The decomposition of anisoin. A mixture of 56 g. of anisoin (m.p. 112-113°), 11.2 g. of potassium cyanide, 75 ml. of 95% ethanol, and 45 ml. of water was heated under reflux for 4 hr. It was then cooled with shaking until crystallization was well under way and then left at 0° overnight. There was recovered 37.5 g. (67%) of material of m.p. 105-111°. The mother liquor was diluted with water and extracted with ether. The ether extract was stirred with saturated sodium bisulfite solution, and from the aqueous phase was recovered 5.8 g. (10%) of anisaldehyde by the addition of sodium carbonate to the bisulfite solution. Removal of the ether from the organic phase left 6.0 g. of viscous red oily material.<sup>12</sup> Acidification of the original

(12) No attempt was made to determine the nature of this material. J. C. Irvine, J. Chem. Soc., 79, 668 (1901) has reported the recovery of a similar by-product of complex nature from the benzoin condensation of ortho-methoxy-benzaldehyde. For the by-products of the benzoin condensation of benzaldehyde see ref. 3, p. 277.

aqueous phase yielded 3.5 g. of a solid of m.p.  $181-183^{\circ}$  which gave no depression when mixed with anisic acid (lit.<sup>11</sup> m.p.  $184^{\circ}$ ). On another similar run which was refluxed for 24 hr., cooling yielded no crystalline anisoin, but a 10% yield of anisaldehyde was recovered.

The "anhydrous" runs. These runs were carried out under conditions similar to those for the Grignard and similar reactions. The glassware was dried overnight at  $125^{\circ}$  before use. Dry nitrogen was used to eliminate moisture from the atmosphere. To the system, being flushed with nitrogen, was added 2 g. of sodium cyanide (dried at  $110^{\circ}$ ), 25 ml. (28 g.) of anisaldehyde, and 40 ml. of anhydrous ethylene glycol dimethyl ether. The runs were heated under reflux for the times indicated in Table II, then stoppered, and maintained at 0° overnight. The anisoin was filtered and washed first with the cold solvent, and then with water to remove sodium cyanide. The yields and melting points are tabulated in Table II.

PHILLIPSBURG, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

# Phosphinemethylenes.<sup>1</sup> II. Triphenylphosphineacylmethylenes

### FAUSTO RAMIREZ AND SAMUEL DERSHOWITZ<sup>2</sup>

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The preparation and some properties of triphenylphosphinebenzoylmethylene (III) and triphenylphosphineacetylmethylene (IV) are reported. Previous formulations of these compounds are rejected.

The properties of the phosphinemethylenes<sup>3</sup>  $(R_3P=CXY \leftrightarrow R_3P^+-C^-XY)$ , such as their color, their stability, and their ability to react with aldehydes and ketones,<sup>4</sup> seem to be closely related to the distribution of the negative charge in the molecule.

$$R_{a}P = CXY + H_{2}O \longrightarrow R_{2}(YXHC)PO + RH \text{ or } R_{a}PO + CH_{2}XY$$
$$R_{a}P = CXY + R'R''CO \longrightarrow R_{a}PO + R'R''C = CXY$$

During an investigation<sup>5</sup> into the structure and properties of the phosphinemethylenes we have ex-

amined two types, I and II, which owe their remarkable stability to the incorporation of the negative charge in a nonbenzenoid (I) and a benzenoid (II) aromatic system. The observed dipole moment of triphenylphosphoniumcyclopentadienylide (I)<sup>1</sup> (7.0 D) is consistent with its representation as a resonance hybrid to which pentacovalent (Ia) and tetracovalent (Ib) phosphorus structures make roughly equal contributions. I was stable toward concentrated alkali and unreactive toward carbonyl functions. II could be hydrolyzed to triphenylphos-



<sup>(1)</sup> A convenient way of naming the compounds herein discussed is based on the name "phosphinemethylene" for the parent formulation  $H_3P=CH_2$  (cf. ref. 3 and Collected Formula Index of Chem. Abs.). Thus,  $(C_6H_5)_3P=CH_2$  would be triphenylphosphinemethylene,  $(C_6H_5)_3P=CH_-C_5H_5$ , triphenylphosphinebenzoylmethylene. The compounds could be named as derivatives of phosphorane, PH<sub>5</sub> [cf. Chem. Eng. News, **30**, 4515 (1952)]. Thus,  $(C_6H_5)_3P=CH_-CO_6H_5$  would be triphenylphonebenzoylbe triphenylphosphorane, PH<sub>5</sub> [cf. Chem. Eng. News, **30**, 4515 (1952)]. Thus,  $(C_6H_5)_3P=CH_-CO_6H_5$  would be triphenylphonebenzoylbe triphenylbe triphenylphonebenzoylbe triphenylbe triphenyl

<sup>(2)</sup> From part of the Ph.D. thesis of S. Dershowitz.

<sup>(3)</sup> G. M. Kosolapoff, Organophosphorus Compounds, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 28, 355.

<sup>(4)</sup> For references see G. Wittig, *Experientia*, 12, 41 (1956); and ref. 5 of this paper.

<sup>(5) (</sup>a) F. Ramirez and S. Levy, J. Am. Chem. Soc., 79, 67 (1957); (b) F. Ramirez and S. Dershowitz, J. Am. Chem. Soc., 78, 5614 (1956).

phine oxide and hydroquinone on prolonged heating with dilute alkali.

This paper deals with a closely related system of phosphinemethylenes: the phosphineacylmethylenes,<sup>1</sup> III and IV.

In early investigations, Michaelis and Kohler,<sup>6</sup> studied the action of aqueous alkali on phenacyltriphenylphosphonium bromide (V) and acetonyltriphenylphosphonium chloride (VI). The resulting compounds, m.p. 181° and 200°, respectively, were formulated as cyclic derivatives of pentacovalent phosphorus, VII and VIII, to account for the extra molecule of water apparently disclosed by the elementary analyses. Later, Kröhnke<sup>7</sup> commented on the stability of the benzoyl derivative (VII, in the early formulation) toward alkali. Recently, Wittig and Schöllkopf<sup>8</sup> described the infrared spectra of these so-called "phosphonium betaines" m.p. 181° and 200°. Accepting the empirical formulas deduced by Michaelis,<sup>6</sup> the phosphonium betaines were formulated<sup>8</sup> as IX and X, with pentacovalent phosphorus. The lack of free C-OH and P-OH and the remarkable shift of the carbonyl frequency<sup>8</sup> were taken as evidence for the "chelated" formulas IX and X.



In our hands, the crystalline substance, m.p. 178-180°, obtained on treatment of phenacyltriphenylphosphonium bromide (V) with alkali was found to have the formula C<sub>26</sub>H<sub>21</sub>OP; it is therefore regarded as triphenylphosphinebenzoylmethylene (IIIa  $\rightarrow$  IIIb). The substance, m.p. 205–206°, obtained from acetonyltriphenylphosphonium chloride (VI) corresponded to the formula  $C_{21}H_{19}OP$ and is regarded as triphenylphosphineacetylmethylene (IVa  $\rightarrow$  IVb). We have confirmed the striking shift of the carbonyl frequency reported by Wittig.<sup>8</sup> The strongest band in the infrared spectrum of the benzoyl derivative III was found at 6.60  $\mu$ ; the corresponding band for the acetyl derivative, IV, was at 6.54  $\mu$ . The low carbonyl frequencies are not unreasonable in the light of the electronic distribution expressed in formulas III and IV.

The ultraviolet absorption spectra of the phosphinemethylenes III and IV are shown in Figs. 1, 2, and 3. The marked bathochromic effect of the benzoyl group is evident. In the hydroxylic solvent some protonation of the phosphinemethylenes is likely; this effect is apparent from a comparison of the curves in ethanol and acetonitrile.



<sup>(6)</sup> A. Michaelis and E. Kohler, Ber., 32, 1566 (1899).

<sup>(7)</sup> F. Kröhnke, Chem. Ber., 83, 291 (1950); cf. footnote 4.

<sup>(8)</sup> G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954). The "phosphonium betaine," m.p. 200°, derived from acetonyltriphenylphosphonium bromide, exhibited a very sharp band at 6.55  $\mu$  in the infrared (KBr).



Both phosphinemethylenes, III and IV, could be hydrolyzed by prolonged heating in aqueous ethanol with or without added alkali. The intermediate in these hydrolyses may be of type IX and X with pentacovalent phosphorus.<sup>5</sup> Reaction with benzaldehyde was observed in hot tetrahydrofuran. The products—triphenylphosphine oxide and benzalacetophenone (from III) or benzalacetone (from IV)—were isolated in high yields. Wittig<sup>4,8</sup> has interpreted analogous reactions as involving intermediates of type XI and XII.



The behavior of the phosphinemethylenes in alkylation reactions is of interest. With ethyl iodide both III and IV underwent O-alkylation exclusively. The resulting (2-ethoxystyryl) - triphenylphosphonium iodide (XIII) and (2-ethoxypropenyl)triphenylphosphonium iodide (XIV) (Figs. 1 and 2) were cleaved to the corresponding phenacyltriphenylphosphonium iodide (XV) and acetonyltriphenylphosphonium iodide (XVI) with hydriodic acid. The phosphonium enol ethers XIII and XIV were cleaved to triphenylphosphine oxide and the corresponding enol ethers XVII and XVIII by hot alkali. These alkaline hydrolyses resemble those previously reported<sup>5b</sup> for analogous O-ethers derived from phosphinemethylenes of type II.

The dipole moments of the phosphineacylmeth-

ylenes III and IV were found<sup>9</sup> to be 5.45 and 5.54 D, respectively.



#### EXPERIMENTAL<sup>10</sup>

Phenacyltriphenylphosphonium bromide (V). Phenacyl bromide (8.35 g.) was added in portions to a chloroform (75 ml.) solution of triphenylphosphine (10.89 g.). The solution was filtered into one liter of anhydrous ether. The precipitate was collected and dried. Yield: 15 g. m.p. 267-269°. The analytical sample obtained by crystallization from water had m.p. 269-271°;  $\lambda_{max.}^{B:OH}$  253 m $\mu$  ( $\epsilon$  15,700) 276 m $\mu$  ( $\epsilon$  5200); bands (KBr) at 3.87 (m), 6.08 (strong est), 6.32 (m), 6.80 (m), 7.02 (s), 7.30 (w), 7.60 (m), 7.75 (m), 9.05 (s) and 10.10 (s)  $\mu$ .

Ânal. Calc'd for C28H22BrOP: C, 67.7; H, 4.8. Found: C, 67.6; H, 5.1.

The bromide appears to crystallize in a different form, m.p. 279-280°, from methanol-ethyl acetate. This form, when recrystallized from water, melted again at 269-271°. The I.R. spectra of both forms (KBr) are identical.

Alkaline treatment of phenacyltriphenylphosphonium bromide (V). A mixture of phenacyltriphenylphosphonium bromide (V) (1.0 g.), 5% methanolic potassium hydroxide (40 ml.) and some water was heated to reflux for 2 days. The mixture was cooled, diluted with water, and extracted with ether. The residue obtained on removal of the ether was stirred with petroleum ether. The insoluble portion (0.495 g., m.p. 147-152°) was shown to be triphenylphosphine oxide. The petroleum ether solution was evaporated and the residue was dissolved in 95% ethanol (5 ml.) and treated with an aqueous alcoholic solution of 2,4-dinitrophenylhydrazonium sulfate. The precipitate (0.475 g.) was shown to be acetophenone-2,4-dinitrophenylhydrazone (m.p. and mixed m.p. with authentic sample  $243-247^\circ$ ). A mixture of bromide V (7.2 g.) and 5% aqueous sodium

A mixture of bromide V (7.2 g.) and 5% aqueous sodium hydroxide (80 ml.) also gave triphenylphosphine oxide (4.0 g.) after 42 hr. at reflux temperature.

Triphenylphosphinebenzoylmethylene (III). A mixture of phenacyltriphenylphosphonium bromide (V) (7.5 g.) and 10% aqueous sodium carbonate (300 ml.) was shaken for 15 hr. The mixture was filtered and the insoluble portion was taken up in hot benzene (200 ml.). Some unreacted bromide (0.5 g.) was removed by filtration; addition of petroleum ether to the benzene filtrate afforded 5.8 g. of phosphinemethylene III m.p. 178–180°. For further purification, a benzene solution of the phosphinemethylene III was boiled in order to remove retained water. Concentration and dilution with petroleum ether afforded 4.45 g. of pure III m.p. 178–180°. The analytical sample was dried at 70° (0.1 mm.);  $\lambda_{\text{max.}}^{\text{EudH}}$ , 268 m $\mu$  ( $\epsilon$  6900), 274 m $\mu$  ( $\epsilon$  7100) and 318 m $\mu$ 

<sup>(9)</sup> The dipole moments were measured by Prof. M. T. Rogers, of Michigan State University and will be the subject for a separate communication.

<sup>(10)</sup> Microanalyses by Micro-Tech Laboratories, Skokie, Ill., and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

( $\epsilon$  11,900); bands (KBr) at 6.32 (m), 6.60 (strongest), 6.80 (m), 7.02 (s) and 9.05 (s)  $\mu$ .

Anal. Cale'd for  $C_{20}H_{21}OP$ : C, 82.1; H, 5.6; M.W. 380. Found: C, 82.1; H, 5.7; mol. wt. 369 (isothermal distillation in benzene).

The phosphinemethylene III could be prepared from the bromide V in lower yield (84%) using 5% aqueous sodium hydroxide for 30 min. at steam bath temperature.

When the phosphinemethylene III (0.08 g.) was shaken with 10% aqueous hydrobromic acid, the original bromide V (0.095 g., m.p. 266-269°) was produced.

Phenacyltriphenylphosphonium iodide (XV). A mixture of the phosphinemethylene III (0.50 g.) and 5% aqueous hydriodic acid (35 ml.) was shaken (ca. 30 min.) and filtered. The insoluble iodide was stirred with warm benzene (to remove unreacted III) and filtered. The crude iodide (0.60 g.) had m.p. 247-254°. Recrystallization from methanolethyl acetate gave the iodide XV m.p. 259-260°;  $\lambda_{max.}^{EOB}$ 222 m $\mu$  ( $\epsilon$  44,500), 254 m $\mu$  ( $\epsilon$  16,200) and 276 m $\mu$  ( $\epsilon$  5900). Bands (KBr) at 3.80 (m-s), 6.08 (strongest), 6.30 (m), 6.80 (m), 7.02 (s), 7.60 (m), 8.35 (s), 9.02 (s), and 10.10 (s)  $\mu$ . Anal. Calc'd for C<sub>28</sub>H<sub>22</sub>IOP: C, 61.4; H, 4.4. Found: C, 61.0; H, 4.7.

The sample m.p. 259-260° melted at 240-242°, when recrystallized from water. The I.R. spectra were identical (KBr).

Hydrolysis of triphenylphosphinebenzoylmethylene (III). A solution of phosphinemethylene (1.0 g.) in 30% aqueous ethanol (80 ml.) was refluxed for 10 hr. The solution was diluted with 40 ml. of water and extracted with ether. Removal of the ether gave a residue, part of which (0.60 g.) was insoluble in petroleum ether and was shown to be triphenylphosphine oxide. The petroleum ether soluble portion afforded acetophenone, identified as its 2,4-dinitrophenylhydrazone (0.62 g.).

Reaction of triphenylphosphinebenzoylmethylene (III) with benzaldehyde. A solution of phosphinemethylene III (3.05 g.) and benzaldehyde (0.838 g.) in tetrahydrofuran (100 ml.) was refluxed for 30 hr. The oily residue obtained on removal of the solvent was taken up in 95% ethanol and treated with an aqueous ethanolic solution of 2,4-dinitrophenylhydrazonium sulfate. The crude 2,4-dinitrophenylhydrazone weighed 3.10 g.; after recrystallization from methanol-chloroform it had m.p. 248-250°; if a trace of hydrochloric acid was present during the recrystallization the m.p. was 169-174°. This behavior, as well as the spectra in the U.V. and I.R. identifies the product as benzalacetophenone-2,4-dinitrophenylhydrazone.

The phosphinemethylene III failed to react with cyclohexanone under similar conditions.

(2-Ethoxystyryl)-triphenylphosphonium iodide (XIII). A mixture of triphenylphosphinebenzoylmethylene (III) (0.70 g.) and freshly distilled ethyl iodide was refuxed for 7 hr. The crystalline substance which separated (0.92 g., m.p. 170–184°) was collected and was then shaken with 10% aqueous potassium carbonate (100 ml.) for some time. The insoluble material was collected and treated with 30 ml. benzene. The insoluble iodide XIII (0.85 g.) had m.p. 175–177°. The analytical sample had m.p. 176–178° (from chloroform-benzene-petroleum ether);  $\lambda_{\rm max}^{\rm EtoH}$  222 mµ ( $\epsilon$  45,400) and 270 mµ ( $\epsilon$  21,200). Bands (KBr) at 6.25 (m), 6.40 (strongest), 8.80 (w), 7.02 (s), 7.65 (s), 9.05 (s) and 9.20 (s) µ.

Anal. Calc'd for  $C_{28}H_{26}IOP$ : C, 62.7; H, 4.9. Found: C, 63.1; H, 5.0.

When the phosphinemethylene III was alkylated with ethyl iodide in anhydrous methanol solution, a mixture of phenacyltriphenylphosphonium iodide (XV) and (2-ethoxystyryl)-triphenylphosphonium iodide (XIII) was obtained. This can be explained as follows:

$$(C_{\mathfrak{s}}H_{\mathfrak{s}})_{\mathfrak{s}}P.CH.CO.C_{\mathfrak{s}}H_{\mathfrak{s}} + CH_{\mathfrak{s}}OH \xrightarrow{(+)} (C_{\mathfrak{s}}H_{\mathfrak{s}})_{\mathfrak{s}}P.CH_{\mathfrak{s}}CO.C_{\mathfrak{s}}H_{\mathfrak{s}} + CH_{\mathfrak{s}}O^{(-)}$$

$$CH_{3}^{(-)} + C_{2}H_{3}I \longrightarrow CH_{3}OC_{2}H_{5} + I^{(-)}$$

No C-alkylation was observed.

Treatment of (2-ethoxystyryl)-triphenylphosphonium iodide (XIII) with acid. A mixture of (2-ethoxystyryl)-triphenylphosphonium iodide (XIII) (0.50 g.) and 5% aqueous hydriodic acid (30 ml.) was refluxed for 15 hr. The mixture was cooled and filtered and the collected solid (0.45 g., m.p. 210-235°) was divided into two portions: (a) one portion (0.25 g.) was recrystallized and was shown to be phenacyltriphenylphosphonium iodide (XV) by comparison with an authentic sample. (b) The second portion (0.20) was shaken (several hours) with 10% aqueous sodium carbonate (25 ml.) affording a solid from which 0.08 g. of triphenylphosphinebenzoylmethylene (III) was obtained on recrystallization (benzene-petroleum ether).

Treatment of (2-ethoxystyryl)-triphenylphosphonium iodide (XIII) with alkali. A mixture of iodide XIII (4.8 g.) and 5%methanolic potassium hydroxide containing ca.5% of water was refluxed for 15 hr. Water was added (30 ml.) and the mixture was extracted with ether. The residue obtained by distillation of the ether was stirred with petroleum ether, yielding 2.1 g. of insoluble triphenylphosphine oxide. The oil obtained after removal of the petroleum ether was distilled (bath temperature  $95^{\circ}/15$  mm.) giving  $\alpha$ -ethoxy-styrene (XVII) as a colorless oil. This material had  $n_{\rm D}^{2\circ}$ 1.5312 and decolorized, instantaneously, a chloroform solution of bromine. Its infrared spectrum (in chloroform) had no carbonyl absorption. When the material was treated with an aqueous methanolic solution of 2,4-dinitrophenylhydrazonium sulfate, containing excess sulfuric acid, no immediate precipitate was observed. After several minutes on the steam bath, acetophenone-2,4-dinitrophenylhydrazone was formed.

Acetonyltriphenylphosphonium chloride (VI). A solution of triphenylphosphine (10.0 g.) and chloroacetone (3.25 g.) in chloroform (ca. 30 ml.) was refluxed for 45 min. The solution was filtered into anhydrous ether (300 ml.) and the solid collected. Yield: 11.2 g., m.p. 234–237°. Analytical sample: m.p. 237–238° (from chloroform-benzene-petroleum ether);  $\lambda_{\rm maxi}^{\rm scot}$  255 m $\mu$  ( $\epsilon$  3600), 262 m $\mu$  ( $\epsilon$  3700), 268 m $\mu$  ( $\epsilon$  4000) and 275 m $\mu$  ( $\epsilon$  3100); bands (KBr) at 3.68 (m), 5.92 (strongest), 6.32 (m), 6.80 (m), 7.02 (s), 7.40 (s), 8.70 (s), 9.05 (s), and 10.05 (s)  $\mu$ .

Anal. Cale'd for C<sub>21</sub>H<sub>20</sub>ClOP: C, 71.1; H, 5.7. Found: C, 70.9; H, 5.9.

Triphenylphosphineacetylmethylene (IV). A mixture of acetonyltriphenylphosphonium chloride (VI) (1.3 g.) and 10% aqueous sodium carbonate was shaken for 8 hr. The solid was collected and dried; yield, 1.07 g., m.p. 199–202°. The analytical sample of IV had m.p. 205–206° (from methanol-water) and was dried at 70°/0.1 mm.;  $\lambda \frac{\text{Etoff}}{\text{mext.}}$ , 268 m $\mu$  ( $\epsilon$  6600), 275 m $\mu$  ( $\epsilon$  6500) and 288 m $\mu$  ( $\epsilon$  5700); bands (KBr) at 6.54 (strongest), 6.80 (m), 7.02 (s), 7.28 (m), 9.05 (s) and 10.22 (s)  $\mu$ .

Anal. Calc'd for  $C_{21}\dot{H}_{19}OP$ : C, 79.3; H, 6.0; mol. wt. 318. Found: C, 79.0; H, 5.9; mol. wt. 329 (isothermal distillation in benzene).

The phosphinemethylene IV precipitated (in 75% yield) upon addition of 5% aqueous sodium hydroxide to an aqueous solution of chloride VI.

Treatment of the phosphinemethylene IV (0.35 g.) in methanol solution (25 ml.) with a few drops of concentrated hydrochloric acid regenerated the phosphonium chloride VI (0.36 g.; m.p. 233-236°), obtained by concentration of the methanol solution and dilution with ethyl acetate.

Acetonyltriphenylphosphonium iodide (XVI). Shaking triphenylphosphineacetylmethylene (IV) (0.30 g.) and 5% aqueous hydriodic acid (25 ml.) for 30 min. at room temperature gave the iodide (0.35 g., m.p. 202–205°). Analytical sample: m.p. 207–209° (from water);  $\lambda_{\text{max}}^{\text{EvoH}}$  262 mµ ( $\epsilon$  4000), 268 mµ ( $\epsilon$  4000) and 276 mµ ( $\epsilon$  3100).

Anal. Calc'd for C<sub>21</sub>H<sub>10</sub>IOP: C, 56.5; H, 4.5. Found: C, 56.7; H, 4.7.

Hydrolysis of triphenylphosphineacetylmethylene (IV). The phosphine methylene IV (1.1 g.) in 40 ml. of water was heated to reflux for 12 hr. The resulting white solid (0.925 g.) was shown to be triphenylphosphine oxide.

Reaction of triphenylphosphineacetylmethylene (IV) with benzaldehyde. A solution of the phosphinemethylene IV (1.1 g.) and benzaldehyde (0.367 g.) in tetrahydrofuran was refluxed for 48 hr. The solvent was removed, the residue was dissolved in 95% ethanol and the solution was treated with an aqueous methanolic solution of 2,4-dinitrophenylhydrazinium sulfate. The precipitate was recrystallized (m.p. 218-221°) and was identified as benzalacetone-2,4dinitrophenylhydrazone.

The phosphinemethylene IV failed to react with cyclohexanone under similar conditions.

(2-Ethoxypropenyl)-triphenylphosphonium iodide (XIV). A mixture of phosphinemethylene IV (1.0 g.) and freshly distilled ethyl iodide (20 ml.) was refluxed for 7 hr. The solid which precipitated (0.40 g.) had m.p.  $163-165^{\circ}$  and was recrystallized from methanol-ethyl acetate without change in m.p.:  $\lambda_{max.}^{\text{EcOH}} 220 \text{ m}\mu$  ( $\epsilon$  44,900), 252 m $\mu$  ( $\epsilon$  13,700) and shoulder at 275 m $\mu$  ( $\epsilon$  3800). Bands (KBr) at 6.30 (w), 7.02 (m), 7.48 (m) and 9.00 (s).

Anal. Cale'd for C23H24IOP: C, 58.2; H, 5.1. Found: C, 58.4; H, 5.2.

Hydrolysis of (2-ethoxypropenyl)-triphenylphosphonium iodide (XIV) with acid. The iodide XIV (0.65 g.) and 5%aqueous hydriodic acid (20 ml.) were heated to reflux for 15 hr. The solid formed was collected and had m.p. 206-208° (0.56 g.). It was shown to be acetonyltriphenylphosphonium iodide (XVI) by mixed m.p. and comparison of I.R. spectra.

Hydrolysis of (2-ethoxypropenyl)-triphenylphosphonium iodide (XIV) with alkali. A mixture of iodide (7.9 g.) and 5% aqueous methanolic potassium hydroxide was refluxed for 15 hr. Water was added and the precipitated solid was collected; it weighed 4.05 g. (m.p. 146-150°) and was shown to be triphenylphosphine oxide. The filtrate was extracted with ether. Fractionation of the ether solution gave isopropenyl ethyl ether, which (1) decolorized bromine-inchloroform instantaneously and (2) gave no precipitate with an aqueous-methanolic solution of 2,4-dinitrophenylhydrazinium sulfate. After the solution was warmed and allowed to stand overnight, acetone-2,4-dinitrophenylhydrazone (0.48 g., m.p. 119-124°). was precipitated. Comparison with an authentic sample confirmed the identity.

Ultraviolet absorption spectra. The spectra of the phosphinemethylenes III and IV show variations in hydroxylic and aprotic solvents (cf. Figs. 1, 2, and 3). The molecular extinction coefficients ( $\epsilon$ ) at  $\lambda$  max. in 95% ethanol are recorded above. The corresponding values in dry acetonitrile are, for III: 267 m $\mu$  ( $\epsilon$  6000), 275 m $\mu$  ( $\epsilon$  5500) and 328 m $\mu$  ( $\epsilon$  10,200); for IV: 275 m $\mu$  ( $\epsilon$  4700) and 295 m $\mu$ ( $\epsilon$  4400).

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NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## Some Monomeric Organosilicon Compounds of High Thermal Stability

## HENRY GILMAN AND JACK J. GOODMAN

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A number of monomeric organosilicon compounds possessing high thermal stability was synthesized. Some organic groups found to impart this property were the *p*-phenoxyphenyl, *m*-tolyl, *m*-trifluoromethylphenyl, and *p*-trimethylsilylphenyl. The molecules containing the 9-fluorenyl group were not promising in this respect. Compounds studied were of the types  $(C_6H_5)_8SiR_4, (C_6H_5)_8SiR_5, C_{12}H_{22}SiR_4, HSiR_4, and SiR_4.$ 

Incidental to studies concerned with the thermal stability of monomeric organosilicon compounds,<sup>1</sup> an examination has been made of the synthesis of a series of  $R_4Si$ ,  $R_3R'Si$ , and  $R_2R_2'Si$  compounds. In these syntheses both Grignard reagents and organolithium compounds were used. The organolithium compounds were prepared by direct reaction with lithium metal, by halogen-metal interconversion reactions using *n*-butyllithium, and by the direct replacement of hydrogen in a metalation reaction.

Preliminary or orienting screening for thermal stabilities indicates that the following groups tend to increase thermal stability: *p*-phenoxyphenyl, *m*-tolyl, *m*-trifluoromethylphenyl, and *p*-trimethylsil-ylphenyl.

#### EXPERIMENTAL

Diphenyl-bis-(p-phenoxyphenyl)-silane. To 105 ml. of an ethereal solution containing 0.090 mole of n-butyllithium<sup>2</sup> was slowly added 75 ml. of an ethereal solution containing 22.4 g. (0.090 mole) of p-bromophenyl phenyl ether.<sup>3</sup> The temperature of the reaction was maintained at  $-15^{\circ}$ . Color Test II<sup>4</sup> was negative after 2 hr. Then there was slowly added 50 ml. of an ethereal solution containing 9.60 g. (0.038 mole) of diphenyldichlorosilane. The reaction mixture was allowed to come to room temperature and stirred overnight. Color Test I<sup>5</sup> was negative at that time and a white solid was suspended in the reaction mixture. Hydrolysis with 200 ml. of was resulted in two clear liquid layers. The ether layer was separated and a solid began to precipitate from it. There was filtered 8.4 g. of a white solid melting

<sup>(1)</sup> Burkhard, Rochow, Booth, and Hart, Chem. Revs., 41, 97 (1947); Post, Silicones and Other Organosilicon Compounds, Reinhold Publishing Corp., New York, N. Y., 1949; Rochow, An Introduction to the Chemistry of the Silicones, 2nd ed., John Wiley & Sons, New York, N. Y., 1951; Gilman and Dunn, Chem. Revs., 52, 77 (1953).

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<sup>(3)</sup> Gilman, Langham, and Moore, J. Am. Chem. Soc., 62, 3277 (1940).

<sup>(4)</sup> Gilman and Swiss, J. Am. Chem. Soc., 62, 1847 (1940).

<sup>(5)</sup> Gilman and Schulze, J. Am. Chem. Soc., 47, 2002 (1925).