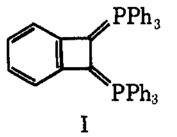
Communications

See Editorial, *J. Org. Chem.*, **37**, No. 13, 4A (1972).

Reductive Condensation of Unsaturated Phosphonium Salts with Carbonyl Compounds. Possible Generation of a Reactive 1,2-Bisylide

Summary: Reaction of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexene-2 dibromide with benzaldehyde and lithium affords 1,4-diphenylbutadiene, possibly *via* an intermediate 1,2-bisylide.

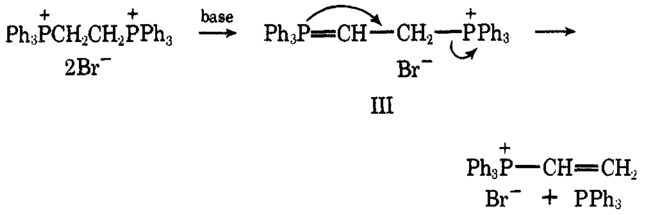
Sir: Phosphorus 1,3- and 1,4-bisylides are useful for double Wittig condensation,[1] but the analogous 1,2-bisylides have not been studied extensively. The only 1,2-bisylide known which is sufficiently reactive for Wittig condensation, 1,2-bis(triphenylphosphoranyl)benzocyclobutene[2] (I), can be prepared in the usual way from the bisphosphonium salt and base. However, attempted preparation of simpler 1,2-bisylides such as II by the above method affords triphenylvinylphosphonium halide and triphenylphosphine (*via* the monoylide III) at temperatures as low as −70°.[3-5]



I

$Ph_3P{=}CHCH{=}PPh_3$

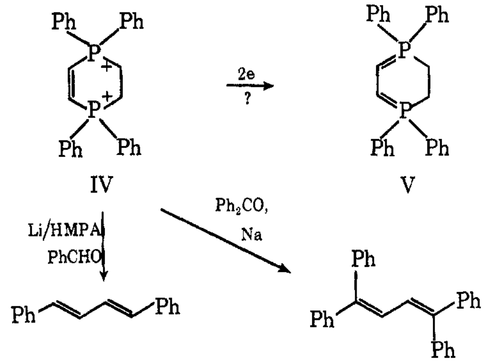
II



$$\overset{+}{Ph_3P}CH_2CH_2\overset{+}{P}Ph_3\ 2Br^- \xrightarrow{\text{base}} Ph_3P{=}CH{-}CH_2{-}\overset{+}{P}Ph_3\ Br^- \longrightarrow Ph_3\overset{+}{P}{-}CH{=}CH_2\ Br^- + PPh_3$$

III

A potential route to 1,2-bisylides which avoids intermediates capable of elimination is based on the hypothesis that two-electron reduction of vinylene bisphosphonium salts would afford the desired bisylides. Thus, treatment of the known 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexene-2 dibromide (IV)[6] with a reducing metal might be expected to form the cyclic bisylide V.[7]



In apparent agreement with the above proposal, treatment of IV with lithium/hexamethylphosphoramide in the presence of benzaldehyde, or with sodium and benzophenone in tetrahydrofuran, affords moderate yields of the expected Wittig products, *trans,-trans*-1,4-diphenylbutadiene and 1,1,4,4-tetraphenylbutadiene, respectively, in addition to complex polar products. However, we have been unable to obtain direct evidence that V is an intermediate in these reactions. Treatment of powdered IV with Li/HMPA at 20° slowly produces a characteristic orange solution, but subsequent addition of benzaldehyde to this solution does not afford any diphenylbutadiene. Furthermore, reaction of IV with Li/HMPA in the presence of cyclohexanone affords none of the derived Wittig product. Similar behavior has been noted for the 1,2-bisylide I which is also unstable at room temperature and does not form simple Wittig products with acetone.[2a]

Although the formation of dienes strongly implicates a Wittig betaine intermediate such as VI, we must note that other rationales can account for the generation of VI which do not involve the bisylide V. The reduction potentials of IV,[8] benzaldehyde, and benzophenone[9] are comparable; so it is possible that electron transfer to the carbonyl component is the first step. Nucleophilic addition of benzaldehyde radical anion to IV (by analogy to the addition of simpler nucleophiles[5,10]) would then produce a species VII which may react with a second mole of lithium and benzaldehyde to form VI (Scheme I).[11] On the basis of this rationale, the failure of cyclohexanone to form a Wittig product can be attributed to its unfavorable reduction potential.

Benzophenone ketyl also reacts with vinyltriphenylphosphonium bromide to form 1,1,4,4-tetraphenylbutadiene. According to the radical anion mechanism outlined in Scheme I, the ylide VIII is an intermediate, and Wittig condensation followed by dehydration leads to the observed diene. An alternate pathway involving electron transfer to the vinylphosphonium salt can also account for generation of VIII. We are not aware

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[1] A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 20.

[2] (a) A. T. Blomquist and V. J. Hruby, *J. Amer. Chem. Soc.*, **86**, 5041 (1964); *ibid.*, **89**, 4996 (1967). (b) P. J. Garratt and K. P. C. Vollhardt, *Chem. Commun.*, 1143 (1971).

[3] G. Wittig, H. Eggers, P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1958).

[4] Treatment of 1,2-bis(triphenylphosphonio)ethane dibromide with butyllithium at −70° in tetrahydrofuran followed by benzaldehyde affords ~10% 1-phenyl-1-heptene as the sole Wittig product. This substance results from addition of butyllithium to vinyltriphenylphosphonium bromide, by analogy to the work of Seyferth and Fogel.[5]

[5] D. Seyferth and J. Fogel, *J. Organometal. Chem.*, **6**, 205 (1966).

[6] A. M. Aguiar and H. Aguiar, *J. Amer. Chem. Soc.*, **88**, 4090 (1966).

[7] The recently reported electrochemical reduction of IV[8] to 1,1,4,4-tetraphenyl-1,4-phosphoniacyclohexane dibromide may prove to be the first example of generation of V. The protic solvent used is expected to protonate V to the observed saturated salt.

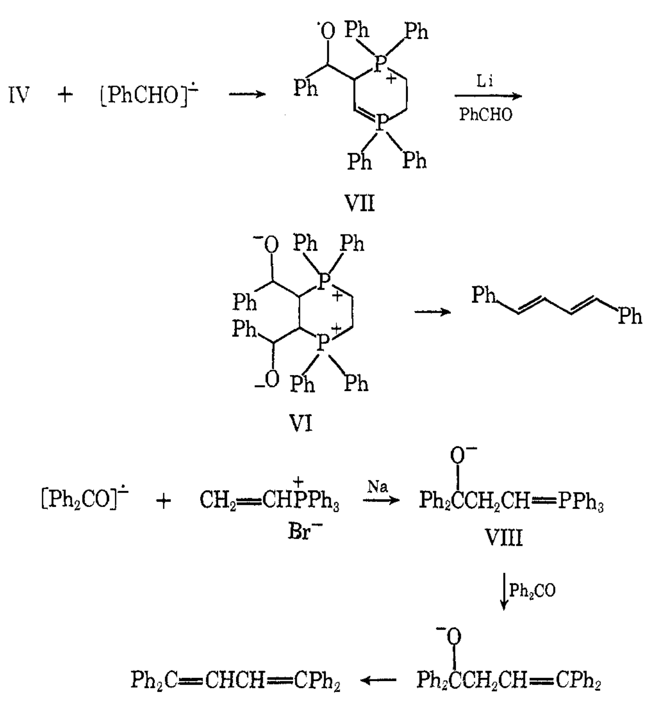
[8] J. H. Stocker, R. M. Jenevein, A. Aguiar, C. W. Prejean, and N. A. Portnoy, *Chem. Commun.*, 1478 (1971).

[9] P. H. Given and M. E. Peover, *J. Chem. Soc.*, 385 (1960).

[10] E. E. Schweizer and W. S. Creasy, *J. Org. Chem.*, **36**, 2244 (1971), and references therein; J. R. Shutt and S. Trippett, *J. Chem. Soc. C*, 2038 (1969).

[11] Alternately, nucleophilic addition of benzaldehyde or benzophenone dianion to IV could be invoked.

SCHEME I



of any direct analogy for the intermediate ylide radical (from one-electron transfer) or ylide anion (two-electron transfer) required for this mechanism.[12]

Studies are in progress to extend the scope of the diene synthesis to aliphatic carbonyl compounds. We are also exploring metal reductions of other vinyl-substituted tetravalent phosphorus compounds with the aim of devising reagents which are synthetically equivalent to phosphorus 1,2-bisylides.

Acknowledgment.—We thank the National Science Foundation for support of this research. We are also grateful to Professor A. M. Aguiar for his help with experimental procedures.

[12] The condensation of styrene radical anion and acetone constitutes a rather remote precedent for this rationale, although not for the organophosphorus intermediates: J. K. Kochi, *J. Org. Chem.*, **28**, 1960 (1963).

[13] Alfred P. Sloan Foundation Fellow, 1971–1973.

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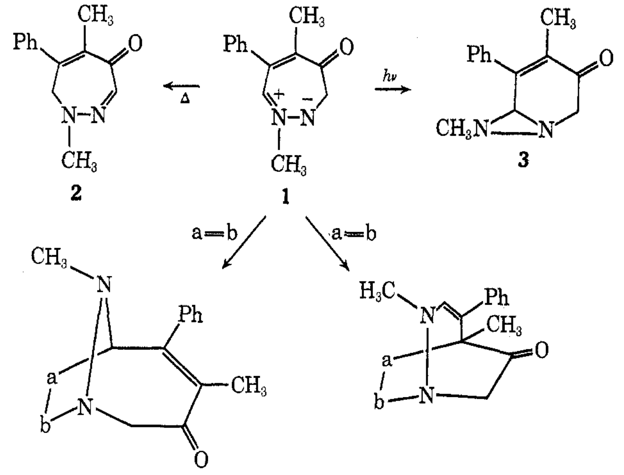
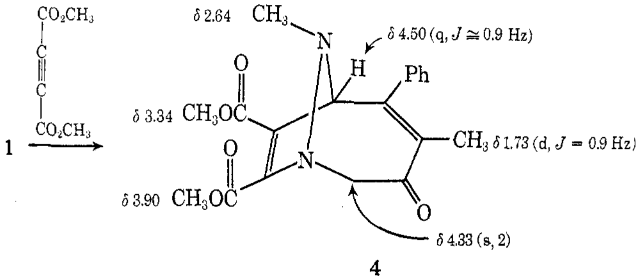
Heterocyclic Studies. 35. Cycloaddition Reactions of a 1,2-Diazepinium Betaine. 1,3- and 1,5-Dipolar Addition in a Vinylogous Azomethine Imine[†1]

Summary: Betaine **1** with acetylenedicarboxylic ester undergoes 1,3-cycloaddition, and with ketene or aryl isocyanates, 1,5-cycloaddition; the isocyanate products rearrange to 1,3 cycloadducts.

Sir: The 1-methyl-2,3-dihydrodiazepinium betaine **1** undergoes thermal sigmatropic rearrangement to the 1,7-dihydrodiazepinone **2** ($k_1^{\mathrm{MeOH},25°}$ 2.4×10^{-4} sec^{-1}) and a photochemical 4-π electrocyclic reaction to **3**.[2] In addition to these intramolecular processes, **1** presents the unusual possibility of dipolar cycloaddition reactions involving either the 4-π azomethine imine system or the 6-π system extending from C-5 to N-2. We now report both of these types of additions.



A mixture of the red betaine **1** [prepared in 90% yield by alkylation of the parent dihydrodiazepinone with $(CH_3)_3O^+BF_4^-$ in acetone][3] and excess dimethyl acetylenedicarboxylate was stirred for 30 min and the deep red solution was chromatographed on silicic acid. The colorless adduct **4**, mp 102°, was isolated in 33% yield. The bicyclic system of **4** was very sensitive to base but was quite stable to acid; heating in 12 *N* HCl led only to hydrolysis of one ester group.



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The thermal rearrangement of **1** to **2** places a severe restriction on bimolecular reactions of **1**. With less reactive dipolarophiles such as methyl propiolate or methyl maleate, adducts were not obtained, and only **2** was isolated.

The possibility of addition to the extended π system of **1** in a $[_{\pi}6_s + _{\pi}4_s]$ process was explored with several dienes including furan and hexachlorocyclopentadiene, but again only **2** was formed and no adducts were detected. Another symmetry-allowed mode of cycloaddition for the extended azomethine imine would be a $[_{\pi}6_s + _{\pi}2_a]$ process, analogous to the numerous $[_{\pi}2_s + _{\pi}2_a)$ cycloaddition that have been observed with

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[†] Attention is called to the possibility of including supplementary data; *e. g.*, see footnote 3 of this communication and editorial. F. D. G.

[1] Supported by Grant GP-9322 from the National Science Foundation.

[2] M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, **90**, 4738 (1968).

[3] Complete experimental details on all compounds described in this communication will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington D. C. 20036, by referring to code number JOC-72-2640. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.