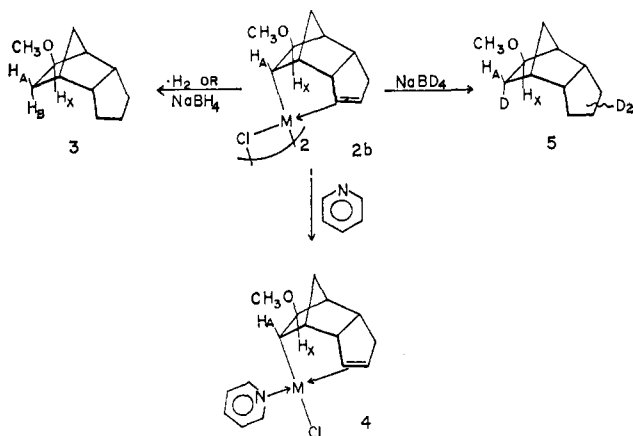


pyridine derivative **4** ( $M = \text{Pt}$  or  $\text{Pd}$ ). Reaction of **2b** with pyridine under conditions employed for the formation of the corresponding toluidine derivatives<sup>1</sup> produced **4**.<sup>8</sup> Chloro-bridged dimers such as **2** are readily split by amines, without alteration of the remainder of the complex, to give derivatives of this type.<sup>1</sup> The important signal in the n.m.r. spectrum was a poorly resolved doublet at  $\tau$  6.25, which may be assigned to the proton,  $H_X$ , on the carbon bearing the methoxy group. The observed coupling constant,  $J_{AX} = 2$  c.p.s. (width at half-height = 3 c.p.s.), is that expected for a  $120^\circ$  dihedral angle<sup>9</sup> and is consistent with the coupling,  $J_{AX'}$  exhibited by the saturated ether **3**. The coupling constant  $J_{BX}$  for **3** is 6.8 c.p.s.<sup>7</sup>



Reduction of **2** ( $M = \text{Pt}$  or  $\text{Pd}$ ) with sodium borodeuteride provided the saturated deuterated methyl ether **5** by a stereospecific *cis* replacement of platinum with deuterium. The *endo* configuration of the deuterium was determined by the  $H_X$  doublet at  $\tau$  6.55,  $J_{AX} = 2.3$  c.p.s.

The position of the 2,3-double bond in relation to the methoxy or metal point of attachment has not been determined by this sequence, but models show that a double bond on the metal side of the molecule affords the best angle and distance for efficacious coordination. Complex **2** has therefore been pictured as such.

**Acknowledgments.** This research was supported in part from a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this Fund.

(8) Satisfactory analytical data have been obtained for all compounds described herein.

(9) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

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## 1,4-Dihydropyridine

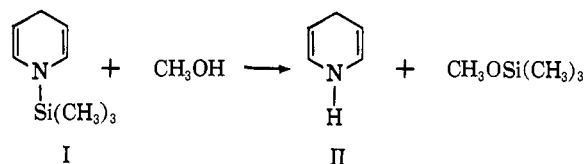
Sir:

Several N-alkyl- and N-aryl-substituted dihydropyridines are known, but none of the five isomeric unsubstituted dihydropyridines has ever been reported.<sup>1-3</sup> We wish to report the preparation of 1,4-dihydropyridine.

(1) F. Bohlman, *Chem. Ber.*, **85**, 390 (1952).

(2) R. A. Barnes in "Pyridine and Derivatives," Vol. I., E. Klingsberg, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p. 77.

1-Trimethylsilyl-1,4-dihydropyridine<sup>4,5</sup> [I, b.p.  $57^\circ$  (6.7 mm.),  $n_D^{25}$  1.4389,  $d_4^{25}$  0.89, mol. wt. 153 (mass spectroscopy)] on treatment with methanol yielded methoxytrimethylsilane and 1,4-dihydropyridine.



Five milliliters of **I** was treated with 1.25 ml. of methanol containing 0.1% KOH, and the product was immediately separated into fractions by vacuum transfer at  $-20$  to  $30^\circ$ . The distillate was collected in liquid-nitrogen-cooled traps, approximately 3 cc. of methoxytrimethylsilane, 0.2 cc. of methanol (excess), 0.1 cc. of hexamethyldisiloxane, 0.1 cc. of pyridine, and 0.5 cc. of 1,4-dihydropyridine (**II**) being collected. A solid residue of approximately 2 cc. was not distillable. The dihydropyridine was a colorless slightly viscous liquid which v.p.c. analysis showed to contain about 5% impurities, mainly methanol and pyridine. None of the dihydropyridine passed through the v.p.c. column. A 20% solution in deuteriobenzene was used for infrared and n.m.r. spectra and a cyclohexane solution was used for ultraviolet spectra. In these solutions, when excluded from air, the dihydropyridine was stable for several days but the neat material solidified and turned orange in a few minutes to hours at room temperature. A second preparation, half the size of the first and made in ethyl ether, reacted in a manner identical with the first preparation and furnished material for C, H, and N analyses.<sup>6</sup> Efforts to measure the refractive index and boiling point of the material were unsuccessful due to its rapid solidification.

The ultraviolet and infrared spectra were in good agreement with those of other dihydropyridines.<sup>3</sup> Compound **I** has an ultraviolet maximum at  $288 \text{ m}\mu$  ( $\epsilon$  1309) and compound **II** has a maximum at  $278 \text{ m}\mu$  ( $\epsilon$  2500). The principal infrared absorptions were (in  $\text{cm}^{-1}$ ) at 3060 ( $=\text{CH}$ ), 2965 ( $\text{CH}_3$ ), 2820 ( $\text{CH}_2$ ), and 1675 ( $\text{C}=\text{C}$ ); for **II** (in  $\text{C}_6\text{D}_6$ ) the absorptions were at 3450 (NH), 3060, 2820, and 1680.

The proton magnetic spectra of **I** and **II** were recorded with a Varian A-60 spectrometer. Measurements were made on solutions containing 10-15% of the compounds in deuteriobenzene. Shifts were measured relative to the residual protons of deuteriobenzene. These have been converted to shifts relative to tetramethylsilane by noting that the residual protons of deuteriobenzene appear 429 c.p.s. ( $\delta = 7.15$  p.p.m.) downfield from tetramethylsilane. The results are summarized in Table I, together with data reported for three closely related compounds.

The spin-spin splitting patterns of the protons of **I** agree with those reported for the analogous protons of compound **IV**. The spin-spin splitting patterns of the protons of **II** indicate strong coupling between the N-H

(3) E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **27**, 3764 (1962).

(4) Formed by the palladium-catalyzed addition of trimethylsilane to pyridine. Details of the preparation and further reactions of this compound and related isomers will appear in a future paper.

(5) *Anal.* Calcd. for  $\text{C}_8\text{H}_{13}\text{NSi}$ : C, 62.8; H, 9.8; N, 9.15; Si, 18.2. Found: C, 62.8; H, 9.8; N, 9.1; Si, 18.1.

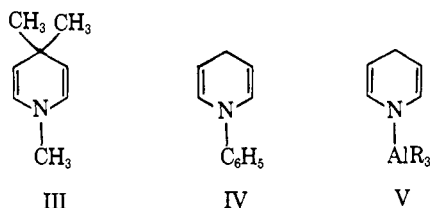
(6) *Anal.* Calcd. for  $\text{C}_8\text{H}_7\text{N}$ : C, 74.1; H, 8.6; N, 17.3. Found: C, 73.3; H, 8.4; N, 16.7.

**Table I.**<sup>a</sup> Chemical Shifts (p.p.m.)

Compound	Protons at positions		
	2	3	4
I	5.87	4.50	3.05
II <sup>b</sup>	5.73	4.42	3.15
III <sup>c</sup>	5.51	4.11	...
IV <sup>d</sup>	6.27	4.53	2.98
V <sup>e</sup>	6.70	4.30	3.30

<sup>a</sup> Estimated precision  $\pm 0.03$  p.p.m. <sup>b</sup> The signal due to the N-H proton has not been identified. <sup>c</sup> No solvent (see ref. 3). <sup>d</sup> Solvent  $\text{CCl}_4$ : M. Saunders and E. Gold, *J. Org. Chem.*, **27**, 1439 (1962). <sup>e</sup> Solvent pyridine: P. Lansbury and J. Peterson, *J. Am. Chem. Soc.*, **85**, 2236 (1963).

proton and protons 2 and 3. No evidence of coupling between the N-H proton and protons 4 is observed.



Compounds I and II have to be rigorously excluded from air since oxygen readily reacts with both materials. Methanolysis of I under neutral conditions is a slow reaction requiring several days to go to completion, but with base or acid the reaction is rapid and vigorous, often causing further reaction of the dihydropyridine.

**Acknowledgment.** We are indebted to Dr. J. B. Bush, Jr., for assistance in interpretation of the n.m.r. spectra, and to Dr. R. S. McDonald for assistance in interpretation of the infrared spectra.

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## The Second-Order Beckmann Reaction of an $\alpha$ -(Methylthio) Ketone Oxime

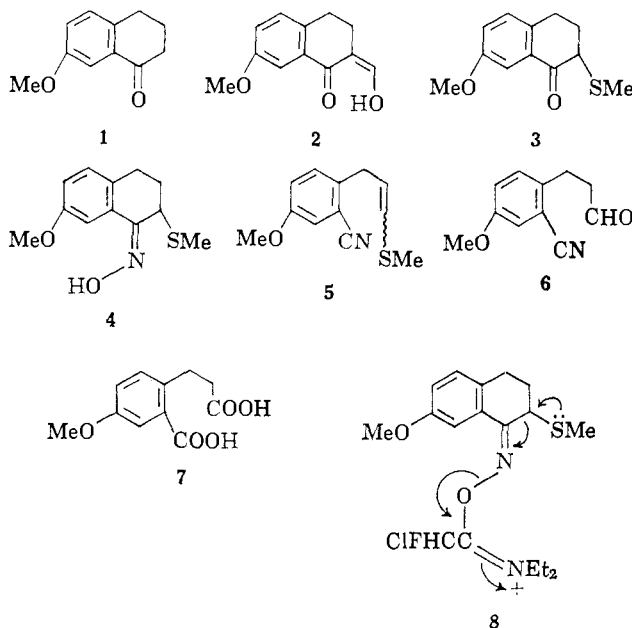
Sir:

We describe here a novel sequence of apparent general applicability to the purpose of oxidative cleavage of the bond between a ketone group and an adjacent methylene. This cleavage is useful in two ways, *viz.*, that direction of cleavage is governed by the steric control over product stability typical of Claisen-type condensations,<sup>1,2</sup> and that the termini of the cleaved bond are left in different oxidation states so that they may readily be separately modified.

7-Methoxytetralone (**1**) was formylated by the action of ethyl formate in tetrahydrofuran in the presence of sodium methoxide to yield the hydroxymethylene ketone **2**,<sup>3,4</sup> m.p. 31.2–32.0°. The hydroxymethylene

(1) G. Stork and R. K. Hill, *J. Am. Chem. Soc.*, **79**, 495 (1957).  
(2) For a recent example of a formylation clearly not governed by the stability of the more stable enolate, see P. Grafen and R. B. Turner, *Tetrahedron Letters*, 3935 (1964), and S. W. Pelletier, R. L. Chappell, and P. C. Parthasarathy, *ibid.*, 41 (1965).  
(3) Acceptable analyses and concordant spectra have been obtained for all new compounds.  
(4) V. S. Gaiind, R. P. Gandhi, I. C. Lakhumna, and S. M. Mukherji, *J. Indian Chem. Soc.*, **33**, 1 (1956), report 2 as a liquid; semicarbazone, m.p. 210°. We find for the semicarbazone m.p. 199.7–200.6°; isoxazole, m.p. 75–76.5°.

ketone was treated<sup>5</sup> with methyl thioisylate<sup>6</sup> and potassium acetate in ethanol to afford the 2-methoxy-7-methoxytetralone<sup>3</sup> (**3**), m.p. 70–70.6°. The crude yield in the two steps is quantitative; the yield of first crop after two recrystallizations is 59%. With hydroxylamine hydrochloride and sodium hydroxide in boiling ethanol, **3** afforded a single oxime<sup>3</sup> **4**, m.p. 107.9–108.8°, in 64% yield. Its infrared spectrum displayed the usual pair of bands for free and intramolecularly hydrogen-bonded hydroxyl at 2.79 (sharp) and 3.06  $\mu$  (broad, strong). Its n.m.r. spectrum showed the following absorptions (in p.p.m. on the  $\delta$ -scale): =NOH, broadened singlet at 9.13<sup>7</sup> (its position being concentration dependent); -SMe, sharp singlet at 2.15; CHSMe, triplet centered at 4.82,  $J = 3.7$  c.p.s.



The oxime **4** was subjected to the Beckmann rearrangement of second order<sup>8</sup> under various conditions, to give methyl 3-(2-cyano-4-methoxyphenyl)prop-1-enyl thioether<sup>3</sup> (**5**) as a semisolid mixture of *cis* and *trans* isomers. The assignment of structure to **5** rests on elemental analysis and i.r. and n.m.r. spectra. The infrared spectrum displays a sharp band at 4.48  $\mu$  (-CN) and new bands<sup>9</sup> at 10.31 and 10.73  $\mu$ , one of which should be assigned to the *trans*-disubstituted double bond. The n.m.r. spectrum displays complex absorption in the vinyl region: at least 15 bands between 5.14 and 6.25, and two sharp singlets for the sulfur-bound methyl groups, at 2.19 and 2.28, area ratios (by integration) 1.7:1.

The vinyl thioether **5** was subjected to hydrolysis by the action of a 1:1 solution of 15% aqueous perchloric acid in ethanol for 30 min. on the steam bath. Conditions vigorous enough to hydrolyze the thioether are

(5) L. G. S. Brooker and S. Smiles, *J. Chem. Soc.*, 1723 (1926).  
(6) D. T. Gibson, *ibid.*, 2637 (1931).  
(7) *Cf. inter alia*, N. S. Bhacca, *et al.* "NMR Spectra Catalogue," Vol. 2, Varian Associates, Inc., Palo Alto, Calif., 1963, spectra numbers 501 and 614.  
(8) (a) *Cf. inter alia*, R. K. Hill, *J. Org. Chem.*, **27**, 29 (1962); (b) A. Hassner and W. A. Wentworth, *Chem. Commun.*, 44 (1965). The footnotes of these two references constitute a useful bibliography.  
(9) *Cf.* L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 46.