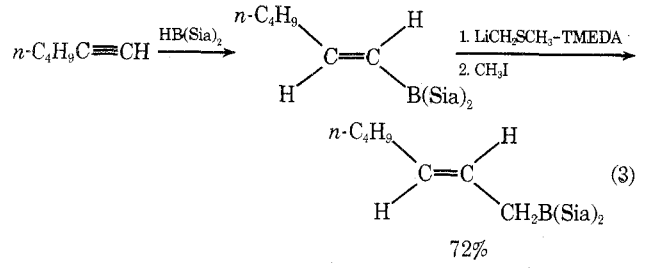

Sia = 3-methyl-2-butyl

rently exploring the scope and limitations of this highly promising synthesis as well as the possibility of applying the homologation procedure to the organoborane ring expansion.

The following procedure is representative. To a solution of 10 mmol of thiomethoxymethyllithium–TMEDA in hexane prepared by the literature procedure[4] and placed in a 100-ml flask equipped with a septum inlet, a magnetic stirring bar, and an outlet connected to a mercury bubbler was added 2.44 ml (10 mmol) of tri-*n*-butylborane in 10 ml of THF at 0°. After the mixture stirred for 1 hr at 0°, 1.87 ml (30 mmol) of methyl iodide was added at 0°, and the reaction mixture was stirred for 6 hr at 25°. After addition of *n*-hexadecane as an internal standard, the mixture was oxidized with 10 ml each of 3 *N* sodium hydroxide and 30% hydrogen peroxide. After the aqueous layer was saturated with potassium carbonate, GLC examination (Carbowax 20M) indicated the presence of *n*-pentanol (9.7 mmol), 1-butanol (17.8 mmol), 2-butanol (1.5 mmol), and a trace of 2-methyl-1-butanol. In a separate run, the reaction mixture was examined by GLC (SE-30) before oxidation. There was present di-*n*-butylmono-*n*-pentylborane (93%) accompanied by two minor by-products (~15% of the total products). This product was identified by GLC isolation followed by alkaline hydrogen peroxide oxidation which produced a mixture of the alcohols in a ratio almost identical with that reported above. Essentially no tri-*n*-butylborane remained unreacted.

Acknowledgment. We thank the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Syracuse University for support of this work.

References and Notes

(1) The reactions of α-lithiobenzyl sulfides and α-lithiothio acetals with organoboranes have recently been reported: (a) T. Mukaiyama, S. Yamamoto and M. Shiono, *Bull. Chem. Soc., Japan*, **45**, 2244 (1972); (b) S. Yamamoto, M. Shiono, and T. Mukaiyama, *Chem. Lett.*, 961 (1973); (c) E. Negishi and T. Yoshida, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973.
(2) Prepared by the addition of 1 equiv of *n*-butyllithium to methyl phenyl sulfone in THF at 0°.
(3) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).
(4) D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967).
(5) R. Damico, *J. Org. Chem.*, **29**, 1971 (1964).
(6) These complexes are stable at 25° for at least several hours. On heating, they undergo slow decomposition reactions. The precise courses of such reactions have not been examined in detail.
(7) Tri-*n*-butylborane contains ~15% of di-*n*-butylmono-*sec*-butylborane and 1–2% of mono-*n*-butyldi-*sec*-butylborane. Although two minor products that accompanied di-*n*-butylmono-*n*-pentylborane have not been identified, the GLC pattern is nearly identical with the original three-peak pattern.
(8) The reaction of **2** with methyl fluorosulfonate produced **4** in 14% yield: unpublished results obtained with K. W. Chiu.
(9) (a) J. J. Tufariello and L. T. C. Lee, *J. Am. Chem. Soc.*, **88**, 4757 (1966); (b) J. J. Tufariello, P. Wojtkowski, and L. T. C. Lee, *Chem. Commun.*, 505 (1967); (c) W. K. Musker and R. R. Stevens, *Tetrahedron Lett.*, 995 (1967).
(10) Our repeated attempts to achieve the one-carbon homologation of thexyldi-*n*-pentylborane via the reaction with dimethylsulfonium methylide[9b] have been unsuccessful.
(11) K. Hirai, H. Matsuda, and Y. Kishida, *Tetrahedron Lett.*, 4359 (1971).
(12) Such a possibility is currently under investigation.
(13) A few stereospecific syntheses of stereochemically defined α-thioallyllithiums were reported recently: (a) J. F. Biellman and J. B. Ducep, *Tetrahedron Lett.*, 3707 (1969); (b) ref 11.

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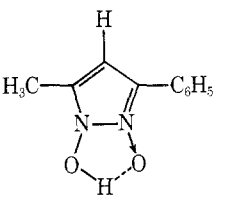
Isolation of a New 1-Hydroxypyrazole 2-Oxide via Chelation

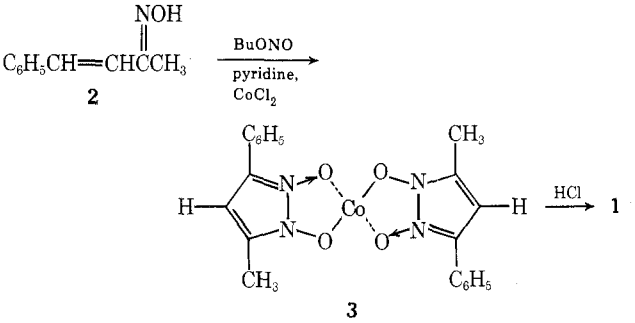
Summary: The isolation of 1-hydroxy-3(5)-phenyl-5(3)-methylpyrazole 2-oxide via a metal complex by nitrosation of benzalacetone oxime in the presence of cobaltous chloride is reported, and the intermediacy of this compound in the formation of 3,4-diazacyclopentadienone derivatives is demonstrated.

Sir: We wish to report the isolation of 1-hydroxy-3(5)-phenyl-5(3)-methylpyrazole 2-oxide (**1**). Although several 1-hydroxypyrazole 2-oxides have been prepared by Freeman and Gannon,[1] this is the first case in which the pyrazole ring is not fully substituted.



1

The procedure used in the isolation of **1** involved the preparation of a solution in aqueous ethanol of benzalacetone oxime (**2**), pyridine, and cobaltous chloride[2] in a molar ratio of 1:1:0.5. This solution was treated with 1.3 equiv of *n*-butyl nitrite which was added in three equal portions at 90-min intervals. The crude precipitate, chiefly the cobalt chelate (**3**),[3] was extracted with warm, concentrated HCl, and an insoluble by-product was filtered off.[4] Upon dilution of the filtrate with water and cooling, **1** was isolated in 33% yield.

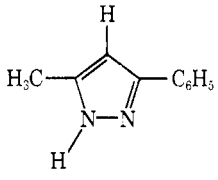


2 **3**

The product was only sparingly soluble in most solvents, but with aqueous KOH it formed a stable salt which was readily purified by recrystallization from ether–tetrahydrofuran. A pure sample of **1** regenerated from the potassium salt was a white solid, melting with decomposition at 182°. (Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.14; H, 5.31; N, 14.72.

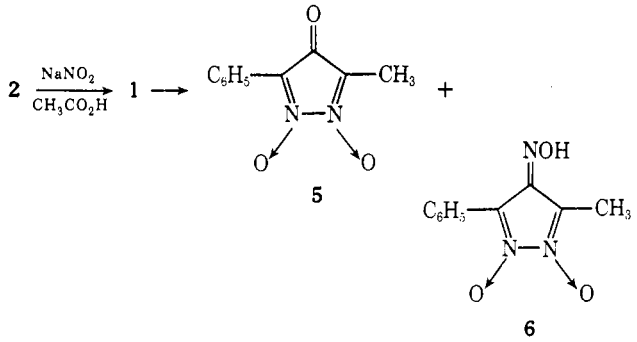
Found: C, 62.88; H, 5.35; N, 14.54.) The compound yellowed slowly upon exposure to air and light.

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



5

6

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.

Acknowledgment. The authors are grateful to the Donors of the Petroleum Research Fund, administered by the Americal Chemical Society, for partial support of this research.

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.
(6) B. Sjollema, *Justus Liebigs Ann. Chem.*, **279**, 248 (1894).
(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