precipitate appeared and the originally light yellow supernatant became essentially colorless. After standing for a day the precipitate was filtered off, dried *in vacuo* (2.11 g.), placed in the cup of a Soxlet extractor and extracted for 4 hr. with methylene chloride. The residue in the cup (1.09 g.) was digested with hot water, filtered, washed, and dried yielding 0.50 g. of black material which gave no green boron flame and contained 93.5% tin.

The benzene and methylene chloride solutions were combined and evaporated to dryness, yielding 1.46 g. (68%) of quite impure tetraphenyltin, m.p. 178–210°. Recrystallization from toluene left 0.72 g. (34%) of tetraphenyltin, m.p. 222–225°, undepressed upon admixture with an authentic sample.

With benzoquinone. A solution of 2.71 g. (0.00993 mole) of diphenyltin in 10 ml. of benzene was added to 10 ml. of benzene containing 1.07 g. (0.00993 mole) of benzoquinone. Within 2 min. the solution turned a dark green; a dark green precipitate appeared and the supernatant became greenish yellow within 5 min. After 0.5 hr. a white precipitate began to appear. After 8 hr. the product was heated on the steam bath for 15 min. and filtered. The precipitate was washed with benzene and dried; 3.24 g. (86%).

Anal. Calcd. for $C_{16}H_{14}SnO_2$: C, 56.75; H, 3.70; Sn, 31.16. Found: C, 56.35; H, 3.96; Sn, 31.32, 31.45.

Hydrogen chloride was passed through a suspension of 1.50 g. of the product in methylene chloride until the originally dense precipitate became flocculent. The product mixture was filtered and the filtrate evaporated near dryness, digested with 3 ml. of petroleum ether (b.p. 40–60°), filtered, and cooled. Crystals of diphenyltin dichloride which formed were filtered off and dried in air; 0.92 g. (67.5%), m.p. 40–43° undepressed upon admixture with an authentic sample.

With benzoyl peroxide. To a solution of 0.77 g. (3.13 mmoles) of benzoyl peroxide in 10 ml. of benzene was added 1.70 g. (6.25 mmoles) of diphenyltin. A slightly exothermic reaction occurred. Crystals began to appear after 15 min. After standing overnight 2.0 g. (81%) of 1,1,2,2-tetraphenyl-1,2-dibenzoxyditin, m.p. 172–177° was obtained. Recrystallization from benzene provided an analytical sample, 1.41 g., m.p. 184–185°, undepressed when mixed with a sample prepared from the reaction of diphenyltin dihydride with benzoic acid.[11]

Anal. Calcd. for $C_{38}H_{30}O_4Sn_2$: C, 57.92; H, 3.84; Sn, 30.12. Found: C, 57.82; H, 3.79; Sn, 30.25, 30.28.

With dibenzyldisulfide. To 20 ml. of a benzene solution containing 5.46 g. (20.0 mmoles) of diphenyltin was added 4.93 g. (20.0 mmoles) of dibenzyldisulfide. The resulting mixture was heated under reflux for 7.5 hr., cooled, and filtered. The solvent was removed at reduced pressure, leaving 9.6 g. (92%) of light yellow diphenyltin dithiobenzylate, n_D^{26} 1.6610.

Anal. Calcd. for $C_{26}H_{24}S_2Sn$: C, 60.13; H, 4.66; S, 12.35; Sn, 22.86; mol. wt., 519.3. Found: C, 60.02; H, 4.70; S, 12.57; Sn, 22.58; mol. wt. 497.4 (cryoscopic in benzene).

Reaction of diphenyltin dithiobenzylate with iodine. To a suspension of 3.12 g. (6.00 mmoles) of diphenyltin dithiobenzylate in 5 ml. of methanol was added a solution of 1.52 g. (6.00 mmoles) of iodine in 10 ml. of methanol. All of the iodine was consumed. The solution was evaporated to dryness leaving the theoretical weight of a mixture of diphenyltin diiodide and dibenzyl disulfide. This was dissolved in 20 ml. of ether, cooled in an ice bath, and 2.37 g. (30.0 mmoles) of pyridine was added. The precipitate which appeared was filtered and washed with warm ether. It was dried in the air for 0.5 hr., m.p. 138–142°. Upon further drying in a vacuum desiccator for 3 days, there remained 2.7 g., m.p. 70–72°, undepressed upon admixture with authentic diphenyltin diiodide.

Anal. Calcd. for $C_{12}H_{10}I_2Sn$: Sn, 22.54. Found: Sn, 22.74, 22.62.

The ether filtrate was warmed to remove the ether and the resulting solid, 1.25 g. (84%), m.p. 67–70°, was recrystallized from ethanol, yielding 0.94 g., m.p. 69–71°, undepressed upon admixture with authentic dibenzyl disulfide.

Polymerization initiated by nitrobenzene. To a solution of 2.21 g. (0.00810 mole) of diphenyltin in 10 ml. of benzene was added 0.85 ml. (0.0114 mole) of nitrobenzene. The mixture was allowed to stand overnight, filtered, and dried. The bright yellow precipitate weighed 2.10 g. and contained 40.8% tin. This may be low because of adsorbed nitrobenzene, whose odor was very apparent. Another similar experiment provided a product containing 41.9% tin.

Polymerization initiated by benzil. A solution of 2.10 g. (10.0 mmoles) of benzil and 2.73 g. (10.0 mmoles) of diphenyltin was allowed to stand at room temperature for a week. The yellow solid was filtered off, washed with ether, and dried; 2.12 g., 78%; tin, 43.07%.

Acknowledgment. We thank K. V. Nahabedian and J. H. Polevy for technical assistance.

DURHAM, N. H.

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Cleavage Reactions of Phosphinemethylenes

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As part of a program of research in organophosphorus chemistry, an attempt was made to prepare bisphosphinemethylenes which would be stable under ambient conditions. Attempts to effect mutual resonance stabilization of two phosphinemethylene groups in the same molecule either by conjugation through an ethylenic double bond or by cross-conjugation through a carbonyl group were unsuccessful. However, a bisphosphinemethylene with no conjugation between the two ylide linkages was prepared in which the two phosphorus-carbon semipolar bonds were stabilized by α-ester carbonyl groups.

Attempts to alkylate the ylide-like compounds resulting from reaction of tertiary phosphines with benzalmalononitrile resulted in cleavage of these complexes into the original benzalmalononitrile and the methiodide of the tertiary phosphine.

Phosphinemethylenes (ylides) may be prepared by treating phosphonium compounds, in which at least one hydrogen is present on a carbon bound to phosphorus, with a base.[1] Ordinary phosphinemethylenes (in which R′ is alkyl or hydrogen) are unstable to air and moisture, which tend to cleave them into tertiary phosphine oxides (and

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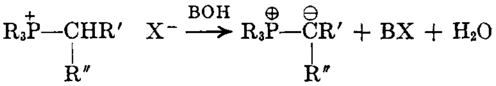
[1] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 28.

hydrocarbons).[2] If R′ is an electron-withdrawing group which can provide resonance stabilization



$$R_3\overset{+}{P}-\underset{R''}{C}HR'\ \ X^- \xrightarrow{BOH} R_3\overset{\oplus}{P}-\underset{R''}{\overset{\ominus}{C}}R' + BX + H_2O$$

of the phosphorus-carbon semipolar bond, the stability is markedly increased. Examples of this type of ylide are $(C_6H_5)_3\overset{+}{P}-R$, where R = $-\overset{-}{C}HCOCH_3$,[3] $-\overset{-}{C}HCOC_6H_5$,[3] $-\overset{-}{C}HCOOC_2H_5$,[4] $-\overset{-}{C}(COOC_2H_5)_2$,[5] $-\overset{-}{C}(COCH_3)COOC_2H_5$,[5] $-\overset{-}{C}(CN)COOC_2H_5$,[6] $-\overset{-}{C}(CN)_2$,[5] $\underline{CH{=}CH-CH{=}CH-\overset{-}{C}}-$,[7] or $\underline{C_6H_4-\overset{|}{C}^{-}-C_6H_4}$.[8]

In such compounds as these the carbon-phosphorus semipolar bond is in resonance with an electron acceptor, such as the cyclopentadienyl anion or a carbonyl or nitrile group in the α-position. To test the possibility of stabilizing two ylide linkages with the same carbonyl group, acetone-1,3-bistriphenylphosphonium chloride (I) was synthesized and treated with aqueous sodium carbonate. Instead of the bisylide, triphenylphosphine oxide and the stable monoylide, triphenylphosphineacetylmethylene, were obtained. Apparently resonance stabilization by the carbonyl group was insufficient to accommodate both phosphinemethylene linkages.

$$\underset{\text{I}}{(C_6H_5)_3\overset{+}{P}CH_2COCH_2\overset{+}{P}(C_6H_5)_3}\ \ 2\,Cl^- \xrightarrow{Na_2CO_3} (C_6H_5)_3P{=}O + (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCOCH_3$$

To determine whether two ylide linkages, when conjugated through an ethylenic double bond, could afford resonance stabilization for one another, 2-butenebistriphenylphosphonium bromide was treated with aqueous sodium carbonate. The bisylide was not isolated. Cleavage by a path different from the one already described for the ylide from I gave triphenylphosphine and a phosphonium salt isolated as the perchlorate which was assigned structure II.

$$(C_6H_5)_3\overset{+}{P}CH_2CH{=}CHCH_2\overset{+}{P}(C_6H_5)_3\ \ 2\,Br^- \xrightarrow{Na_2CO_3}$$

$$(C_6H_5)_3P + (C_6H_5)_3\overset{+}{P}CH{=}CH-CH{=}CH_2\ \ Br^- \xrightarrow{NaClO_4}$$

$$\underset{\text{II}}{(C_6H_5)_3\overset{+}{P}CH{=}CH-CH{=}CH_2\ \ ClO_4^-} \xrightarrow{H_2}$$

$$\underset{\text{III}}{\underset{ClO_4^-}{(C_6H_5)_3\overset{+}{P}CH_2CH{=}CHCH_3}}$$

The elemental analysis of II was in excellent agreement with the proposed structure. Hydrogenation of II gave crotyltriphenylphosphonium perchlorate (III), which, under the mild conditions employed, did not undergo further reduction. The perchlorate (II) decolorized aqueous potassium permanganate and (very slowly) a solution of bromine in methylene chloride. In our hands, it failed to undergo diene condensation with maleic anhydride and tetracyanoethylene.

The infrared spectrum of II showed unsaturation other than that in the aromatic rings, but the end vinyl group was not indicated as strongly as is usually expected. Crotyltriphenylphosphonium perchlorate (III) showed unsaturation due only to the aromatic system. The failure of the aliphatic double bond in III to show up is not surprising, since a single *trans* double bond may absorb very weakly in the infrared region.

The band for aromatic absorption in II was broader than the one in III and was unsymmetrical, suggesting that it contained more than one component. This observation is consistent with the postulated structure of II, in which the conjugated aliphatic system should produce two bands in this region.

The failure of the end vinyl group in II to produce strong bands may be because the actual structure of II is a hybrid involving resonance of the conjugated aliphatic system with the triphenylphosphonium group.[9]

$$[(C_6H_5)_3\overset{+}{P}CH{=}CH-CH{=}CH_2 \longleftrightarrow (C_6H_5)_3P{=}CH-CH{=}CH-\overset{+}{C}H_2]\ \ ClO_4^-$$

The mechanism for this seemingly abnormal cleavage may be very similar to the one given by Wittig[10] for the cleavage of ethanebistriphenyl-

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(2) G. M. Kosolapoff, *Organophosphorus Compounds*, Wiley, New York, 1950, p. 29.

(3) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(4) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).

(5) L. Horner and H. Oediger, *Chem. Ber.*, **91**, 437 (1958).

(6) J. A. Ford, Jr., unpublished observation.

(7) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 6167 (1957).

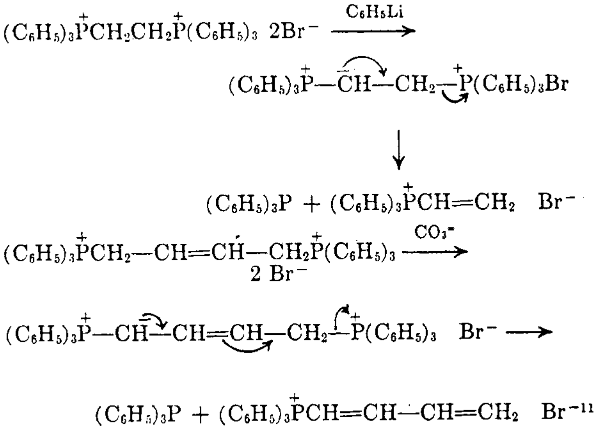
(8) L. A. Pinck and G. E. Hilbert, *J. Am. Chem. Soc.*, **69**, 718 (1947).

(9) The NMR spectra of the protons in the butyl, crotyl, and butadienyltriphenylphosphonium perchlorates have been examined by R. L. Griffith and J. K. O'Loane, of these Laboratories, using a 60-mc./sec. Dual Purpose V-4302 Spectrometer (Varian Associates). Solutions (10 and 20%) in acetonitrile and methylene chloride with 3% tetramethylsilane as an internal standard were used.

The bands for the hydrogens, other than those attached to the phenyl rings, for the butadienyl compound have a chemical shift relative to tetramethylsilane of −5.50 to −7.14 p.p.m. These data show that all these protons are attached to ethylenic carbon atoms.

(10) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

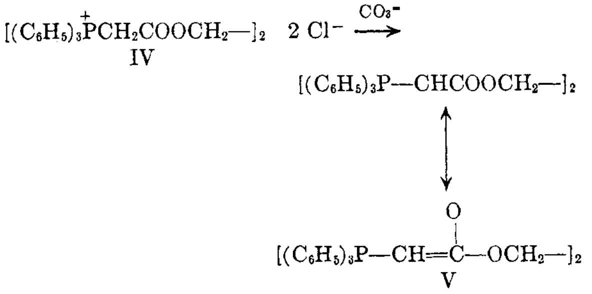
phosphonium bromide (of which the starting material for II is a vinylog) into triphenylphosphine and vinyltriphenylphosphonium bromide.



$$(C_6H_5)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(C_6H_5)_3\ 2Br^- \xrightarrow{C_6H_5Li} (C_6H_5)_3\overset{+}{P}-\overset{-}{C}H-CH_2-\overset{+}{P}(C_6H_5)_3Br \rightarrow (C_6H_5)_3P + (C_6H_5)_3\overset{+}{P}CH=CH_2\ Br^-$$

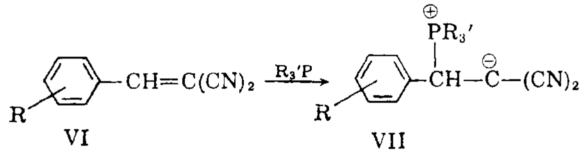
$$(C_6H_5)_3\overset{+}{P}CH_2-CH=CH-CH_2\overset{+}{P}(C_6H_5)_3\ 2\,Br^- \xrightarrow{CO_3^=} (C_6H_5)_3\overset{+}{P}-CH-CH=CH-CH_2-\overset{+}{P}(C_6H_5)_3\ Br^- \rightarrow (C_6H_5)_3P + (C_6H_5)_3\overset{+}{P}CH=CH-CH=CH_2\ Br^-$$[11]

Treatment of 3,6-dioxa-2,7-dioxooctane-1,8-bistriphenylphosphonium chloride (IV) with sodium carbonate gave a stable bisylide, 2,5-dioxa-1,6-dioxo-1,6-hexanebistriphenylphosphinemethylene (V). The ylide linkages in V are stabilized by α-ester carbonyl groups just as they were in some of the previously mentioned stable ylides.[4-6]



$$\underset{IV}{[(C_6H_5)_3\overset{+}{P}CH_2COOCH_2-]_2\ 2\,Cl^-} \xrightarrow{CO_3^=} [(C_6H_5)_3P-CHCOOCH_2-]_2 \leftrightarrow \underset{V}{[(C_6H_5)_3P-CH=\overset{O}{\overset{|}{C}}-OCH_2-]_2}$$

Closely related to the ylides just described are the resonance-stabilized compounds (VII) formed by the addition of tertiary phosphines to benzalmalononitriles (VI).[12] Substitution of electron-withdrawing groups in the benzene ring of VI enhanced the tendency for adduct formation while electron-releasing groups decreased or eliminated it.[13] In keeping with this statement, we readily obtained the adducts VIIa, VIIb, and VIIc with tributylphosphine and p-chlorobenzalmalononitrile (VIa), p-nitrobenzalmalononitrile (VIb), and 2,4-dichlorobenzalmalononitrile (VIc), respectively, but recovered only starting material by treating the phosphine with 3,4-dimethoxybenzalmalononitrile (VId).

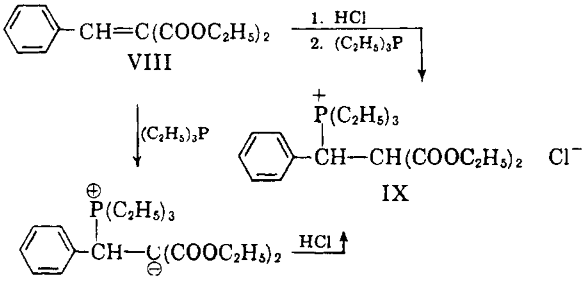


VI VII

VIa. R = p-Cl
b. R = p-NO$_2$
c. R = 2,4-di-Cl
d. R = 3,4-di-CH$_3$O

VIIa. R = p-Cl, R' = n-C$_4$H$_9$
b. R = p-NO$_2$, R' = n-C$_4$H$_9$
c. R = 2,4-di-Cl,
R' = n-C$_4$H$_9$

Evidence supporting structure VII was the fact that diethyl benzalmalonate (VIII) gave the same phosphonium chloride (IX) when treated first with hydrogen chloride and then triethylphosphine as it did when treated with these reagents in reverse order.[14]



VIII IX

As the benzalmalononitrile-tertiary phosphine adducts as well as those from VIII gave phosphonium salts on treatment with hydrogen chloride, C-alkylation was attempted with methyl iodide in methanol upon the adducts of tributylphosphine and VIa, VIb, and VIc. The unexpected result was cleavage of the adducts to methyltributylphosphonium iodide and the original benzalmalononitrile.

EXPERIMENTAL[15]

Materials. 2-Butenebistriphenylphosphonium bromide was obtained from Dr. M. Stern, of Distillation Products Industries. Tri-n-butylphosphine was purchased from Westvaco Mineral Products, Division of Food Machinery and Chemical Corp., and 1-chloro-2-butene from Aldrich Chemical Co. All other materials were Eastman Organic Chemicals, White Label Grades.

Acetone-1,3-bistriphenylphosphonium chloride (I). A solution of 40 g. (0.15 mole) of triphenylphosphine and 9.6 g. (0.076 mole) of 1,3-dichloroacetone in 450 ml. of chloroform was refluxed for 2 hr., poured into a beaker, concentrated to a volume of 150 ml., diluted with 300 ml. of acetonitrile, concentrated until crystallization started, cooled, and filtered to give 30.4 g. of white crystals. Two recrystallizations from chloroform-acetonitrile gave 6.3 g. (7.9%), m.p. 266–267° dec., in a sealed capillary, with gradual decomposition starting at 256°.

Anal. Calcd. for $C_{39}H_{34}Cl_2OP_2$: C, 72.0; H, 5.2; Cl, 10.9. Found: C, 70.0, 70.3; H, 5.5, 5.3; Cl, 10.4.

Perchlorate (from methanol), m.p. 289–291°, with gradual darkening from 279°.

Anal. Calcd. for $C_{39}H_{34}Cl_2O_9P_2$: C, 60.1; H, 4.36; Cl, 9.12. Found: C, 60.0; H, 4.3; Cl, 9.4.

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(11) After completion of this work, a review article on phosphinemethylenes was published by U. Schöllkopf [*Angew. Chem.*, **71**, 260 (1959)], who described the same reaction and the same mechanism. The work appeared originally in a dissertation by H. Burger, University of Tübingen, 1957.

(12) L. Horner and K. Klüpfel, *Ann.*, **591**, 69 (1955).

(13) L. Horner and K. Klüpfel, *Ann.*, **591**, 71 (1955).

(14) L. Horner and K. Klüpfel, *Ann.*, **591**, 90 (1955).

(15) Melting points were determined on a Fisher-Johns apparatus, unless otherwise noted, and are corrected.

Treatment of I *with sodium carbonate.* A filtered solution of 6.3 g. (0.0097 mole) of I in 150 ml. of distilled water was added, dropwise with stirring, to a solution of 20 g. (0.16 mole) of sodium carbonate monohydrate in 180 ml. of distilled water. After addition was complete, the mixture was stirred for 5 hr. and the pale yellow solid filtered, washed with distilled water, and dried. This solid (4.8 g.) was slurried in 100 ml. of boiling anhydrous ether, filtered, and dried. The residue (2.8 g.) was recrystallized from 100 ml. of ethyl acetate to give 1.4 g., m.p. 205–207°, m.m.p. with triphenylphosphineacetylmethylene 205–208°.[5] The ether filtrate from slurrying of the crude reaction product was evaporated to dryness. The residue (1.9 g., m.p. 140–150°) was recrystallized from 150 ml. of cyclohexane to give 1.1 g., m.p. 140–150°. The infrared spectrum of this material showed a bathochromically shifted carbonyl group and several strong bands similar to those of triphenylphosphine oxide. It was nearly identical with the infrared spectrum of a mixture of 67% triphenylphosphine oxide and 33% triphenylphosphineacetylmethylene.

Treatment of 2-butenebistriphenylphosphonium bromide with sodium carbonate. To 49.6 g. (0.400 mole) of sodium carbonate monohydrate in 446 ml. of distilled water (10% solution) was added, dropwise with stirring, a slurry of 29.6 g. (0.0400 mole) of 2-butenebistriphenylphosphonium bromide in 200 ml. of distilled water. The mixture was stirred overnight after completion of the addition. The pink solid was filtered, washed with distilled water, and dried to give 8.7 g. (82%) of triphenylphosphine, m.p. and m.m.p. 79–80°. To the aqueous filtrate was added, dropwise with stirring, a solution of 20 g. (0.16 mole) of sodium perchlorate in 30 ml. of distilled water. A brown gum separated gradually. It was broken up periodically with a metal spatula. After the solution had been stirred for 4 hr., the gum had changed to a yellow solid which was filtered, washed with distilled water, and vacuum-dried at 35° to give 13.8 g. of II (83%), m.p. 135–148°.[9] It decolorized cold, aqueous potassium permanganate, but attempts to show unsaturation by Diels-Alder condensation with maleic anhydride and tetracyanoethylene were unsuccessful.

Anal. Calcd. for $C_{22}H_{20}ClO_4P$: C, 63.6; H, 4.83; Cl, 8.57; P. 7.47. Found: C, 64.0; H, 4.8; Cl, 8.4; P, 7.8.

Three recrystallizations of 6.0 g. of this crude product from ethanol, using large quantities of Norit, gave 1.27 g. of yellow crystals, m.p. 182–184°.

Crotyltriphenylphosphonium perchlorate (III). A. A solution of 1.0 g. of II in 50 ml. of acetonitrile was shaken overnight with 0.05 g. of platinum oxide at room temperature in a Parr shaker at an initial hydrogen pressure of 50 lb. The catalyst was then removed by filtration, fresh catalyst was added, and the shaking continued overnight. After filtration of the catalyst and concentration of the filtrate on a 60° water bath under water-pump vacuum, the residue was recrystallized four times from absolute ethanol to give 0.16 g. of III, m.p. and m.m.p. with authentic III 178–180°

Anal. Calcd. for $C_{22}H_{22}ClO_4P$: C, 63.3; H, 5.29; Cl, 8.52. Found: C, 63.5; H, 5.2; Cl, 8.3.

B. A solution of 26.2 g. (0.100 mole) of triphenylphosphine, 9.1 g. (0.100 mole) of crotyl chloride, and 100 ml. of absolute ethanol was refluxed overnight, concentrated under water-pump vacuum on a 60° water bath, and the white solid residue slurried with ethyl acetate, filtered, and dried to give 28.4 g. (80%) of crotyltriphenylphosphonium chloride, m.p. 214–219°.

Anal. Calcd. for $C_{22}H_{22}ClP$: C, 74.8; H, 6.24; Cl, 10.1. Found: C, 74.9; H, 6.4; Cl, 9.8.

A solution of 10.0 g. (0.0283 mole) of this salt in 100 ml. of distilled water was added in one portion to a solution of 10 g. of sodium perchlorate in 100 ml. of distilled water. The mixture was allowed to stand 1 hr. The white solid was broken up, filtered, washed with distilled water, and sucked dry. Three recrystallizations from 100-ml. portions of absolute ethanol gave 7.3 g. of colorless crystals (62%), m.p. 178–181°.

Anal. Calcd. for $C_{22}H_{22}ClO_4P$: C, 63.3; H, 5.29; Cl, 8.52. Found: C, 63.7; H, 5.4; Cl, 9.7.

3,6-Dioxa-2,7-dioxoheptane-1,8-bistriphenylphosphonium chloride (IV). A solution of 10.8 g. (0.0500 mole) of ethylene glycol bischloroacetate, 26.2 g. (0.100 mole) of triphenylphosphine, and 100 ml. of absolute ethanol was refluxed 24 hr., concentrated under water-pump vacuum on a hot water bath and the residue slurried with ethyl acetate (100 ml.), filtered, washed with ethyl acetate, and air-dried overnight to give 36.3 g. (98%) of crude product, m.p. 100–140°. An analytical sample, m.p. 138–142° (with slow effervescence), was prepared by recrystallization from acetonitrile-2-butanone. The crude product was pure enough for the synthesis of V.

Anal. Calcd. for $C_{42}H_{38}Cl_2O_4P_2$: C, 68.2; H, 5.14; Cl, 9.61. Found: C, 67.4; H, 5.4; Cl, 8.9.

2,5-Dioxa-1,6-dioxo-1,6-hexanebistriphenylphosphinemethylene (V). A solution of 20.8 g. (0.028 mole) of crude IV in 75 ml. of distilled water was added, dropwise with vigorous stirring, to a solution of 35 g. (0.28 mole) of sodium carbonate monohydrate in 315 ml. of distilled water (10% solution). The mixture was stirred 2 hr. after addition was complete, and the pale yellow solid was filtered, washed with distilled water, and dried to give 15.4 g., m.p. 121–125°. Recrystallization from 1:1 benzene-ligroin (b.p. 66–75°) (170 ml.) gave 12.5 g. (67%) of IV, m.p. 127.5–128.5°. A further recrystallization from the same solvent system did not improve the melting point.

Anal. Calcd. for $C_{42}H_{36}O_4P_2$: C, 75.8; H, 5.41; P, 9.31. Found: C, 75.8; H, 5.9; P, 9.0.

p-Chlorobenzalmalononitrile-tributylphosphine adduct (VIIa). Nine and four-tenths grams (0.050 mole) of *p*-chlorobenzalmalononitrile[16] was dissolved by gentle warming in 100 ml. of *p*-dioxane. To the solution was added 10 g. (0.050 mole) of tributylphosphine. The solution, which had turned bright yellow, was allowed to cool and the sides of the container were scratched to start crystallization. The cream-colored solid was filtered, washed with *p*-dioxane, and allowed to stand overnight in a dry-box under nitrogen to give 16.3 g. (83%) of XV, m.p. 121–123°.

Anal. Calcd. for $C_{22}H_{32}ClN_2P$: C, 67.5; H, 8.19; Cl, 9.08; N, 7.16. Found: C, 67.1; H, 8.0; Cl, 9.4; N, 7.6.

Adducts VIIb from *p*-nitrobenzalmalononitrile[16] and tributylphosphine (m.p. 116–119°; yield, 94%; *anal.* calcd. for $C_{22}H_{32}N_3O_2P$: C, 65.8; H, 8.0; N, 10.5; found: C, 64.7; H, 7.9; N, 10.6) and VIIc from 2,4-dichlorobenzalmalononitrile[17] and tributylphosphine (m.p. 121–124°; yield, 88%. *Anal.* calcd. for $C_{22}H_{31}Cl_2N_2P$: C, 62.1; H, 7.3; Cl, 16.7; N, 6.6; found: C, 62.1; H, 6.9; Cl, 16.8; N, 6.8) were prepared in the same manner.

Attempted methylation of VIIa. A solution of 10 g. (0.026 mole) of XV, 10 ml. of methyl iodide, and 100 ml. of methanol was placed in a refrigerator for 2 days. The colorless crystals were filtered, washed with methanol, and dried to give 4.6 g. (94%) of X, m.p. and m.m.p. with authentic X, 158–160°. Evaporation of the filtrate and recrystallization of the residue from acetone-ether gave 6.3 g. (71%) of methyltributylphosphonium iodide, m.p. 130–132° (lit.[18] m.p. 133.5°).

By a similar procedure, attempted methylation of 10 g. (0.025 mole) of VIIb gave 2.0 g. (40%) of VIb, m.p. 154–158° (m.p. and m.m.p. with VIb 158–159° after recrystallization from acetone-ether). Methyltributylphosphonium iodide was not isolated in this instance.

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Likewise attempted methylation of 10 g. (0.024 mole) of VIIc gave 4.3 g. (80%), of VIc, m.p. 147–149° (m.m.p. with VIc 149–150° after recrystallization from acetone), and 4.5 g. (54%) of methyltributylphosphonium iodide. m.p. 132°.[18]

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Reduction of Schiff Bases. III. Reduction with Dimethylamine Borane

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A number of Schiff bases with various functional groups such as chloro, nitro, hydroxy, methoxy, carbethoxy, sulphonamido, and carboxy were prepared and reduced to the respective secondary amines by using dimethylamine borane in glacial acetic acid. The yields of the secondary amines generally ranged from 80–97%. None of the other functional groups were affected under the conditions used during the course of the reduction. The stoichiometry of the reaction was shown to be three moles of Schiff base to one mole of dimethylamine borane and indicated that borane was the probable reducing agent.

The reduction of Schiff bases to form secondary amines has been accomplished by catalytic hydrogenation[1] and by various chemical methods such as magnesium in methanol.[2] More recently it has been shown that lithium aluminum hydride[3]

TABLE I

SECONDARY AMINES

Ar—CH$_2$—NH—Ar′ (I-XIV)

Ar—CH$_2$—NH—CH$_2$—CH$_2$—NH—CH$_2$—Ar′ (XV–XVII)

Ar	Ar′		M.P. (Corr.)	Yield, %	Method	Recryst. Solvent
Phenyl	Phenyl	I	37.5–38.0[a]	84.2[b]	—	—
Phenyl	*p*-Chlorophenyl	II	47.5–48.0[a]	97.4	B	Ethanol
p-Chlorophenyl	*p*-Chlorophenyl	III	70.0–70.5[a]	89.5	A	Ethanol
Phenyl	*o*-Chlorophenyl	IV	39.5–40.0[a]	83.6[c]	—	—
p-Nitrophenyl	*p*-Nitrophenyl	V	189.0–189.5[d]	89.2	A	—
m-Nitrophenyl	*m*-Nitrophenyl	VI	136.5–137.0[a]	94.5	A	—
m-Nitrophenyl	*o*-Nitrophenyl	VII	167.0–167.5[e]	89.3	A	Ethanol
p-Methoxyphenyl	Phenyl	VIII	63.5–64.0[f]	90.9	B	Ethanol
m-Hydroxyphenyl	Phenyl	IX	101.0–102.0[a]	82.0	B	Ethanol
Phenyl	*p*-Hydroxyphenyl	X	88.0–89.0[g]	94.0	B	Methanol
Phenyl	*p*-Methoxyphenyl	XI	49.0–50.0[a]	90.1	A	Ethanol
Phenyl	*p*-Carbethoxyphenyl	XII	96.5–97.0[h]	92.8	A	Ethanol
Phenyl	*p*-Sulfonamidophenyl	XIII	170.0–171.0[i]	79.5	A	—
p-Methoxyphenyl	*p*-Phenylmercaptoacetic acid	XIV	131.5–133.0(d)[j]	84.5	B	Methanol
p-Methoxyphenyl	*p*-Methoxyphenyl	XV	—[k]	71.3	B	—
p-Nitrophenyl	*p*-Nitrophenyl	XVI	78.0–78.5	71.0	B	Methanol
p-Chlorophenyl	*p*-Chlorophenyl	XVII	—[l]	84.0	B	—

[a] J. H. Billman and A. C. Diesing, *J. Org. Chem.*, **22**, 1069 (1957). [b] Amine purified by formation of the hydrochloride, m.p. 214–215°, yield based on hydrochloride, 90.0%. [c] Amine purified by formation of the hydrochloride. [d] C. Paal and C. Benker, *Ber.*, **32**, 1256, (1899) reported m.p. 192°. [e] *Anal.* Calcd. for N: 15.39; Found 15.55; also infrared spectra indicates reduction of the Schiff base. [f] O. J. Steingart, *Ann.*, **241**, 337, reported m.p. 64.5°. [g] M. Bakunin, *Gazz. Chim. Ital.*, **36II**, 213, 218. [h] Aladar Skita and Werner Stuhner, Ger. Patent No. **716,668**, Dec. 24, 1941. [i] Schiff base m.p. 176°, reduction proven by infrared spectra and mixed m.p.; E. Miller, H. J. Rock, and M. L. Moore, *J. Am. Chem. Soc.*, **61**, 1199 (1939) reported m.p. 169–174°. [j] *Anal.* Calcd. for S: 10.56; Found 10.58. [k] Isolated as the dihydrochloride. [l] Isolated as the diacetate, m.p. 139–140°.

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(3) Part II: J. H. Billman and K. N. Tai, *J. Org. Chem.*, **23**, 535 (1958).