Complex with Toluene: *Anal.* Calcd. for $C_{28}H_{28}SiSn \cdot C_8H_8$: Si + Sn, 24.32. Found: Si + Sn, 24.56.

Complex with Pyridine: *Anal.* Calcd. for $C_{28}H_{28}SiSn \cdot C_5H_5N$: Si + Sn, 24.85. Found: Si + Sn, 25.03.

Complex with Dioxane: *Anal.* Calcd. for $C_{28}H_{28}SiSn \cdot C_4H_8O_2$: Si + Sn, 24.49. Found: Si + Sn, 24.68.

1,1′4-4′-Tetraphenyl-1-stanna-4-germanacyclohexane.—Equimolecular amounts of diphenyltin dihydride (5.50 g., 0.02 mole) and diphenyldivinylgermane (5.60 g.) were heated together for 4 hr. at 65° and for 8 hr. at 80°. The partly solid reaction mixture was taken up in a small volume of petroleum ether. Filtration yielded 3.45 g. of a solid which melted at 110–115°. Recrystallization from ethanol (twice) raised the m.p. to 124–125°; yield of pure product 1.92 g. (17%). The infrared spectrum revealed the presence of C_6H_5–Ge (band at 1080 cm.$^{-1}$), of C_6H_5–Sn (band at 1065 cm.$^{-1}$) and of $-CH_2-$ (doublet at 2860 cm.$^{-1}$), but there was no evidence for Sn–H (band at 1825 cm.$^{-1}$) or $GeCH=CH_2$ (band at 952 cm.$^{-1}$).

Anal. Calcd. for $C_{28}H_{28}GeSn$: C, 60.42; H, 5.02; Ge + Sn, 34.56; mol. wt., 5.56. Found: C, 60.19; H, 5.19; Ge + Sn, 34.74; mol. wt. (Rast), 545.

Complex with Toluene: *Anal.* Calcd. for $C_{28}H_{28}GeSn \cdot C_7H_8$: Ge + Sn, 29.52. Found: Ge + Sn, 29.59.

1,1′,2,4,4′,5-Hexaphenyl-1,4-distannacyclohexane.—Phenylacetylene (7.1 g., 0.07 mole) was added dropwise to a rapidly stirred solution of 19.2 g. (0.07 mole) of diphenyltin dihydride in 50 ml. of *n*-pentane. When the spontaneous evolution of heat had ceased the reaction mixture was refluxed for 2 hr. Thereupon the solvent was removed and the residue was heated at 100° for 6 hr. Upon cooling, a brittle product (26.0 g.) was obtained which melted at *ca.* 70–90°.

When a solution of 10.0 g. of this product in 150 ml. of 1-butanol was rapidly cooled, 2.5 g. of a white powder precipitated which melted at 70–72° (sintering at 68°).

Anal. Calcd. for $C_{40}H_{36}Sn_2$: C, 63.71; H, 4.81; Sn, 31.49; mol. wt., 754. Found: C, 63.44; H, 5.05; Sn, 31.79; mol. wt. (Rast), 780.

The mother liquor after 3 days at room temperature had deposited 2.7 g. of a crystalline solid which after recrystallization from acetic acid melted at 144–145°. The infrared spectra of both compounds were very similar in the region of 3500–680 cm.$^{-1}$. There was no evidence of Sn–H (band at 1825 cm.$^{-1}$) or of $SnCH=CHC_6H_5$ (band at 985 cm.$^{-1}$).

Anal. Calcd. for $C_{40}H_{36}Sn_2$: C, 63.71; H, 4.81; Sn, 31.49; mol. wt., 754. Found: C, 63.77; H, 5.08; Sn, 31.69; mol. wt. (Rast), 817.

Acknowledgment.—The authors are indebted: to Prof. G. J. M. van der Kerk, Director of this Institute, for encouragement; to Dr. E. S. Hedges, Director of the International Tin Research Council, for his supporting interest; to Mr. H. A. Budding for able experimental assistance.

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES, UNIVERSITY OF HEIDELBERG]

The Organometallic Alkylidene Reaction

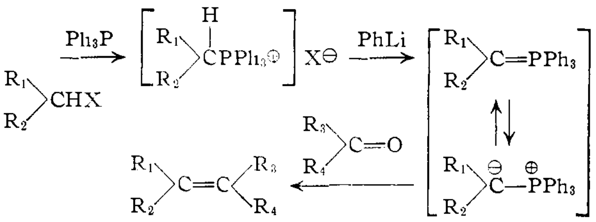
BY MALCOLM C. HENRY[1] AND GEORGE WITTIG

RECEIVED APRIL 25, 1959

The analog of the reaction between triphenylphosphine-methylene and carbonyl compounds to form the corresponding ethylenic compounds has been studied with quaternary compounds of arsenic, antimony and bismuth. The reaction with the arsenic alkylidene, in contrast to the phosphorous alkylidene, yields with benzophenone predominantly the corresponding aldehyde along with smaller amounts of the corresponding ethylenic compound. With the stibonium alkylidene only the corresponding aldehyde is produced. A new reaction has been utilized to produce triaryl-alkyl-quaternary salts of some of the group 5 elements using trimethyloxonium boron tetrafluoride.

The reaction between triarylphosphine alkylidenes and carbonyl compounds has proved to be, because of its specificity and good yields, widely applicable for the conversion of carbonyl compounds into their ethylenic entities.[2,3] Satisfactory results have also been obtained with compounds containing hydroxyl and acetoxy groups in addition to the carbonyl function,[4,5] and in the conversion of different types of saturated and α,β-unsaturated steroidal ketones to the corresponding methylene compounds. The reaction in many instances offers the most accessible route from such carbonyls to the corresponding methylenic compounds. Levine[6] and Wittig[7] have described a modification of the alkylidene reaction whereby aldehydes may be synthesized by way of their enol ethers.

We have attempted to substitute for phosphorus the other members of the group 5A elements, namely arsenic, antimony and bismuth. Benzophenone was selected as the second reactant.



Triphenylmethylarsonium halides have been previously synthesized by Michaelis[8] and Steinkopf[9] using the direct reaction between triphenylarsine and methyl halides. No method was available for the synthesis of triphenylmethylstibonium or bismuthonium salts since methyl halides do not add directly to triphenylstibine and triphenylbismuth. However, trimethyloxonium boron tetrafluoride, $[(CH_3)_3O^+][BF_4^-]$, an active methylating agent described by Meerwein,[10] reacts readily with triphenylstibine to yield the quaternary boron tetrafluoride, which is easily converted to the corresponding iodide. Triphenylbismuth reacts with the reagent, but does not produce the analogous "onium" salt under the conditions used. The

---

[1] U. S. Quartermaster Research and Engineering Command. Pioneering Research Division, U. S. Army, Natick, Mass.; work carried out at the University of Heidelberg, Heidelberg, Germany, under the auspices of a Secretary of the Army Research Fellowship.

[2] G. Wittig, *Experientia*, **12**, 41 (1956); *Angew. Chem.*, **68**, 505 (1956).

[3] U. Schöllkopf, *ibid.*, **71**, 260 (1959).

[4] R. Sondheimer and R. Mechoulam, THIS JOURNAL, **79**, 5029 (1957).

[5] G. Wittig, "Festschrift, Prof. Dr. Arthur Stoll," Birkhauser Basel, Switzerland, 1957.

[6] S. Levine, THIS JOURNAL, **80**, 6150 (1958).

[7] G. Wittig and E. Knauss, *Angew. Chem.*, **71**, 127 (1959).

[8] A. Michaelis, *Ann.*, **321**, 141 (1902).

[9] W. Steinkopf and G. Schwen, *Ber.*, **54**, 2973 (1921).

[10] H. Meerwein, *J. prakt. Chem.*, **147**, 257 (1937).

reaction of the triphenylmethylarsonium halides and the triphenylmethylstibonium iodide takes place readily in dry ether as does the subsequent reaction of the alkylidene with benzophenone. In the case of the arsenic salt four products are formed, triphenylarsine, diphenylacetaldehyde, triphenylarsine oxide and diphenylethylene. The former two are always formed in equimolar amounts as are the latter two, thus indicating that the two pairs are formed together, probably by two different routes. It would appear that after the initial formation of the alkylidene II that the reaction with benzophenone could produce an intermediate (III) that by rearrangement produces the triphenylarsine oxide and the diphenylethylene in equimolar amounts. Apparently the intermediate can also rearrange by an alternate route, possibly by formation of an unstable epoxide ring which reopens to form the diphenylacetaldehyde. Table I summarized the results obtained and shows that the halide ion used in the initial salt has but little effect on the reaction and further that in the case of the stibonium salt only triphenylarsine and diphenylacetaldehyde are produced, although traces of triphenylarsine oxide and diphenylethylene were detected.

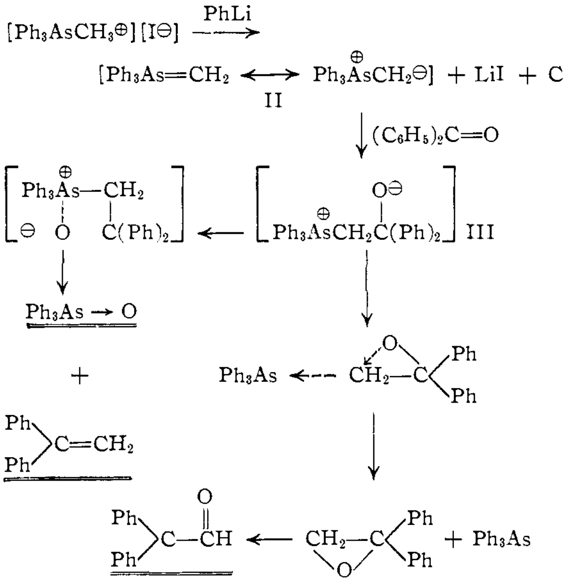


TABLE I

PRODUCTS OF REACTION BETWEEN $Ph_3(CH_3)MeI$, Ph_2CO AND PhLi

10 mmoles reactants, 60° reflux, 12 hours, sealed Schlenk tube

	Ph_2CO un-reacted	Ph_3Me	Ph_2-CHCHO	Ph_3MeO	$Ph_2C{=}CH_2$
$Ph_3(CH_3)AsI$	1.1	6.9	6.8	2.0	2 1
$Ph_3(CH_3)AsBr$	1.5	6.9	6.5	2 3	2.4
$Ph_3(CH_3)SbI$	0.2	9.1	9.2	Trace	Trace

Experimental[11]

Triphenylmethylarsonium Iodide.—A molar excess of methyl iodide was added to an alcoholic solution of triphenylarsine and refluxed for several hours according to the method of Michaelis[8]; m.p. 174–175°.

Anal. Calcd. for $C_{19}H_{18}AsI$: C, 50.91; H, 4.03. Found: C, 50.99; H, 4.10. Mohr titration (silver nitrate), 1:1 molar ratio with salt.

Triphenylmethylarsonium Bromide.—A sealed Schlenk tube containing a solution of triphenylarsine in excess methyl bromide was allowed to stand for two weeks according to the procedure of Steinkopf[9]; white crystalline product, m.p. 194–195°.

Anal. Calcd. for $C_{19}H_{18}AsBr$: C, 56.87; H, 4.74. Found: C, 56.80; H, 4.73; Mohr titration (silver nitrate), 1:1 molar ratio with salt.

Triphenylmethylstibonium Iodide.—Trimethyloxonium boron tetrafluoride, prepared according to the method of Meerwein,[10] was treated with triphenylstibine in liquid sulfur dioxide solution, stirred and allowed to stand for several hours. The sulfur dioxide was evaporated slowly, the resulting white mass dissolved in alcohol and the triphenylmethylstibonium boron tetrafluoride precipitated with ether. Recrystallization from boiling water produced the pure salt, m.p. 133–134°. A heated, saturated aqueous solution of this salt in the presence of a molar excess of sodium iodide upon cooling produced triphenylmethylstibonium iodide, m.p. 124–124.5°.

Anal. Calcd. for $C_{19}H_{18}SbI$: C, 46.45; H, 3.64. Found: C, 46.18; H, 3.60.

Typical Reaction Conditions.—A Schlenk tube of suitable size was evacuated, dried and filled with dry nitrogen. A weighed amount of the dry triphenylmethylarsonium or stibonium salt was added and then suspended in dry diethyl ether. An equimolar amount of phenyllithium was added; the Schlenk tube was sealed and allowed to react for 12 hours with shaking. After an equimolar amount of benzophenone (dissolved in ether) had been added, the Schlenk tube was resealed, placed in a 60° oil-bath and refluxed for 12 hours. The contents were hydrolyzed with 6 *N* HCl, washed with water, dried and the ether evaporated. The resulting residue or viscous oil was chromatographed on a neutral alumina (Merck) column. The solvent sequence most useful was petroleum ether (30–40°), petroleum ether (60–80°), diethyl ether and methanol.

Alkylidene Reaction using Triphenylmethylarsonium Iodide.[12]—The reaction, using 10 mmoles of triphenylmethylarsonium iodide, phenyllithium and benzophenone, respectively, and the subsequent isolation of the reaction products were carried out as described above. Triphenylarsine was the first reaction product eluted from the column (2.09 g.); recrystallized from methanol, m.p. 60–61°. Mixed melting point with authentic sample gave no depression. Comparison with infrared spectrum of authentic sample and precipitation of the $HgCl_2 \cdot Ph_3As$ insoluble complex were used as confirmatory evidence.

Anal. Calcd. for $C_{18}H_{15}As$: C, 70.61; H, 4.90. Found: C, 70.60; H, 4.95.

The second fraction from the column was diphenylethylene (1.8 g.). High vacuum distillation yielded a pale yellow, almost colorless liquid. Comparison with infrared spectrum of an authentic sample was used as confirmatory evidence.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.33; H, 6.60. Found: C, 93.29; H, 6.62.

The third fraction from the column was diphenylacetaldehyde (1.34 g.). A portion of this was distilled under vacuum and a portion used to form the 2,4-dinitrophenylhydrazone, m.p. 154–155°. Mixed melting point and infrared spectrum of an authentic sample were used as confirmatory evidence.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.72: *H*, 6.12. Found: C, 85.68; H, 5.98.

The fourth fraction, triphenylarsine oxide, was isolated as an insoluble residue from the initial reaction mixture (0.644 g.). Recrystallization from alcohol produced the pure salt, m.p. 191–191.5°. Mixed melting point and infrared spectrum of an authentic sample were used as confirmatory evidence.

Anal. Calcd. for $C_{18}H_{15}AsO$: C, 67.09; H, 4.65. Found: C, 66.90; H, 4.79.

HEIDELBERG, GERMANY

---

[11] Melting points are uncorrected. All solvents were distilled and dried over sodium metal. All reactions were carried out under nitrogen.

[12] Triphenylmethylarsonium bromide and triphenylmethylstibonium iodide reactions were carried out in a similar manner.