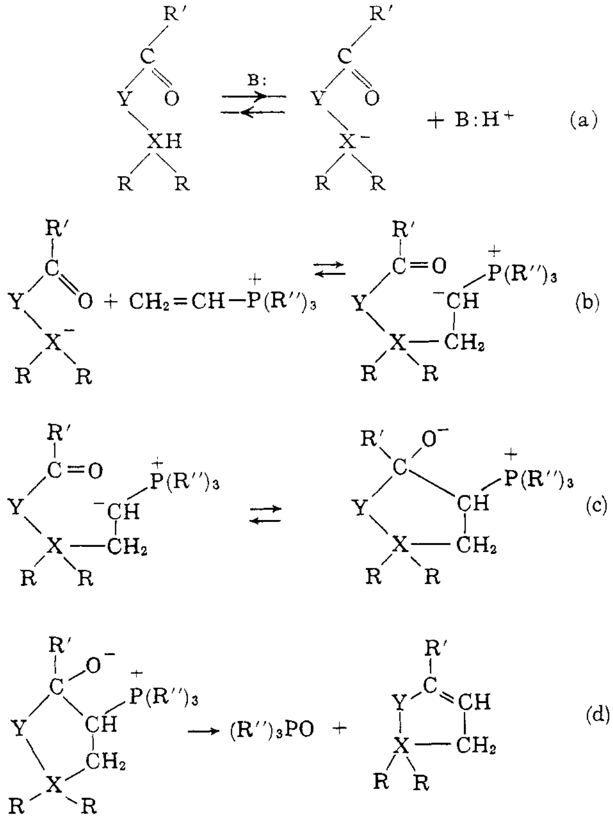
Reactions of Phosphorus Compounds. III. A New General Ring Synthesis from Vinyltriphenylphosphonium Bromide

Sir:

We wish to report a new general heterocyclic and carbocyclic ring synthesis. The common feature of these reactions is a vinyl trisubstituted phosphonium salt. In a recent paper we[1] have demonstrated the ability of vinyltriphenylphosphonium bromide (I) to undergo nucleophilic conjugate addition reactions of a Michael type with ROH, R_2NH, and RSH. In addition to the above mentioned functional groups, –CH and –PH have also been added to vinyltributylphosphonium bromide.[2]

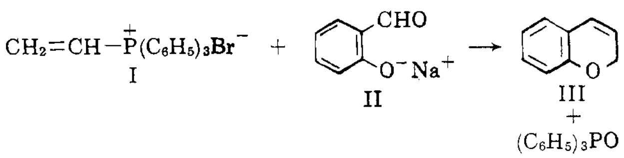
We wish to show that anions of these groups add to vinylphosphonium salts giving phosphorus ylides which will attack any functional groups known to be labile to ylides that are present. A general mechanistic pathway for this reaction may be demonstrated (a–d)



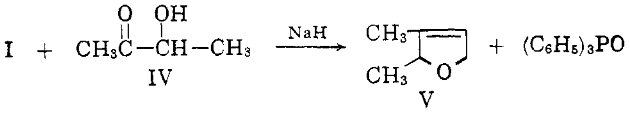
where Y = aliphatic or aromatic, R′ = aliphatic, aromatic, or hydrogen, R = omitted, aliphatic, aromatic, or electron withdrawing groups, X = oxygen, nitrogen, or carbon.[3]

We wish to demonstrate part of this generality by describing the synthesis of two compounds: (A) 3,4-chromene (III) from salicylaldehyde and (B) 2,5-dihydro-2,3-dimethylfuran (V) from acetoin.

(A) Vinyltriphenylphosphonium bromide[1] (I) (0.05 mole) was allowed to react with 0.06 mole of the sodium salt of salicylaldehyde (II) in 200 ml. of freshly distilled salicylaldehyde at 110 ± 10°. for 24 hr. The solution was placed in 1 l. of 10% sodium hydroxide, extracted with ether, dried, and distilled, and gave a 62% yield of 3,4-chromene (III), b.p. 91–93° (13 mm.), $n^{20}{}_D$ 1.5886 (lit.[4] b.p. 49.5–50.0° (1.0 mm.), $n^{20}{}_D$ 1.5879). The infrared[4] and n.m.r. spectra were consistent with the designated structure. A similar reaction using dry acetonitrile as the solvent gave a 71% yield of the 3,4-chromene (III) (by gas phase chromatography) and a 51% yield of triphenylphosphine oxide (melting point and mixture melting point were identical with that of an authentic sample).



(B) Acetoin (IV) (0.175 mole) was placed in a mixture of sodium hydride (0.153 mole) and dry ether (100 ml.). The salt (I) (0.19 mole) was added all at once and then 200 ml. of dry dimethylformamide was added dropwise. The mixture was stirred for 48 hr. at room temperature. An equal volume of water was added; extraction with ether, drying, concentration, and distillation gave a fraction, b.p. 95–120° (atmospheric pressure), weighing 6.61 g., which was shown to be 89% 2,5-dihydro-2,3-dimethylfuran (V) (*i.e.*, a 39% over-all yield). Redistillation gave an analytically pure sample of the dihydrofuran (V), b.p. 104°, (atmospheric pressure), $n^{23}{}_D$ 1.4325. *Anal.* Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.09; H, 10.29. Triphenylphosphine oxide was also isolated in 49% yield.



The n.m.r. spectrum of V (neat) exhibited proton absorption at τ 8.84 p.p.m. (doublet, weight 3), 8.32 p.p.m. (split peak, weight 3), 5.50 p.p.m. (unresolved multiplet, weight 2.9), and 4.58 p.p.m. (unresolved multiplet, weight 0.9). The infrared spectrum was in agreement with the structure assigned.

The generality of this unique reaction for the preparation of heterocyclic and carboxcyclic ring systems will be fully demonstrated in forthcoming papers.

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[1] E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, **29**,1 746 (1964), paper No. II of this series.

[2] P. T. Keough and M. Grayson, *ibid.*, **29**, 631 (1964).

[3] Examples where X = nitrogen or carbon have been demonstrated in these laboratories: K. K. Light and G. J. O'Neill, unpublished results. We are attempting to demonstrate examples where X = sulfur or phosphorus.

[4] W. E. Parham and L. D. Huestis, *J. Am. Chem. Soc.*, **84**, 813 (1962).

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RECEIVED APRIL 30, 1964

The Cleavage of Cyclopropanes by Thallium Triacetate

Sir:

In a recent communication[1] we reported that lead tetraacetate cleaves cyclopropanes to yield 1,3-diacetates and unsaturated monoacetates. We now wish to report that thallium triacetate reacts with cyclopropanes under conditions that are similar to those previously reported for lead tetraacetate. However,

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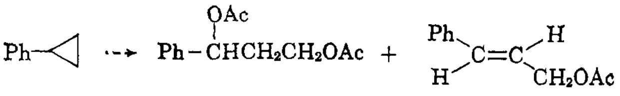
[1] R. J. Ouellette and D. L. Shaw, *J. Am. Chem. Soc.*, **86**, 1651 (1964).

thallium triacetate is very specific in the cleavage reaction and high yields of a single product are observed. We also wish to present evidence in support of a two-step mechanism in which both steps proceed at similar rates. Winstein[2] has reported that thallic triacetate oxidizes cyclohexene and has probed the mechanism of the reaction and stereochemistry of the products.

Phenylcyclopropane is cleaved by thallium triacetate in acetic acid at 75°. In a typical reaction, a solution that was 0.04 M in thallium triacetate and 0.08 M in phenylcyclopropane was allowed to react for 120 hr. The sole products are 1-phenyl-1,3-diacetoxypropane and *trans*-cinnamyl acetate which are obtained in 92% and 8% yields, respectively. The 1-phenyl-1,3-diacetoxypropane was collected and identified by its n.m.r. spectrum. No 2-phenyl-1,3-diacetoxypropane was found. The *trans*-cinnamyl acetate was identified by its v.p.c. retention times on XF-1150 (cyano silicone), QF-1 (fluoro silicone), and SF-96. In the previous work the *trans*-cinnamyl acetate was identified by its n.m.r. and infrared spectra.

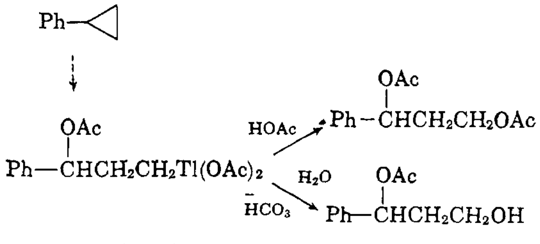


Ethyl cyclopropane was subjected to similar reaction conditions. The ratio of 1,3-diacetoxypentane to 2-ethyl-1,3-diacetoxypropane is approximately 65. Both products were readily separable on Degs and XF-1150. Less than 5% of the reaction product consists of lower molecular weight material (unsaturated monoacetates). By contrast the ratio of 1,3-diacetoxypentane to 2-ethyl-1,3-diacetoxypropane in the lead tetraacetate reaction is 6.

The stereochemistry of the reaction has been examined with norcarane. Norcarane is cleaved to give 2-acetoxymethylcyclohexyl acetate and 1,3-diacetoxycycloheptane in the ratio of 15 to 1. Approximately 5% of the reaction product is of lower molecular weight. By contrast the corresponding ratio in the lead tetraacetate cleavage is 5.3 to 1. The n.m.r. spectrum of the 2-acetoxymethylcyclohexyl acetate was examined to determine the stereochemistry of this product. A sharp singlet at τ 8.10 corresponding to the six hydrogens of the two acetate groups is observed for the *trans* isomer.[4] The *cis* isomer[4] shows two sharp singlets at τ 8.10 and 8.03. Each singlet corresponds to three hydrogens. The signal at τ 8.03 must correspond to the predominantly axial acetoxy group in the *cis* isomer. The reaction product has a sharp singlet at τ 8.10. The *cis* isomer could be detected if it were present to the extent of 2% of the reaction mixture. Thus the cleavage reaction stereospecifically yields the *trans* ring-opened product.

The cleavage reaction can be carried out conveniently with thallic oxide. Under the reaction conditions, thallic oxide is converted to thallium triacetate. This modification avoids the use of the moisture-sensitive thallium triacetate.

That the reaction with thallium triacetate is a two-step process is indicated by the following observations. Aliquots of the reaction mixture of phenylcyclopropane and thallium triacetate were quenched in water at various time intervals. Each sample was extracted with ether and the ethereal solution was washed with sodium bicarbonate. Analysis by v.p.c. showed the presence of a third product of longer retention time than the diacetate. Acetylation of the reaction mixture removes this product and increases the yield of 1-phenyl-1,3-diacetoxypropane. The product is an alcohol which results from the decomposition of the organothallium intermediate under the work-up conditions. As the reaction proceeds the peaks corresponding to the alcohol and diacetate increase while the phenylcyclopropane decreases. The alcohol peak is initially larger than the diacetate peak but decreases with time to a small value. This strongly suggests, that the reaction involves a two-step mechanism, the first step of which is the formation of the organothallium intermediate. The second step is the decomposition of the intermediate. Both steps proceed at measurable rates.



By analogy it appears that the reaction with lead tetraacetate involves an organolead intermediate which decomposes very rapidly and the rate-determining step is the cleavage of the cyclopropane ring. Under similar reaction conditions the attack of mercuric acetate on cyclopropanes would be expected to give stable organomercury compounds. The reaction with mercuric acetate has been observed by Levina.[5-8]

Further work on the direction of cleavage, stereochemistry of cleavage, and elucidation of the mechanism of cleavage by rate studies is in progress.

[2] C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 606 (1963).

[3] Liquid phases obtained from Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

[4] The authors wish to thank Dr. Lloyd Dolby for authentic samples of *cis*- and *trans*-2-acetoxymethylcyclohexyl acetate.

(5) R. Ya. Levina and V. N. Kostin, *Zh. Obshch. Khim.*, **23**, 1054 (1953).

(6) R. Ya. Levina and V. N. Kostin, *Dokl. Akad. Nauk. SSSR*, **97**, 1027 (1954).

(7) R. Ya. Levina, V. N. Kostin, and V. A. Tartakouskii, *Zh. Obshch. Khim.*, **27**, 881 (1957).

(8) R. Ya. Levina, V. N. Kostin, and V. A. Tartakouskii, *ibid.*, **24**, 2998 (1956).

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RECEIVED APRIL 17, 1964

The Electrochemical Oxidation of Formic Acid in the Presence of Dimethylformamide

Sir:

Conway and Dziechiuch[1] have shown that the electrolysis of potassium formate in formic acid gives carbon dioxide and hydrogen, according to the following over-all electrode reactions

$$HCOO^- \longrightarrow CO_2 + H^+ + 2e$$

$$2H^+ + 2e \longrightarrow H_2$$

with the coulombic yield approaching 1 mole of CO_2

[1] B. E. Conway and M. Dziechiuch, *Can. J. Chem.*, **41**, 21 (1963).