

Reactions of Phosphorus Compounds. Part V. Synthesis of Chromenes from Allyltriphenylphosphonium Bromide

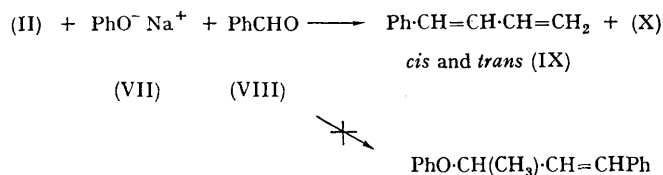
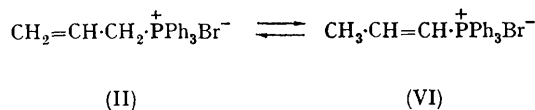
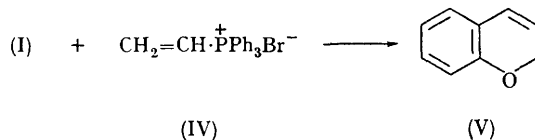
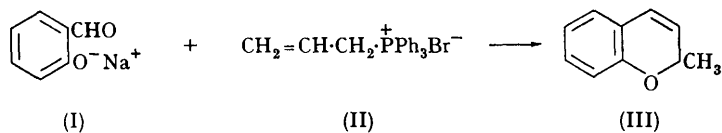
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CONTINUING our interest in the reactions of phosphonium salts¹ we have discovered that the sodium salt of salicylaldehyde (I) and allyltriphenylphosphonium bromide (II) in dimethylformamide react

to give 2-methyl-3-chromene (III) in up to 34% yield.²

Similarly, methallyltriphenylphosphonium bromide (IIa) and the sodium salt of salicylaldehyde



¹ Part IV, E. E. Schweizer and K. K. Light, *J. Amer. Chem. Soc.*, 1964, **86**, 2963.

² Chromene isolated, i.r., g.l.c. matched authentic sample. E. E. Schweizer and R. Schepers, *Tetrahedron Letters*, 1963, **15**, 979.

(I) in dimethylformamide gave 2,2-dimethyl-3-chromene (IIIa) in 40% yield. An analytical sample³ has b.p. 94°/11 mm., n_D^{24} 1.5496.

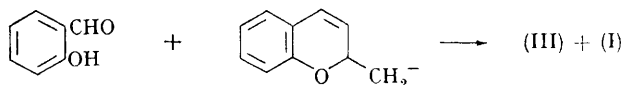
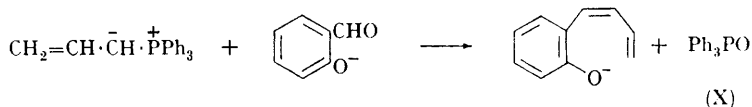
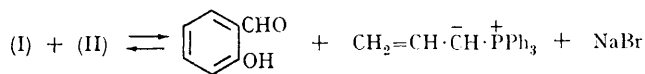
The previously reported⁴ preparation of 3-chromene (V) from vinyltriphenylphosphonium bromide (IV) and (I) initially led to the assumption that the present reaction is the result of an initial base-catalyzed isomerization⁵ of the allyl salt (II) to the corresponding propenyltriphenylphosphonium bromide (VI) followed by a ring closure similar to that described in our previous paper.⁴ Keough and Grayson⁵ have shown, however, that the characteristic Michael additions of

of benzaldehyde (VIII) gives only the two geometric isomers of phenylbutadiene (IX), as indicated by comparison of their infrared spectra with those of published⁷ compounds, and triphenylphosphine oxide (X). None of the phenoxy-adduct (XI), which would be expected if the reaction were the result of an initial isomerization of (II) to (VI) followed by a Michael addition of the phenoxide and then a Wittig reaction with benzaldehyde, was observed.⁸

Thus, the mechanism (I) is suggested as a possibility for this novel reaction.

This unique synthesis of 2-methyl-3-chromene

Mechanism I



vinylphosphonium salts^{5,6} do not occur with the propenyl salt (VI).⁵

We have also shown that the reaction of sodium phenoxide (VII) and the salt (II) in the presence

(III) and 2,2-dimethyl-3-chromene (IIIa) suggests a new ring synthesis from allyltriphenylphosphonium salts. The full synthetic possibilities are being explored.

(Received, February 15th, 1965.)

³ Found: C, 82.35; H, 7.4%. The n.m.r. and i.r. spectra were characteristic for this structure.

⁴ E. E. Schweizer, *J. Amer. Chem. Soc.*, 1964, **86**, 2744.

⁵ P. T. Keough and M. Grayson, *J. Org. Chem.*, 1964, **29**, 631.

⁶ E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, 1964, **29**, 1746.

⁷ O. Grummitt and F. J. Christoph, *J. Amer. Chem. Soc.*, 1951, **73**, 3479.

⁸ The distillation products through and including the triphenylphosphine oxide portions showed no absorption attributable to a phenoxy-ether.