G. With Trimethyl Phosphite.—To 6.2 g (0.05 mole) of trimethyl phosphite dissolved in 100 ml of tetrahydrofuran was added 0.2 mole of I over 0.25 hr. The resulting reaction was mildly exothermic. Subsequent to the complete addition, the reaction mixture was heated at gentle reflux for 1 hr. A Gilman Color Test I[15] was negative at this time.

The reaction mixture was then hydrolyzed with 200 ml of 1.5 *M* ammonium chloride. The organic layer was separated, dried over sodium sulfate, concentrated, and distilled to give 1.4 ml of a mixture boiling over the range 95–120° (0.1 mm). The mixture was shown by gas phase chromatography to contain *ca.* 60% of VI. The phosphine, for the purpose of analysis, was converted to the corresponding phosphine sulfide. An analytical sample of the sulfide was obtained by gas phase chromatography.

Anal. Calcd for $C_6H_{15}PS_4$: C, 29.26; H, 6.1; S, 52.02. Found: C, 29.0; H, 6.2; S, 51.3.

The structure assignment of tris(methylthiomethyl)phosphine sulfide was positively confirmed by spectral analysis: H^1 nmr signals centered at τ 6.93 (methylene, doublet, J = 6.8 cps), and 7.66 (methyl, singlet) in the correct area ratios and a mass spectrum of the material had an intense parent peak at *m/e* 245.9792 (by a peak matching technique) which corresponds closely to a calculated *m/e* of 245.9794.

H. With Triphenyl Phosphite.—To 31 g (0.1 mole) of triphenyl phosphite dissolved in 100 ml of tetrahydrofuran was added, over 0.5 hr, 0.3 mole of I. Subsequent to the complete addition, the reaction was heated at gentle reflux for 2 hr and then stirred over night at room temperature. Work-up of the reaction mixture as described above gave 11.2 g (52%) of VI, bp 120–126° (0.3 mm). The purity of this material was shown to be >98% by gas phase chromatographic analysis. An H^1 nmr spectrum of VI exhibited signals at τ 7.27 (>PCH_2, doublet, J = 4 cps) and 7.8 (SCH_3, singlet) in the correct area ratios. Also, the material gave tris(methylthiomethyl)phosphine sulfide (see above experiment) on treatment with sulfur.

Reaction of *n*-Decyl Methyl Sulfide with *n*-Butyllithium–TMEDA.—To a solution of 0.05 mole of the *n*-butyllithium–TMEDA complex there was added, at room temperature, 9.4 g (0.05 mole) of *n*-decyl methyl sulfide. During a total reaction time of 4 hr, a white precipitate formed.

The reaction mixture was then carbonated by pouring onto a Dry Ice–ether slurry and worked up by standard procedures. The neutral fraction was dried over sodium sulfate, concentrated, and distilled under reduced pressure to give 2.63 g (37.5%) of 1-decene, bp 66–70° (*ca.* 15 mm), as evidenced by infrared and gas phase chromatographic analysis.

The acid fraction on concentration gave 1.96 g (17%) of decylthioacetic acid, mp 48–50°. A crystallization from hexane gave the analytical sample, mp 51–53°.

(15) H. Gilman and F. Shulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

Anal. Calcd for $C_{12}H_{24}O_2S$: C, 62.07; H, 10.35; S, 13.79. Found: C, 62.0; H, 10.6; S, 14.5.

The experimental neutralization equivalent of the acid was found to be 226 (theoretical, 232).

An H^1 nmr spectral analysis of the compound confirmed the structure assignment: signals centered at τ 0.1 (acid), 6.76 (SCH_2CO_2), 7.34 (CH_2CH_2S, triplet, J = 6 cps), 8.7 [$SCH_2(CH_2)_8$], and 9.1 (CH_2CH_3, triplet) in the correct area ratios.

Reaction of (2-Methylbutyl)methyl Sulfide with *n*-Butyllithium–TMEDA.—The reactants, in equimolar ratios (0.05 mole), were stirred at room temperature for 18 hr. The small quantity of precipitate that formed during this time was recovered by filtration. The filtrate was then carefully quenched with D_2O with any gas evolved being passed through a solution of bromine in carbon tetrachloride.

The organic phase was separated and distilled (again evolved gas scrubbed by passing through a Br_2–CCl_4 trap) to give 1.26 g (10.7%) of partially deuterated starting olefin. A small quantity of the olefin was purified by glpc and shown by mass spectral analysis to contain 99.0% d_0 and 0.9% d_1.

The solvents from the preceding distillation were shaken with the Br_2–CCl_4 solution to remove any 2-methyl-1-butene. Subsequent to the destruction of excess bromine with aqueous sodium sulfite, the organic phase was distilled to give 9.8 g (42%) of 1,2-dibromo-2-methylbutane, bp 67–69° (*ca.* 15 mm), $n^{25}D$ 1.5049. An H^1 nmr spectral analysis confirmed the structure assignment: signals centered at τ 6.2 (singlet, CH_2Br), 8.1 (quartet, J = 7 cps, CH_3CH_2), 8.2 (singlet, $BrCCH_3$), and 8.95 (triplet, J = 7 cps, CH_3CH_2).

Anal. Calcd for $C_5H_{10}Br_2$: C, 26.09; H, 4.35; Br, 69.56. Found: C, 25.4; H, 4.6; Br, 70.1.

Registry No.—I, 10415-47-1; III, 10428-55-4; VI, 10428-56-5; VII, 10428-57-6; $[(CH_3)_3N^+CH_2]_2$ $2I^-$, 10428-58-7; tetrahydrofuran, 109-99-9; trimethylsulfonium iodide, 2181-42-2; diphenylmethyl(methylthiomethyl)phosphonium iodide, 10428-59-8; diphenyl(methylthiomethyl)phosphine sulfide, 10428-60-1; dimethyl(trimethylsilylmethyl)sulfonium iodide, 3607-00-9; (2-hydroxypentyl)dimethylsulfonium iodide, 10428-61-2; tris(methylthiomethyl)phosphine sulfide, 10428-62-3; decylthioacetic acid, 10428-63-4; 1,2-dibromo-2-methylbutane, 10428-64-5.

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Reaction of Butylmagnesium Bromide with Ketones

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Addition of an ether solution of *n*-butylmagnesium bromide to acetone in ether gave *n*-butane (I) and *n*-butyldimethylcarbinol (II). When acetone was added to the Grignard reagent, a large amount of *n*-octane was produced along with I and II. Addition of methanol or acetic acid to the Grignard reagent also caused the formation of *n*-octane. The carbinol II was easily produced at the higher temperature as well as at the higher concentration of the Grignard reagent. A factor determining the reactivity of a ketone toward the Grignard reagent is the steric effect of the alkyl group of the ketone.

In the course of our study on the anionic polymerization of α,β-unsaturated carbonyl compounds with an organometallic catalyst, we noticed that, the lower the concentration of *n*-butyllithium was, the more significant were the changes that appeared in the reaction mode of the lithium alkyl toward the unsaturated carbonyl compounds.[1] A similar situation seems also to be true for a reaction mode of Grignard reagent in such a small concentration range.

By adding an ether solution of *n*-butylmagnesium bromide to acetone in ether, there was observed the formation of *n*-butane, *n*-butyldimethylcarbinol and, sometimes, a very small amount of *n*-octane. The formation of *n*-butane was not due to the destruction of the Grignard reagent with the small quantity of water present in ether and acetone, since the concentration

(1) N. Kawabata and T. Tsuruta, *Makromol. Chem.*, **86**, 231 (1965).

of water was less than 0.4 mmole $l.^{-1}$ in ether and less than 0.001% in acetone, and, moreover, the reactivity of water toward the Grignard reagent was only three times larger than that of acetone. This Grignard reagent contained originally no *n*-butane, which was confirmed by a reaction with diethyl oxalate at 20°, where only a trace of *n*-butane was observed. Isopropyl alcohol, diacetone alcohol, and pinacol were not produced, but a small quantity of triacetone dialcohol was found, which was probably produced by the action of the alkoxide I'.[2]

As shown in Table I, the alkoxide I' did not decrease by reactions such as condensation and polymerization. Distribution of products between *n*-butylmagnesium bromide and acetone or methyl ethyl ketone under various conditions is shown in Table II or III.

TABLE I

REACTION OF *n*-BUTYLMAGNESIUM BROMIDE WITH ACETONE AT 20°[a]

Reaction time, sec	*n*-Butyldimethylcarbinol, mole/l.
12	0.0167
25	0.0166
40	0.0166
52	0.0164
93	0.0167

[a] The Grignard reagent was added to acetone in ether; [n-C_4H_9MgBr], 0.0241 mole/l.; [CH_3COCH_3], 0.540 mole/l.

TABLE II

REACTION OF *n*-BUTYLMAGNESIUM BROMIDE WITH ACETONE[a]

n-C_4H_9MgBr, mole/l.	Temp, °C	Products distribution, %[b] I/(I + II)	II/(I + II)
0.0130	20	33.6	66.4
0.0194	20	32.5	67.5
0.0259	20	30.0	70.0
0.0389	20	29.8	70.2
0.0518	20	27.4	72.6
0.0128	−30	68.0	32.0
0.0255	−30	61.9	38.1
0.0383	−30	57.7	42.3
0.0638	−30	53.4	46.6

[a] The Grignard reagent was added to acetone in ether; [CH_3COCH_3], 0.540 mole/l. [b] I, *n*-butane; II, *n*-butyldimethylcarbinol.

TABLE III

REACTION OF *n*-BUTYLMAGNESIUM BROMIDE WITH METHYL ETHYL KETONE[a]

n-C_4H_9MgBr, mole/l.	$CH_3COC_2H_5$, mole/l.	Temp, °C	Products distribution, %[b] I/(I + III)	III/(I + III)
0.0122	0.43	20	26.0	74.0
0.0189	0.43	20	23.8	76.2
0.0368	0.43	20	20.4	79.6
0.0504	0.43	20	18.0	82.0
0.0249	0.030	20	23.1	76.9
0.0249	0.214	20	24.9	75.1
0.0249	0.434	20	23.1	76.9
0.0249	0.661	20	26.5	73.5
0.0248	0.43	−30	58.9	41.1
0.0265	0.43	−30	55.7	44.3
0.0370	0.43	−30	49.7	50.3
0.0620	0.43	−30	44.2	55.8

[a] The Grignard reagent was added to methyl ethyl ketone in ether. [b] I, *n*-butane; III, *n*-butylmethylethylcarbinol.

(2) V. Grignard and M. Dubien, *Compt. Rend.*, **177**, 299 (1923).

The total yields of products amount to 95–100% of the calculated values. The difference between them are presumably due to the formation of *n*-octane.

The yield of the carbinols increased as the concentration of *n*-butylmagnesium bromide increased as shown in Table II and Table III. That suggests a higher reaction order with respect to the Grignard reagent for addition compared with that for metalation. Grignard reagents are considered to exist as equilibrium mixtures of monomeric and dimeric forms in ether solution.[3] The dimeric forms or two molecular species of the reagent may be considered to be used in the transition state of the addition reaction, while one molecular species in the metalation reaction. On the other hand, the concentration of the ketones had no influence on the distribution of products. It was also found that a lower temperature favored the formation of *n*-butane.

As shown in Table IV, when acetone was added to an ether solution of *n*-butylmagnesium bromide, a large amount of *n*-octane was produced along with the normal reaction products. This Grignard reagent did not contain originally either *n*-octane or *n*-butyl bromide. The yield of *n*-octane became higher in the lower concentration range of the Grignard reagent. *n*-Octane formation seems to suggest that free radicals might be formed in the reaction. In accordance with this observation, Maruyama has detected free radicals in his electron spin resonance (esr) spectra in the reactions between Grignard reagents and the derivatives of benzophenone or acetophenone and some other ketones and nitriles.[4] Addition of methanol or acetic acid to an ether solution of *n*-butylmagnesium bromide also caused the formation of *n*-octane in 57 and 45% yields, respectively.

TABLE IV

REACTION OF *n*-BUTYLMAGNESIUM BROMIDE WITH ACETONE AT 20°[a]

n-C_4H_9MgBr, mole/l.	Products distribution, %[b] I/(I + II + 2IV)	II/(I + II + 2IV)	2IV/(I + II + 2IV)
0.0122	17.2	13.1	69.7
0.0182	22.5	36.8	40.7
0.0243	29.8	52.9	17.3
0.0486	23.4	70.0	6.6

[a] Acetone was added to the Grignard reagent; [CH_3COCH_3], 0.540 mole/l. [b] I, *n*-butane; II, *n*-butyldimethylcarbinol; IV, *n*-octane.

As shown in Table V, the ratio of carbinols formed by the addition of the Grignard reagent to an ether solution of acetone and methyl ethyl ketone mixture is proportional to the ratio of the amount of the ketones. We conclude that the addition of the Grignard reagent to ketones is a first-order reaction as to ketones. Relative reactivities of ketones toward *n*-butylmagnesium bromide were determined by competitive reactions from eq 1 and are summarized in Table VI.

As shown in Figure 1 and Table VII, there was observed a straight-line relationship between the relative reactivity of the methyl alkyl ketone, $RCOCH_3$, and the rate constant of Michael addition of lauryl mercaptan (LSH) to methyl α-alkylacrylate, $CH_2{=}C(R)$-CO_2CH_3[5] (eq 2).

(3) E. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.*, **86**, 4363 (1964).
(4) K. Maruyama, *Bull. Chem. Soc. Japan*, **37**, 897 (1964).
(5) R. Fujio and T. Tsuruta, *Kogyo Kagaku Zasshi*, **69**, 925 (1966).

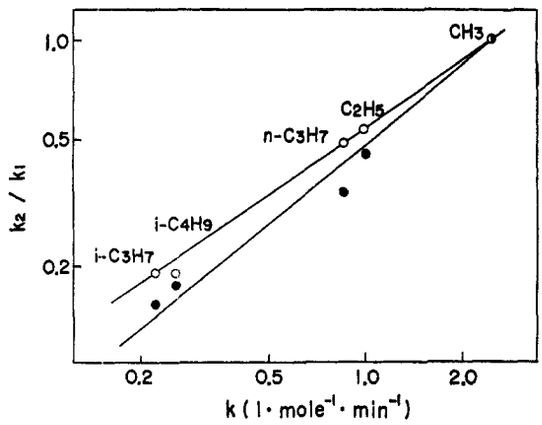


Figure 1.—Plots of k_2/k_1 against k: ○, in diethyl ether; ●, in tetrahydrofuran.

TABLE V

DETERMINATION OF RATE ORDER CONCERNING KETONE FOR ADDITION REACTION OF *n*-BUTYLMAGNESIUM BROMIDE TO KETONE[a]

$CH_3COC_2H_5/CH_3COCH_3$[b] (=α)	1.58	0.792	0.388
n-Butylmethylethylcarbinol/ *n*-butyldimethylcarbinol (=β)	0.839	0.433	0.197
$\beta/\alpha = k_2/k_1$	0.53	0.55	0.51

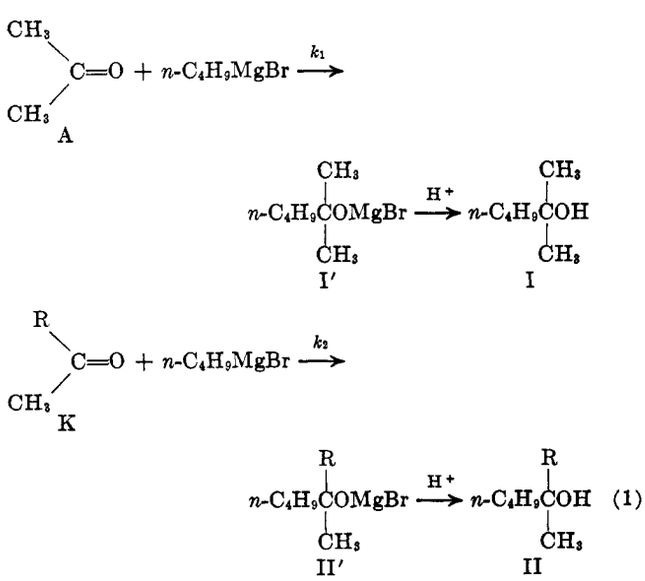
[a] The Grignard reagent was added to the mixture of the ketones in ether; [n-C_4H_9MgBr], 0.0260 mole/l., 20°. [b] Quantities of the ketones used were as *ca.* 20 times much as that of the Grignard reagent, and they were considered to be constant during the reaction.

TABLE VI

RELATIVE REACTIVITIES OF METHYL ALKYL KETONES TOWARD *n*-BUTYLMAGNESIUM BROMIDE AT 20°[a]

	Relative reactivity k_2/k_1	
Methyl alkyl ketone	In diethyl ether[b]	In tetrahydrofuran[c]
CH_3COCH_3	1.00	1.00
$CH_3COC_2H_5$	0.53	0.44
CH_3CO n-C_3H_7	0.48	0.32
CH_3CO i-C_3H_7	0.19	0.15
CH_3CO i-C_4H_9	0.19	0.17

[a] The Grignard reagent was added to the mixture of the ketones in ether or tetrahydrofuran. [b] [n-C_4H_9MgBr], 0.0260 mole/l. [c] [n-C_4H_9MgBr], 0.0325 mole/l.



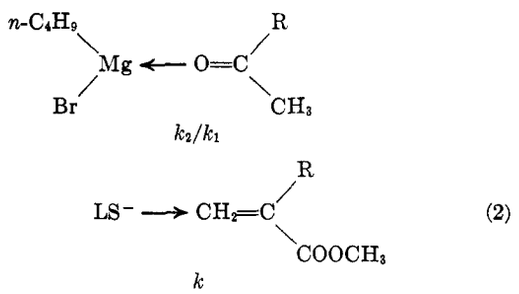
relative reactivity k_2/k_1 = IIA/IK

TABLE VII

RATE CONSTANTS OF MICHAEL ADDITION REACTION OF LAURYLMERCAPTAN TO METHYL α-ALKYLACRYLATES IN ETHYL ALCOHOL[a]

α-Alkyl group	k,[b] l. mole^{-1} min^{-1}	$\Delta\Delta H^*$,[b] cal mole^{-1}	$\Delta(T\Delta S^*)$,[c] cal mole^{-1}
CH_3	2.52	0	0
C_2H_5	1.016	200	−200
n-C_3H_7	0.868	200	−300
i-C_3H_7	0.227	500	−800
i-C_4H_9	0.262	500	−500

[a] [LSH], 0.120 mole/l.; [acrylate], 0.04 mole/l.; [EtOK], 0.008 mole/l. [b] T = 303°K. [c] T = 298°K.



Since the two reactions are opposite in the direction of electron displacement, the fact that k_2/k_1 had a positive linearity with k seems to show the factor determining the relative reactivity of a ketone toward the Grignard reagent is the steric effect of the alkyl group when the carbonyl–oxygen coordinates to the magnesium of the Grignard reagent.

Experimental Section

Materials.—Diethyl ether and tetrahydrofuran were distilled over sodium–potassium alloy. Ketones were dried over drierite and purified by fractionation with 30-cm Vigreaux column. *n*-Butyl bromide was washed with sulfuric acid, then with water, and distilled over calcium hydride under reduced pressure. Ether solutions of *n*-butylmagnesium bromide were prepared in 98–100% yield from 0.13 mole of *n*-butyl bromide and 0.14 g-atom of magnesium turnings, obtained from Merck and Co. Ltd., the purity of which was 99.5%. Tetrahydrofuran solutions of *n*-butylmagnesium bromide were made by mixing one volume of the Grignard reagent obtained above and one volume of tetrahydrofuran. Nitrogen gas was purified by passing through a tube containing active copper at 170° and dried on phosphorus pentoxide. Preparation of reagents and other experiments were conducted under a nitrogen atmosphere.

Analyses.—The purity of the reagents used was checked by a vapor phase chromatography (vpc), where a 0.5 × 3 m stainless column packed with polyethylene glycol 20,000 (30 wt %) on 40–60 mesh Celite 545 was used. Yields of the products were also measured by vpc with calibration curves. For the determination of the carbinols was used the same column described above, and for the determination of *n*-butane was used the column packed with the mixture of polyethylene glycol 20,000 and silicone D. C. 550 (30 wt %) on 80–100 mesh Celite 545 (volume ratio was 1:2). The calibration curve of *n*-butane was made from the area ratio of *n*-butane to diethyl ether, *n*-butane being prepared from the reactions between various amounts of *n*-butylmagnesium bromide and α-naphthol in ether. The calibration curves of the carbinols were made from the area ratios of them to *p*-cymene or cumene added as an internal standard material.

The sum of the amount of *n*-butane and the carbinol was in accordance with the quantity determined by an acid–base titration and also with the amount of *n*-butyl bromide used as follows: *n*-butyl bromide used 0.0260 mole/l.; titration 0.0264 mole/l.; found, [*n*-butane] = 0.0085 mole/l. and [*n*-butyldimethylcarbinol] = 0.0178 mole/l. The calibration curve of *n*-butane once made is useful for the determination of the concentration of *n*-butylmagnesium bromide.

Procedure.—An ether solution of *n*-butylmagnesium bromide was added from a buret to a magnetically stirred ether solution of ketone within 1.2 sec, and the reaction was stopped with acetic acid 1 min after the addition of the reagent. Inverse addition of acetone was conducted with a syringe.

The rate constants, k, of Michael addition of LSH to $CH_2{=}C(R)CO_2CH_3$ were calculated from eq 3. Here the concentration of LSH was determined by an iodometry. The reaction was conducted at various temperatures, and the ΔH^* and the ΔS^* were obtained from Arrhenius plots.[5]

$$LSH + B \overset{K_1}{\rightleftharpoons} LS^- + BH^+$$

$$LS^- + CH_2{=}C(R)CO_2CH_3 \overset{k_2}{\rightleftharpoons} LSCH_2\bar{C}(R)CO_2CH_3$$

$$\frac{-d[LSH]}{dt} = k[LSH][CH_2{=}C(R)CO_2CH_3] \qquad (3)$$

$$k = K_1k_2[B]/[BH^+]$$

Registry No.—I, 625-23-0; II (R = Et), 5582-82-1; *n*-butylmagnesium bromide, 693-03-8; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; CH_3CO *n*-C_3H_7, 107-87-9; CH_3CO *i*-C_3H_7, 563-80-4; CH_3CO *i*-C_4H_9, 108-10-1; laurylmercaptan, 112-55-0; methyl α-methylacrylate, 80-62-6; methyl α-ethylacrylate, 2177-67-5; methyl α-propylacrylate, 3070-66-4; methyl α-isopropylacrylate, 3070-67-5; methyl α-isobutylacrylate, 3070-69-7.

Organophosphorus Chemistry. IV. The Reactions of Trialkyl Phosphites with α-Halo Ketones[1]

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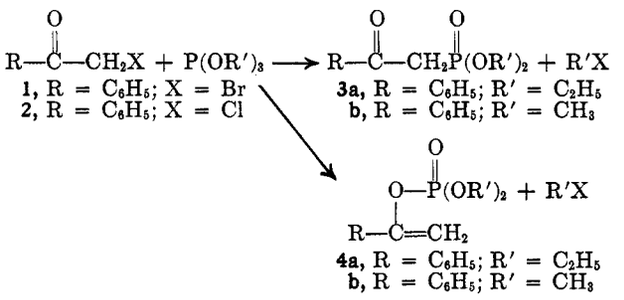
The course of the reactions of certain phenacyl halides and of α-halocyclohexanones with triethyl phosphite, *i.e.*, to form ketophosphonates and/or enol phosphates (Perkow reaction), is not significantly altered by the initial presence of alcohols. Thus, these reactions probably do not proceed *via* initial attack of phosphorus on halogen. Phenacyl bromides give only enol phosphates and no ketophosphonates in reaction with trialkyl phosphites in the presence of acetic acid. A possible mechanism for these reactions is presented and its relationship to the mechanism of the Perkow reaction is discussed. The evidence presented strongly suggests that the Perkow reaction involves initial attack of trialkyl phosphite on carbonyl carbon followed by rearrangement to oxygen.

The reactions of α-halo ketones with trialkyl phosphites lead to ketophosphonates **3** (Arbusov reaction) and enol phosphates **4** (Perkow reaction)[3] (Scheme I).

SCHEME I



We and others have found that the reaction of numerous α-bromo ketones with triphenylphosphine in the presence of methanol, acetic acid, or other prototropic reagents leads to the dehalogenated ketone in high yield.[4,5] These reactions appear to proceed by nucleophilic displacement on bromine by the phosphine assisted by proton transfer to the incipient carbanion. They may also involve a prior protonation or hydrogen-bond formation on the carbonyl oxygen which then makes attack on bromine more feasible. The reactions of α-bromo ketones with triphenylphosphine in anhydrous solvents may also proceed by initial attack on bromine to give enolate bromophosphonium ion pairs which recombine to give either keto- or enol triphenylphosphonium salts and their further reaction products.[5] Ketotriphenylphosphonium salts may also be formed, in some cases at least, by SN2 displacement of bromide ion by triphenylphosphine in aprotic solvents.

Results and Discussion

We now wish to present evidence which indicates that the formation of ketophosphonates most likely occurs by SN2 displacement of halide ion even in the presence of alcohols. Furthermore we have found evidence that enol phosphate formation proceeds most likely by initial attack at carbonyl carbon followed by rearrangement of the phosphorus to carbonyl oxygen[6a] (Scheme II).

2-Bromoacetophenone (**1**) reacts with triethyl phosphite in 1,2-dimethoxyethane ("glyme") or without solvent to give mainly the ketophosphonate **3a** and less of diethyl 1-phenylvinyl phosphate **4a** (Table I). Reaction in the initial presence of ethanol gives a com-

(1) (a) Part of the research was performed at Lehigh University. (b) This investigation was supported in part by Grant No. GP-1354 from the National Science Foundation and AF-AFOSR-938-65 from the Directorate of Chemical Sciences, Air Force Office of Scientific Research. We also acknowledge with thanks the award of funds for a Varian A-60 nmr spectrometer from the National Science Foundation and the award (to M. A.) of the Althouse (1963–1964) and Hornor (1964–1966) Fellowships at Lehigh University.

(2) Address to which correspondence should be sent.

(3) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

(4) (a) I. J. Borowitz and L. I. Grossman, *Tetrahedron Letters*, 471 (1962); (b) H. Hoffman and H. J. Diehr, *ibid.*, 583 (1962); (c) S. Trippett, *J. Chem. Soc.*, 2337 (1962); (d) P. A. Chopard, R. F. Hudson, and G. Klopman, *ibid.*, 1379 (1965).

(5) (a) I. J. Borowitz and R. Virkhaus, *J. Am. Chem. Soc.*, **85**, 2183 (1963); (b) I. J. Borowitz, K. Kirby, and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966).

(6) (a) A similar pathway for the mechanism of the Perkow reaction has been proposed by P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965). Our work, which had begun before publication of this paper, is mainly based on systems not studied by these authors. (b) This conclusion is supported by current kinetic studies, especially when compared with related studies in the triphenylphosphine–phenacyl bromide system. We also find that the enolate of acetophenone is phosphorylated mainly on oxygen.[7]

(7) S. Firstenberg, research in progress.