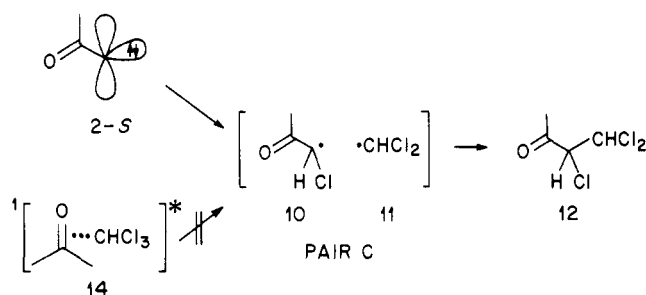


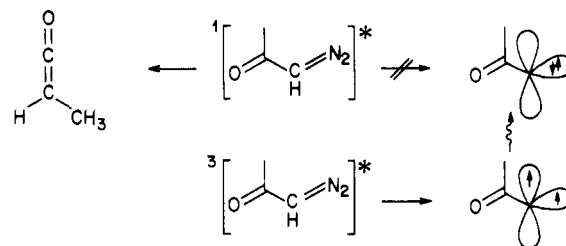
the sensitizer, though resulting in smooth decomposition, failed to generate any observable nuclear spin polarization. Consequently, the CIDNP effects are linked to the sensitizer. One can envisage several direct mechanisms how the sensitizer could generate pair C in the singlet state. Mechanisms involving diffusion-controlled reactions of the initially excited singlet state of the sensitizer, e.g., energy transfer to, or exciplex formation with the diazo compound, are eliminated because of the short lifetime of this state.¹⁵ Ground-state association of **1** and **3**, which might lead to an excited-state complex, is ruled out because neither uv nor NMR spectra show evidence for it. Finally, a mechanism involving an excited-state complex, **14**, between sensitizer and trichloromethane,¹⁶ is eliminated because it can form pair C only by a very specific quenching reaction without precedent. Therefore, we conclude that pair C is generated by singlet acetylmethylene, 2-S, which arises via intersystem crossing of 2-T.



This assignment implies that the intersystem crossing rate of 2-T and its rate of reaction with CHCl_3 are of the same order of magnitude. A similar conclusion is suggested for the photosensitized decomposition of **1** in cyclohexane/ CHCl_3 . This reaction led to polarized geminate coupling products initiated via both hydrogen abstraction by 2-T ($\rightarrow 6,9$) and via chlorine abstraction by 2-S ($\rightarrow 12$). However, we were able to offset the balance between the rates of reaction and of intersystem crossing by choosing appropriate substrates. Only one polarized coupling product, **7**, was observed in cyclohexene/ CHCl_3 ; apparently, 2-T reacts considerably faster with cyclohexene than with CHCl_3 and its overall rate of hydrogen abstraction is substantially greater than its rate of intersystem crossing to 2-S. In contrast, sensitized decomposition of **1** in CCl_4 produced polarized 3,4,4,4-tetrachlorobutan-2-one (**13**, E), whose signal direction indicated that it was generated predominantly from a singlet precursor. In this case, the intersystem crossing of 2-T is faster than its reaction with CCl_4 . This finding confirms that chlorine abstraction by triplet carbenes, though observed occasionally,^{10b,17} is not generally favorable.

The conclusion that 2-S is formed during the photosensitized decomposition of **1**, and that it reacts with chlorocarbons by chlorine abstraction bears significance for the mechanism of the Wolff rearrangement of **1**. The formation of ketenes upon direct irradiation of diazoketones is formulated frequently via singlet ketocarbenes.² In the case of **1**, the direct photolysis is known to produce methylketene,³ but we failed to observe any intermolecular products. Consequently, 2-S is eliminated as an intermediate in the Wolff rearrangement of **1** and the mechanistic alternative, methyl migration concerted with loss of nitrogen,² must be favored.

In summary, we have investigated the photodecomposition of diazoacetone and have observed reactions of acetylmethylene in the triplet and the singlet state. Acetylmethylene was eliminated as an intermediate in the Wolff rearrangement of diazoacetone. The mechanistic conclusions in this system are more detailed than for most other diazo compounds. Usually, the photoreactions of diazo compounds are discussed as carbene reactions although the participation of excited states of



the diazo compound cannot be ruled out. When simultaneous involvement of singlet and triplet carbenes is postulated, it is usually not clear whether intersystem crossing occurs in the diazo compound or, after loss of nitrogen, in the carbene. In the system discussed here, the involvement of excited-singlet diazoacetone is ruled out. Therefore, it is quite clear that 2-S and not 1-S is the precursor for **12** and **13**, and that intersystem crossing can only occur from 2-T to 2-S. This observation does not in itself establish 2-S as the lower lying state but it rules out the possibility that 2-S lies appreciably above 2-T. The question, which of these states is the ground state, is currently under investigation.

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The Thermal Dimer and Ketene Cycloadduct of $\Delta^{1,4}$ -Bicyclo[2.2.0]hexene¹

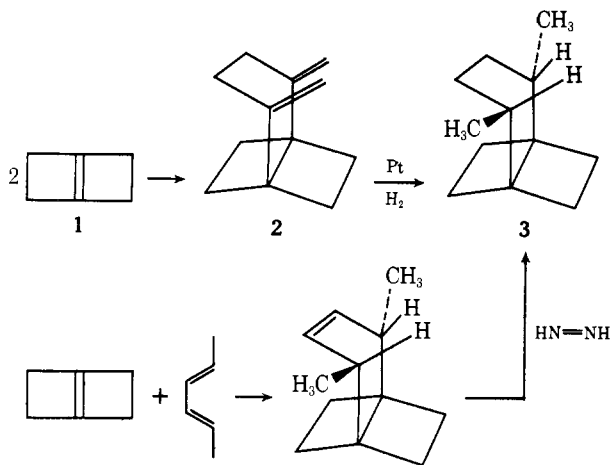
Sir:

We have previously reported that $\Delta^{1,4}$ -bicyclo[2.2.0]hexene (**1**) disappears spontaneously by a process which appears to obey second-order kinetics.² It did not give the expected ring opened product 1,2-dimethylenecyclobutane. We now have investigated the thermal reaction in more detail.

The electrolysis of 1-bromo-4-chlorobicyclo[2.2.0]hexane in dimethylformamide at -15 to -20° gave a solution of **1** which could be extracted into pentane. The pentane solution

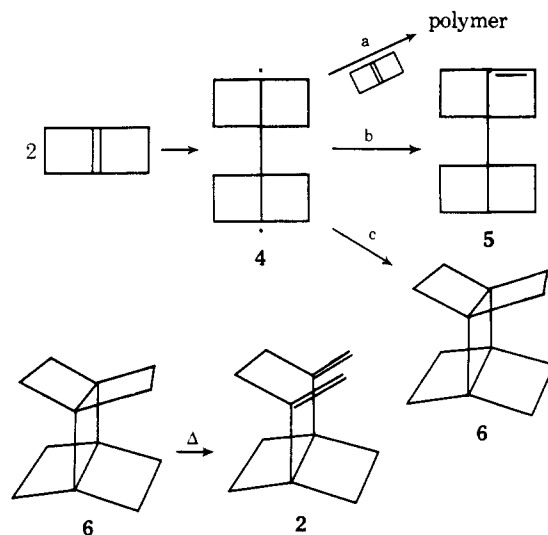
was allowed to stand at room temperature for 24 h. The insoluble polymer which precipitated was filtered, and evaporation of the solvent gave a single product in 25–50% yield which was homogeneous by gas chromatography. The mass spectrum and elemental analysis³ indicate the molecular formula $C_{12}H_{16}$. The proton NMR spectrum (270 MHz) had bands at δ 4.79 (2 H, s), 4.57 (2 H, d, $J = 1.8$ Hz), 2.33 (4 H, s), and 2.28 (8 H, AA'BB', $J = 3.3, 9.6$ Hz). The infrared spectrum contained a C=C stretching vibration at 1641 cm^{-1} . The carbon NMR spectrum (20 MHz) revealed six bands (δ rel to $\text{Me}_4\text{Si} = 0$, relative intensity): δ 30.4 (43), 33.7 (26), 46.7 (9), 106.9 (25), and 154.1 (6). The ^1H NMR bands at δ 4.79 and 4.57,⁴ the C=C stretch in the ir spectrum⁵ and the ^{13}C NMR bands at δ 106.9 and 154.1^{6,7} are consistent only with the presence of two equivalent, unsymmetrically substituted $\text{C}=\text{CH}_2$ subunits. The fact that only six carbon resonances are found necessitates a plane of symmetry, and the carbon shifts at δ 30.4 and 46.7 are similar to those found in compounds with a bicyclo[2.2.0]hexane fragment.^{8,9} Based on these assignments, a reasonable structure for this compound is 2,5-dimethylenetricyclo[4.2.2.0^{1,6}]decane (**2**).

In order to establish the structure of **2**, we have performed the Diels-Alder reaction between **1** and *trans,trans*-2,5-hexadiene. Reduction of the product with diimide gave *cis*-2,5-dimethyltricyclo[4.2.2.0^{1,6}]decane (**3**). The same dimethylpropellane was obtained by hydrogenation of **2** over platinum black.



It was not possible to devise a mechanism by which **2** is produced in a single step. A reasonable sequence involves initial bimolecular reaction to give a diradical species, **4**, which then has several options.¹⁰ It may add another molecule of olefin and continue the polymerization process (route a), abstract a hydrogen to give the "ene" product (**5**) (route b), or close to give the pentacyclopentane **6** (route c). Route a can account for the large (50–75%) amount of polymer formed in this reaction; however, no low molecular weight products have been isolated to characterize this reaction path. The "ene" reaction, route b, has been observed previously with cyclopropene;¹¹ however, the formal "ene" product is itself a highly strained olefin and capable of undergoing further reactions, making the detection of any products quite difficult. However, the formation of **6** is confirmed by the isolation of **2**, a compound obtained by retro[2 + 2]cycloaddition of **6**. Since the [2.2.2]propellane reported by Eaton and Temme undergoes ring cleavage at 25° with a half-life of 28 min,¹² **6** would be expected to do so at an even lower temperature.

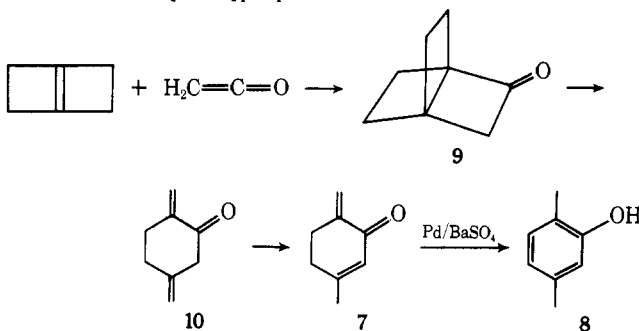
The dimerization of **1** is unique in that the other reported examples of thermal olefin dimerization occur in compounds in which the double bond is subjected to severe torsional strain. Adamantene,¹³ homoadamant-1-ene,¹⁴ and norborn-1-ene¹⁵ have structures which necessitate large torsional angles be-



tween the p orbitals. In **1**, the angle must be zero, and p-p overlap should not be significantly different from that of a normal olefin. Thus the reactivity of **1** is due primarily to angle bending rather than torsional strain.

In order to further examine the reactivity of **1**, a solution of **1** in methylene chloride was stirred at -78° while approximately 100 g of freshly prepared ketene was bubbled through the mixture. The solution was warmed to room temperature over the period of 1.5 h. Excess ketene and methylene chloride were evaporated, and the residue was passed through alumina and eluted with pentane and ether. The ether fraction contained one major component. The mass (M^+ , = 122), ir (1672 (s), 1625 (s), 935 (m), 880 cm^{-1} (m)), uv (λ_{max} MeOH 255 nm ϵ 13 400), and NMR ((CDCl_3 , 270 MHz); δ 6.02 (1 H, s), 5.97 (1 H, s), 5.28 (1 H, s), 2.73 (2 H, t, $J = 6.6$ Hz), 2.39 (2 H, t, $J = 6.6$ Hz), 2.01 (3 H, s)) spectra are consistent with 3-methyl-6-methylenecyclohex-2-en-1-one (**7**). Identification was confirmed by rearrangement over Pd/BaSO_4 ^{16,17} to 2,5-dimethylphenol (**8**) and comparison of the 270-MHz NMR, ir, and uv spectra with that of authentic **8**.

A reasonable mechanism for the formation of **7** involves [2 + 2] cycloaddition of ketene to **1**¹⁸ to give tricyclo[2.2.2.0^{1,4}]octan-2-one (**9**) followed by ring cleavage to give 2,5-dimethylenecyclohexanone (**10**). In the reaction mixture **10** undergoes a hydrogen migration to form the conjugated dienone. The isolation of **7** provides strong evidence for the formation of a [2.2.2]propellane-2-one.

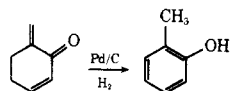


The cycloaddition reactions of **1** have the potential of giving a variety of interesting strained molecules. These reactions are the subject of a continuing study.

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- (10) The scheme is consistent with the observed second-order disappearance of **1**. If one applies the steady state approximation, one obtains a term for initiation and dimerization which is second order in **1** and a term for polymerization which has a higher order dependence on **1** and is determined by the nature of the chain termination step. In the preparative experiments the ratio of dimerization of polymerization was 1:1. The kinetic experiments were carried out at a lower concentration of **1** which should then give close to second-order kinetics.
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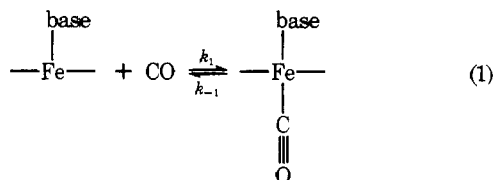
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Received December 18, 1975

Dual Pathways of Heme Protein Model Compound Reactions with Carbon Monoxide

Sir:

The reactions of carbon monoxide with heme proteins¹ or their five-coordinate model compounds^{2–4} are usually written as the simple association-dissociation process shown below (direct association mechanism).



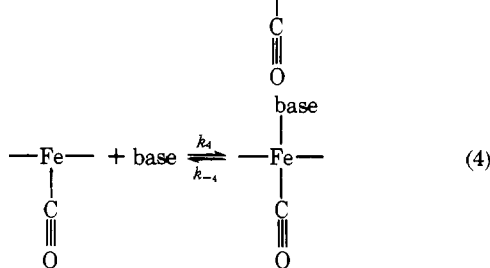
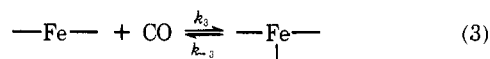
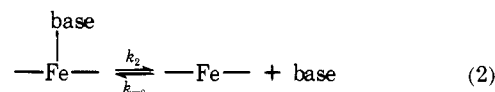
We have recently reported⁴ definitive kinetic evidence for this pathway for compound **1** (see Table I) in water at pH > 7. We now report evidence for a different base-elimination mechanism (eq 2–4) in reactions of heme-base compounds with carbon monoxide.

When compound **1** in aqueous CTAB is titrated with acid its Soret band shows an isosbestic change from that of five-coordinate heme (416 nm at pH 9) to that of four-coordinate heme (408 nm, broad, at pH 2)⁵ and indicates an apparent $\text{p}K_a$ of 3.5.⁶ Over the range pH 2–9 the visible spectrum of the

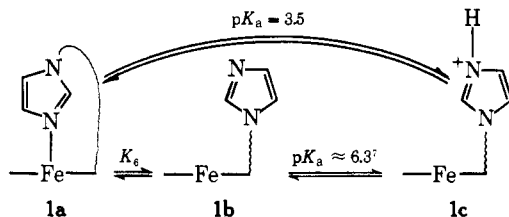
Table I

Compound	R	(l'_{obsd}) ^{a, b} l. mol ⁻¹ s ⁻¹	$\text{p}K_a$ ^c
1	H	1.0×10^7	3.6
2	CH ₃	1.3×10^8	6.5
Mesoheme dimethyl ester		3.5×10^8	

^a The observed second-order rate constant for heme-carbon monoxide reaction was measured by the flash photolysis method as a pseudo-first-order reaction in varying concentrations of excess carbon monoxide. ^b Reactions were observed at pH 7.3 in water containing 2% cetyltrimethylammonium bromide (CTAB) and about 10^{-4} M sodium dithionite. ^c $\text{p}K_a = \text{pH}$ at which the proximal base is half coordinated to iron(II) and the other half protonated.



corresponding carbon monoxide complex, **1**-CO, is unchanged. This means that at pH ≤ 2.5 , the proximal imidazole in **1** remains complexed with iron only if carbon monoxide is also complexed.⁵ It also implies that four-coordinate heme, **1c**, produced in acidic media must complex carbon monoxide before the imidazole can coordinate (base-elimination mechanism).



The kinetic data for **1** strengthen this implication. At a carbon monoxide concentration of 2×10^{-5} M the rate constant for combination with carbon monoxide (l'_{obsd}) increases from 1×10^7 l. mol⁻¹ s⁻¹ at pH 7 to 3.5×10^8 l. mol⁻¹ s⁻¹ at pH 2.5.⁴ Since the rate constant obtained at pH 2.5 is identical with that obtained for mesoheme dimethyl ester, the reaction of **1** at pH 2.5 with carbon monoxide presumably proceeds via a reaction of **1c** with carbon monoxide ($l'_{\text{obsd}} = k_8$), yielding, as the final product, **1a**-CO, and not **1c**-CO.