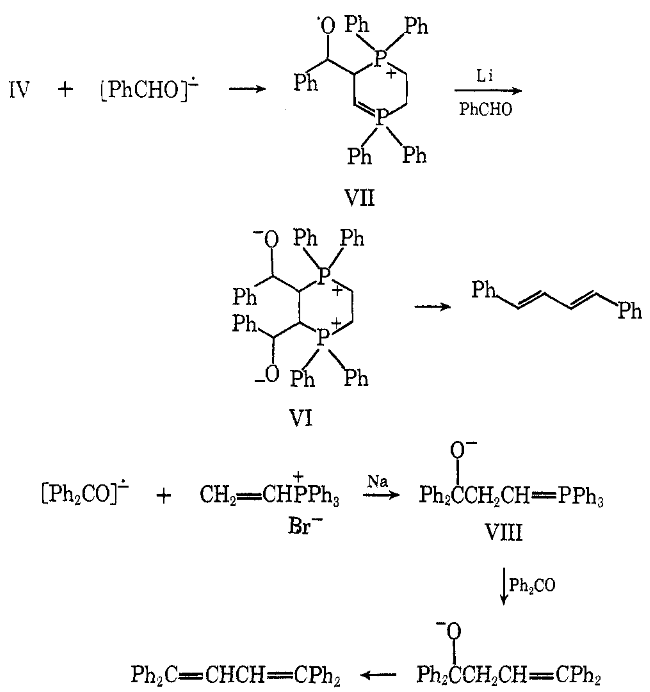
SCHEME I



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.

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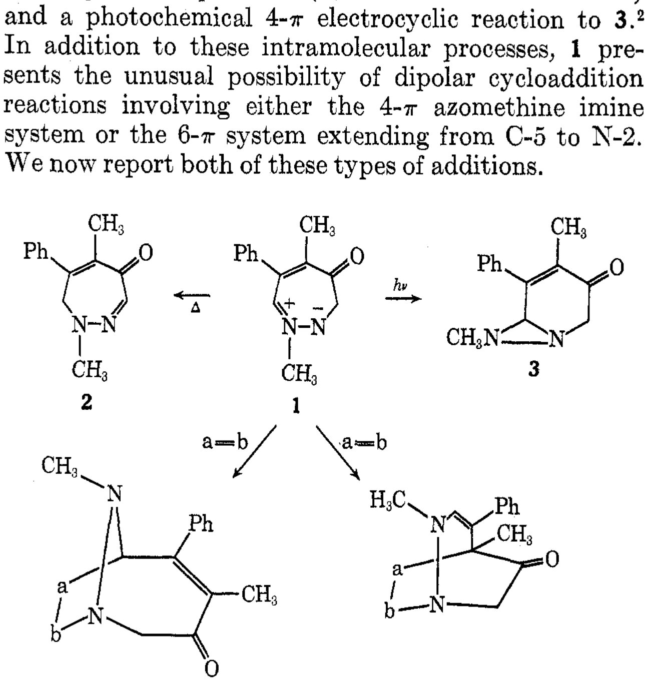
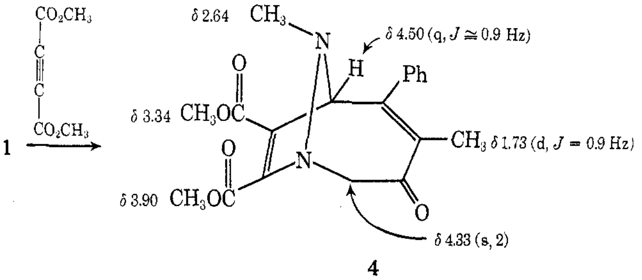
Heterocyclic Studies. 35. Cycloaddition Reactions of a 1,2-Diazepinium Betaine. 1,3- and 1,5-Dipolar Addition in a Vinylogous Azomethine Imine[†][1]

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.

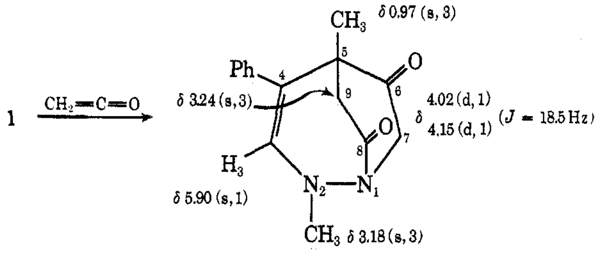
[1] Supported by Grant GP-9322 from the National Science Foundation.

[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.

heteroallenes such as ketenes[4] and isocyanates.[5] This approach proved quite fruitful.

A solution of **1** in CH_2Cl_2 was decolorized in a few seconds by a stream of ketene, and evaporation gave the colorless adduct **5** (84%). Attachment of the ketene bridge at C-5 of **1** is clearly indicated by the high-field methyl signal. The only previous 1,5-dipolar cycloaddition of this type appears to be that observed in the reaction of *o*-diazo oxides and ketenes to give benzo-1,4,5-oxadiazepines;[6] in this case, however, 1,3-cycloaddition to the diazo group would give a nonbenzenoid product, and the 1,5-cycloaddition product is therefore strongly favored owing to product stability.



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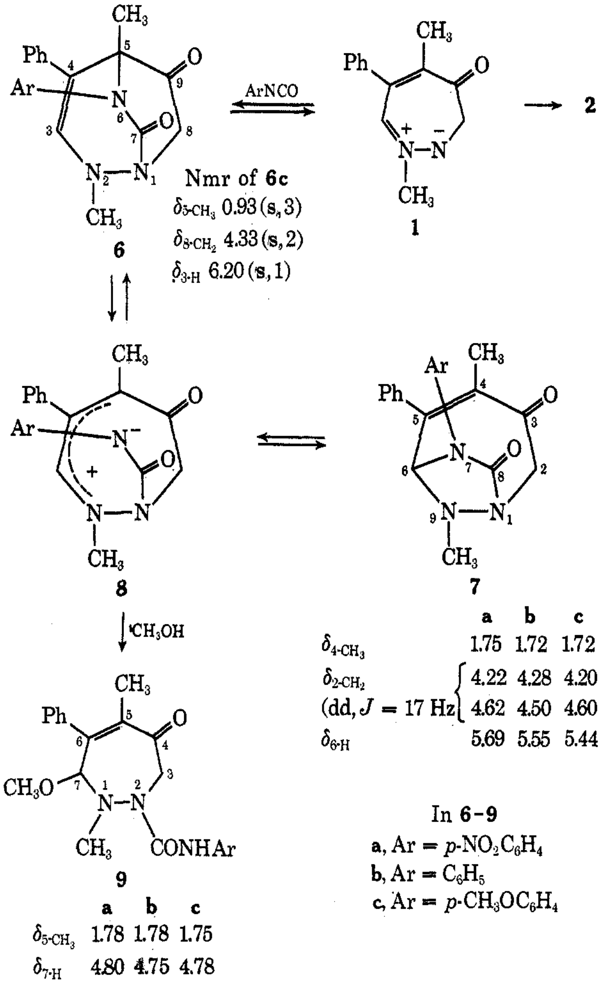
Reactions of **1** with aryl isocyanates at 25° gave the 1,3-dipolar adducts **7a–c** (50–70%); the relative rates were p-$NO_2 \gg p$-$H > p$-OCH_3. With *p*-methoxyphenyl isocyanate, a second compound was seen in the nmr spectrum of the reaction mixture, and an impure sample of this product was crystallized from a reaction at 0°. The nmr spectrum indicated the 1,5 cycloadduct **6c**. Solutions of **6c** at room temperature became orange in a few seconds and then faded; **7c** was then isolated. The nmr spectra of such solutions of **6c** initially showed small peaks due to the betaine **1** and then progressively the formation of **7c** and the rearrangement product **2** in a ratio of ~2.5:1. Reactions of **6c** and phenyl or *p*-nitrophenyl isocyanate gave the adducts **7b** and **7a**, respectively.

The presence of the other 1,5 adducts, **6a** and **6b**, was detected by nmr in solutions of **1** and isocyanates at −20°, but rearrangement to **7a,b** occurred rapidly on warming.

On heating the 1,3 adduct **7b** in a melt at 170°, phenyl isocyanate could be distilled, and the rearrangement product **2** was isolated in 66% yield.[7] The 1,3 adducts reacted in boiling methanol to give methoxy compounds considered to be **9**;[8] the relative rates were again p-$NO_2 > p$-$H > p$-OCH_3. Reaction of the 1,5 adduct **6c** in methanol at 25° gave the *p*-methoxy derivative **9c** and the 1,3 adduct **7c** (~2:1).

We interpret these observations in terms of a reversible concerted $[_{\pi}6_s + {}_{\pi}2_a]$ addition to form the 1,5 cycloadducts **6**, followed by rearrangement of **6** to the more stable 1,3 adducts **7** *via* the dipolar intermediate **8**. This intermediate presumably also gives rise to the methoxytetrahydrodiazepinones **9** by addition of methanol. The greater stability of the *p*-methoxyphenyl 1,5 adduct **6c** is attributed to the higher energy of intermediate **8c** relative to **8a** or **8b**. A similar sequence has been proposed for reactions of chlorosulfonyl isocyanate and dienes, which leads by $[_{\pi}2_s + {}_{\pi}2_a]$ addition to vinylazetidinones and thence by thermal rearrangement to dihydropyridones or dihydropyrans.[5]



Nmr of **6c**
$\delta_{5\text{-}CH_3}$ 0.93 (s, 3)
$\delta_{8\text{-}CH_2}$ 4.33 (s, 2)
$\delta_{3\text{-}H}$ 6.20 (s, 1)

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	a	**b**	**c**
$\delta_{4\text{-}CH_3}$	1.75	1.72	1.72
$\delta_{2\text{-}CH_2}$ (dd, J = 17 Hz)	4.22 4.62	4.28 4.50	4.20 4.60
$\delta_{6\text{-}H}$	5.69	5.55	5.44

9

	a	**b**	**c**
$\delta_{5\text{-}CH_3}$	1.78	1.78	1.75
$\delta_{7\text{-}H}$	4.80	4.75	4.78

In **6–9**
a, Ar = p-$NO_2C_6H_4$
b, Ar = C_6H_5
c, Ar = p-$CH_3OC_6H_4$

According to the mechanism we suggest for the reactions of **1** with isocyanates, the $[_{\pi}6_s + {}_{\pi}2_a]$ addition to **6** is more rapid than $[_{\pi}4_s + {}_{\pi}2_s]$ addition leading directly to **7**, and the former process is presumably highly concerted. To assess the extent of charge developed in the isocyanate during these additions, the following second-order rate constants for the disappearance of **1** were measured in chloroform at 20° for five isocyanates.[9]

Ar	$k \times 10^2\ M^{-1}\ sec^{-1}$
p-CH_3O	1.62 ± 0.07
p-CH_3	1.37 ± 0.03
p-H	2.07 ± 0.06
m-Cl	3.68 ± 0.27
p-Cl	3.49 ± 0.26

From these data, a Hammett ρ value of 0.69 ± 0.13 was obtained with a correlation coefficient of 0.95. If the rate for *p*-methoxyphenyl isocyanate is omitted

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(4) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).

(5) E. J. Moriconi and W. C. Meyer, *J. Org. Chem.*, **36**, 2841 (1971), and many other references given there.

(6) W. Reid and R. Dietrich, *Ann.*, **666**, 113, 135 (1963); W. Reid and K. Wagner, *ibid.*, **681**, 45 (1965).

(7) Similar reversibility has been observed with 1,3-dipolar adducts from aryl isocyanates and azomethine imines derived from isoquinoline: R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 584 (1963).

(8) The 7-methoxy-1,2,3,7-tetrahydrodiazepinone structures **9** appear more compatible with the nmr values than the allylic isomers (5-methoxy-1,2,3,5-tetrahydrodiazepinone), but the latter alternative is not rigorously excluded by the data available.

(9) The reactions were run under pseudo-first-order conditions with isocyanate in excess, following the disappearance of **1** at 436 nm.

(*vide infra*), the data give a ρ value of 0.83 ± 0.13 and a correlation coefficient of 0.98. When compared with ρ values reported for the addition of alcohols to aryl isocyanates, 2.46 ± 0.16[10] and 1.98 ± 0.10,[11] the cycloadditions appear to involve very little (negative) charge development in the transition state, *i.e.*, a highly concerted reaction.

The rates of cycloaddition of aryl isocyanates to α,*N*-diphenylnitrone have a distinct minimum near $\sigma = 0$ with ρ values of -1.8 ± 1.1 and $+1.41 \pm 0.23$ for electron-donating and electron-withdrawing substituents, respectively.[12] These data have been interpreted as indicating a concerted but not synchronous addition mechanism,[12] and a similar conclusion may be drawn for the cycloadditions of **1**, in which *p*-anisyl isocyanate also reacts faster than *p*-tolyl isocyanate, and a significantly smaller ρ value is observed.

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[10] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 743 (1947).

[11] M. Kaplan, *J. Chem. Eng. Data*, **6**, 272 (1961).

[12] D. M. Zavisza, Ph.D. Thesis, Clark University, 1967; *Diss. Abstr.*, **28** (5), 1869-B (1967).