

content initially present in **3** and **4** was found either in the product olefins or in the dimethyl-*n*-butylamine. This result precludes all mechanisms other than an intramolecular elimination and also the exchange of hydrogen in the dimethyl-*n*-butylamine under the reaction conditions. The results of this study are thus analogous to those reported<sup>2</sup> when KNH<sub>2</sub> was used as the base. The observation of both olefins being derived completely by a syn  $\alpha',\beta$  elimination allows the direct measure of the kinetic isotope effect for the formation of both olefins (Table I). The isotope effects are comparable with those observed in liquid ammonia with LiNH<sub>2</sub> as the base. Thus, the *cis*/*trans* ratio of olefins is not markedly affected by a difference in base strength of the RLi. However, a measurable difference in product composition exists from our results in liquid ammonia despite the fact that identical ylide mechanisms are operating in both cases.

The increase in the amount of *cis* olefin formed when the solvent polarity was decreased on going from liquid ammonia to diethyl ether suggested the possibility of a solvent effect. Treatment of **2** with *n*-butyllithium, *sec*-butyllithium, and *tert*-butyllithium for 24 hr at 25° in pentane solvent afforded *cis*/*trans* ratios of 66/34, 59/41, and 60/40, respectively. A fourfold increase in the amount of solvent did not alter the *cis*/*trans* ratio when *n*-butyllithium was the base. However, when the *n*-butyllithium concentration was increased by a factor of 4 and the *sec*-butyllithium concentration was increased by a factor of 2.5, the observed *cis*/*trans* ratios were 85/15 and 87/13, strongly suggesting the intervention of a surface phenomenon in this heterogeneous reaction medium. Deuterium labeling experiments with *n*-butyllithium clearly established that the  $\alpha'\beta$  mechanism was also operating in pentane solvent.

Thus, the different ratios of *cis*- and *trans*-cyclooctene formed under different reaction conditions does not have the mechanistic significance that previous investigators have ascribed to it. One explanation for the change in product composition could be an aggregation phenomenon. This should be particularly true in non-polar solvents such as pentane where the nitrogen ylide will be destabilized and many form a heterogeneous aggregate with the alkyllithium reagents. The degree of association of the carbanion basic center of the ylide intermediate with the lithium alkyl could influence its effective basicity, thereby increasing the amount of the more stable *cis* stereoisomer. Finally, it should be emphasized that not all trimethylalkylammonium salts undergo  $\alpha'\beta$  elimination reactions in liquid ammonia solvent. In the *exo*-norbornyl system elimination with LiNH<sub>2</sub> in liquid ammonia proceeds principally by an E2 pathway.<sup>7</sup>

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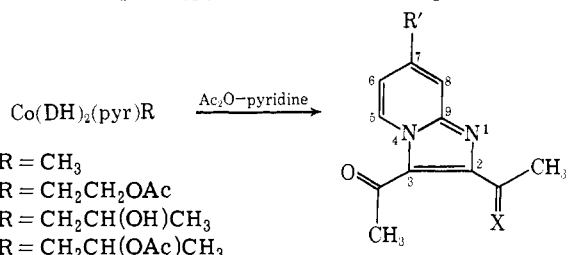
(7) Unpublished results.

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## Degradation of Alkyl(pyridine)cobaloximes to Derivatives of Imidazo[1,2-*a*]pyridine

Sir:

We have found that on prolonged exposure to acetic anhydride in pyridine the alkyl(pyridine)cobaloximes<sup>1</sup> (**1**–**3**) undergo a remarkable degradation to a derivative (**4**) of imidazo[1,2-*a*]pyridine. For example, treatment



- 1, R = CH<sub>3</sub>
- 2, R = CH<sub>2</sub>CH<sub>2</sub>OAc
- 3, R = CH<sub>2</sub>CH(OH)CH<sub>3</sub>
- 5, R = CH<sub>2</sub>CH(OAc)CH<sub>3</sub>

- 4, X = N(OAc); R' = H
- 6, X = N(OH); R' = H
- 7, X = (NO<sub>2</sub>)<sub>2</sub>; R' = H
- 8, X = N(OAc); R' = CH<sub>3</sub>

DH<sub>2</sub> = dimethylglyoxime

of 2-hydroxypropyl(pyridine)cobaloxime (**3**) with acetic anhydride (10 mol equiv) in pyridine for 24 hr at room temperature gives 2-acetoxypropyl(pyridine)cobaloxime<sup>2</sup> (**5**) in excellent yield. However, if the reaction is run for a longer time then the **5** initially formed reacts further. After 9 days at room temperature (or 2 days at 60°), analysis of the reaction mixture shows the absence of **5** and the presence of the new compound **4**<sup>3–5</sup> which has been isolated<sup>6</sup> in yields up to 30%. Compound **4** was easily deacetylated (catalytic NaOCH<sub>3</sub>–CH<sub>3</sub>OH, 20°, overnight) giving **6**<sup>4,7</sup> which on oxidation with concentrated nitric acid (5 min, 20°) gave a quantitative yield of a geminal dinitro compound **7**.<sup>4,8</sup> Hence, **6** contains the structural unit C=NOH, which is O-acetylated in **4**. The presence of a 2-pyridoneimine system in **4**, **6**, and **7** was inferred from the characteristic<sup>9</sup> splitting patterns in the nmr signals due to the protons of their pyridine ring.

(1) Alkyl(base)cobaloximes are bis(dimethylglyoximate)cobalt complexes with an alkyl group and a Lewis base as axial ligands. For a review of their chemistry, see G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

(2) B. T. Golding, H. L. Holland, U. Horn, and S. Sakrikar, *Angew. Chem., Int. Ed. Engl.*, **9**, 959 (1970).

(3) Mp 112°; C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub><sup>4</sup>; nmr<sup>8</sup> (CDCl<sub>3</sub>)  $\delta$  2.27 (s, 3 H, OCOCH<sub>3</sub>), 2.57 (s, 3 H, CH<sub>3</sub>), 2.64 (s, 3 H, CH<sub>3</sub>), 7.08 (d of d, 1 H,  $J_{56} + J_{57} = 13.5$  Hz, 6-*H*), 7.49 (d of d, 1 H,  $J_{57} = 6.5$ ,  $J_{78} = 8.9$  Hz, 7-*H*), 7.73 (d, 1 H,  $J_{78} = 8.9$  Hz, 8-*H*), 9.69 (d, 1 H,  $J_{56} = 6.9$  Hz, 5-*H*); ir (CHCl<sub>3</sub>) 1770, 1640 cm<sup>-1</sup>.

(4) Satisfactory combustion analyses (C, H, and N) and high-resolution mass spectral data have been obtained for this compound.

(5) Spectral assignments are made on the basis of the structure rigorously established later.

(6) **4** was obtained by evaporating the reaction mixture and extracting the residue with dichloromethane, followed by chromatography on silica gel, evaporation, sublimation (ca. 100° (0.001 mm)), and recrystallization. In subsequent preparations, the crude sublimate of **4** was deacetylated to **6**, which was recrystallized (ethyl acetate). This procedure gives higher yields of pure material.

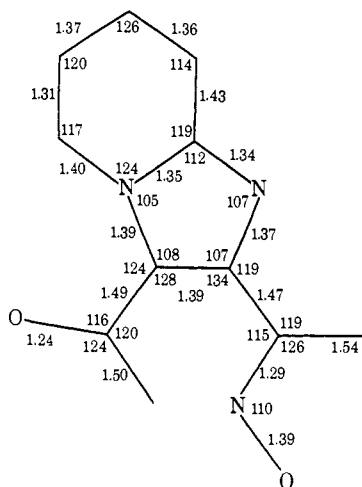
(7) Mp 191°; C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub><sup>4</sup>; nmr similar to that of **4** excepting the loss of the signal at  $\delta$  2.27 and the gain of a signal at 9.30 (br, 1 H, OH); ir (CHCl<sub>3</sub>) free and bonded O–H stretch at 3583 and 3320 (br) cm<sup>-1</sup>, respectively; uv (CH<sub>3</sub>OH)  $\lambda_{\text{max}}$  219 (sh,  $\epsilon$  16,800), 227 ( $\epsilon$  17,350), 252 ( $\epsilon$  25,000), and 311 nm ( $\epsilon$  7,510).

(8) Mp 177°; C<sub>11</sub>H<sub>10</sub>N<sub>3</sub>O<sub>5</sub><sup>4</sup>; nmr<sup>8</sup> (CDCl<sub>3</sub>)  $\delta$  2.65 (s, 3 H, CH<sub>3</sub>), 2.70 (s, 3 H, CH<sub>3</sub>), 7.31 (d of d, 1 H,  $J_{78} = 11.3$ ,  $J_{57} = 7.0$  Hz, 7-*H*), 7.71 (d, 1 H,  $J_{78} = 11.3$  Hz, 8-*H*), 7.83 (t, 1 H,  $J_{56} + J_{57} = 14.0$  Hz, 6-*H*), 8.91 (d, 1 H,  $J_{56} = 6.7$  Hz, 5-*H*); ir (CH<sub>2</sub>Cl<sub>2</sub>) 1656, 1580 (C(NO<sub>2</sub>)<sub>2</sub>) cm<sup>-1</sup>.

(9) See e.g., W. W. Paudler and H. L. Blewitt, *Tetrahedron*, **21**, 353 (1965).

From the spectroscopic data and chemical transformations described so far a unique structure for **4** cannot be defined. We therefore undertook a single-crystal X-ray analysis of **6** which secures the structure shown in Figure 1 and Chart I.<sup>10,11</sup> Now the structures of **4**<sup>11</sup> and **7**<sup>11</sup> follow unambiguously.

Chart I. Bond Lengths (Ångstroms) and Bond Angles (Degrees)<sup>a</sup>



<sup>a</sup>  $R = 0.089$ . The nine atoms of the ring system form a least-squares plane with standard deviation 0.011 Å. The nonhydrogen atoms of the  $\text{CH}_3\text{CO}-\text{C}$  group form a plane with standard deviation 0.009 Å; torsional angle with the ring system, 12.4°. The five nonhydrogen atoms of the  $\text{CH}_2\text{C}(\text{NOH})-\text{C}$  group form a plane with standard deviation 0.002 Å; torsional angle with the ring system, 60.0°.

A distinguishing feature of the nmr spectra of **4** and **6** is the low-field resonance due to H-5, deshielded by the peri carbonyl<sup>12</sup> [in the X-ray structure (Figure 1 and Chart I) this is oriented as shown, almost in the plane of the ring system ( $\varphi = 12.4^\circ$ ), and we assume that this situation persists for solutions of **4** and **6** in chloroform]. In **7** the deshielding is markedly lowered, because the bulky 1,1-dinitroethyl group (relative to  $\text{CH}_3\text{C}=\text{NO}-$  in **4** and **6**) causes the planar rotamer to be less populated. In support of this argument, carbonyl stretching frequencies indicate less conjugation of the carbonyl group with the heteroaromatic system of **7** ( $\nu$  1656  $\text{cm}^{-1}$ ) compared with **4** and **6** ( $\nu$  1640  $\text{cm}^{-1}$  for both compounds).

The formation of compound **4** is probably a general reaction of alkyl(pyridine)cobaloximes since **1** and **2** behaved similarly to **3** on treatment with acetic anhydride in pyridine, although they react more slowly. A homolog (**8**) of **4** is obtained (16% yield) by reacting 2-hydroxypropyl(4-methylpyridine)cobaloxime with acetic anhydride in 4-methylpyridine for 2 days at 60°. Compound **4** is not formed from bromo(pyridine)cobaloxime under similar conditions, nor is it produced from dimethylglyoxime and acetic anhydride in pyr-

(10) Crystal data: orthorhombic; space group  $Pbca$ ;  $a = 16.402$ ,  $b = 13.463$ , and  $c = 9.735$  Å;  $Z = 8$ . Observed reflections (520) ( $I/\sigma(I) > 5.0$ ) were collected on a Stoe two-circle diffractometer, with Mo  $K\alpha$  radiation and graphite monochromator. The structure was solved by direct methods and refined to a current  $R$  factor of 0.089 with anisotropic temperature factors for all nonhydrogen atoms and isotropic temperature factors for hydrogen atoms.

(11) **4**, 2-(1-(*E*)-acetoxyminoethyl)-3-acetylimidazo[1,2-*a*]pyridine; **6**, 2-(1-(*E*)-hydroxyminoethyl)-3-acetylimidazo[1,2-*a*]pyridine; **7**, 2-(1,1-dinitroethyl)-3-acetylimidazo[1,2-*a*]pyridine.

(12) For analogous examples see R. M. Acheson and D. A. Robinson, *J. Chem. Soc. C*, 1633 (1968) and W. K. Anderson and A. E. Friedman, *Can. J. Chem.*, **49**, 668 (1971).

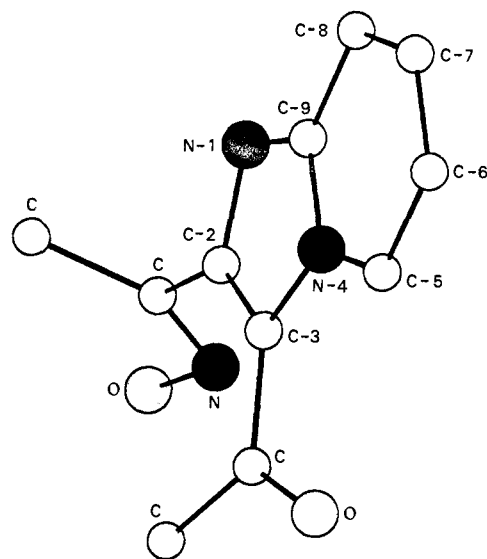


Figure 1.

idine containing cobaltous acetate.<sup>13</sup> The production of compounds **4** and **8** involves an oxidation of a dimethylglyoxime unit; the yield of **4** obtained from **3** is insensitive to the presence or absence of oxygen and the oxidant must therefore be the cobaltic ion of the complex. Exposure of reaction mixtures to light does not increase the yield of **4**. We are investigating the mechanism of formation of **4** from alkyl(base)cobaloximes, with particular reference to the role and fate of the alkylcobalt group of the substrate and to possible template effects around cobalt.

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(13) Dimethylglyoxime di-*O*-acetate is produced in these reactions and is also a by-product in the formation of **4**.

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## Structural Index for Elemental Solids

Sir:

We have discovered an index for s-p bonded elemental solids which separates covalent, fcc, hcp, and bcc structures. The index is based on the pseudopotential of an atomic core in a solid, which may be approximated by the Pauli-force model potential<sup>1-3</sup>

$$V = -Z/r + \sum_l [\hat{l}(\hat{l} + 1) - l(l + 1)]P_l/2r^2 \quad (1)$$

Here  $Z$  is the net core charge,  $l$  is the angular momentum quantum number of a valence orbital,  $\hat{l} = \hat{l}(l)$  is an  $l$ -dependent parameter obtained from atomic spectral data,<sup>1,2</sup> and  $P_l$  is the  $l$ -projection operator. A physical interpretation of (1) and a tabulation of  $\hat{l}$  values for

(1) G. Simons and A. Bloch, submitted to *Phys. Rev.*

(2) G. Simons, *Chem. Phys. Lett.*, **12**, 404 (1971).

(3) G. Simons, *J. Chem. Phys.*, **55**, 756 (1971).