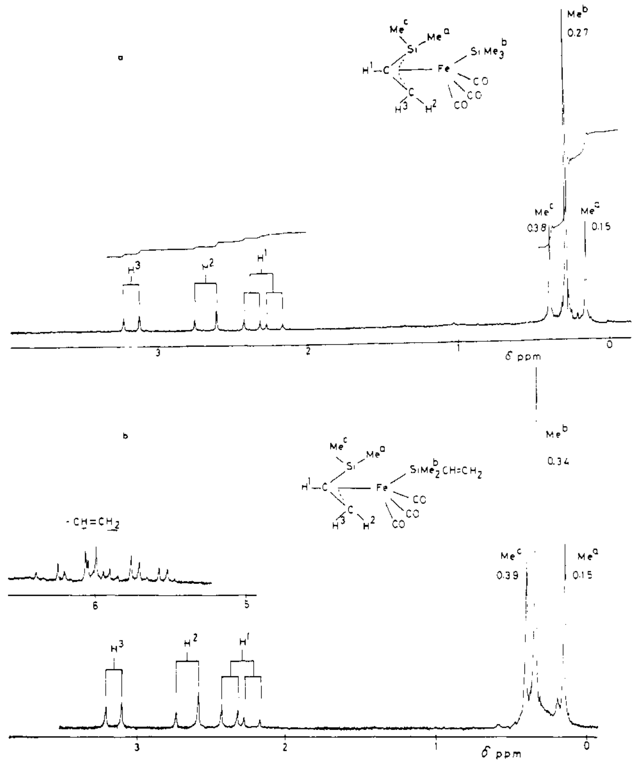

Figure 1. The ^{1}H NMR spectra of (a) **2a** and (b) **2b**.

vinyl protons because of the coordination to the iron atom. Thus, H^1 is observed at δ 2.29 ppm as a doublet of doublets with spin–spin coupling constants of 15.0 and 10.0 Hz. The chemical shifts of other vinyl protons, H^2 and H^3, are observed at δ 2.68 (doublet, $J = 15.0$ Hz) and 3.17 (doublet, $J = 10.0$ Hz), respectively. The proton decoupled ^{13}C NMR spectrum showed three C-Si signals at δ (vs. $Me_4Si = 0$) − 3.0, −1.0, and 0.0 with relative intensity of 1:3:1, two vinyl carbons at δ 43.0 and 46.0 and carbonyl carbons at δ 212. A mass spectrum of **2a** (25 eV) showed inter alia the molecular ion $C_{10}H_{18}O_3Si_2Fe^+$ at m/e 298 and ions corresponding to the successive loss of three CO at m/e 270, 242, and 214. In its IR spectrum (film) three $\nu_{C=O}$ bands were observed at 2025, 1995, and 1975 cm^{-1}. These bands correspond nicely to those of π-allyltricarbonyliron halides which reportedly exhibited three $\nu_{C=O}$ bands between 2095 and 1980 cm^{-1}.[6] An absorption at 1315 cm^{-1} with medium intensity is interesting to note. The $\nu_{C=C}$ frequency of the coordinated double bond in the π-allyl complex is known to appear at about 100 cm^{-1} lower frequency than that of the free C=C.[7] Therefore, if the $\nu_{Si=C}$ value at 1407 cm^{-1} reported by Barton and McIntosh[8] is valid.[9] the absorption at 1315 cm^{-1} can be assigned to the frequency of the coordinated Si=C bond.

By a similar treatment with enneacarbonyldiiron (190 mg, 0.52 mmol) 1,2-divinyltetramethyldisilane (**1b**, 190 mg, 1.12 mmol) gave the corresponding yellow complex (**2b**) in 60% yield, bp 42.0 °C (10^{-3} mmHg). The ^{1}H spectrum of **2b** (Figure 1b) showed three CH_3-Si signals at δ 0.15 (3 H, s), 0.34 (6 H, s), and 0.39 (3 H, s) and three coordinated vinyl protons at δ 2.27 (1 H, dd, $J = 14.0$ and 10.0 Hz, H^1), 2.66 (1 H, d, $J = 14.0$ Hz, H^2), and 3.15 (1 H, d, $J = 10.0$ Hz, H^3). In addition to these signals, **2b** showed a multiplet at δ 5.50–6.50 (3 H) corresponding to a free vinyl group. The molecular ion, $C_{11}H_{18}O_3Si_2Fe^+$ at m/e 310, which loses three CO successively, was also observed. The IR spectrum of **2b** exhibited three $\nu_{C=O}$ at 2025, 1995, and 1975 cm^{-1}, an absorption at 1310 cm^{-1} (vide supra), and absorptions due to a free vinyl group at 1600 and 940 cm^{-1}. Again these spectroscopic data are fully in agreement with the structure indicated. Anal. Calcd for **2a** ($C_{10}H_{18}Si_2O_3Fe$): C, 40.27; H, 6.08. Found: C, 40.43; H, 5.86. Calcd for **2b** ($C_{11}H_{18}Si_2O_3Fe$): C, 42.58; H, 5.85. Found: C, 42.86; H, 5.67.

The spectroscopic evidence reported here suggests strongly that compounds **2a** and **2b** do indeed contain the η^3-1-silapropenyl ligand. However, ultimate proof of the structure should be given by an x-ray crystal-structure determination. Actually, we have examined the reaction of enneacarbonyldiiron with a variety of vinyldisilanes to obtain crystalline derivatives, but at this moment analytically pure samples have been obtained only for **2a** and **2b**. The reaction of **2** with other donors, for example, with triphenylphospine, resulted in the substitution of η^3-1-silapropenyl and silyl groups rather than CO to give bis(triphenylphosphine)tricarbonyliron.

$$2 + 2PPh_3 \rightarrow Fe(CO)_3(PPh_3)_2$$

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes. We also thank O. L. Chapman for a preprint.[10]

References and Notes

(1) Chemistry of Organosilicon Compounds 95.
(2) W. le Noble, "Highlights of Organic Chemistry", Marcel Dekker, New York, N.Y., 1974, Chapter 10.
(3) J. E. Bulkowski, N. D. Miro, D. Sepelak, and C. H. Van Dyke, *J. Organomet. Chem.*, **101**, 267 (1974).
(4) W. Malisch and P. Panster, *J. Organomet. Chem.*, **64**, C5 (1974).
(5) (a) F. J. Impastato and K. G. Ihrman, *J. Am. Chem. Soc.*, **83**, 3726 (1961); (b) M. L. H. Green and P. L. Nagy, *J. Chem. Soc.*, 189 (1963); (c) R. F. Heck and C. R. Boss, *J. Am. Chem. Soc.*, **86**, 2580 (1964); (d) F. M. Chaudhari, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 2255 (1967); (e) D. H. Gibson and D. K. Erwin, *J. Organomet. Chem.*, **86**, C31 (1975); (f) A. N. Nesmeyanov, Yu. A. Ustynyuk, I. I. Kritskaya, and G. A. Shchembelov, *ibid.*, **14**, 395 (1968).
(6) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **226**, 1927 (1962).
(7) M. L. H. Green, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, Chapter 2.
(8) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972).
(9) The result of Barton and McIntosh has been questioned.[10] However, the ab initio calculation predicted the stretching vibration of Si=C for $H_2Si{=}CH_2$ to be 1490 cm^{-1}.[11]
(10) O. L. Chapman, C.-C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tumey, *J. Am. Chem. Soc.*, in press.
(11) H. B. Schlegel, S. Wolfe, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 246 (1975).

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Received June 23, 1976

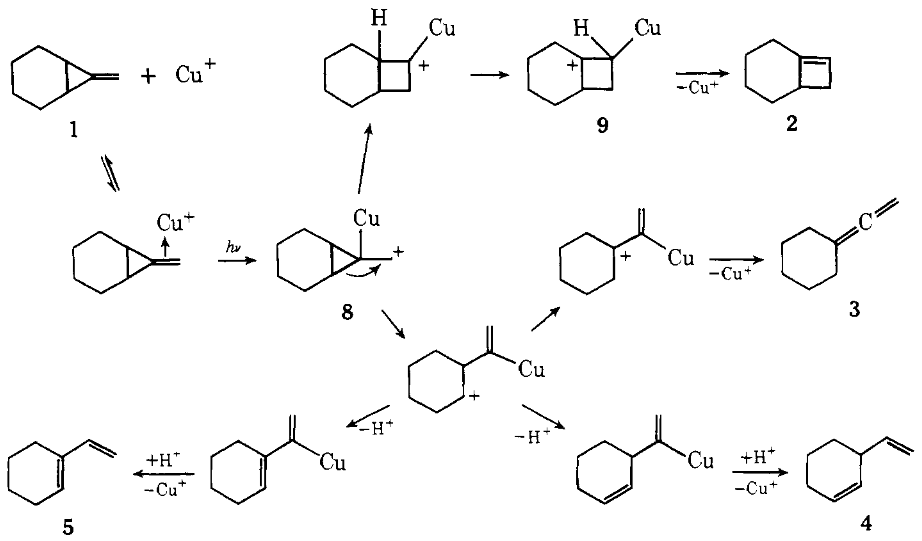
Copper(I) Catalysis of Olefin Photoreactions. Photorearrangement and Photofragmentation of 7-Methylenenorcarane

Sir:

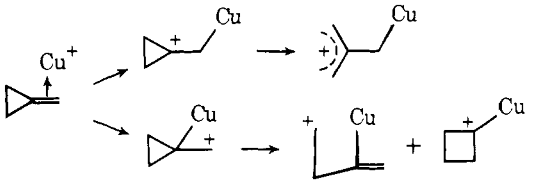
Recently we have been concerned with discovering and understanding organic photochemical reactions which require transition metals as catalysts.[1] Olefin photoreactions which are catalyzed by salts of copper(I)[2] are especially interesting since the salts form isolable olefin complexes,[3] and since the olefin–metal interaction almost certainly plays a key role in the photochemical process. We now report that the photochemistry of 7-methylenenorcarane (**1**) in the presence of copper(I) is characterized by a plethora of novel molecular transformations involving carbon skeletal reorganizations, a new class of copper catalyzed photochemical process.

Our previous studies elucidated some mechanistic details of olefin photodimerization catalyzed by copper(I) salts.[1d] However, the precise nature of the olefin–catalyst–light interaction responsible for reaction is not known. The present study of photolysis of methylene cyclopropane **1** in the presence

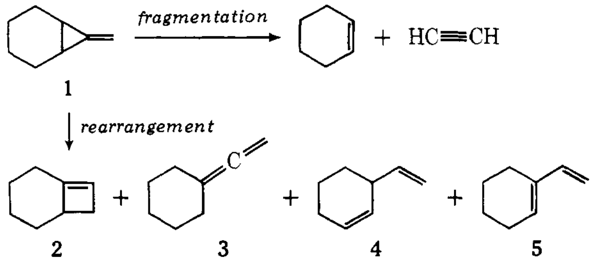
Scheme I



of copper(I) was initiated to test a mechanistic hypothesis. Thus, a mechanism which might account for copper catalysis of olefin photoreactions involves preliminary *photocupration,* light induced transformation of a μ^2-copper(I) olefin complex into a μ^1-β-copper(I) carbenium ion intermediate. This would produce either cyclopropyl or cyclopropyl carbinyl carbenium ion intermediates from a methylene cyclopropane. Skeletal rearrangements might then ensue via well-known reactions of these types of carbenium ions.[4,5]

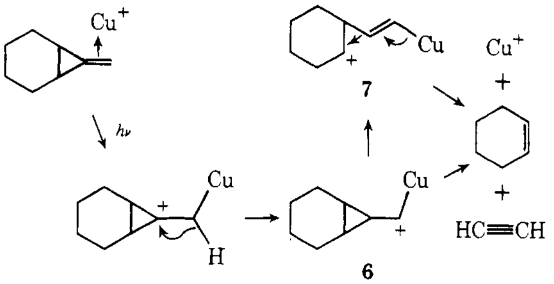


Formation of a (1:1) copper-olefin complex which rapidly exchanges free and coordinated olefin is indicated by the effect of added copper(I) on the ^{1}H NMR spectrum of **1**.[6] Olefin complexes of copper trifluoromethanesulfonate (CuOTf) exhibit two strong UV absorption bands, one at 233–241 nm (ϵ_{max} 2500–3600) and one at 272–282 nm (ϵ_{max} 1500–2100).[3] Therefore, **1** was irradiated in ether solution in the presence of CuOTf (0.08 equiv) with short wavelength, Rayonette RPR 254, UV lamps. Cyclohexene, acetylene, bicyclo[4.2.0]oct-1(7)-ene (**2**), and *unsym*-pentamethyleneallene (**3**) were obtained as major products along with traces of 3-vinylcyclohexene (**4**) and 1-vinylcyclohexene (**5**) (eq 1). All products were isolated by gas–liquid phase chromatography and identified by comparison of retention times (DC 710 on chromosorb column except for acetylene for which a Porapak column was utilized) and proton magnetic resonance spectra with those of authentic samples.[7] No reaction occurs in the absence of CuOTf and the reaction stops abruptly upon cessation of irradiation. The ratio of products **2–5** was monitored from 24 to 70% conversion of **1** and found to be 1.00 (**2**):0.41 (**3**):0.14 (**4**):0.10 (**5**) (±0.01) while that of cyclohexene varied gradually from 1.8 after 24% conversion of **1** to 1.4 after 70% conversion.

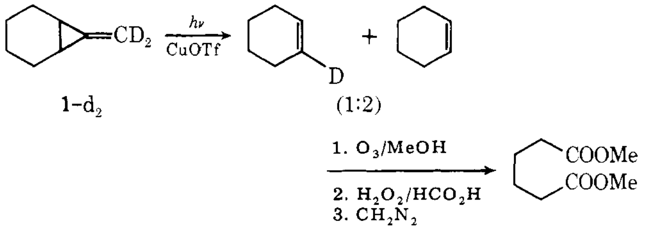


(1)

Formation of cyclohexene and acetylene by a photofragmentation reaction resembles the mercury sensitized, gas phase photofragmentation of methylene cyclopropane which gives principally ethylene and acetylene.[8] While photochemical reactions of olefins promoted by copper(I) often resemble those induced by triplet sensitizers,[1,2] different products are sometimes obtained. These differences may be ascribed to the influence of association of the photoexcited olefins with sensitizer or copper(I). The copper catalyzed photofragmentation could involve an ionic mechanism leading to a copper–carbene complex **6**[9] (eq 2). The free carbene corresponding to the copper–carbene complex **6** is known to fragment to cyclohexene and acetylene.[10] Alternatively, a stepwise process via **7** could be involved in the fragmentation of **6**. However, a deuterium labeling experiment indicates that a more complex process may be involved in the copper catalyzed photofragmentation. Thus, cyclohexene produced from the photolysis of **1**-d_2 in which the vinyl hydrogens are replaced by deuterium is 30–40% monodeuterated. The ^{1}H NMR spectrum of this product suggests that deuterium has replaced a vinyl hydrogen. This was confirmed by conversion to dimethyl adipate which was deuterium free. Deuterium scrambling into the six-membered ring was *not* found for recovered **1**-d_2 or for any of the rearrangement products from **1**-d_2 (vide infra). A mech-



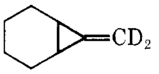
(2)



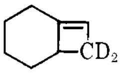
anism which can explain the interesting deuterium migration is unclear.

Since copper salts catalyze photocyclization of 1,3-butadiene to give cyclobutene,[2h,1] we examined the possibility that **2** might be produced indirectly from **1** via copper(I) catalyzed photocyclization of **5**. A mixture of **1**-d_2 (vide infra) and **5** (3:2) was irradiated in ether solution with CuOTf. Mass spectral analysis of the **2** produced showed it to be at least 94% **2**-d_2. Thus, photocyclization of **5**, which would give **2**-d_0, is not an important pathway for formation of **2** from **1**. Moreover, the invariance of the ratio of the products **2–5** during the course of the reaction implies that the products are all primary and stable under the reaction conditions.

The products **2**, **3**, **4**, and **5** can be explained by a mechanism involving initial light induced cupration of **1** to give a cyclopropylcarbinylcarbenium ion intermediate **8** (Scheme I). This mechanism is consistent with the deuterium substitution pattern found in the products **10–13** from rearrangement of **1**-d_2. The position of deuterium substitution in **11–13**, but not **10**, is evident from a comparison of their ^{1}H NMR spectra with those of the unlabeled analogues **3–5**. The deuterium substitution pattern in **10** was demonstrated by conversion to **13** upon vapor phase pyrolysis in a sealed tube.



1-d$_2$



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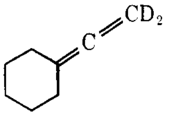

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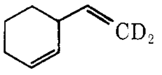

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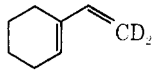

13

The cyclopropyl carbinyl to cyclobutyl rearrangement in the **8** to **2** transformation is especially characteristic and strongly supportive of a process requiring a vacant vicinal orbital, e.g., carbenium ion **8** or metallocarbenium ion **6**.[5] Significantly, such rearrangements are unknown for cyclopropyl carbinyl radicals.[11] Alternative mechanisms, e.g., involving excited state intermediates, have not been rigorously excluded. However, copper free excited state intermediates seem unlikely since the rearrangement types reported above have never been observed for electronically excited methylenecyclopropanes.[8,12] Clearly, photocupration must now be seriously considered as a possible key step in all olefin photoreactions catalyzed by copper salts.[13]

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this research. We thank Professor M. S. Newman and Dr. V. J. Lee for spectra of *unsym*-pentamethyleneallene. We thank Professor J. D. Roberts for stimulating discussions.

References and Notes

(1) (a) R. G. Salomon and N. El Sanadi, *J. Am. Chem. Soc.*, **97,** 6214 (1975); (b) R. G. Salomon and J. K. Kochi, *Tetrahedron Lett.*, 2529 (1973); (c) *J. Am. Chem. Soc.*, **96,** 1137 (1974); (d) R. G. Salomon, K. Floting, W. E. Streib, and J. K. Kochi, *ibid.*, **96,** 1145 (1974).

(2) (a) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87,** 2596 (1965); (b) D. J. Trecker, J. P. Henry, and J. E. McKeon, *ibid.*, **87,** 3261 (1965); (c) D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKeon, *ibid.*, **88,** 3021 (1966); (d) H. Nozaki, Y. Nisikawa, M. Kawanisi, and R. Noyori, *Tetrahedron*, **23,** 2173 (1967); (e) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Am. Chem. Soc.*, **91,** 2608 (1969); (f) J. A. Deyrup and M. Betkouski, *J. Org. Chem.*, **37,** 3561 (1972); (g) J. Meinwald and B. E. Kaplan, *J. Am. Chem. Soc.*, **89,** 2611 (1967); (h) R. Srinivasan, *ibid.*, **85,** 3048 (1963); (i) I. Haller and R. Srinivasan, *ibid.*, **88,** 5084 (1966); (j) R. N. Warrener and J. B. Bremner, *Rev. Pure Appl. Chem.*, **16,** 117 (1966); (k) J. E. Baldwin and R. H. Greeley, *J. Am. Chem. Soc.*, **87,** 4514 (1965); (l) R. Srinivasan, *ibid.*, **86**, 3318 (1964); (m) A. Angel, Ph.D. Thesis, University of Arizona, 1972.

(3) R. G. Salomon and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 559 (1972).

(4) (a) P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, **80,** 2024 (1958); (b) E. E. Schweizer and W. E. Parham, *ibid.*, **82,** 4085 (1960); (c) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87,** 4006 (1965); (d) C. H. DePuy, L. G. Schnack, and J. W. Hauser, *ibid.*, **88,** 3343 (1966).

(5) (a) R. Breslow in "Molecular Rearrangementsj', Vol. I, P. deMayo, Ed., Wiley, New York, N.Y., 1963, p 233; (b) N. C. Deno, *Prog. Phys. Org. Chem.*, **2,** 129 (1964); (c) M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16,** 321 (1965); (d) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87,** 1331 (1965); (e) M. Vogel and J. D. Roberts, *ibid.*, **88,** 2262 (1966); (f) P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88,** 2321 (1966); (g) Z. Majerski, M. Nikoletic, S. Borcic, and D. E. Sunko, *Tetrahedron,* **23,** 661 (1967). (h) The available data do not limit the order of 1,2-carbon and 1,2-hydride shifts producing **2** to that of Scheme I. Alternatively, hydride shift to give **6** (eq 2) could precede a carbon shift leading to **9** and thence **2.**

(6) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95,** 1889 (1973).

(7) (a) Bicyclo[4.2.0]octene-1(7): J. C. Duggan, U.S. Patent 3 660 342; *Chem. Abstr.*, **77,** P19256z (1972); (b) *unsym*-pentamethyleneallene: W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20,** 95 (1955); (c) 3-vinylcyclohexene: N. F. Cywinski, *J. Org. Chem.*, **30,** 361 (1965); (d) 1-Vinylcyclohexene: K. Suga, S. Watanabe, and K. Kamma, *Can. J. Chem.*, **45,** 933 (1967).

(8) R. K. Brinton, *J. Phys. Chem.*, **72,** 321 (1968).

(9) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95,** 3300 (1973).

(10) W. Kirmse and K. H. Pook, *Chem. Ber.*, **98,** 4022 (1965).

(11) J. D. Roberts, private communication.

(12) (a) J. C. Gilbert and J. R. Butler, *J. Am. Chem. Soc.*, **92,** 7493 (1970); (b) A. S. Kende, Z. Goldschmidt, and R. F. Smith, *ibid.*, **92,** 7606 (1970).

(13) These possibilities will be elaborated in the full paper.

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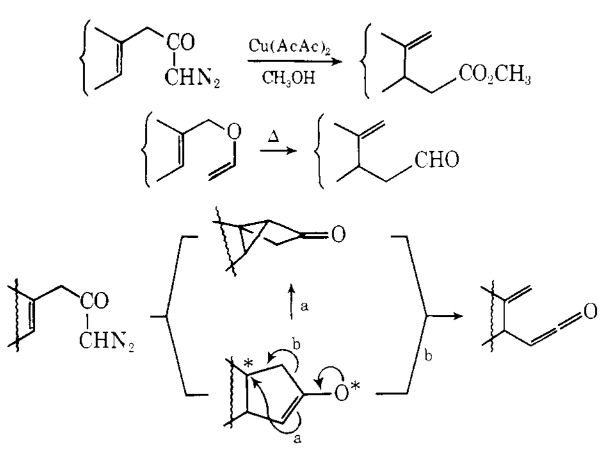
Received July 6, 1976

Stereochemical Consequences of the Vinylogous Wolff Rearrangement

Sir:

In recent communications we[1] and Lokensgard, O'Dea, and Hill[2] reported that the copper catalyzed decomposition of β,γ-unsaturated diazoketones efficiently leads via a novel skeletal rearrangement to γ,δ-unsaturated acid derivatives. This transformation, a synthetic alternative to the Claisen rearrangement of allyl vinyl ethers, was termed by us the vinylogous Wolff rearrangement.[3] A reasonable reaction pathway for this transformation[1,2] involves formation of a bicyclo[2.1.0]pentane intermediate via insertion of the diazocarbon into the β,γ-olefin. Fragmentation of this intermediate would then lead to a β,γ-unsaturated ketene.[4] A refinement of this scheme allows for either the insertion or fragmentation processes to proceed in a stepwise manner as shown below.



In view of the potential synthetic importance of the vinylogous Wolff rearrangement, we wish to report here the results of our investigation on the steric course of this transformation with three diazoketones (**1a–3a**). The required unsaturated diazoketones (**1a–3a**) were prepared in the usual manner from