified by its copper salt, m.p. 194.5–195.5° (reported m.p. 195–196°).[18]

Conversion of Metallo-β-hydroxy Esters (II) to Acetophenone, Benzoylacetone and Dypnone.—The alkyl β-hydroxy-β-phenylbutyrate (0.1 to 0.2 mole) dissolved in twice its volume of anhydrous solvent was added dropwise during 10–20 minutes to a liquid ammonia suspension of an equivalent (plus 5%) of sodium amide or lithium amide. A hot water-bath was applied and the ammonia driven off while 100–150 ml. of ether or other solvent was being added. After refluxing and stirring for appropriate periods the reaction mixture was cooled and decomposed with ice-cold 3 *N* hydrochloric acid. The organic layer was washed with 1 *N* hydrochloric acid, saturated sodium bicarbonate solution and water, and combined with solvent extracts of the aqueous layers. The organic solution was dried over drierite and the solvent distilled. The residue was fractionated *in vacuo*.

The yields of products and recovered β-hydroxy esters are given in Table I. The acetophenone boiled at 78–82° (10 mm.); m.p. of 2,4-dinitrophenylhydrazone 248–250° (reported m.p. 249–250°).[19] The benzoylacetone boiled at 137–140° (5 mm.) and melted, after recrystallization from ethanol–water, at 60–61° (reported m.p. 60°)[17]; it was further identified by the mixed melting point method, by a strong enol test with ferric chloride, and by its copper chelate, m.p. 194.5–195.5° (reported m.p. 195–196°).[18] The recovered β-hydroxy esters boiled at 143–145° (15 mm.) (for ethyl ester), 136–137° (10 mm.) (for *t*-butyl ester), and 134.5–135.5° (10 mm.) (for isopropyl ester). These recovered β-hydroxy esters were evidently uncontaminated with appreciable amounts of benzoylacetone since they gave negative enol tests with ferric chloride. The dypnone boiled at 173–176° (3 mm.) and was identified by its phenylhydrazone, m.p. 181–182° (reported m.p. 176°).[20]

Anal. Calcd. for $C_{12}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.31; H, 6.52; N, 8.85.

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(12) Although the extent to which the sodio esters and acetophenone undergo direct metal–hydrogen exchange without first undergoing the aldol condensation was not established, there seems little doubt that such direct exchange occurs to a greater extent with the sodio esters than with the lithio esters which were shown first to exhibit largely the aldol condensation.

(13) With the relatively large isobutyrate anion, this metal–hydrogen exchange ("enolization" of the ketone) was observed exclusively even when M is lithium (ref. 4). Similarly, with relatively complex ketones, this side-reaction occurred preferentially to the Reformatsky condensation; M. S. Newman, This Journal, **64**, 2131 (1942).

(14) Unpublished results of F. W. Swamer and C. R. Hauser.

(15) C. R. Hauser, B. E. Hudson, B. Abramovitch and J. C. Shivers, *Org. Syntheses*, **24**, 19 (1944).

(16) G. Schroeter, *Ber.*, **37**, 1093 (1904).

(17) H. Meerwein and D. Vossen, *J. prakt. Chem.*, **141**, 149 (1934).

(18) W. Wislicenus and W. Stoeber, *Ber.*, **35**, 545 (1902).

(19) N. R. Campbell, *Analyst*, **61**, 393 (1936).

(20) M. Delacre, *Bull. acad. roy. Belg.*, [3] **20**, 469 (1896).

Relative Solubilities of Lithio and Sodio Salts of β-Hydroxy Esters in Ether.—A solution of 14.8 g. (0.0625 mole) of *t*-butyl β-hydroxy-β-phenylbutyrate in 25 ml. of ether was added during 3 minutes to a stirred suspension of 0.0625 mole of lithium amide in 100 ml. of liquid ammonia, and the ammonia driven off rapidly by means of a hot water-bath as 40 ml. of ether was being added. As soon as the liquid ammonia had evaporated (about 5 minutes), 3 g. of filter aid (Hyflo Supercel) was added and the mixture filtered rapidly with suction. The solid remaining on the funnel, less the tared weight of the filter aid, weighed 0.4 g., corresponding to only 2% of insoluble lithio salt. Distillation of the solvent from the clear filtrate yielded a glassy, viscous residue which, after sucking dry under vacuum, weighed 14.6 g., corresponding to 97% of ether soluble lithio salt.

When ethyl β-hydroxy-β-phenylbutyrate was similarly converted to its sodio salt by sodium amide and the mixture filtered under the above conditions, the material on the funnel corresponded to 9% of insoluble sodio salt and that obtained on evaporation of the filtrate, to 88% of soluble sodio salt.

Ethyl α-Bromoacetate with Acetophenone and Zinc.—Treatment of 83.5 g. (0.5 mole) of ethyl α-bromoacetate, 73.2 g. (0.61 mole) of acetophenone, 40 g. (0.62 mole) of purified zinc dust and 100 ml. of anhydrous benzene under the conventional Reformatsky conditions,[9] (refluxed 1.25 hours), gave 62.3 g. (60%) of ethyl β-hydroxy-β-phenylbutyrate, b.p. 143.5–145.5° (15 mm.).

When the same quantities of reactants (using purified 20–30 mesh granulated zinc) were refluxed for a total of 29 hours in benzene and toluene (50 ml. of each), and the reaction mixture allowed to stand another 23 hours (the majority of the zinc dissolving within the first hour), there was isolated only 1.2 g. (1%) of ethyl β-hydroxy-β-phenylbutyrate, b.p. 133–136° (10 mm.). In addition there was obtained 2.2 g. (6%) of benzoylacetone, b.p. 129–132° (10 mm.), 33.0 g. (49%) of dypnone, b.p. 156–158° (1 mm.), and 10.2 g. of dark viscous residue. The β-diketone was identified by its positive enol test and copper salt, m.p. 194–195° (reported m.p. 195–196°).[18] The dypnone was identified by its phenylhydrazone, m.p. 181.5–182.5° (see above).

DURHAM, N. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Analogs of Hexaphenylethane. II.* Triphenylmethyltriphenylsilane

BY A. G. BROOK, HENRY GILMAN AND L. S. MILLER

RECEIVED APRIL 2, 1953

Triphenylmethyltriphenylsilane, a very stable solid showing no tendency to dissociate into free radicals, has been isolated in 40–70% yield from the reaction of triphenylmethylsodium or -lithium with triphenylhalosilanes. Its synthesis is accompanied by the formation of from 8–15% of the isomeric *p*-triphenylsilylphenyldiphenylmethane. When attempts were made to prepare triphenylmethyltriphenylsilane from triphenylsilylpotassium and triphenylchloromethane, the only products obtained were hexaphenyldisilane and hexaphenylethane, isolated as the peroxide. These products were shown conclusively to have arisen as the result of a halogen–metal interconversion, a phenomenon not previously observed with silicon compounds.

The well known and much studied dissociation of the hexaarylethanes into triarylmethyl radicals has given rise to considerable speculation as to whether analogous compounds containing other group IVB elements dissociate similarly. Numerous studies have been made on some of the members of this series, namely, the symmetrical disilanes, digermanes, distannanes and diplumbanes, but little attention has been paid to the unsymmetrical members containing two different group IVB elements, particularly in the case where only one carbon atom has been replaced.

Evidence is lacking for the dissociation of the hexaaryldisilanes[1] or digermanes,[2] but certain evidence, particularly cryoscopic and ebullioscopic molecular weight determinations, has been presented which suggests that the hexaaryl- and hexaalkyldistannanes[3] and -diplumbanes[4] dissociate to some extent, although this dissociation is not detected by magnetic susceptibility measurements.

Of the possible unsymmetrical hexaaryl compounds, only triphenylsilyltriphenyltin,[5] triphenylmethyltriphenyltin[6] and triphenylmethyltriphenyllead[6] have been prepared. Of these, the dissociation of the first has not been studied, while on the basis of cryoscopic molecular weight determinations in benzene, the second appears not to dissociate, while the latter appears to be about 50% dissociated at low concentrations.

No reports have been made of attempts to prepare triphenylmethyltriphenylsilane, the carbon–silicon analog of hexaphenylethane. The present investigation concerns the synthesis of this compound and a study of its properties, in particular its tendency to dissociate. A similar study of triphenylmethyltriphenylgermane is now in progress in this Laboratory.

Two alternative syntheses of triphenylmethyltriphenylsilane appeared to be possible, as outlined in equations 1 and 2.

$$(C_6H_5)_3C\text{–}M + (C_6H_5)_3Si\text{–}X \longrightarrow (C_6H_5)_3C\text{–}Si(C_6H_5)_3 + MX \quad (1)$$

$$(C_6H_5)_3Si\text{–}K + (C_6H_5)_3C\text{–}Cl \longrightarrow (C_6H_5)_3C\text{–}Si(C_6H_5)_3 + KCl \quad (2)$$

When triphenylchloro- or -bromosilane is treated with one mole equivalent of triphenylmethylsodium or -lithium, two isomeric products (I and IV) are obtained in ratios varying from about 3:1 to 9:1, depending on the conditions, each of which has the correct analysis for the desired triphenylmethyltriphenylsilane. The higher melting compound, which melts at about 330–335°, was identi-

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* For paper I, of this series see H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 3762 (1953).

[1] (a) W. Schlenk, J. Renning and G. Racky, *Ber.*, **44**, 1178 (1911); W. C. Schumb and C. M. Saffer, THIS JOURNAL, **61**, 363 (1939); (b) H. Gilman and G. E. Dunn, *ibid.*, **73**, 5077 (1951); H. Gilman and T. C. Wu, *ibid.*, **75**, 3762 (1953).

[2] P. W. Selwood, THIS JOURNAL, **61**, 3168 (1939); G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

[3] H. Morris, W. Byerly and P. W. Selwood, THIS JOURNAL, **64**, 1727 (1942); C. A. Kraus and W. V. Sessions, *ibid.*, **47**, 2361 (1925).

[4] R. Preckel and P. W. Selwood, *ibid.*, **62**, 2765 (1940); T. Midgley, C. A. Hochwalt and G. Calingaert, *ibid.*, **45**, 1821 (1923); E. Krause, *Ber.*, **54**, 2560 (1921).

[5] H. Gilman and S. D. Rosenberg, THIS JOURNAL, **74**, 531 (1952).

[6] J. C. Bailie, *Iowa State Coll. J. Sci.*, **14**, 8 (1939) [*C.A.*, **34**, 6241 (1940)]; see also J. C. Bailie, Doctoral Dissertation, Iowa State College, 1938.