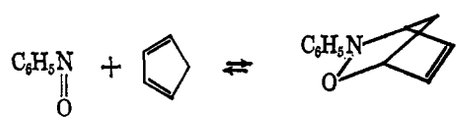
small, except for methanol where the equilibrium is shifted somewhat to the 1,3 cycloadduct. Although methanol could not be employed as a solvent in the determination of the reaction rate in Table I, the reported[4] value for ethanol falls in the same range. The interpretation of the influence of methanol on the equilibrium constant is not immediately apparent.

In order to determine the thermodynamic parameters the equilibrium constant was measured at several temperatures in dichloromethane, as summarized in Table III. A plot (Figure 1) of log K *vs.* $1/T$ provided the

TABLE III

EQUILIBRIUM CONSTANT DETERMINATION IN DICHLOROMETHANE AT VARIOUS TEMPERATURES



Temp, ±0.1°	K^a (av)	No. of detn
25	13.23	4
20	21.04	3
15	31.37	4
10	49.20	3

[a] Maximum deviation from average value 1.1%.

standard heat of reaction from the slope of the straight line, using the Gibbs–Helmholtz equation. The standard heat of reaction was found to be −14.8 kcal/mole, the standard entropy change −44.6 eu, and the standard free energy change −1.5 kcal at 25°.

The standard entropy change is of the order of magnitude reported for "conventional" Diels–Alder reactions,[3] although a bit on the low side. On the other hand, the standard heat of reaction is somewhat on the high side.

Since at low temperature (about −70°) the 1,4-cycloadduct of 1,3-cyclopentadiene and nitrosobenzene can be isolated,[9,10] an opportunity was provided to study a retrograde 1,4 cycloaddition reaction at convenient temperatures. The rate of the dissociations was found to follow the sample first-order rate equation at the initial intervals of time, since the rate of dissociation of the cycloadduct was fast compared with the rate of formation of the cycloadduct or around room temperature. However, the difficulties encountered in the purification of the cycloadduct, because of its tendency to revert to its components, precluded measurement of the rate constant with the accuracy necessary to obtain meaningful data.

(9) N. L. Hepfinger, Ph.D. Dissertation, University of Pittsburgh, 1963.
(10) G. Kresze and G. Schulz, *Tetrahedron*, **17**, 7 (1961).

Experimental Section

The technique of the spectrophotometric kinetic measurements have been described in detail in previous papers.[5-7]

1,3-Cyclopentadiene (bp 39–40°, $n^{22}D$ 1.4446) was prepared by pyrolytic depolymerization and distillation of the commercially available dicyclopentadiene at atmospheric pressure.[11] The purity of the monomer was ascertained by gas–liquid partition chromatography. The Perkin-Elmer Model 154 gas chromatograph was also used for this analysis with 20% QF-1 on Chromosorb P 30–60 mesh column packing. The gas–liquid partition chromatographic analyses of the cyclopentadiene was carried out at two different column temperatures (~100 and ~180°) to ascertain the absence of impurities such as cyclopentane or polymerized cyclopentadiene. In each case a single peak was obtained.

3-Phenyl-2-ox-3-azabicyclo[2.2.1]hept-5-ene was prepared by the reaction between nitrosobenzene (5.35 g, 0.05 mole), and 1,3-cyclopentadiene (29.7 g, 0.45 mole), in diethyl ether (50 ml). The reaction mixture was allowed to stand for 12 hr at about −5° in an ice–salt bath. The solvent was then evaporated under vacuum at ice-bath temperature and the residue was extracted with five 50-ml portions of cold pentane. The pentane extracts were cooled to −70° in a Dry Ice–acetone bath until crystallization was complete, then filtered through a jacketed sintered-glass funnel which was cooled with powdered Dry Ice. The funnel was immediately closed with a tight-fitted one-hole stopper through which nitrogen gas was admitted. Drying of the product was achieved by passing cold dry nitrogen through the colorless crystals. The product was further purified by repeating the same sequence. The samples used for kinetic studies were recrystallized twice, mp 32° (lit.[9,10] 32–34°), yield 72–75%.

(11) G. Wilkinson, *Org. Syn.*, **36**, 31 (1956).

Reactions of α-Keto *p*-Toluenesulfonates with Trialkyl Phosphites[1]

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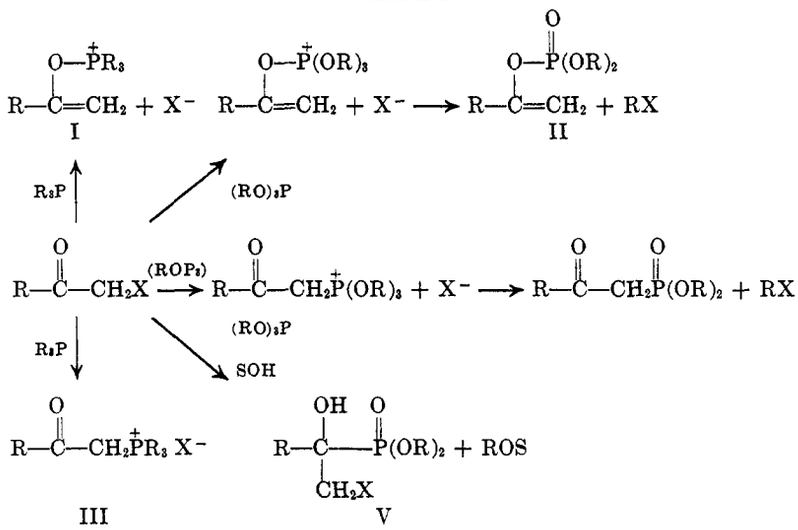
The α-keto *p*-toluenesulfonates, $RCOCH_2OSO_2C_6H_4CH_3$, R = C_6H_5, CH_3, $(CH_3)_3C$, have been allowed to react with trimethyl and/or triethyl phosphite. In all cases vinyl phosphates, the Perkow reaction product, were formed. Reactions of two of these *p*-toluenesulfonates, R = C_6H_5, $(CH_3)_3C$, with triphenylphosphine and tributylphosphine, respectively, yielded the C-phosphonium salts. No enol phosphonium salts were detected. These results are discussed from a mechanistic point of view and are related to the mechanisms of the Perkow reaction and similar displacement processes.

The reactions of α-halocarbonyl compound with various phosphorus containing nucleophiles have been the subject of extensive study.[2] The products formed from these reactions are of several general structural types. It has become increasingly clear that the product(s) obtained from any given reaction depend on the nature of the nucleophile, the structure of the α-halocarbonyl compound and the reaction conditions. Typical products from the reaction of a trialkyl phosphite and an α-halo ketone are the vinyl phosphate, II, the Perkow reaction product, and an α-keto phosphonate, III, the Arbusov reaction product; when alcohols or acetic acid is present, α-hydroxy phosphonates, V, are

(1) This research has been supported by the National Science Foundation under NSF GP202 and GP4997.

(2) For general reviews, see (a) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961); (b) B. Miller, "Topics in Phosphorus Chemistry," Vol., 2, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons Inc., New York, N. Y., 1965, pp 178–187.

SCHEME I

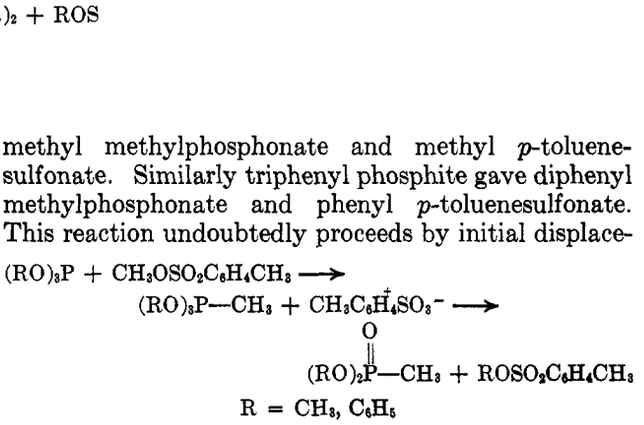


often formed. Trisubstituted phosphines react to give enol phosphonium salts, I, and phosphonium salts, III (see Scheme I).

Recent studies of these reactions have been particularly concerned with their mechanisms. It has long been recognized that α-halocarbonyl compounds provide a variety of positions for nucleophilic attack and that these reactions can proceed simultaneously and thus lead to a variety of products. In the case of phosphorus containing nucleophiles this also holds true. It is also becoming increasingly evident that modifications in the nucleophilicity of the phosphorus atom has a profound effect on its mode of reaction.[3] In particular trisubstituted phosphites differ in their reactivity and mode of reaction from trisubstituted phosphines. In the reactions of these substances with α-halocarbonyl compounds structurally similar products are often obtained and for this reason it has often been assumed that similar products, for example enol-phosphonium salts and vinyl phosphates, arise by similar reaction mechanisms. Although this kind of reasoning may lead to valid conclusions it is by no means certain that it will.

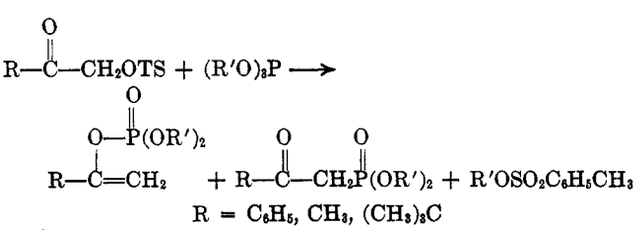
One of the suggested paths for the reaction of an α-halo ketone with a trisubstituted phosphite or phosphine involves nucleophilic displacement on halogen to give a halophosphonium salt and an enolate ion. Product formation then proceeds by further reaction of these ions. It was the purpose of this work to investigate reactions of α-substituted ketones which possess a good leaving group but whose properties are such that nucleophilic displacement reactions upon it were not feasible. The leaving group chosen was *p*-toluenesulfonate. This well-known leaving group behaves similarly to halogen in most displacement reactions except that displacement reactions on an oxygen of the sulfonate are not known, whereas nucleophilic displacement on halogen is well documented.[4]

Earlier work has shown that methyl *p*-toluenesulfonate reacts with trimethyl phosphite to give dimethyl methylphosphonate and methyl *p*-toluenesulfonate. Similarly triphenyl phosphite gave diphenyl methylphosphonate and phenyl *p*-toluenesulfonate. This reaction undoubtedly proceeds by initial displacement on the methyl carbon atom to give a pair of ions which then react to give the observed products.[5] These results show clearly that normal displacement reactions do occur between phosphites and *p*-toluenesulfonates and thus confidence can be had that the α-keto *p*-toluenesulfonates can also react in a conventional manner if no alternatives are presented to them.



Results and Discussion

The *p*-toluenesulfonate esters were prepared by allowing an α-halo ketone to react with silver *p*-toluenesulfonate in acetonitrile. Three esters were prepared. They were the phenacyl, acetonyl, and pinacolyl derivatives. These materials were then allowed to react with triethyl and/or trimethyl phosphite under a variety of conditions. Product analyses were conducted in the main by nmr spectroscopy. Known reactions of the phosphites with α-halo ketones were employed to obtain standard samples for nmr comparison studies. Attempts to analyze reaction mixtures by glpc led to erratic results. Toward the end of this investigation an instrument with glass injection ports was obtained. This gave reliable and reproducible results. Un-



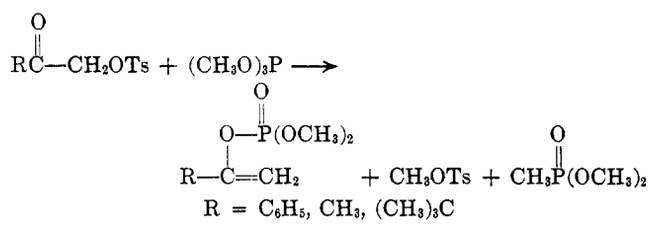
(3) (a) J. I. G. Cadogan, *Quart. Rev.* **16**, 208 (1962); (b) Reference 2b. (c) R. G. Harvey and E. R. DeSombre in "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 57–111.

(4) (a) R. N. Hazeldine and B. O. West, *J. Chem. Soc.*, 3631 (1956); (b) D. W. Grisley, Jr., *Tetrahedron Letters*, 435 (1963).

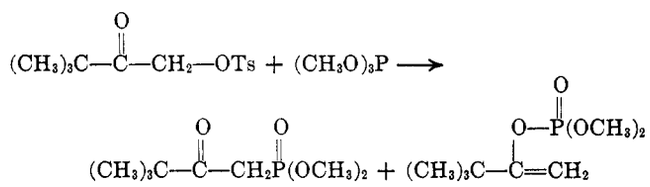
(5) (a) T. C. Myers, S. Preis, and E. V. Jensen, *J. Am. Chem. Soc.*, **76**, 4172 (1954); (b) D. B. Denney and J. Giacin, *Tetrahedron Letters*, **No. 26**, 1747 (1964).

fortunately, most of the vinyl phosphates had decomposed so except for a few isolated cases analyses for vinyl phosphates is based on nmr evidence. Phosphonates were analyzed for both by nmr and glpc.

Reaction of phenacyl, acetonyl and pinacolyl *p*-toluenesulfonates with trimethyl phosphite at room temperature yielded vinyl phosphates. Methyl *p*-toluenesulfonate which was formed during the reaction

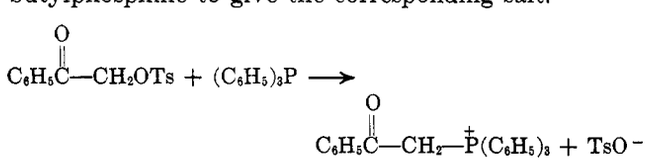


reacted with trimethyl phosphite to give dimethyl methylphosphonate and to regenerate methyl *p*-toluenesulfonate. The phenacyl *p*-toluenesulfonate was allowed to react with triethyl phosphite at room temperature. Again vinyl phosphate was formed. No keto phosponate was obtained as a product of this reaction at the temperature used. Reaction of pinacolyl *p*-toluenesulfonate with excess trimethyl phosphite at reflux yielded a mixture of the vinyl phosphate and the phosphonate. This phosphonate was also formed to the apparent exclusion of the vinyl phosphate when



bromopinacalone was allowed to react with trimethyl phosphite at *ca.* 100° or at room temperature.

Reaction of phenacyl *p*-toluenesulfonate with triphenylphosphine both in the presence and absence of excess methanol yielded the phosphonium salt. Similarly pinacolyl *p*-toluenesulfonate reacted with tri-*n*-butylphosphine to give the corresponding salt.

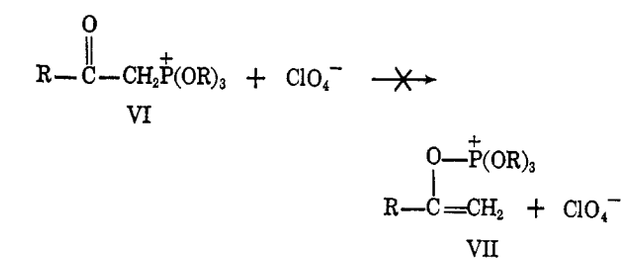


The results of these experiments have an important bearing on the mechanisms of the formation of vinyl phosphates and phosphonates. The ready and almost exculsive formation of vinyl phosphates from the reactions of the *p*-toluenesulfonate esters demonstrates clearly that an α-halogen is not required for this reaction. It should be noted that one might expect formation of phosphonates at higher temperatures and this was observed in the reaction of pinacolyl *p*-toluenesulfonate with trimethyl phosphite. At room temperature the *p*-toluenesulfonates react much like α-chloro ketones which give little or no phosphonates; they do give increasing amounts of phosphonates as the temperature is raised.

It has been suggested[6] that vinyl phosphate and phosphonate are formed by displacement on halogen to give an enolate ion and an halotrialkoxyphosphonium cation. These are then postulated to combine to give ions, I and III. Such a reaction path for the *p*-toluenesulfonate reactions would require displacement by the nucleophile on an oxygen of the ester. This kind of displacement process is without precedent and there seems to be no reason or need for suggesting it here.

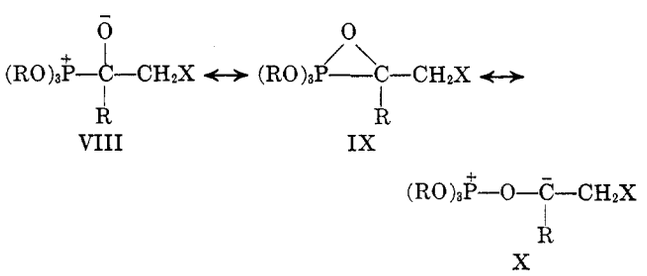
The results of these experiments do not prove that α-halo ketones do not react with phosphites by displacement on halogen, however, in view of the correspondence of the reaction products to the products of the *p*-toluenesulfonate reactions consideration of alternative mechanisms seems imperative.

Recently, Hudson and co-workers[7] have discussed the mechanism of formation of vinyl phosphate. They have shown that salts, VI, are stable and show no



tendency to rearrange to, VII, under conditions of the Perkow reaction. They conclude therefore that salts, VI, are not intermediates in the Perkow reaction. On the basis of studies of the reactions of several halogenated ketones these workers have concluded that attack by phosphite on the carbonyl group is the most likely initial step in vinyl phosphate formation. The results from the *p*-toluenesulfonate reactions support this contention.

The exact details of the reaction of the carbonyl group with the trialkyl phosphite are still obscure. At various times it has been suggested that the initial attack involves addition to the carbonyl carbon to give VIII which rearranges *via* IX to X which then loses X^- to



give the enol phosphonium salt. Alternatively rearrangement with simultaneous expulsion of X^- can be considered. The other major mechanistic proposal involves attack by the phosphite on the carbonyl oxygen with simultaneous expulsion of X^-. As yet no experimental distinction has been made between these various proposals, however, it should be pointed out that phosphorus containing nucleophiles are different from the more common nucleophiles in that they can form pentacovalent substituted compounds or intermediates. This may well be the key to an understanding of the Perkow reaction. Attack by the phosphite may give the resonance hybrid of which VIII, IX, and

(6) (a) A. J. Speziale and L. R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962); (b) I. J. Borowitz and R. Virkhaus, *ibid.*, **85**, 2183 (1963); (c) B. Miller, *J. Org. Chem.*, **28**, 345 (1963).

(7) (a) P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965); (b) R. F. Hudson and G. Salvadori, in press.

X are major contributors. Reaction of this hybrid with SOH can lead to hydroxy phosphonates, V, whereas in the absence of hydroxylic solvents decomposition to enol phosphonium salts, I, occurs.

This mechanism also accounts for the very real difference in reactivity and mode of reactions of phosphites and phosphines. Addition of a trisubstituted phosphine to a carbonyl group undoubtedly occurs, however, it is known that trialkyl- and triaryldialkoxyphosphoranes are very unstable[8] and thus one expects very little or no contribution from IX to the addition product. If this is required for the formation of the vinyl phosphonium salt then the lack of formation of such products can be understood.

The phosphines react in an entirely normal fashion with the α-keto *p*-toluenesulfonates studied. Exclusive phosphonium salt formation is consistent with direct displacement on carbon. A similar observation has been made by Hoffman and Beller.[9] They have found that the *p*-toluenesulfonate of benzoin reacts with triphenylphosphine to give the β-keto phosphonium salt. By contrast α-benzoylbenzyl chloride gave only enol phosphonium salt. This reaction involves attack on halogen which may, in some cases at least, proceed with simultaneous phosphorus–oxygen bond formation.[10]

In summary it seems reasonable to conclude that the reaction of trialkyl phosphites with simple α-haloketones and aldehydes proceeds by addition to the carbonyl group. A pentasubstituted intermediate may be formed which decomposes to an enol phosphonium salt. It should be noted that α-halo compounds which can yield very stable anions by displacement on halogen could well react in this manner with a trisubstituted phosphite. Similarly hydroxylic solvents may change the position of displacement.[7b] Clearly caution is required in attempting to reach general mechanistic conclusions in this series of reactions.

Experimental Section[11]

Phenacyl *p*-Toluenesulfonate.—To a stirred solution of 31.0 g (0.11 mole) of silver *p*-toluenesulfonate in 150 ml of dry purified acetonitrile was added dropwise 22.1 g (0.11 mole) of phenacyl bromide in 40 ml of acetonitrile. After the addition the mixture was heated at 50° with stirring for 3 days. The cooled reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was triturated with chloroform which was evaporated to give crude phenacyl *p*-toluenesulfonate. Recrystallization from carbon tetrachloride afforded material, mp 100–101° (lit.[12] 99–100°) in 70% yield. The infrared spectrum was in accord with that expected for the proposed structure. The nmr spectrum was also in complete accord with that expected: aromatic absorptions centered at 7.6, CH_2 at 5.3, and CH_3 at 2.4 ppm. The areas under these absorptions were in the correct ratio.

Acetonyl *p*-Toluenesulfonate.—A mixture of 4.11 g (0.03 mole) of bromoacetone and 8.43 g (0.03 mole) of silver *p*-toluenesulfonate was heated in dry acetonitrile for 10 hr at 60°. Concentration and extraction of the residue with 40–50 ml of hot carbon tetrachloride afforded a solution of the product which was isolated by distillation bp 139–140° (0.15 mm). There was obtained 2.2 g, 31% of product. The infrared spectrum had carbonyl absorption at 5.7 μ. The nmr spectrum showed single peaks at 2.08 ppm (alkylmethyl protons), 2.39 ppm (aromatic methyl protons), 4.45 ppm (methylene protons), and a typical A_2B_2 pattern centered at 7.45 ppm (aromatic protons). The areas were in accord with the proposed structure.

The preparation was difficult to duplicate and on several occassions no product was obtained. This compound has been obtained as a low melting, 27–28°, solid by reaction of diazoacetone with *p*-toluenesulfonic acid.[12]

Pinacolyl *p*-Toluenesulfonate.—A mixture of 10.7 g (0.06 mole) of bromopinacolone and 16.7 g (0.06 mole) of silver *p*-toluenesulfonate in 100 ml of acetonitrile was heated under reflux with stirring for 24 hr. Filtration followed by evaporation of the solvent afforded a residue which was triturated with ether. Evaporation of the ether and cooling of the residue afforded a solid which was recrystallized twice from ether–pentane. There was obtained 4.2 g, 25%, of pinacolyl *p*-toluenesulfonate, mp 70–71°.

Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.75; H, 6.71; S, 11.8. Found: C, 57.41; H, 6.96; S, 11.55.

The infrared spectrum had carbonyl absorption at 5.7 μ. The nmr spectrum had peaks at 1.10 ppm (alkyl methyl protons), 2.40 ppm (aromatic methyl protons), 4.83 ppm (methylene protons), and an A_2B_2 pattern centered at 7.51 ppm (aromatic protons). The areas were in accord with the proposed structure.

Reaction of Bromopinacolone with Trimethyl Phosphite.—Bromopinacolone[13] (17.9 g, 0.1 mole) was heated with 12.4 g (0.1 mole) of trimethyl phosphite for 20 hr at 90–100°. Distillation of the reaction mixture afforded a major fraction, bp 73–74° (0.25 mm). There was obtained 14.8 g (71%) of dimethyl pinacolylmethylphosphonate. This structure was assigned on the basis of a carbonyl absorption at 5.85 μ in the infrared spectrum and the nmr spectrum which had a doublet at 3.68 ppm (J = 11 cps) (methoxy protons), a doublet at 3.25 ppm (J = 22 cps) (methylene protons), and a singlet at 1.15 ppm (methyl protons). The areas were in accord with those calculated for the proposed structure.

Anal.[14] Calcd for $C_8H_{17}O_4P$: C, 46.15; H, 8.23; P, 14.87. Found: C, 45.19; H, 8.11; P, 14.81.

In another reaction, 2.7 g (0.015 mole) of bromopinacolone and 1.86 g (0.015 mole) of trimethyl phosphite were allowed to stand at room temperature. After 6 days the nmr spectrum indicated that dimethyl pinacolylmethylphosphonate had been formed but that significant quantities of bromopinacolone remained and that dimethyl methylphosphonate had also been formed. Methyl bromide was also present. Excess trimethyl phosphite was added and the mixture was allowed to stand 3 days. At this time a small amount of bromopinacolone remained. Glpc analysis showed that dimethyl pinacolylmethylphosphonate was the major product.

Reaction of Pinacolyl *p*-Toluenesulfonate with Trimethyl Phosphite at Room Temperature.—Pinacolyl *p*-toluenesulfonate (1.35 g, 0.005 mole) was allowed to react at room temperature with 0.62 g (0.005 mole) of trimethyl phosphite. After 8 days the nmr spectrum showed that starting material was present as well as dimethyl methylphosphonate. A multiplet was also present at 4.66 ppm. This has been assigned to the vinyl protons of dimethyl 1-*t*-butylvinyl phosphate. Excess trimethyl phosphite was added to the reaction mixture. After 20 days the nmr spectrum showed that further reaction had occurred but that some starting *p*-toluenesulfonate still remained. Analysis by glpc indicated that no dimethyl pinacolylmethylphosphonate was present. Addition of this compound and reanalyses indicated that it could be detected within the capabilities of the instrument.

Reaction of Pinacolyl *p*-Toluenesulfonate with Trimethyl Phosphite under Reflux.—Pinacolyl *p*-toluenesulfonate (4.65 g, 0.0172 mole) was mixed with trimethyl phosphite (21.3 g, 0.172 mole) and heated under reflux for 4 hr. The nmr spectrum indicated that both dimethyl 1-*t*-butylvinyl phosphate and dimethyl pinacolyl phosphonate were formed. Distillation gave a broad

(8) (a) D. B. Denney, H. Relles, and A. K. Tsolis, *J. Am. Chem. Soc.*, **86**, 4487 (1964); (b) D. B. Denney and H. Relles, *ibid.*, **86**, 3897 (1964); (c) D. B. Denney and S. T. D. Gough, *ibid.*, **87**, 138 (1965); (d) D. B. Denney and H. Relles, *Tetrahedron Letters*, **No. 11**, 573 (1964).

(9) Reported by H. Hoffman and H. J. Diehr, *Angew. Chem.*, **76**, 944 (1964).

(10) D. B. Denney and N. Gershman, *Tetrahedron Letters*, **No. 43**, 3899 (1965).

(11) Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137. Nmr spectra were obtained with a Varian Model A-60 spectrometer using tetramethylsilane, 0 ppm, as internal standard. Gas–liquid phase chromatograms were obtained with a Perkin-Elmer Model 801 gas chromatograph. A 6 ft × 1/8 in. SE-30 column with a helium flow rate of *ca.* 30 ml/minute was used for the analyses.

(12) A. L. Crowther and G. Holt, *J. Chem. Soc.*, 2818 (1963).

(13) Prepared according to the procedure of M. Jackman, M. Klenk, B. Fishburn, B. F. Tullar, and S. Archer, *J. Am. Chem. Soc.*, **70**, 2884 (1948).

(14) The low value obtained for carbon is probably due to the difficulty of its analyses when phosphorus is present.

boiling point range; so arbitrary fractions were taken. Analysis by nmr of these fractions indicated that dimethyl pinacolylphosphonate had been concentrated in one of them. This was confirmed by glpc analysis which showed it to be present.

Reaction of Phenacyl *p*-Toluenesulfonate with Trimethyl Phosphite.—Phenacyl *p*-toluenesulfonate (2.7 g, 0.01 mole) was allowed to react with 1.24 g (0.01 mole) of trimethyl phosphite in 35 ml of ether. The mixture was allowed to stand for 4 days and was then heated under reflux for 2 days. The nmr spectrum of the residue after removal of the ether showed that dimethyl 1-phenylvinyl phosphate was a major product. All of the absorptions of the pure compound were present in the nmr of the residue. The nmr spectrum suggested that no dimethyl phenacylphosphonate was present. Its absence was confirmed by glpc analysis.

Reaction of Acetonyl *p*-Toluenesulfonate with Trimethyl Phosphite.—Acetonyl *p*-toluenesulfonate (0.57 g, 0.003 mole) was allowed to react with trimethyl phosphite (0.31 g, 0.003 mole). After 8 days at room temperature little reaction had occurred. Excess trimethyl phosphite was added. After 5 days the nmr spectrum showed that dimethyl 1-methylvinyl phosphate was present as a major reaction product and that no dimethyl acetylmethylphosphonate was present. This later conclusion was confirmed by glpc analysis.

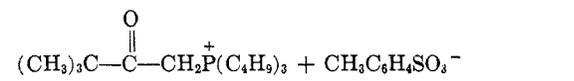
Reaction of Phenacyl *p*-Toluenesulfonates with Triethyl Phosphite.—A solution of 2.7 g (0.01 mole) of phenacyl *p*-toluenesulfonate and 1.66 g (0.01 mole) of triethyl phosphite in 35 ml of dry ether was heated under reflux for 18 hr. The ether was removed and the residue was analyzed by glpc. The vinyl phosphate was identified by its retention time which was the same as that of an authentic sample. No phosphonate was found. Addition of 1% of phosphonate gave rise to a peak which shows that phosphonate would have been detected if present in that amount.

In another experiment under essentially the same conditions, the product was investigated by nmr which indicated that vinyl phosphate was the major product of the reaction.

Reaction of Phenacyl *p*-Toluenesulfonate with Triphenylphosphine.—A solution of 2.9 g (0.01 mole) of phenacyl *p*-toluenesulfonate and 2.56 g (0.01 mole) of triphenylphosphine in 35 ml of benzene was heated under reflux for 3 days. During this time a precipitate formed. The cooled reaction mixture was filtered and the dried solid was recrystallized from ether–chloroform. The product, 4.2 g, softened at 115–120° but resolidified and melted at 146–148°. It is believed that a hydrate was obtained and the melting point behavior is due to this. The infrared spectrum indicated hydroxylic protons were present. The rest of the spectrum was in agreement with that expected. In particular there was carbonyl absorption at 1700 cm^{-1}. The nmr spectrum showed a doublet at 5.9 ppm (J = 13 cps), which is due to the methylene adjacent to the carbonyl group, a singlet at 2.27 ppm, methyl attached to the aromatic ring, and a singlet at 2.9 ppm which is assigned to the water. The aromatic region was obscured by the absorption of the chloroform which was used as solvent.

In another experiment the same quantities of reactants were allowed to react in 35 ml of benzene to which 3 ml of methanol had been added. The same material was obtained.

Reaction of Pinacolyl *p*-Toluenesulfonate with Tributylphosphine.—A solution of 0.67 g (0.003 mole) of pinacolyl tosylate and 0.51 g (0.003 mole) of tributylphosphine in 10 ml of benzene was heated under reflux for 5 hr. The benzene was removed under reduced pressure. The residue had a carbonyl band at 5.8 μ. The nmr spectrum had an A_2B_2 pattern at 7.36 ppm (aromatic hydrogens), a doublet at 4.16 ppm (J = 12 cps) (methylene adjacent to a carbonyl and positive phosphorus), singlet at 2.28 ppm (aromatic methyl), and a singlet at 1.31 ppm (t-butyl hydrogens). There were also peaks due to n-butyl hydrogens. The areas under these peaks were in accord with the assigned structure following.



$$(CH_3)_3C{-}C(=O){-}CH_2\overset{+}{P}(C_4H_9)_3 + CH_3C_6H_4SO_3^-$$

The Reaction of Dihydropyran with Substituted Benzenesulfonyl Azides[1a]

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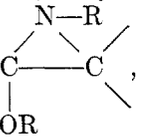
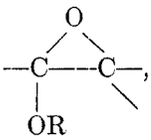
The addition of arylsulfonyl azides to dihydropyran was studied. The products obtained from this reaction were shown to be N-(arylsulfonyl)-δ-pentanimido lactones by nmr and infrared spectra and by hydrolysis studies. Hydrolysis of these compounds gave the corresponding substituted benzenesulfonamide and δ-valerolactone, isolated as its hydrazide. Eight new imido lactones were prepared.

The desire to prepare 1,2-epiimino sugars from glycals prompted an investigation of the reaction of arylsulfonyl azides with the model system, dihydropyran. The desired nitrogen analogs,  , of an epoxy ether,  , have been reported by Hatch and Cram[2] to be an intermediate in the rearrangement of ketoxime O-sulfonates to amino ketones (the Neber reaction). Lloyd and Roberts[3] found that 3,4,6-tri-O-acetyl-2-deoxy-1,2-(2,4-dinitrophenylepi-imino)-α-D-glucopyranoside was formed in small yields when 3,4,6-tri-O-acetyl-2-deoxy-2-(2,4-dinitrophenylamino)-α-D-glucopyranosyl bromide was treated with pyridine in ethanol.

Alder and Stein[4] were among the first investigators to report the formation of a substituted aziridine *via* thermal decomposition of the triazoline intermediate which is formed from the addition of phenyl azide to dicyclopentadiene. Caronna and Palazzo[5] found that a nitro group on the benzene ring of the phenyl azide makes the triazoline intermediate so unstable that it decomposes at once to the aziridine. Franz and Osuch[6] recently reported that azides of type RN_3 (R = $C_6H_5SO_2$–, p-$CH_3C_6H_4SO_2$–, CH_3SO_2–, $(C_6H_5)_2P(\rightarrow O)O$–, $(C_2H_5)_2NSO_2$–, and $N_3SO_2C_6H_4OC_6H_4SO_2$–) react with norbornene, dicyclopentadiene, and 3,6-endomethylenetetrahydrophthalic anhydride to yield aziridines and imines without pyrolysis of an intermediate triazoline. They found, in agreement with

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