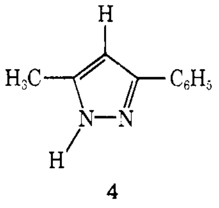
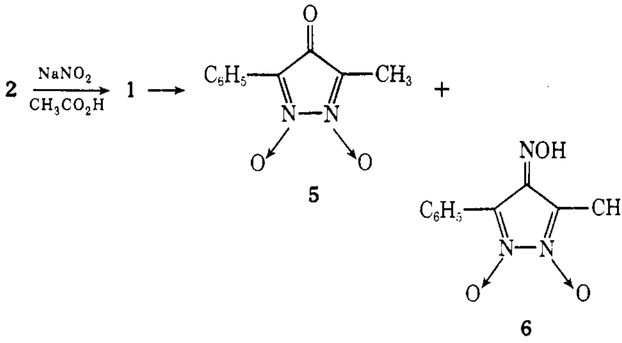
Found: C, 62.88; H, 5.35; N, 14.54.) The compound yellowed slowly upon exposure to air and light.

The chemical properties (acidity, chelation) and spectral characteristics of 1 agree with those of previously reported 1-hydroxypyrazole 2-oxides.[1b] The infrared spectrum closely resembled that of a sample of 1-hydroxypyrazole-3(5)-phenyl-4,5(3)-dimethylpyrazole 2-oxide, while the NMR spectrum (CF_3CO_2H) showed signals at δ 7.80–8.90 (m, 5, C_6H_5), 6.47 (s, 1, pyrazole C-4 proton), and 2.52 (s, 3, CH_3).[5] The heterocyclic structure was confirmed by reduction of 1 with zinc in refluxing acetic acid to 3(5)-phenyl-5(3)-methylpyrazole (4), identified by comparison with an authentic sample.[6]



4

Although 1 has not been isolated previously, its intermediacy has been inferred in the nitrosation of 2 with sodium nitrite in acetic acid to give 2-phenyl-5-methyl-3,4-diazacyclopentadienone 3,4-dioxide (5) and the corresponding oxime (6).[7] In a preliminary investigation of its chemical reactivity, 1 was subjected to nitrosation under conditions approximating those reported for the conversion of 2 to 5 and 6. When the nitrosation was performed under an inert atmosphere, the main product was 6, while the ketone (5) was the major product when the reaction mixture was kept saturated with oxygen during the nitrosation. These results support the intermediacy of 1 in the synthesis of 5 and 6 as proposed by Freeman.



We are currently pursuing further investigations into the synthesis and reactivity of 1 and analogous compounds.

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References and Notes

[1] (a) J. P. Freeman and J. J. Gannon, *J. Heterocycl. Chem.*, **3**, 544 (1966); (b) J. P. Freeman and J. J. Gannon, *J. Org. Chem.*, **34**, 194 (1969).

[2] We believe, as proposed by Freeman,[7] that **1** is present during the nitrosation of **2**, even in the absence of the metal, but undergoes further reaction under nitrosating conditions. Cobalt(II), under basic conditions, simply traps the anion of **1** by forming a very insoluble chelate which is removed from the nitrosating medium before further reaction occurs. The formation of such chelates with 1-hydroxypyrazole 2-oxides has been reported for a variety of metal ions,[1b] and we are investigating the behavior of other metal ions in place of cobalt(II) in our reaction.

[3] The chelate (**3**) was isolated from the crude product mixture after extraction with methanol in a Soxhlet extractor for several hours. The insoluble residue recovered from the Soxhlet thimble was identical in the infrared with an analytical sample of **3**,[5] a violet solid, subsequently prepared by treatment of the potassium salt of **1** with aqueous $CoCl_2$.

[4] The by-product was identified as the oxime (**6**). In the absence of the metal ion, the reaction gave **6** in 42% yield, and no isolable quantities of **1** were detected.

[5] Spectra were obtained using a Beckman IR-8 infrared spectrophotometer and a Hitachi Perkin-Elmer R 20 60-MHz NMR spectrometer.

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[7] J. P. Freeman, J. J. Gannon, and D. L. Surbey, *J. Org. Chem.*, **34**, 187 (1969).

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Synthetic Organic Photochemistry. VII. Six-Atom Photochemical Ring Expansions[1]

Summary: The photolysis of 2-(2-cyclopropylcyclopropyl)cycloalkanones leads to a six-atom ring expansion in a single step.

Sir: Traditional methods for the ring expansion of carbocyclic systems most frequently involve one atom ring expansions.[2] We have been engaged for some time in a program aimed at developing methods by which rings can be expanded by several atoms in a single step. Previously we have reported examples of two atom photochemical ring expansions of 2-alkenyl-[3] and 2-alkynylcycloalkanones[4] and three atom photochemical ring expansions of 2-cyclopropyl-[5] and 2-oxiranylcycloalkanones.[6] In order to increase the utility of the photochemical method of ring expansion we have sought to prepare systems which combine two of the above types of structural features and herein report our initial studies in this area.

A 2-(2-cyclopropylcyclopropyl)-cycloalkanone such as 1 is an attractive model system because it can potentially undergo a six atom photochemical ring expansion either by a one photon (path a, Scheme I) or by a two photon process (path b).[7] The route illustrated in Scheme II, which makes use of a recently reported synthesis of α,β-unsaturated aldehydes using 1,3-bis(methylthio)-allyllithium,[8] provided an efficient method for the preparation of **1a** and **1b** from the corresponding cycloalkene oxides.

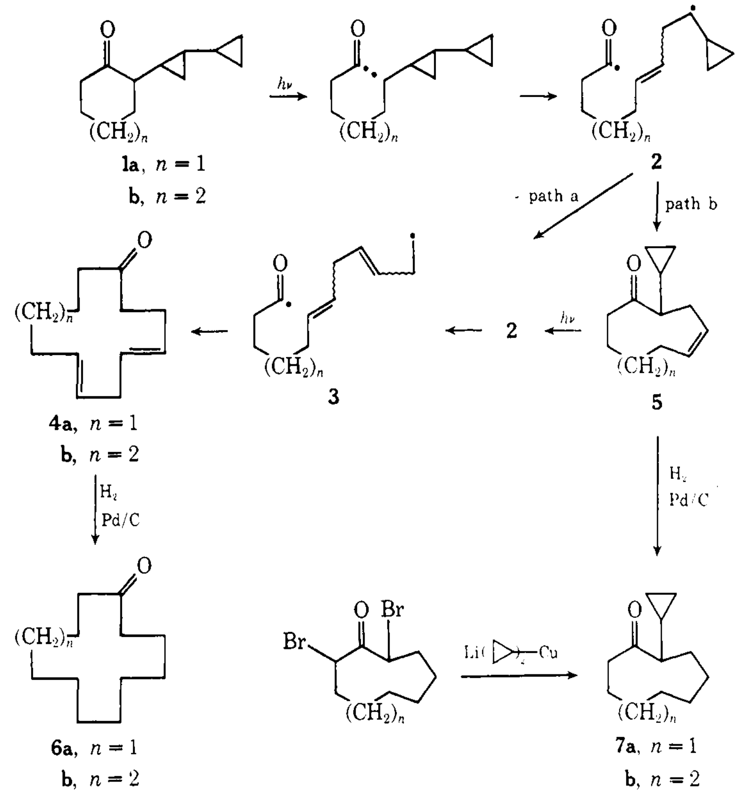
Irradiation of a dilute solution of **1a** [$\lambda_{max}^{isooctane}$ 293 nm (ϵ 34)] through Pyrex until approximately 80% of **1a** had disappeared gave a mixture which on vpc analysis was found to contain at least five products. Because of the large number of potential cis and trans double bond isomers of 4 and 5 no attempt was made to resolve the mixture. The crude photoproduct was distilled and reduced by catalytic hydrogenation over palladium on charcoal to give in 78% overall yield a mixture which contained 19% of the starting ketone **1a**, 61% cyclododecanone **6a** and 20% 2-cyclopropylcyclononanone **7a**.

A similar irradiation of 1b [$\lambda_{max}^{isooctane}$ 294 nm (ϵ 50)] to 75% disappearance of the starting material followed by hydrogenation of the distilled crude photoproduct gave in 86% overall yield a mixture of starting ketone **1b** (25%), cyclo-

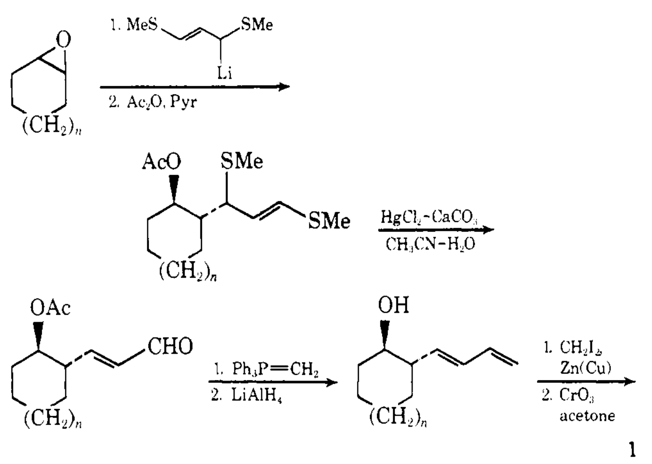
Table I
Product Composition in Photolysis of 1a

	% in Reduced Photomixture	
Time, hr	7a	6a
1	3.5	8
2	9.6	17
3	12	23

Scheme I



Scheme II



tridecanone **6b** (51%), and 2-cyclopropylcyclodecanone **7b** (24%).[9]

In an effort to determine qualitatively whether the six atom ring expanded products 4 arose by way of a one photon process (path a, Scheme I) or by two consecutive three atom ring expansions (path b) the photolysis of **1a** was stopped at low conversion and the composition of the reduced photoproduct was determined (Table I). The results of these experiments indicate that the six atom ring expanded product is a primary photoproduct because little of it would be expected to be formed early in the reaction by a two photon process as the starting ketone would be absorbing most of the light. Through the early part of the reaction the six atom and three atom ring expanded products are formed in an approximately 2:1 ratio. Since in the final product the composition is ~3:1 it appears that later in the reaction some of **5a** is being converted to **4a**.

References and Notes

(1) Supported in part by grants from the National Science Foundation and the Alfred P. Sloan Foundation.

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(7) Although we have illustrated the three atom ring expansions[5,6] as diradical processes they can also be considered to be excited state allowed $[{}_{\sigma}2_{s} + {}_{\sigma}2_{s}]$ cycloadditions: R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Velag Chemie, Weinheim/Bergst., Germany, 1970.

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(9) Authentic samples of the cyclopropyl ketones **7a** and **7b** were prepared by reaction of the appropriate α,α'-dibromocycloalkanone (**8**) with lithium dicyclopropylcopper; cf. G. H. Posner and J. J. Sterling, *J. Amer. Chem. Soc.*, **95**, 7788 (1973).

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