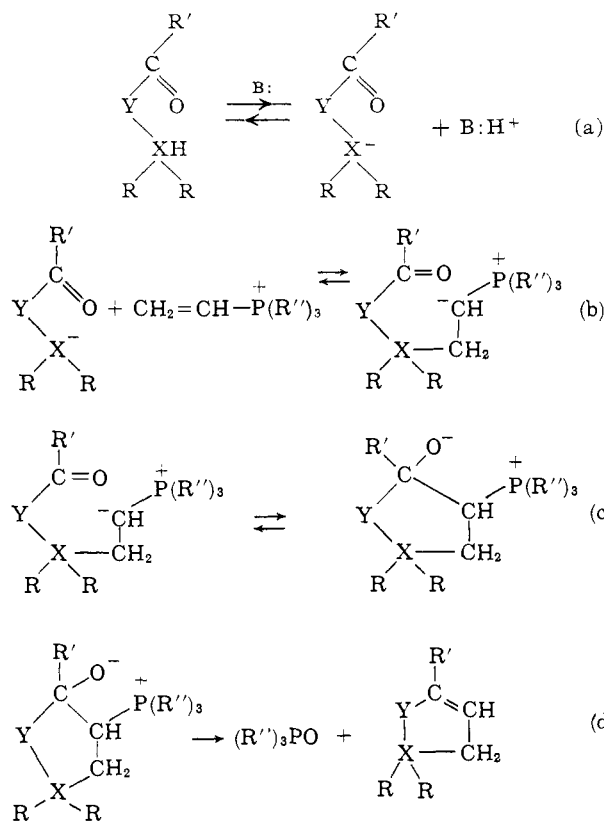


### Reactions of Phosphorus Compounds. III. A New General Ring Synthesis from Vinyltriphenylphosphonium Bromide

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<sup>1</sup> have demonstrated the ability of vinyltriphenylphosphonium bromide (I) to undergo nucleophilic conjugate addition reactions of a Michael type with ROH, R<sub>2</sub>NH, and RSH. In addition to the above mentioned functional groups, -CH and -PH have also been added to vinyltributylphosphonium bromide.<sup>2</sup>

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)

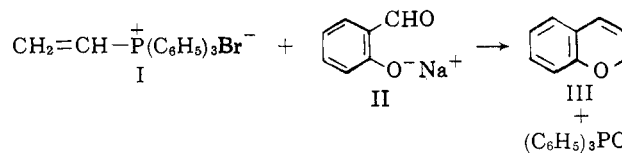


where Y = aliphatic or aromatic, R' = aliphatic, aromatic, or hydrogen, R = omitted, aliphatic, aromatic, or electron withdrawing groups, X = oxygen, nitrogen, or carbon.<sup>3</sup>

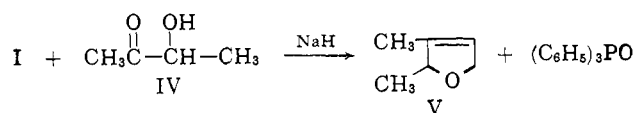
We wish to demonstrate part of this generality by describing the synthesis of two compounds: (A) 3,4-chromene (III) from salicylaldehyde and (B) 2,5-dihydro-2,3-dimethylfuran (V) from acetoin.

(A) Vinyltriphenylphosphonium bromide<sup>1</sup> (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  $110 \pm 10^\circ$ . for 24 hr. The solu-

tion 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.  $91-93^\circ$  (13 mm.),  $n_{\text{D}}^{20}$  1.5886 (lit.<sup>4</sup> b.p.  $49.5-50.0^\circ$  (1.0 mm.),  $n_{\text{D}}^{20}$  1.5879). The infrared<sup>4</sup> 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.  $95-120^\circ$  (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.  $104^\circ$ , (atmospheric pressure),  $n_{\text{D}}^{25}$  1.4325. Anal. Calcd. for C<sub>8</sub>H<sub>10</sub>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  $\tau$  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 carbocyclic ring systems will be fully demonstrated in forthcoming papers.

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

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### The Cleavage of Cyclopropanes by Thallium Triacetate

Sir:

In a recent communication<sup>1</sup> 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,

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

(1) E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, **29**, 1746 (1964), paper No. 11 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.