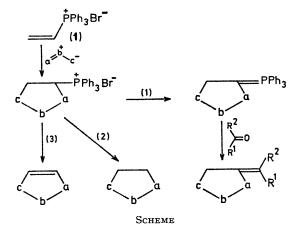
The Synthetic Utility of Adducts of 1,3-Dipolarophiles with Vinyl Phosphonium Salts

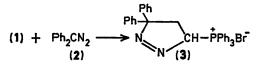
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Summary 3,3-Diphenyl-5-triphenylphosphonio- Δ^1 -pyrazoline bromide and 4-triphenylphosphonio- Δ^1 -pyrazoline bromide were prepared and generalized reactions for 1,3-dipolar adducts of vinyl phosphonium salts were suggested and illustrated using the aforementioned species.

WE report our work on 1,3-dipolar additions to vinyl triphenyl phosphonium salts, a technique recently used¹ to obtain heterocyclic systems. We show that this may be a general reaction and may allow the use of a series of secondary steps with the initial adduct which will yield further products as shown in the Scheme.



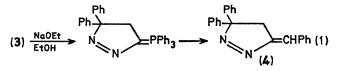
An example of each of the three reactions (1, 2, and 3) predicted above has been studied.



On allowing diphenyldiazomethane (2) to react with

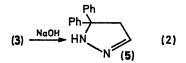
† The analytical and spectral data for all the new compounds reported are in agreement with the structures shown.

vinyl triphenylphosphonium bromide (1) in methylene chloride a quantitative yield of 3,3-diphenyl-5-triphenyl-phosphonio- Δ^1 -pyrazoline bromide (3)[†] was obtained.

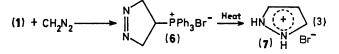


On treating (3) with sodium ethoxide in ethanol followed by benzaldehyde, the normal Wittig reaction product (4)was obtained (65% yield).

The reaction of (3) with 10% sodium hydroxide yielded the expected 5,5-diphenyl-3*H*-pyrazoline (5) in 87% yield.



Heating 4-triphenylphosphonio- Δ^1 -pyrazoline bromide (6), produced in 90% yield from the reaction between (1) and diazomethane, gave a quantitative yield of triphenylphosphine and pyrazoline hydrobromide (7).



Thus it has been shown that 1,3-dipolar additions to vinyl phosphonium salts are readily accomplished. Furthermore, the initial adducts may be treated in a variety of ways, (see Scheme) which increases the synthetic use of vinylphosphonium salts. Pathways other than those shown in the Scheme are possible, and this was demonstrated by

(3)
$$\xrightarrow{\text{Heat}}$$
 Ph₂C=CH CH₂PPh₃Br⁻
(8)

carrying out the thermal degradation of the salt (3) which forms 3,3-diphenyl allyl-1-triphenylphosphonium bromide (8) in greater than 84% yield. We thank the Public Health Service for a grant.

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¹ E. Zbiral, M. Rasberger, and H. Hengstberger, Annalen, 1969, 725, 22.