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 10   11   12   13
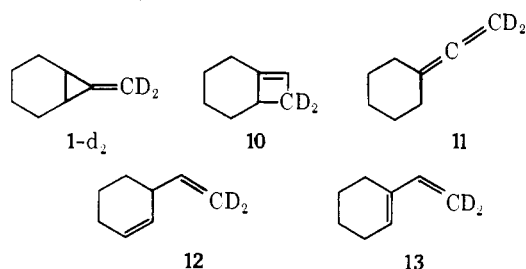
The cyclopropyl carbinyl to cyclobutyl rearrangement in the **8** to **2** transformation is especially characteristic and strongly supportive of a process requiring a vacant vicinal orbital, e.g., carbenium ion **8** or metallocarbenium ion **6**.[5] Significantly, such rearrangements are unknown for 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]

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## 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.
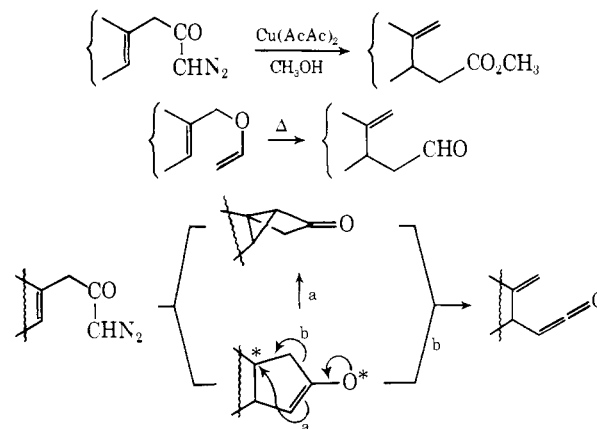

In view of the potential synthetic importance of the vinylogous Wolff rearrangement, we wish to report here the results of our investigation on the steric course of this transformation with three diazoketones (**1a**–**3a**). The required unsaturated diazoketones (**1a**–**3a**) were prepared in the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

the corresponding β,γ-unsaturated ethyl esters (**1b**–**3b**)[5] ((a) 5% aqueous NaOH, 2 h; (b) $SOCl_2$; (c) 3 equiv of CH_2N_2) which were available through condensation of either cyclohexanone, 4-*tert*-butylcyclohexanone, or 2,6-dimethylcyclohexanone with the lithium enolate of ethyl acetate as described by Rathke.[6] Subsequent dehydration ($SOCl_2$:pyridine 1:1, 2 h) led selectively to the endocyclic isomer. Introduction of the methyl group of **2b** was effected utilizing the LDA:HMPA procedure reported recently by Rathke[7] and Schlessinger.[8]


a, R = CHN_2
b, R = OCH_2CH_3
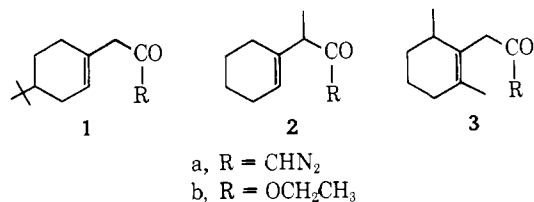
Treatment of **1a** with a catalytic amount of $CuSO_4$ or $Cu(AcAc)_2$[2] in boiling cyclohexane containing 1% methanol led to **4** and **5** in 26 and 39% yield,[9] respectively. The structure and stereochemical assignments were established after VPC resolution by direct comparison of the IR and NMR spectra of **4** and **5** with those obtained recently by Trost and Strege.[10] Similar decomposition of diazoketone **2a** led to a mixture of **6**[5] and **7**[5] in 24 and 35% yield, respectively. Confirmation of structures **6** and **7** was obtained by their $RuO_4/NaIO_4$ oxidation[11] in aqueous acetone to the methyl ester of 2-oxocyclohexane acetic acid, while the stereochemical disposition of the methyl substituents was established utilizing lanthanide shift reagents. Here the olefinic methyl resonance (δ 1.58) of **7** underwent a greater downfield shift relative to the methyl resonance (δ 1.57) of **6** when equimolar solutions of **6** and **7** were progressively doped with the shift reagent, $Eu(fod)_3$.[12] Furthermore, the olefinic resonance (δ 5.10) of **6** experienced a larger deshielding effect compared to the same signal (δ 5.12) in ester **7**.
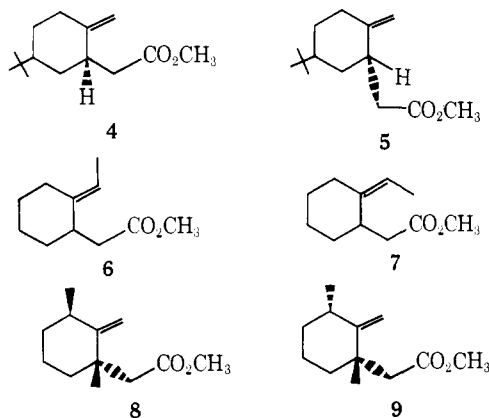
Interestingly the final example (**3a**) in our study, unlike the previous two cases which displayed little or no stereoselectivity, gave a 9:1 mixture of esters **8**[5] and **9**[5] in an overall yield of 41%. Since the spectroscopic properties of these unknown esters were insufficient to establish conclusively the stereochemical relationship of the 1,3-dimethyl substituents, a chemical correlation of **8** and **9** with the previously known enone **10**[13] was effected. To this end $RuO_4/NaIO_4$ oxidation[11] of pure **8** and **9** followed by esterification with CH_2N_2 led to **11**[5] and **12**,[5] respectively. In each case only a single γ-ketoester was formed. Equilibration of either pure **11** or **12** with $NaOCH_3$ in boiling MeOH led to the same mixture; i.e., 65:35, respectively. Although both ketoesters were also unknown, a tentative structure assignment based on the NMR spectra data was now

possible. For example, the resonance of the equatorial methyl substituent at C-1 in **11** experiences a small, expected[14,15] upfield shift (Δ 0.25 ppm) relative to that of the C-1 axial methyl in **12**. Likewise, the equatorial methylene group at C-1 in **12** appears upfield (Δ 0.30 ppm) compared to the axial counterpart in **11**.

Continuing the chemical correlation, homologation of ester **9** to **13**[5] via a photochemical initiated Wolff rearrangement[16] proceeded without incident ((a) NaOH; (b) $SOCl_2$; (c) 3 equiv of CH_2N_2; (d) $h\nu$, MeOH). Subsequent $RuO_4/NaIO_4$ oxidation of both **13** and **10**, followed in the case of **10** by CH_2N_2 esterification, led in both instances to the same[17] ketoester (i.e., **14**[5]). On this basis then, the major and minor products of the vinylogous Wolff rearrangement of **3a** are assigned structures **8** and **9**, respectively.
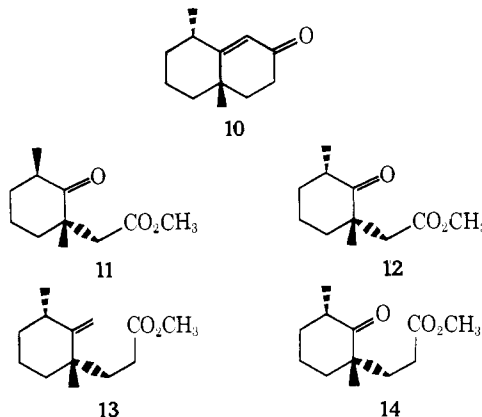

A brief comment at this point concerning the observed stereoselectivity is in order. Examination of molecular models of **1a** reveals that approach by the diazocarbon to the β,γ-olefin from either side is sterically unencumbered while one of the two possible reactive conformations in diazoketones **2a** and **3a** appears to lead to considerable nonbonded interaction. This nonbonded interaction in **2a** arises from a 1,3-interaction between the side chain methyl and the ring methylene groups. Interestingly, only **3a** displays high stereoselectivity[18] in the vinylogous Wolff rearrangement, while **1a** and **2a** are almost completely nonstereoselective. These results are explicable in terms of the described mechanism. That is, during the fragmentation step of the vinylogous Wolff rearrangement, diazoketone **2a** has ample opportunity to lose the postulated selectivity resulting from initial addition to the β,γ-olefinic bond, while the stereochemical outcome of **1a** and **3a** is determined via the initial bond formation step. Alternatively, if the fragmentation step is stereospecific, the lack of selectivity with **2a** must derive from the initial insertion. Further studies on the vinylogous Wolff rearrangement are in progress in our laboratory.

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i

ii
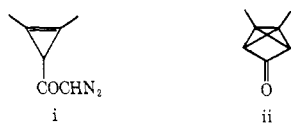
More recently Zimmerman and Little reported that when the copper catalyzed decomposition of iii was carried out in the absence of methanol an intermediate, as yet unidentified, is formed. This intermediate displays an infrared band at 5.60 μ (1785 cm^{-1}). Upon methanolysis ester iv is formed in addition to a variety of other products: H. E. Zimmerman and R. D. Little, J. Am. Chem. Soc., 96, 4623 (1974).

iii

iv
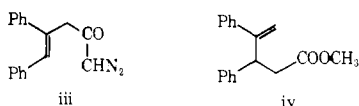
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I

II

III

a, R = H
b, R = OCH₂CH₂O
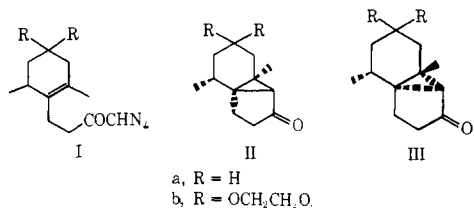
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Received May 28, 1976

The Photochemical Reactions of Azidopentaamminechromium(III). Evidence for a First Transition Series Coordinated Nitrene Intermediate

Sir:

The recent discovery by Basolo and co-workers of an efficient photoinduced reaction mode involving nitrenes[1] has revived considerable interest in the photochemical reactions of azido complexes of transition metals.[2] In contrast to the redox mode observed in the photolysis of $Co(NH_3)_5N_3^{2+}$,[3] the rhodium(III) and iridium(III) analogues reacted principally via a coordinated nitrene, $M(NH_3)_5NH^{3+}$, pathway.[1] The difference in reaction modes with the heavier metals was attributed to less favorable +2 oxidation states and increased sta-
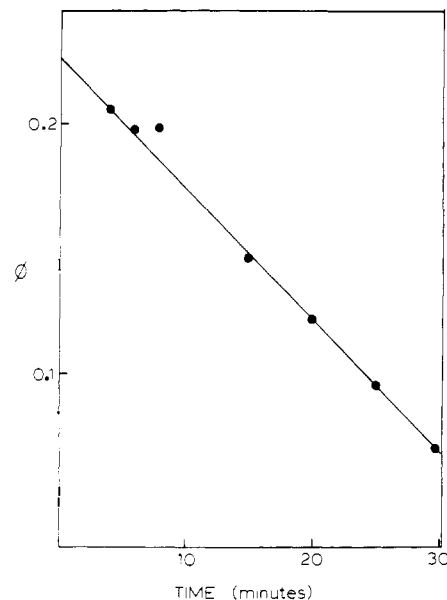

Figure 1. Dependence of the $Cr(NH_3)_5NH_2Cl^{3+}$ quantum yield on irradiation time; initial concentration of $[Cr(NH_3)_5N_3](ClO_4)_2$ is 2.8×10^{-3} M in 0.3 M HCl, $I_0 \sim 10^{-5}$ einstein l.$^{-1}$ min^{-1}.

bilization of the nitrene intermediates by additional $d\pi-p\pi$ bonding.[1c] As yet, however, nitrene intermediates have not been detected in the photochemical reactions of first transition series azidopentaammine complexes. Analogous to rhodium(III) and iridium(III) complexes, the +2 oxidation state of acidopentaamminechromium(III) is less favorable. Moreover, previous investigations of thermal substitution reactions of $Cr(NH_3)_5N_3^{2+}$ have indicated that the Cr–N bond is unusually stable.[4] With these observations in mind, we have reexamined the 313-nm photolysis of $Cr(NH_3)_5N_3^{2+}$ to determine if nitrene intermediates occur.

Previous investigations of the ligand-field photosensitivity of $Cr(NH_3)_5N_3^{2+}$ have established aquation of ammonia as the predominant process,[4] whereas irradiation in the LMCT region, $\lambda \leq 330$ nm, resulted in a general decline in the ultraviolet absorption spectrum and the evolution of N_2 gas.[5] When acidic or neutral solutions of $Cr(NH_3)_5N_3^{2+}$ are exposed to 313-nm radiation,[6] the quantum yield of dissappearance of $Cr(NH_3)_5N_3^{2+}$, determined from the decrease in absorbance at 280 nm and/or 265 nm, was 0.48; in excellent agreement with the previous determination of 0.45.[5] Also, azide ion was not detected in the photolyte.[7] Contrary to the previous report,[5] however, the inability of the photolyte to reduce $Co(NH_3)_6^{3+}$, $Co(NH_3)_5Cl^{2+}$, or $Co(NH_3)_5Br^{2+}$ and flash photolysis studies indicate photoredox decomposition is not a major reaction pathway. When degassed 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solutions containing 10^{-4} to 10^{-2} M NaI were exposed to a filtered (10^{-2} M NaI) 210-J flash, 20% of the complex was decomposed and N_2 was formed, yet no transient absorbance of I_2^- was observed.[2a,3b,8] Although the absence of an I_2^- absorbance indicates photoredox does not occur, its absence was further confirmed by flash photolysis. A degassed 10^{-3} M $Cr(NH_3)_5N_3^{2+}$ solution was exposed to a filtered (10^{-2} M NaI) 250-J flash and analyzed at 740 nm, the absorption maximum of $Cr(H_2O)_6^{2+}$.[9] Spectra recorded before and after the flash indicated 50% of the complex was decomposed by the flash, but no transient absorbance was observed. Assuming a minimum signal to noise ratio of 2:1, the absence of an absorbance establishes that photoredox accounts for less than 12% of the overall photochemical reaction.

The previous study which proposed a photoredox mechanism reported the yield of N_2 to be essentially the expected 1.5 mol of N_2 per mole of complex decomposed. However, we find the