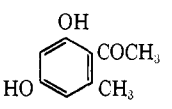
$C_6H_5COCH_2COCH_2COCH_2COCH_2COC_6H_5$
6

$C_6H_5COCH_2COCH_2COC_6H_5$
7

The utility of the β-keto ester condensation reaction for synthesis of large polycarbonyl compounds will depend upon its applicability with aliphatic keto esters, especially with acetoacetic ester. The sodium salt of methyl acetoacetate was treated with dianion **2** and with dilithioacetylacetone to give tetraketones **8**[7] and **9**, respectively, in yields of 30 and 31%. The structure of **9**, mp 38–42°, was supported by spectra and elemental analyses and by cyclization to resorcinol **10**.[10]

$CH_3COCH_2COCH_2COCH_2COR$
8, R = C_6H_5
9, R = CH_3



10

Self-condensation of methyl acetoacetate was not observed in either of these acylation reactions, indicating that proton abstraction from the 4 position of methyl sodioacetoacetate by diketone dianions is not a significant reaction under the present conditions.[16]

The reactions of enolate salts of β-keto esters with strong nucleophiles represent a generally unrecognized, if not novel, class of anionic condensation reactions. We are presently studying the use of these acylating agents for synthesis of poly-β-carbonyl compounds containing six, seven, and more carbonyl groups, as well as surveying the reactions of other negatively charged electrophiles to determine their potential usefulness in organic synthesis.

(16) See K. G. Hampton, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **28**, 1946 (1963).

(17) Career Development Awardee of the U. S. Public Health Service (GM-27103). Research support by the U. S. Public Health Service (GM-12848) is gratefully acknowledged.

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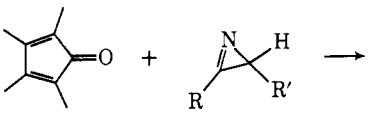
The Mechanism of Azepine Formation in the Cycloaddition of 1-Azirines to Cyclopentadienones[1]

Sir:

Recently we described the cycloaddition of 1-azirines **1** to cyclopentadienones **2** to give 3*H*-azepines **6**.[2] A possible mechanism for this reaction was proposed[2,3] involving first a Diels–Alder type addition to produce **3** followed by formation of an azanorcaradiene intermediate **4**, which then undergoes a 1,5-hydrogen shift.[2] An analogy to step **3** → **4** is provided by the facile loss of CO in the conversion of norbornadien-7-ones to benzenes.[4]

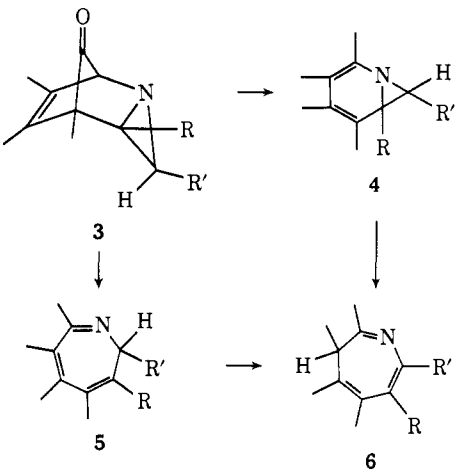
An equally plausible mechanism involves opening of the aziridine ring in **3** with simultaneous loss of CO. This would lead to a 2*H*-azepine **5** which can be converted into **6** by a 1,5-hydrogen shift.

(1) Cycloadditions. XI. For the previous paper in this series, see A. Hassner, M. J. Haddadin, and A. B. Levy, *Tetrahedron Lett.*, in press.
(2) D. J. Anderson and A. Hassner, *J. Amer. Chem. Soc.*, **93**, 4339 (1971).
(3) V. Nair, *J. Org. Chem.*, **37**, 802 (1972).
(4) S. Yankelevich and B. Fuchs, *Tetrahedron Lett.*, 4945 (1967), and references therein.



2 **1**

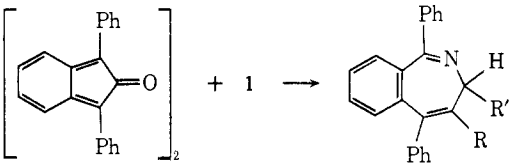
a, R = C_6H_5; R′ = H
b, R = C_6H_5; R′ = Me
c, R = C_6H_5; R′ = C_6H_5
d, R = Et; R′ = Et



3 **4** **5** **6**

A differentiation between these two pathways should be possible if one chooses a substrate in which participation by the double bond during the loss of CO in step **3** → **4** is energetically unfavorable. The benzocyclopentadienone[5] **7** represents such a case, in which formation of an azanorcaradiene and ultimately of a 3*H*-azepine requires disruption of benzene resonance.

Indeed, cycloaddition of azirines **1a–c** to 1,3-diphenylinden-2-one (**7**) proceeded cleanly to produce the 2*H*-azepines **8a–c**. Further heating of **8** at 260° did not



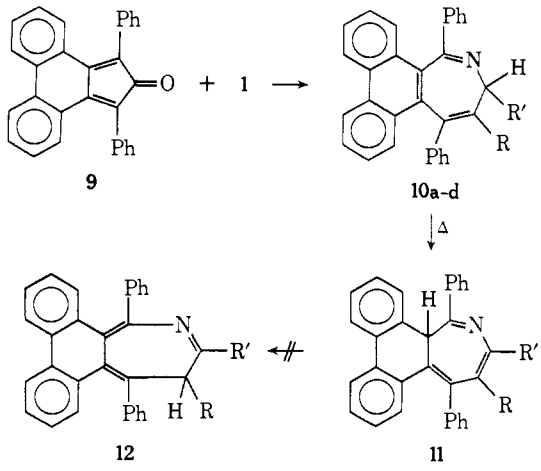
7 **8**

a, R = Ph; R′ = H
b, R = Ph; R′ = CH_3
c, R,R′ = Ph

cause isomerization to 3*H*-azepines. These results, however, do not mitigate against a 3*H*-azepine as a primary product which had isomerized to the more stable **8**.

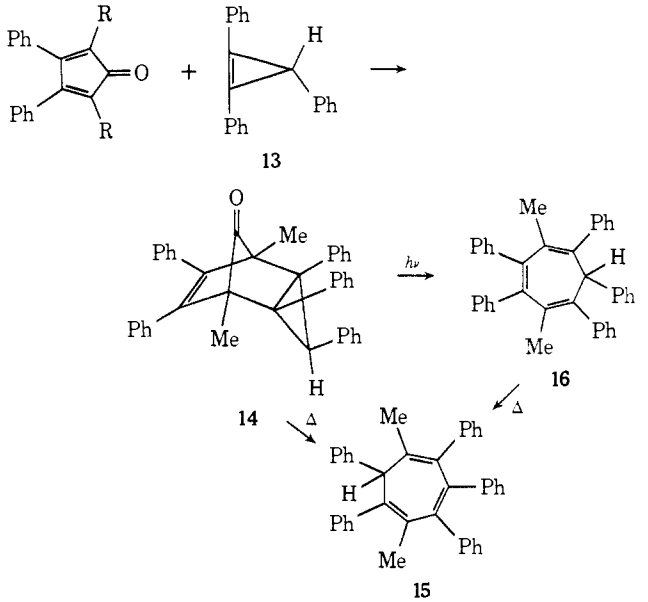
Since the delocalization energy in the phenanthrene center ring is much lower than in benzene, we investigated the cycloaddition of phencyclone **9** with azirines **1a–d**. The reaction was carried out in refluxing toluene or xylene and gave the 2*H*-azepines **10** in 50–80% yield. The structure of azepines **8** and **10** was immediately apparent from their nmr spectra. For example, in **8b** and **10b** the azepine ring proton appeared as a quartet (J = 6.5 Hz) and the methyl group as a doublet (J = 6.5 Hz). Similarly, in **8a** and **10a** the two azepine ring protons appeared as two doublets (J = 9 and 10 Hz, respectively, for **8a** and **10a**) at 25°, indicating slow inversion of the 2*H*-azepine ring on the nmr time scale.

(5) J. M. Holland and D. W. Jones, *J. Chem. Soc. C*, 608 (1971).



Further heating of 2*H*-azepines **10** in triglyme (or neat) afforded the 3*H*-azepines **11** *via* a symmetry-allowed 1,5-hydrogen shift. This isomerization also proceeded in the presence of potassium *tert*-butoxide in refluxing glyme. Benzoazepines **8** were inert to these conditions. The structures of **11** were evident from their nmr spectra. An isomeric 3*H*-azepine structure **12** was readily excluded, since there was no coupling of the ring proton in **11a** or **11d**.[6]

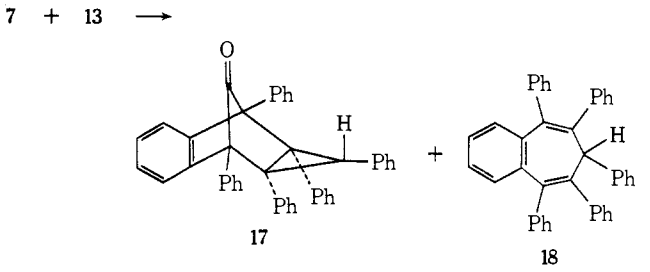
These results are consistent with pathway **3** → **5** → **6**. Additional evidence for this mechanism was obtained by further studies of analogous cyclopropene cycloadditions. The cyclopropene adduct **14**, which on heating in toluene affords cycloheptatriene **15**, produced



the symmetrical cycloheptatriene **16** (equivalent methyl groups in the nmr) on photochemical decarbonylation. Heating **16** in toluene led to formation of **15** in 75% yield, by a 1,5-hydrogen shift; hence **15** is probably a secondary thermolysis product of **14**.

On the basis of other studies[7] on the thermal decarbonylation of bridged ketocyclopropyl systems related to **14**, it is expected that for a concerted electrocyclic opening of the three-membered ring with loss of CO (step **3** → **5**), more efficient orbital overlap in the transition state is obtained with an endo rather than an exo configuration.

It is highly probable then that addition of azirines **1** to cyclopentadienones **2** occurs preferentially from the endo side. In support of this contention is our ability to isolate, in a 1:4 ratio, the exo adduct **17** and cycloheptatriene **18** from the cycloaddition of triphenyl-



cyclopropene **13** to **7**. Unlike **14**, adduct **17** is stable to 300°.

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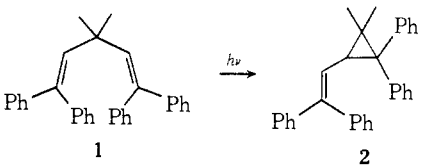
Evidence for Requirement of the Second π Bond in the Di-π-methane Rearrangement and the Observation of Excited Singlet 1,4-Phenyl Migration. Mechanistic and Exploratory Organic Photochemistry. LXXII[1]

Sir:

In our earlier efforts we uncovered a basic type of excited state behavior characteristic of molecules having two π moieties attached to an sp^3-hybridized carbon;[2] we termed this the di-π-methane rearrangement.[2b,3] Subsequently this rearrangement has proven to be of exceptional generality. Typifying the rearrangement is the transformation of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**1**)[4] (eq 1). Our mechanism



(1)

involves initial bonding between the two π moieties.

In contrast, Woodward and Hoffmann[5] have suggested that the reaction is a $_{\sigma}2_a + {}_{\pi}2_a$ or $_{\sigma}2_s + {}_{\pi}2_s$ process, a mechanism in which only one π bond plays a role.

The present report contains evidence describing (1) the necessity of the second π bond for facile rearrange-

(6) J. I. G. Cadogan and R. K. Mackie, *J. Chem. Soc. C*, 2819 (1969), showed that $J_{2,3}$ in 3*H*-azepines is *ca.* 5 Hz.

(7) B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Amer. Chem. Soc.*, **89**, 5964 (1967).

(1) For paper LXXI of the series note H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 7806 (1972).

(2) (a) H. E. Zimmerman and G. L. Grunwald, *ibid.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. S. Sherwin, *ibid.*, **89**, 3932 (1967).

(3) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

(4) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 98-99.