give the product **30** (53 mg). Recrystallization was effected from a mixture of ether and pentane; mp 99–100°, $[\alpha]_D$ −43° (*c* 0.38, methanol). *Anal.* Calcd for $C_{18}H_{21}N_5O_3$: C, 60.82; H, 5.95; N, 19.70. Found: C, 60.92; H, 5.85; N, 19.71.

Registry No.—**2**, 18908-30-0; **3**, 18908-31-1; **4**, 18908-32-2; **5**, 18908-33-3; **6**, 18908-35-5; **9**, 18908-34-4; **11**, 18908-36-6; **12**, 18908-37-7; **13**, 18908-38-8; **14**, 18908-39-9; **16**, 18908-40-2; **17**, 18908-41-3; **18**, 14199-62-3; **19**, 18908-43-5; **20**, 18908-44-6; **22**, 18908-45-7; **23**, 18908-46-8; **24a**, 18908-47-9; **25**, 18908-48-0; **27**, 18902-56-2; **28**, 18908-49-1; **29**, 18908-50-4; **30**, 18908-51-5.

Transalkylation of Phosphonates. Equilibrium Studies

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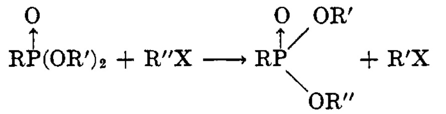
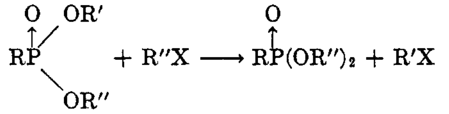
The reaction between alkylating agents and phosphonates (reactions 1 and 2) was found to proceed at a considerably lower temperature than previously reported. Use of a primary alkyl iodide as the alkylating agent results in a reasonably rapid and clean reaction at 130°, but a temperature as low as 70° can bring about slow interconversion; alkyl tosylates react somewhat faster than the corresponding iodides. Performing the reaction in a sealed tube results in establishment of equilibrium; equilibrium distributions agree closely with calculated values over a rather wide range of initial concentrations. The equilibrium data indicated that phosphonate exchange in the absence of external alkylating agent, reaction 3, should be a random, or entropy-controlled process; this was verified experimentally. The use of transalkylation equilibria as a means of obtaining free energy data for alkyl iodides and tosylates is discussed. Transalkylation can be used as a convenient means of synthesis of phosphonate esters, but the magnitude of the equilibrium constants for the reactions must be considered when planning such syntheses.

The reaction between alkylating agents and esters of pentavalent phosphorus acids (transalkylation) has been studied several times in this decade.[1–8] Reactions 1 and 2 illustrate the phosphonate case. There can be

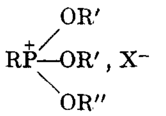


$$\mathrm{R\overset{\overset{O}{\uparrow}}{P}(OR')_2 + R''X \longrightarrow R\overset{\overset{O}{\uparrow}}{P}(OR')(OR'') + R'X} \qquad (1)$$



$$\mathrm{R\overset{\overset{O}{\uparrow}}{P}(OR')(OR'') + R''X \longrightarrow R\overset{\overset{O}{\uparrow}}{P}(OR'')_2 + R'X} \qquad (2)$$

little doubt that these reactions proceed by nucleophilic attack by the phosphoryl oxygen,[1–5,7] producing alkoxyphosphonium salts as intermediates.[6,8] For reaction 1, the intermediate would be



$$\mathrm{R\overset{+}{P}(OR')_2(OR''),\ X^-}$$

Owing to the fact that the reported reaction conditions for transalkylation use high temperatures and long reaction times, it is easy to conclude that the reaction is of somewhat limited scope and utility.[9] It was therefore somewhat surprising to find phosphonate transalkylation at the temperature of refluxing propyl iodide (*ca.* 100°). Specifically, a mixed Michaelis–Arbuzov reaction between trimethyl phosphite and propyl iodide was attempted, with the hope of preparing dimethyl propylphosphonate. The phosphite was added slowly to a large excess of boiling propyl iodide contained in a distilling apparatus arranged in such a manner as to allow rapid removal of methyl iodide, minimizing formation of dimethyl methylphosphonate.[10] Analysis of the product by glpc and nmr indicated not only dimethyl propylphosphonate and dimethyl methylphosphonate, but also substantial amounts of the transalkylated materials, methyl propyl methylphosphonate, dipropyl methylphosphonate, methyl propyl propylphosphonate, and dipropyl propylphosphonate. This somewhat surprising result prompted additional studies on the generality and usefulness of the transalkylation reaction.

Results and Discussion

Generality of Phosphonate Transalkylation.—In order to establish the approximate lower temperature limit for transalkylation, various alkyl iodide–phosphonate mixtures were refluxed for 24 hr. The results are shown in Table I. The rather large reactivity difference as a function of alkylating agent must be almost

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(1) H. J. Harwood and D. W. Grisley, Jr., *J. Amer. Chem. Soc.*, **82**, 423 (1960).

(2) A. N. Pudovik, A. A. Muratova, T. I. Konnova, T. Feoktistova, and L. N. Levkova, *Zh. Obshch. Khim.*, **30**, 2624 (1960); *Chem. Abstr.*, **55**, 15332*a* (1961).

(3) R. G. Laughlin, *J. Org. Chem.*, **27**, 1005 (1962).

(4) H. G. Henning, G. Hilgetag, and G. Busse, *J. Prakt. Chem.*, **33**, 188 (1966).

(5) J. I. G. Cadogan, R. K. Mackie, and J. A. Maynard, *J. Chem. Soc., C*, 1356 (1967).

(6) H. Teichmann, M. Jatkowski, and G. Hilgetag, *Angew. Chem. Intern. Ed. Engl.*, **6**, 372 (1967).

(7) H. J. Harwood, M. L. Becker, and R. R. Smith, *J. Org. Chem.*, **32**, 3882 (1967).

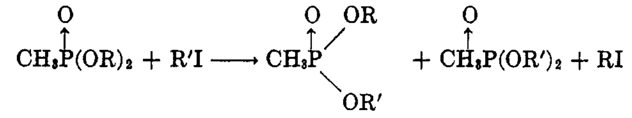
(8) L. V. Nesterov and R. I. Mutalapova, *Tetrahedron Lett.*, 51 (1968).

(9) Pudovik[2] uses 160–165° to realize the reaction of butyl iodide and diethyl ethylphosphonate; Laughlin[3] uses 170° for the reaction of dodecyl iodide and dimethyl ethylphosphonate. Henning[4] found that triphenylphosphine catalyzed the reaction such that somewhat lower temperatures and shorter reaction times could be used.

(10) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, p 121.

Table I

Generality of Phosphonate–Alkyl Iodide Exchange[a]



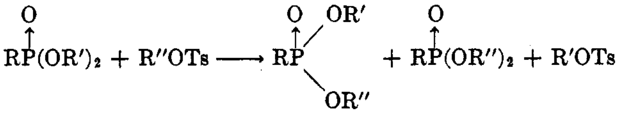
$$CH_3\overset{O}{\overset{\uparrow}{P}}(OR)_2 + R'I \longrightarrow CH_3\overset{O}{\overset{\uparrow}{P}}(OR)(OR') + CH_3\overset{O}{\overset{\uparrow}{P}}(OR')_2 + RI$$

			% yield[b]		
Case	R	R′	$CH_3\overset{O}{\overset{\uparrow}{P}}(OR)_2$	$CH_3\overset{O}{\overset{\uparrow}{P}}(OR)(OR')$	$CH_3\overset{O}{\overset{\uparrow}{P}}(OR')_2$
1[c]	CH_3	$n\text{-}C_4H_9$	12	42	46
2[c]	CH_3	$n\text{-}C_3H_7$	70	25	5
3[d]	CH_3	C_2H_5	94	6	Trace
4[d]	C_2H_5	CH_3	100	0	0
5[d]	C_3H_7	C_2H_5	98	2	0

[a] After 24-hr reflux. [b] Yields are normalized to 100%; in all cases, a material balance of over 90% was realized. [c] Phosphonate–iodide ratio of 1:10. [d] Phosphonate–iodide ratio of 1:20.

Table II

Phosphonate–Alkyl Tosylate Exchange[a]



$$R\overset{O}{\overset{\uparrow}{P}}(OR')_2 + R''OTs \longrightarrow R\overset{O}{\overset{\uparrow}{P}}(OR')(OR'') + R\overset{O}{\overset{\uparrow}{P}}(OR'')_2 + R'OTs$$

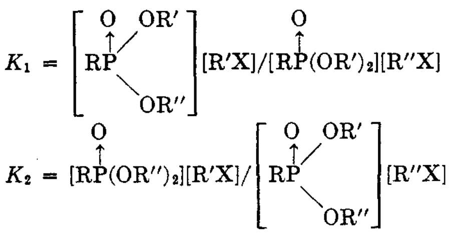
				% yield[b]		
Case	R	R′	R″	$R\overset{O}{\overset{\uparrow}{P}}(OR')_2$	$R\overset{O}{\overset{\uparrow}{P}}(OR')(OR'')$	$R\overset{O}{\overset{\uparrow}{P}}(OR'')_2$
1[c]	CH_3	CH_3	C_2H_5	2	23	75
2[c]	CH_3	CH_3	C_3H_7	4	29	67
3[d]	CH_3	C_2H_5	CH_3	9	45	46
4[d]	C_2H_5	C_2H_5	CH_3	11	46	43
5[d]	C_3H_7	C_3H_7	CH_3	14	57	29

[a] Temperature, 130–140°. [b] See footnote b, Table I. [c] Phosphonate–tosylate ratio of 1:20; reaction time, 7 hr. [d] Phosphonate–tosylate ratio of 1:5; reaction time, 3.5 hr.

entirely due to the reaction temperature;[11] consistent with previous reports, only the transalkylation with butyl iodide proceeds at fast enough rate under these conditions for convenient use. However, it is interesting to note that even the temperature of refluxing ethyl iodide (*ca.* 70°) is sufficient for noticeable reaction. Thus it would appear that transalkylation at 70–100° proceeds at a rate somewhat too slow for convenient synthetic application, but fast enough to be troublesome when performing certain Michaelis–Arbuzov and related reactions.

In an effort to find a method to introduce more rapidly methyl, ethyl, and propyl groups, the corresponding alkyl tosylates were studied. Owing to the similar behavior of alkyl halides and tosylates in nucleophilic substitution reactions, it was felt that their reactivity toward phosphonates would not be too different.[12] Furthermore, the higher reaction temperature allowed by the phosphonate–alkyl tosylate system should prove highly advantageous. The results of a number of such transalkylations are found in Table II. Clearly the results are in agreement with all expectations; indeed, the tosylate exchange should prove to be a convenient synthetic procedure. This will be discussed in more detail subsequently.

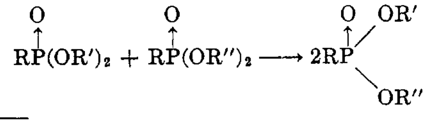
Equilibrium Studies.—Comparison of cases 1 and 3 in Table II demonstrates the reversibility of the transalkylation reaction. Indeed, the intervention of alkoxyphosphonium salts as *bona fide* intermediates as suggested in the introductory remarks requires the reaction to be reversible. Two independent equilibrium expressions completely define the system under



$$K_1 = \left[R\overset{O}{\overset{\uparrow}{P}}(OR')(OR'')\right][R'X]/[R\overset{O}{\overset{\uparrow}{P}}(OR')_2][R''X]$$

$$K_2 = [R\overset{O}{\overset{\uparrow}{P}}(OR'')_2][R'X]/\left[R\overset{O}{\overset{\uparrow}{P}}(OR')(OR'')\right][R''X]$$

investigation.[13] Dividing these expressions provides the derived equilibrium expression for phosphonate exchange in the absence of "external" alkylating agent (reaction 3).



$$R\overset{O}{\overset{\uparrow}{P}}(OR')_2 + R\overset{O}{\overset{\uparrow}{P}}(OR'')_2 \longrightarrow 2R\overset{O}{\overset{\uparrow}{P}}(OR')(OR'') \quad (3)$$

---

[11] Owing to the large excess of alkyl halide, the temperature of the boiling mixture is quite close to the boiling point of the pure halide.

[12] Laughlin, however, was unsuccessful in an attempt to transalkylate dimethyl methylphosphonate with octadecyl tosylate at 200°.[9]

[13] Henceforth it is assumed that R″ > R.

TABLE III

EQUILIBRATION OF METHYLPHOSPHONATE–ALKYL IODIDE MIXTURES, METHYL–*n*-PROPYL CASE[a]

	Reactant ratio[b]			Product distribution[c,d]		
Case	P	CH_3	C_3H_7	$CH_3\overset{\overset{O}{\uparrow}}{P}(OCH_3)_2$	$CH_3\overset{\overset{O}{\uparrow}}{P}{<}^{OCH_3}_{OC_3H_7}$	$CH_3\overset{\overset{O}{\uparrow}}{P}(OC_3H_7)_2$
1[e]	1	2	2	6.4 (6.2)	38.4 (38.2)	55.2 (55.6)
2[f]	1	2	2	5.7	38.3	56.0
3[e]	1	2	1.33	17.5 (17.5)	49.7 (49.5)	32.8 (33.0)
4[e]	1	2	0.66	46.2 (46.4)	43.1 (43.9)	10.7 (9.7)
5[f]	1	3	2	8.3 (9.2)	43.0 (43.1)	48.7 (47.7)
6[e]	1	4	2.66	6.1 (6.2)	38.2 (38.3)	55.7 (55.4)
7[e]	1	2	6	0.2 (0.2)	9.9 (9.7)	89.8 (90.1)

[a] Temperature, 130°; time, 140 hr. [b] Reactant composition is found by determining the identity of reactant phosphonate (footnotes *e* and *f*) and allocating remaining alkyl groups to iodine. [c] Footnote *b*, Table I. [d] The calculated values in parentheses are for $K_1 = 18.3$, $K_2 = 4.3$. [e] Dimethyl methylphosphonate. [f] Dipropyl methylphosphonate.

In order to study quantitatively the question of equilibrium, a number of sealed-tube reactions were performed on esters of methylphosphonic acid ($R = CH_3$) using both alkyl iodides and tosylates. Table III shows equilibrium data for the methyl–propyl case ($R' = CH_3$; $R'' = n\text{-}C_3H_7$).

Calculated yields[14] of all materials, including alkyl iodides[15] are in excellent agreement with the experimentally determined values over a rather wide range of initial concentrations. Thus it would appear that the neglect of activity coefficients when computing transalkylation equilibrium constants is permissible. A number of equilibrations were studied in order to determine the sensitivity of K_1 and K_2 to structure. The results are given in Table IV. In every case, agreement between experimentally determined and calculated distributions was excellent.

TABLE IV

EQUILIBRIUM DATA—METHYLPHOSPHONATE TRANSALKYLATION[a]

R′	R″	X[b]	K_1	K_2	K_1/K_2
CH_3	C_2H_5	I	26.0	6.0	4.3
CH_3	C_3H_7	I	18.3	4.3	4.3
CH_3	C_2H_5	OTs	1.87	0.44	4.3
CH_3	C_3H_7	OTs	1.94	0.44	4.4

[a] Temperature, 130°. [b] Equilibration time, 120–140 hr for iodides, 24–40 hr for tosylates.

It is important to notice that the value of the derived equilibrium constant for reaction 3, K_1/K_2, is quite close to the value $K_1/K_2 = 4$, calculated for a random distribution of substituents, *both* for the methyl–ethyl and methyl–propyl cases. Thus the results indicate that the equilibrium constant for reaction 3 should be almost totally controlled by entropy, with essentially zero enthalpy. This prediction was confirmed by allowing equimolar amounts of dimethyl and dipropyl methylphosphonate to react in the presence of a catalytic amount of methyl tosylate. After 20 days at 130° the mixture contained 24.4% dimethyl methylphosphonate, 24.4% dipropyl methylphosphonate, and 51.1% methyl propyl methylphosphonate; the composition of the mixture was unchanged after 20 additional days. The equilibrium constant thus obtained was 4.4, in excellent agreement with the derived constants found in Table IV, cases 2 and 4. The behavior of reaction 3 is consistent with a number of "redistribution" reactions studied by Van Wazer and associates.[16–19]

The values for K_1 and K_2 which correspond to a random distribution of substituents are 2 and 0.5, respectively. Thus it is clear that the transalkylation with iodides is not strictly entropy controlled in the cases studied, while the tosylate transalkylations closely approximate random scrambling. The obvious conclusion is that the tosylates have more nearly equal free energies of formation than do the iodides. Unfortunately, a rather thorough search of the literature revealed no useful free-energy data for alkyl iodides and tosylates. Consequently, it is suggested that the phosphonate transalkylation might be used profitably in the study of free-energy relationships in homologous series of alkyl halides and related derivatives. Thus, assuming an equilibrium constant of 4 for all reactions of type 3 gives −1110 cal for the $\Delta G°$ of the reaction.[20] If the free energy of formation of a cross-product is assumed to be 555 cal more negative than that of either unscrambled material, then $K_1 = 18.3$ for the methyl iodide–propyl iodide system gives $\Delta\Delta G°_{CH_3I-C_3H_7I} = -1773$ cal, while $K_2 = 4.3$ gives −1723 cal, for an average of −1748 cal. In the same manner, $\Delta\Delta G°_{CH_3I-C_2H_5I} = -2022$ cal at 130°.[21] As a cross-check on the consistency of these values, the ethyl–propyl transalkylation was studied. At 130°, the $\Delta\Delta G°_{C_2H_5I-C_3H_7I}$ should be 274 cal; using 555 cal as the free-energy difference between phosphonates as described above gives $K_1 = 1.4$, $K_2 = 0.36$. The experimentally determined constants were in complete agreement; the

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[14] A computer program was written to solve the two equilibrium expressions by successive approximations. A FORTRAN IV listing is available upon request.

[15] For the sake of brevity, analytical data for methyl and propyl iodide were not included in Table III.

[16] K. Moedritzer, G. M. Burch, J. R. Van Wazer, and H. K. Hofmeister, *Inorg. Chem.*, **2**, 1152 (1963).

[17] L. C. D. Groenwehge and J. H. Payne, *J. Amer. Chem., Soc.*, **81**, 6357 (1959).

[18] For an early quantitative study of an entropy-controlled process, see G. Calingaert and H. A. Beatty, *ibid.*, **61**, 2748 (1939).

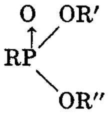
[19] For a recent review of the subject, see J. R. Van Wazer and K. Moedritzer, *Angew. Chem. Intern. Ed. Engl.*, **5**, 341 (1966).

[20] The assumption should be valid in the absence of steric crowding. Research will begin presently to study this matter in more detail.

[21] The assumption that both unscrambled phosphonates have the same free energy of formation may be unjustified. In this event, the $\Delta\Delta G°$ values reported above would be in error.

TABLE V

REFRACTIVE INDEX AND THERMAL CONDUCTIVITY RESPONSE DATA FOR PHOSPHONATES



R	R′	R″	Registry No.	Method of prepn	$n^{20}D$	Thermal response[a]
CH_3	CH_3	CH_3	756-79-6	M-A[b]	1.4136	100
CH_3	CH_3	C_2H_5	18755-36-7	T[c]	1.4136	108[d]
CH_3	C_2H_5	C_2H_5	683-08-9	M-A	1.4141	125
CH_3	CH_3	C_3H_7	683-25-0	T	1.4171	115
CH_3	C_2H_5	C_3H_7	18755-38-9	T		131[d]
CH_3	C_3H_7	C_3H_7	6410-56-6	T	1.4200	140
CH_3	CH_3	C_4H_9	683-32-9	T	1.4222	125[d]
CH_3	C_4H_9	C_4H_9	2404-73-1	T	1.4263	168
C_2H_5	CH_3	CH_3	6163-75-3	T	1.4168	108[d]
C_2H_5	CH_3	C_2H_5	5301-65-5	T	1.4170	116[d]
C_2H_5	C_2H_5	C_2H_5	78-38-6	M-A	1.4166	131
C_3H_7	CH_3	CH_3	18755-43-6	T	1.4214	115[d]
C_3H_7	CH_3	C_3H_7	18755-44-7	T	1.4236	140[d]
C_3H_7	C_3H_7	C_3H_7	1789-95-3	T, M-A	1.4245	150–160[d]

[a] Relative molar response to a thermal conductivity detector, based on 100 for R = R′ = R″ = CH_3. [b] Michaelis–Arbuzov reaction. [c] Transalkylation. [d] Estimated.

best computer fit for four trials was for $K_1 = 1.4$, $K_2 = 0.36$. However, the possibility that this agreement is a fortunate coincidence can not be ignored;[21] additional work is needed in this area.

Synthetic Utility.—The reversibility of the transalkylation can not be ignored when considering synthetic applications. Only in the phosphonate–halide case involving production of a lower boiling halide can the equilibrium be displaced by product removal. The following situations show the advantages and limitations of transalkylation in phosphonate synthesis. It is felt that the methods suggested here compare favorably with current synthetic methods.[22,23]

Preparation of Mixed Phosphonates, RP(→O)(OR′)OR″.—The size of the equilibrium constant for reaction 3 places the upper limit of mixed phosphonate produced during transalkylation at about 50%; the ratio of reactants to get the maximum yield would depend on the size of the equilibrium constants. However, a yield of 40% or better is realized over a rather wide range of initial conditions. Product isolation in small amounts can be routinely performed by glpc, whereas isolation by fractional distillation is successful only if the phosphonates differ in mass by at least three carbon atoms.

Preparation of Phosphonates of the Type RP(→O)(OR′)$_2$.[13]—Dimethyl propylphosphonate is an example of this situation. As mentioned in the introductory remarks, compounds of this type are difficult to prepare by the Michaelis–Arbuzov reaction. A material of considerably higher purity should be realized by performing a transalkylation on dipropyl propylphosphonate. Inspection of the equilibrium constants in Table IV points to methyl tosylate as the preferred alkylating agent. In order to determine the minimum amount of tosylate necessary to get pure product, a computer analysis using hypothetical starting mixtures was performed. The assumption was made that $K_1 = 1.94$ and $K_2 = 0.44$. With a 20:1 ratio of tosylate to phosphonate, the dimethyl propylphosphonate at equilibrium would amount to only 83% of total phosphonate. Rather than go to higher and higher tosylate–phosphonate ratios in order to force the reaction to completion, a "multipass" approach was tried. Between each pass, the phosphonate mixture would be separated from the tosylate mixture and treated with fresh methyl tosylate. Using three passes, each with a 6:1 tosylate–phosphonate ratio, a product of 97% purity should be obtained, whereas a 10:1 ratio should produce a product of 99% purity. Owing to the high-boiling system, the reaction need not be performed in a sealed tube.

Preparation of Phosphonates of the Type RP(→O)(OR″)$_2$.—The preparation of dipropyl methylphosphonate is representative. The Michaelis–Arbuzov reaction of tripropyl phosphite and methyl iodide produces this compound in good purity; the only problem is obtaining reasonably pure tripropyl phosphite. As an attractive alternate, the transalkylation of dimethyl methylphosphonate with propyl iodide is suggested. Two passes using a 6:1 ratio of iodide to phosphonate should produce a material of over 99% purity. This was verified experimentally. Alternately, one pass with a 20:1 iodide–phosphonate ratio should produce a 97–98% pure product.

Extension to Other Systems.—It is reaonable to assume that equilibrium constants for other interchange reactions[24] could be determined. However, the slow rate of reaction in some cases would cause difficulty. For example, the reaction of methyl iodide and ethyl tosylate in a 24:1 ratio at 150° for 100 hr produced only 5% ethyl iodide and methyl tosylate. After 90 hr at 180°, the yield increased to 38%, and it is likely that this does not represent equilibrium. Additional research is under way in this area.

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[22] E. Gryszkiewicz-Trochimowski, M. Bousquet, and J. Quinchon, *Bull. Soc. Chim. Fr.*, 1222 (1961).

[23] N. Thoung, F. Convert, G. Martin, and P. Chabrier, *ibid.*, 1925 (1965).

[24] I. P. Gragerov, *Vopr. Khim. Kinetiki, Kataliza, i Reaktsionnoi Sposobnosti, Akad. Nauk SSSR, Otd. Khim. Nauk*, 36 (1955); *Chem. Abstr.*, **50**, 4599*f* (1956).

Experimental Section

Materials.—All alkyl halides were commercially available; they were redistilled before use. Propyl tosylate was prepared by the usual method; methyl tosylate and ethyl tosylate were obtained from commercial sources, and were recrystallized prior to use. Phosphonates were prepared by the Michaelis–Arbuzov reaction and by transalkylation. Many of the phosphonates are new compounds; the rather routine identification by nmr was based upon peak position, intensity, and multiplicity. Table V contains useful phosphonate data.

Analysis Procedure.—All phosphonates were analyzed by glpc, using a 5 ft × $\frac{1}{8}$ in. stainless steel column containing 4% QF-1 (fluorosilicone) on 80/100 mesh acid-washed and silanized Chromosorb G. Alkyl iodides were analyzed on a 3 ft × 0.25 in. copper column containing 18% tricresyl phosphate on 60/80 mesh untreated firebrick. Two columns were used for preparative work involving phosphonates, a 3 ft × 0.25 in. copper column containing 20% Carbowax 20M on 60/80 mesh untreated firebrick, and a 6 ft × 0.25 in. copper column containing 5% UCON LBX 550 on 80/100 mesh acid-washed and silanized Chromosorb G. A Micro-Tek chromatograph equipped with glass-lined injector block and thermal conductivity detectors was used for both analytical and preparative work. Thermal conductivity response factors are included in Table V; the estimated values are either interpolations or extrapolations from known values.

Reaction Procedure.—The reactions below are representative.

A. Reaction of Diethyl Ethylphosphonate with Methyl Tosylate.—A mixture of 1.66 g (0.01 mol) of diethyl ethylphosphonate and 9.3 g (0.05 mol) of methyl tosylate contained in a 25-ml pear-shaped flask equipped with thermometer, reflux condenser, and drying tube was heated at *ca.* 140° for 3.5 hr. The phosphonate mixture was then separated from the tosylate mixture by vacuum distillation at 0.3–0.5 mm. Glpc analysis of an ether solution of the distillate indicated that the product distribution was 43% dimethyl ethylphosphonate, 46% methyl ethyl ethylphosphonate, and 11% diethyl ethylphosphonate. The over-all recovery of phosphonate was 95%. Analysis of the residual tosylate mixture by nmr indicated a methyl tosylate–ethyl tosylate ratio of 2.8:1, the value predicted from the phosphonate distribution.

B. Reaction of Dimethyl Methylphosphonate with Propyl Iodide.—A mixture of 0.62 g (0.005 mol) of dimethyl methylphosphonate and 1.133 g (0.0067 mol) of propyl iodide was heated in an oil bath at 130 ± 0.5° in a heavy-walled tube for 140 hr. Analysis of the product indicated 17.5% dimethyl methylphosphonate, 49.7% methyl propyl methylphosphonate, and 32.8% dipropyl methylphosphonate; the over-all recovery was 93%. Analysis of the alkyl halides indicated 85.9% methyl iodide and 14.1% propyl iodide, with an over-all recovery of 96%.

C. Preparation of Dipropyl Methylphosphonate.—A mixture of 6.2 g (0.05 mol) of dimethyl methylphosphonate and 51 g (0.30 mol) of propyl iodide was allowed to react in a heavy-walled tube for 96 hr at 130°. The tube was then opened, the contents was placed in a distillation apparatus, and the methyl iodide was distilled. The phosphonate–propyl iodide mixture was then returned to the tube, and additional propyl iodide was introduced such that 0.3 mol was again present. After 48 hr at 130°, the tube was again opened and the product distilled. In this manner, 7 g (78%) of a material boiling at 86–87° (6 mm) was obtained, $n^{20}\text{D}$ 1.4201 [lit.[22] bp 95–96° (10 mm), $n^{20}\text{D}$ 1.4200]. Analysis by glpc indicated a purity of 99.5%.

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Diaryliodonium Salts from Aryllithium Reagents with *trans*-Chlorovinyliodoso Dichloride[1,2]

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A new synthetic route to symmetrical diaryliodonium salts used the low-temperature reaction of *trans*-chlorovinyliodoso dichloride with 2 equiv of aryllithium and gave fair to excellent yields of diphenyliodonium, di-*p*-tolyliodonium, di-1-naphthyliodonium, di-2-naphthyliodonium, di-9-anthryliodonium, and dibenziodolium salts. An extension of this method allows the synthesis of unsymmetrical diaryliodonium salts.

Synthesis of diaryliodonium salts[4] is generally accomplished by the electrophilic attack of a polyvalent

$$\text{Ar}\overset{+}{\text{I}}\text{OH} + \text{Ar'H} \xrightarrow{-\text{H}_2\text{O}} \text{Ar}\overset{+}{\text{I}}\text{Ar'}$$

$$\text{ArICl}_2 + \text{Ar'Li} \xrightarrow[-\text{Cl}^-]{-\text{LiCl}} \text{Ar}\overset{+}{\text{I}}\text{Ar'}$$

iodine species on an aromatic system.[5,6] These syntheses cannot be used, however, if the iodoso compounds cannot be prepared or if they are not stable; 1-naphthyliodoso dichloride is one such example.[6]

Our new approach involved the following steps: (a) preparation of a compound Cl–Z–ICl_2, such that Z represents a masking group inert to ArLi under the reaction conditions; (b) reaction of Cl–Z–ICl_2 with 2 equiv of ArLi, forming Cl–Z–IAr_2; and (c) removal of Z to form $\text{Ar}_2\text{I}^+\text{Cl}^-$. Several considerations lead to the selection of the group –CH═CH– as Z; the reactions can now be formulated more specifically.

There were four reasons for believing in the possibility of the final ionic elimination: (a) the intermediate phenyl(β-chlorovinyl)iodonium chloride with base yields acetylene,[7] (b) the large size of the IAr_2

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(3) Taken from the dissertation of R. A. Nathan to be submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree.

(4) Polyvalent organoiodine compounds: D. F. Banks, *Chem. Rev.*, **66**, 243 (1966).

(5) J. B. Briody, *J. Chem. Soc., B*, 93 (1968).

(6) F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Amer. Chem. Soc.*, **82**, 2948 (1960).

(7) Aryl(*trans*-chlorovinyl)iodonium salts and bis(*trans*-chlorovinyl)iodonium salts are known.[8,9] The authors report that all of these iodonium salts liberate acetylene near their melting points or with acid or base.