solution containing Na_2CO_3 and dried (Na_2SO_4). The residue obtained by evaporation of solvent was dissolved in ether and filtered through 20 g of Merck acid-washed alumina. Upon evaporation and trituration of the residue with benzene 2.5 g of a yellow solid were obtained. Crystallization from benzene gave **3,3,6,6-tetramethyl-1,2,4,5-cyclohexanetetrone (IXa)**, mp 233–235° (very rapid sublimation above 200°). *Anal.* Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.23; H, 6.00.

B. From DMDM by SeO_2 Oxidation in Toluene.—A mixture of DMDM (Ia, 5 g) and SeO_2 (15 g) in 70 ml of toluene was refluxed for 60 hr. After cooling the precipitated material was filtered and the solvent was evaporated. The partly solid residue was taken up in benzene and the insoluble, crystalline material was filtered and purified as above yielding the pure tetrone IXa. Chromatography of the benzene-soluble fraction yielded a small amount of the trione Id.

C. From *trans*-Dihydroxy-DMDM (XIId) by CrO_3 Oxidation.—To a solution of XIId (0.30 g) in 10 ml of acetone at 0° was added 2.2 equiv of Jones reagent. After 5 min at room temperature water-saturated NaCl solution (1:1) was added. After extraction with ether, washing of the extract with saturated NaCl solution, drying, and evaporation of the solvent, 260 mg of a solid yellow residue was obtained. Crystallization from CCl_4 yielded the pure tetrone IXa.

D. From a Mixture of *cis*- and *trans*-Dihydroxy-DMDM (XIIc and d) by CrO_3 Oxidation.—A high yield of the tetrone IXa was obtained when oxidation with CrO_3 was carried out as above on a mixture of XIIc and d, containing mainly the *cis* isomer XIIc (as evidenced by the pmr spectrum of the mixture).

E. From *trans*-Dihydroxy-DMDM (XIId) by Oxidation with N-Bromosuccinimide (NBS).—A mixture of XIId (200 mg) and NBS (400 mg) in 10 ml of CCl_4 was brought to refluxing with an electric bulb. Reaction occurred rapidly with liberation of HBr and some bromine. Bromine disappeared on continued refluxing. After *ca.* 1 hr the mixture was cooled and the succinimide was filtered. The solvent was evaporated, yielding a yellow, oily residue from which crystals separated on standing. These were collected and crystallized from benzene, yielding the pure tetrone IXa.

The tetrone readily formed a hydrate in the presence of water (see below). When the infrared spectrum was taken in KBr, the spectrum of the hydrate was obtained. The physical characteristics of the tetrone IXa are: infrared spectrum, ν_{max}^{Nujol} large CO absorption 5.74–5.90 μ, no OH absorption; ultraviolet spectrum, $\lambda_{max}^{CH_3CN}$ 258 mμ (ϵ 360), *ca.* 287 (sh) (180), and 410 (46); $\lambda_{max}^{CHCl_3}$ 256 mμ (ϵ 185) (sh) and 407 mμ (ϵ 42); pmr spectra may show the two *gem*-dimethyl singlets of the hydrate (see Table I) besides the tetrone single peak. A good spectrum of the tetrone is obtained in $CDCl_3$ at 60° or in benzene at 80° (see Table I) showing only very low peaks of the hydrate.

Bisquinoxaline XI.—A mixture of IXa (21 mg) and *o*-phenylenediamine (25 mg) in 3 ml of acetic acid was refluxed for a few minutes. Water was added to the cooled solution and the precipitated solid was filtered, washed with water, and crystallized from ethanol, mp 267–268°. *Anal.* Calcd for $C_{22}H_{20}N_4$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.70; H, 5.92; N, 16.22. Pmr ($CDCl_3$) showed a 12-proton singlet at δ 2.99 (*gem*-Me_2) and an eight-proton symmetrical multiplet centered at 7.90 (aromatic H).

Tetrone Hydrate (IXb).—By crystallization of the tetrone IXa from water heavy, pale yellow prisms of the tetrone hydrate IXb were obtained, mp *ca.* 170° (when put on the melting block at that temperature) with loss of water and resolidification followed by rapid sublimation of the tetrone. By slow warming from lower temperatures, there was no melting but continuous change into the tetrone. *Anal.* Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 56.11; H, 6.71. Infrared showed ν_{max}^{KBr} 3.02 (OH) and 5.70 μ (CO); ν_{max}^{Nujol} 3.05 (OH) and 5.71 μ(CO); ultraviolet showed $\lambda_{max}^{CH_3CN}$ 262 mμ (ϵ 260), 410 mμ (ϵ 30); pmr showed that the tetrone hydrate (IXb) had a low solubility in $CDCl_3$ at room temperature, but the tetrone singlet at δ 1.42 was not observed in the spectrum of the hydrate (see Table I). Upon warming to 60°, the tetrone singlet appeared together with the two hydrate singlets, and grew slowly with time.

Oxidation of the Tetrone (IXa).—To a solution of IXa (0.3 g) in 20 ml of water was added a solution of periodic acid (2.5 g) in a few milliliters of water. After standing for 1 hr at room temperature ethylene glycol was added to destroy the excess oxidizing agent and the solution was extracted with ether. The extract was washed with sodium thiosulfate solution and with saturated NaCl solution, dried, and evaporated. Crystallization of the residue from ether–pentane gave dimethylmalonic acid, mp 185–190°. Trituration with boiling chloroform raised the melting point to 203–204°. Esterification of the acid with diazomethane yielded oily methyl dimethylmalonate, the pmr spectrum of which showed only two singlets at δ 1.45 and 3.73 (ratio 1:1).

Acknowledgment.—The authors are grateful to Mrs. N. Shoeff for technical assistance, to Dr. N. Danieli for mass spectral determinations, and to Eng. R. Heller for microanalyses.

The Chemistry of Allene. II. The Kinetics of Free-Radical Addition of Hydrogen Bromide

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The kinetics of the free-radical addition of HBr to allene at −78° has been investigated and a mechanism for the reaction is proposed. Bromine atom adds both to the terminal and the central carbon of allene with a ratio of the corresponding rate constants k_1/k_2 = 2.0, *i.e.*, the addition occurs statistically. Reversibility of Br· addition at C_1 and nonreversibility of addition at C_2 of allene accounts for the effects of the reacton conditions on the ratio of terminal and central adducts, [T]/[C]. At constant temperature, [T]/[C] is independent of allene concentration, but is uniquely dependent on the HBr concentration.

The factors influencing the product distribution in free-radical addition to allene are not well understood at present. The point of initial attack of free radicals, *i.e.*, terminal *vs.* center, has also been controversial. The free-radical addition of HBr to allene in the gas phase at room temperature or above gave 2-bromopropene as the only monoadduct.[1,2] The exclusive formation of 2-bromopropene was explained in terms of Br· attacking the terminal carbon then migrating to the center carbon to give a resonance-stabilized radical, followed by hydrogen abstraction to yield the central isomer.[1] The addition of HBr in the liquid phase at room temperature, however, gave small amounts of 3-bromopropene;[2,3] its proportion increased at lower reaction temperatures and at high

(1) P. I. Abell and R. S. Anderson, *Tetrahedron Letters*, **49**, 3727 (1964).

(2) K. Griesbaum, A. A. Oswald, and D. N. Hall, *J. Org. Chem.*, **29**, 2404 (1964).

(3) D. Kovachic and L. C. Leitch, *Can. J. Chem.*, **39**, 3636 (1961).

HBr/allene ratio.[2] To explain these results, several alternate mechanisms were proposed.[2]

The kinetics of the free-radical addition of HBr to allene has been studied to provide answers for the question of terminal *vs.* central attack and to elucidate a reaction mechanism which accounts for the effects of HBr concentration and the reaction temperature on the ratio of the terminal- and central-attack products.

Results and Discussion

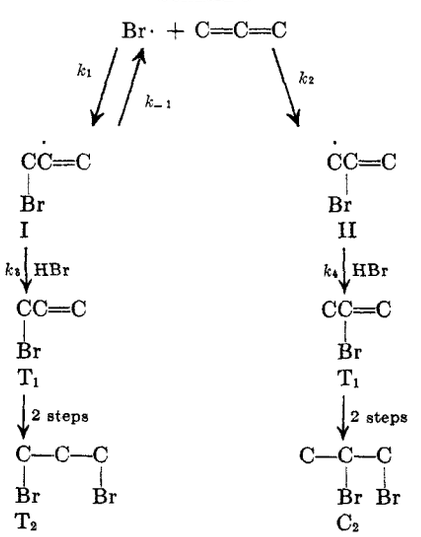
The addition of HBr to allene (1.0 *M*) in pentane at −78° was initiated by Co^{60} γ rays; the initial HBr concentration was varied 40-fold from 0.25 to 10 *M*. It had been reported[2] that at high HBr concentrations, ionic addition occurred to a considerable extent thus complicating the free-radical reaction. Under our experimental conditions no ionic addition was observed as evidenced (a) by the complete absence of the ionic diaddition product, 2,2-dibromopropane,[2,4] in the irradiated samples, and (b) by the failure to detect more than traces of products in nonirradiated blank experiments.

Preliminary experiments established that, at constant HBr concentration, the ratio of terminal- and center-attack products, [T]/[C], is independent of the allene concentration. The report by Griesbaum, Oswald, and Hall[2] that the amount of terminal attack decreased drastically with an increasing excess of allene, could therefore not be verified. The product ratio [T]/[C] at −78° was however uniquely dependent on the HBr concentration.

The results are shown in Figure 1 where the ratio of products [T]/[C], resulting from terminal ([T] = [T_1] + [T_2]) and central ([C] = [C_1] + [C_2]) bromine attack, respectively, is plotted against the average hydrogen bromide concentration. At high HBr concentrations, [T]/[C] is constant, while at low HBr concentrations [T]/[C] falls off to zero.

The simplest mechanism consistent with these results is shown in Scheme I.

SCHEME I



With the usual steady-state approximations for the intermediates I and II, the rate expressions follow.

(4) K. Griesbaum, *J. Am. Chem. Soc.*, **86**, 2301 (1964).

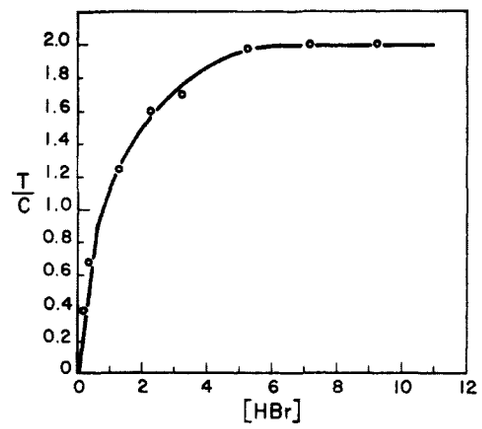


Figure 1.—The effect of HBr concentration on the ratio of terminal and central isomers ([T]/[C]) at −78° in pentane as a solvent.

$$\frac{d[T]}{dt} = \frac{k_1k_3[C{=}C{=}C][Br\cdot][HBr]}{k_{-1} + k_3[HBr]} \quad (1)$$

$$\frac{d[C]}{dt} = k_2[C{=}C{=}C][Br\cdot] \quad (2)$$

After dividing, one obtains

$$\frac{d[T]}{d[C]} = \frac{k_1k_3[HBr]}{k_2(k_{-1} + k_3[HBr])} \quad (3)$$

There are two limiting cases. (a) At high HBr concentrations, $k_3[HBr] > k_{-1}$, and after integration eq 3 reduces to

$$\frac{[T]}{[C]} = \frac{k_1}{k_2} \quad (4)$$

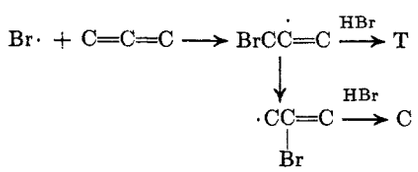
i.e., terminal- and center-attack products are formed at a constant ratio which represents directly the relative rates of attack of bromine at the terminal and central carbon of allene. Our results (Figure 1) shows that [T]/[C] is constant from about 6 *M* HBr and higher, yielding $k_1/k_2 = 2.0$. (b) At low HBr concentrations, eq 3 can be approximated by

$$\frac{d[T]}{d[C]} = \frac{k_1k_3[HBr]}{k_2k_{-1}} \quad (5)$$

Under differential reaction conditions [HBr] is constant and one obtains

$$\frac{[T]}{[C]} = \frac{k_1k_3[HBr]}{k_2k_{-1}} \quad (6)$$

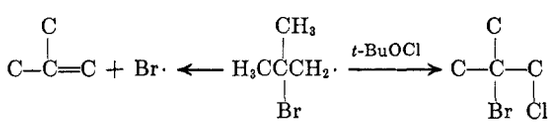
Although our experiments were not carried out under strictly differential conditions, we have used as an approximation the averages of the initial and final HBr concentrations in Figure 1. In agreement with eq 6, [T]/[C] is a linear function of HBr at low concentrations. From the initial slope ($k_1k_3/k_{-1}k_2$) and the obtained value for k_1/k_2, the ratio of rate constants of hydrogen transfer and bromine atom elimination, k_3/k_{-1}, is found[5] to be 1.4 ± 0.3 l. mole^{-1}. The observed HBr dependency (Figure 1) rules out a mechanism which was considered by Abell and Anderson



(5) At constant [HBr], a useful linear form of eq 3 is $[C]/[T][HBr] = (k_{-1}\cdot k_2/k_1k_3 + k_2/k_1)[HBr]$; it gives $k_3/k_{-1} = 1.2$ l. mole^{-1} and $k_1/k_2 = 2.2$.

where Br· adds only to the terminal carbon of allene followed by migration.

Such a mechanism would require [T]/[C] to increase linearly at all HBr concentrations. Our proposed mechanism is consistent with the expected reactivities of the α-bromoalkyl radical intermediates I and II. Based on available data for carbon–bromine[6] and π-bond energies[7] the addition of Br· to the center carbon of allene to give radical II is exothermic by about 11 kcal/mole if it has the conformation and relative instability of a nonresonance-stabilized primary radical. However, rotation by 90° about the C_1–C_2 carbon bond to give a resonance-stabilized allylic radical has probably zero activation energy and occurs therefore very rapidly leading to additional stabilization of the radical. On the other hand, Br· addition to the terminal carbon of allene to yield radical I is less exothermic and $-\Delta H$ is calculated to be ≅9 kcal/mole. The reverse reaction, $BrC\dot{C}{=}C$ (I) → Br· + C=C=C, therefore has an activation energy much less than that required for the corresponding decomposition of radical II and is expected to be close to the endothermicity of the reaction, *i.e.*, ≅9 kcal/mole, in view of the almost zero activation energy for Br· addition. Comparable value of 8.1 kcal/mole was reported for the activation energy of the decomposition of the α-bromoethyl radical,[8] ($BrC\dot{C}$ → Br· + C=C). Bromine elimination from radical I is therefore *quite feasible* on energetic grounds even at −78°.[9] The analogous reaction has been observed with other radicals at the same temperature. The free-radical-induced *cis–trans* isomerization of 2-butene[10] involves reversible addition of Br· to the double bond of butene. Further, Br· elimination from 2-bromo-2-methylpropyl radical has been demonstrated[11] to be competitive with chlorine abstraction from *t*-butylhypochlorite at −78°.



As has been previously pointed out, the center-attack product is increased at higher temperatures. At identical HBr concentrations, the [T]/[C] ratios were reported[2] to be 0.56 (−70°), 0.31 (−40°), and 0.075 (ambient). Such variation with temperature is in accord with our proposed mechanism. The two Br· addition steps are exothermic and of low or zero activation energy; k_1/k_2 is therefore relatively temperature insensitive. The temperature dependence of [T]/[C] is primarily a result of the higher activation energy of k_{-1} relative to that of the hydrogen-transfer step k_3.[12] Thus the formation of the terminal addition product becomes increasingly unfavorable at higher temperature, while no such adverse effect operates for the center adduct. Abell[1] concluded that Br· addition to allene is irreversible since he only observed the center-addition product. His results, however, were obtained in the gas phase, *i.e.*, low HBr concentration, and at relatively high reaction temperature. Both of these effects strongly favor the formation of the center adduct; the initial fast reversible Br· addition at the terminal carbon cannot be ascertained under these conditions.

The value of $k_1/k_2 = 2.0$ obtained suggests that the bromine atom attack on C_1 and C_2 of allene is indiscriminate.

Very similar results have been obtained in the free-radical addition of benzenethiol to allene[13] which also follows a similar mechanism; k_1/k_2 was found to be equal to 2.0 at 130°. Arrhenius plots indicated only a small difference in the activation energies of the two addition reactions ($E_{k_2} - E_{k_1} = 1.1$ kcal/mole).

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 237 double-beam recording spectrophotometer (sodium chloride optics). Nmr spectra were obtained on a Varian Model A60 spectrometer.

In the vapor phase chromatographic analysis, weight per cent of the reaction products were calculated from the corresponding peak areas. Peak areas–weight per cent relationship were determined from calibration using synthetic mixtures of known composition.

Materials.—Commercially available allene (Dow Chemical Co.) used in these studies contained about 5% propylene and traces of chloropropene. Spectrograde pentane was used as a solvent and commercial grade anhydrous hydrogen bromide was condensed and distilled under vacuum before use.

General Procedure for Addition of HBr to Allene.—All the runs were carried out in thick-walled Pyrex ampoules each fitted with a ground joint. Each run was performed on a 25-ml scale. Pentane as a solvent was introduced in each ampoule, which was flushed with a dry steam of nitrogen and connected to a vacuum line which was fitted with two manometers and two 2-l. glass reservoirs for storing allene and HBr, respectively. The ampoule was cooled in liquid nitrogen and evacuated at 10^{-3} mm for 10 min. Allene (1 g) giving a 1 *M* solution and the appropriate volume of HBr were condensed successively. The ampoule was sealed while connected to the vacuum system. The ampoules of various HBr concentrations were kept in a 2-l. Dewar flask at −78°. The reaction was initiated by γ rays from a 3-kcurie Co^{60} source which was in the form of four encapsulated pencils placed in a circle 2.5 in. from the Dewar flask. Irradiation was continued for 2 hr after which time each ampoule was opened and flushed in the dark with a dry steam of nitrogen first at −78° and then at −20° until all the HBr was removed.

Blank runs were carried out applying the same procedure but without irradiation.

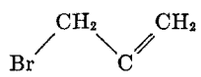
The reaction mixtures were analyzed by vpc using a 12-ft column packed with 20% Carbowax (20,000) on Diatoport P. Helium was used as the carrier gas and the temperature was programmed at 11°/min over the range 80–250°. All the reaction products were identified by comparison of their vpc retention

(6) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," translated by M. Baudart, Princeton University Press, Princeton, N. J., 1958.

(7) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936).

(8) R. Barker and A. Maccoll, *J. Chem. Soc.*, 2839 (1963).

(9) By analogy with the structure proposed for the 1-methylvinyl radical [R. W. Fessenden and R. K. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963)], the structure of radical I can be represented as



whose most probable conformation is that in which the carbon–bromine bond is coplanar with the orbital occupied by the free electron on the central carbon atom, *i.e.*, the conformation most suitable for the Br· elimination.

(10) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **82**, 5354 (1960).

(11) W. O. Haag and E. I. Heiba, *Tetrahedron Letters*, **No. 41**, 3683 (1965).

(12) The activation energy for the reaction ·CH_3 + HBr ⟶ CH_4 + Br· was found to be 2 kcal/mole: [H. C. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, **10**, 305 (1942); E. R. Van Artsadlen G. and B. Kistiakowsky, *ibid.*, **12**, 469 (1944). Based on available bond energy data[6] the reactivity of a methyl radical is comparable with that of a secondary vinylic radical and hence the activation energy for k_3 is expected to be about 2 kcal/mole.

(13) E. I. Heiba, *J. Org. Chem.*, **31**, 776 (1966).

times, and infrared and nmr spectra with those of authentic samples. The over-all conversions were about 40–50% for the runs at high [HBr] and 10–20% for those at low [HBr].

The blank runs showed no reaction except for traces of 2,2-dibromopropane (ionic diadduct) at 8 *M* HBr and higher. No correction for ionic addition was necessary and the reaction products were calculated throughout to be resulting from the free-radical addition of Br· to the terminal or the central carbon of allene.

No isomerization of allene to methylacetylene was observed.

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The Controlled Alkylation of Mono-*n*-alkylphosphines

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The controlled alkylation of mono-*n*-alkylphosphines by methyl and *n*-alkyl halides under a variety of conditions has been investigated. Trialkylphosphines of the type RPR_2' (*R* = *n*-alkyl, R′ = methyl or *n*-alkyl) can be obtained simply and in excellent yields (78–94%) from mono-*n*-alkylphosphines and methyl or *n*-alkyl iodides, using the alcohol corresponding to the alkyl iodide as solvent. With more elaborate control of reaction variables, methyl chloride and dodecylphosphine gave 80 ± 10% yields of dimethyldodecylphosphine; small amounts of dodecyltrimethylphosphonium chloride were also produced. Simple dialkylphosphines can be obtained in good yield by moderately heating methyl or *n*-alkyl iodides and primary phosphines without solvent. Factors involved in the controlled alkylation of mono-*n*-alkylphosphines are discussed. A number of trialkylphosphines have been prepared and characterized by conversion to phosphine oxides and phosphonium salts.

A number of methods are potentially available for the synthesis of simple trialkylphosphines of the type RPR_2' (R = *n*-alkyl, R′ = methyl, or *n*-alkyl).[1,2] Many of these methods are long, tedious, and result in poor over-all yields, or require starting materials that are not readily available or are difficult to handle.[3] In considering possible synthetic routes to trialkylphosphines, the direct conversion of mono- to trialkylphosphines by controlled alkylation appeared promising from the standpoint of directness and simplicity.[4,5] The results of the alkylation of mono-*n*-alkylphosphines with methyl and *n*-alkyl halides are summarized in Table I.

Discussion

The preparation of trialkylphosphines by controlled alkylation of monoalkylphosphines is dependent upon close control of a number of variables. These include the alkylating agent, solvent, temperature, time, reactant ratio, the strength of the acid by-product, and the acid concentration. The role of these factors is best understood by considering the complete alkylation sequence, along with our findings concerning the influence of the reaction variables.

The complete alkylation of primary phosphines involves two types of reactions: (1) alkylation or nucleophilic substitution, and (2) dissociation of the hydrogen halide salts formed by the alkylation reaction. The

$$RPH_2 + R'X \longrightarrow \underset{\text{I}}{[RPH_2R'^+]X^-} \rightleftharpoons HX + \underset{\text{II}}{RPHR'} \xrightarrow{R'X}$$

$$\underset{\text{III}}{[RPHR'_2{}^+]X^-} \rightleftharpoons HX + \underset{\text{IV}}{RPR'_2} \xrightarrow{R'X} \underset{\text{V}}{[RPR'_3{}^+]X^-}$$

individual alkylation steps proceed faster according to the order of nucleophilicity of alkylphosphines: $R_3P > R_2PH > RPH_2$.[6a] On the other hand, dissociation of the hydrogen halide salts becomes more difficult as substitution of alkyl groups occurs.[6b] The successful synthesis of a trialkylphosphine is then dependent upon preparing its hydrohalide salt (III) under conditions such that further dissociation does not occur. If any dissociation of III does occur, then the free trialkylphosphine will be alkylated to the tetraalkylphosphonium salt under the conditions required for the initial alkylation.

Methanol was chosen as solvent for the initial methylation studies, because of its polar character (polar solvents facilitate the alkylation steps) and its relatively nonbasic character (basic solvents facilitate the dissociation reactions). Subsequent methylation studies showed that the reaction was considerably slower in ethanol and produced ethylated by-products to the extent of 8%. The latter factor requires that the alcohol corresponding to the alkyl halide be used.

With regard to the alkylating agent, methyl iodide is not only the most reactive alkyl halide but is essentially nonbasic, and leads to salts of hydrogen iodide, the strongest acid in the series HI, HBr, and HCl. These factors contribute to the successful preparation

(1) L. Maier, *Prog. Inorg. Chem.*, **5**, 84 (1963).

(2) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp 33–36.

(3) (a) W. J. Bailey, S. A. Buckler, and F. Marktscheffel, *J. Org. Chem.*, **25**, 1996 (1960); (b) H. Hellmann and O. Schumacher, *Angew. Chem.*, **72**, 211 (1960), and unpublished results from these laboratories; (c) M. Grayson, P. T. Keough, and G. A. Johnson, *J. Am. Chem. Soc.*, **81**, 4803 (1959); (d) G. Kamai and L. A. Khismatullina, *Zh. Obshch. Khim.*, **26**, 3426 (1956); *Chem. Abstr.*, **51**, 9512*h* (1957).

(4) (a) A. W. Hofmann, *Chem. Ber.*, **6**, 292 (1873). Dialkyl- and trialkylphosphines were prepared by alkylation of mono- and dialkylphosphines, respectively. Information concerning the yields and specificity of these alkylations appears sketchy and has led to some confusion concerning the worth of this method. Information concerning the direct conversion of mono- to trialkylphosphines was not available. (b) Methods utilizing Grignard reagents and alkylphosphonous dichlorides or dialkylphosphinous chlorides or metal phosphides and alkyl halides offer no advantage for the simple trialkylphosphines, since the phosphorus compounds in both cases are generally obtained from the corresponding phosphines. For further discussion of these methods see ref 1, pp 90, 91 and K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushanam, "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 18, 19.

(5) Subsequent to this investigation, a simplified synthesis of trialkylphosphine oxides was developed; see T. H. Siddall and M. A. Davis, *J. Chem. Eng. Data*, **10** (3), 303 (1965). This synthesis coupled with trichlorosilane reduction of the phosphine oxide constitutes an excellent route to simple trialkylphosphines; see H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **98**, 171 (1965).

(6) (a) W. A. Henderson, Jr., and S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 5794 (1960); (b) W. A. Henderson, Jr., and C. A. Streuli, *ibid.*, **82**, 5791 (1960).