

(21,300);  $\lambda_{\max}^{\text{Nujol}}$  3.25, 5.78, 6.12, 6.30, 6.70, 7.96, 8.24 $\mu$ ) and (VIII, R = OH, R<sup>3</sup> = CH<sub>3</sub>; m.p. 186–191°;  $[\alpha]_{\text{D}} +80^{\circ}$ ;  $\lambda_{\max}^{\text{MeOH}}$  276 m $\mu$  (2,000), 285 m $\mu$  (1,800);  $\lambda_{\max}^{\text{Nujol}}$  3.25, 6.10, 6.21, 6.35, 6.67, 7.99  $\mu$ ), respectively. Reduction of VIII (R = OH, R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CO) and VIII (R = OH, R<sup>3</sup> = CH<sub>3</sub>) to the known<sup>9,10</sup> lactams VIII (R = H, R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CO) and VIII (R = H, R<sup>3</sup> = CH<sub>3</sub>) was accomplished using zinc-acetic acid and hydrazine, respectively.

The photolysis mixtures from VI and VII also gave, in each case, another hydroxamic acid. These products (IX; m.p. 205–210° dec.,  $[\alpha]_{\text{D}} -3^{\circ}$ ;  $\lambda_{\max}^{\text{MeOH}}$  230 m $\mu$  (20,000);  $\lambda_{\max}^{\text{Nujol}}$  3.28, 5.75, 6.12, 6.24, 6.30, 6.68, 7.92  $\mu$ ) and (X; m.p. 205–207°;  $[\alpha]_{\text{D}} 0^{\circ}$ ;  $\lambda_{\max}^{\text{MeOH}}$  276 m $\mu$  (2,000), 285 m $\mu$  (1,800);  $\lambda_{\max}^{\text{Nujol}}$  3.28, 6.12, 6.22, 6.34, 6.68, 8.0  $\mu$ ) correspond, respectively, to isomers of (VIII, R = OH, R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CO) and (VIII, R = OH, R<sup>3</sup> = CH<sub>3</sub>).

This difference most probably is due to isomerism at C-13, rather than to the presence of the alternative 17-aza-17a-keto system.<sup>12</sup>

A plausible mechanism (partial structures A-E) can be invoked to account for these photolytic rearrangements. Initial fission of the O-NO bond can lead to the intermediate C-13 nitroso intermediate(s) (C). The formation of the hydroxamic acid (E) from (C) may then follow the path C → D → E (or equivalent process).

(12) The known 13-isoestrone 3-methyl ether (A. Butenandt, A. Wolff and P. Karlson, *Ber.*, **74**, 1308 (1941)) has been converted, via the 17-oxime, to a 13-isolactam identical with the lactam derived from X. This evidence together with other corroborating data will be discussed in a later, detailed publication.

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RECEIVED FEBRUARY 18, 1961

#### THE HYDROGEN VIBRATIONS IN COBALT CARBONYL HYDRIDE. BONDING CONSIDERATIONS.<sup>1</sup>

Sir:

The determination of the frequencies and the character of the hydrogen vibrations in HCo(CO)<sub>4</sub> would be important in establishing the nature of the bonding in this interesting molecule. Previous work has shown that the infrared bands at 703<sup>2-4</sup> and 331<sup>4</sup> cm.<sup>-1</sup> arise from vibrations which involve substantial motion of the hydrogen atom. Since the C and/or O atoms also participate substantially in these modes in the hydride and/or deuteride,<sup>4</sup> a salient question is whether the 703 cm.<sup>-1</sup> vibration involves Co-H bending motion<sup>4</sup>

or Co-H stretching motion.<sup>3,5</sup> If the former were true, one would expect at least one hydrogen vibration at a frequency much greater than 703 cm.<sup>-1</sup>. This question has been investigated previously by examining the infrared spectrum of films of HCo(CO)<sub>4</sub> and DCo(CO)<sub>4</sub> on a silver chloride window at -196°.<sup>3</sup> It was reported that no bands were observed in the region of ~1400 cm.<sup>-1</sup> in the deuteride.<sup>3</sup> Now, if there were no fundamental in the deuteride at ~1400 cm.<sup>-1</sup>, there could be no "pure" Co-H stretching vibration in the hydride near ~1950 cm.<sup>-1</sup>, where bands have been observed.<sup>2,8</sup>

This question now has been reexamined by studying the infrared spectrum of gaseous HCo(CO)<sub>4</sub> and DCo(CO)<sub>4</sub> at pressures up to 20 mm. in cells with effective path lengths as great as 5 meters. Special attention was paid to the region between 1000 and 2000 cm.<sup>-1</sup>. Among the bands observed in this region for HCo(CO)<sub>4</sub> is one with easily resolvable PQR structure at 1934 cm.<sup>-1</sup> (previously reported<sup>2,8</sup>) and a weaker, somewhat broad, band at 1400 cm.<sup>-1</sup>. The samples of DCo(CO)<sub>4</sub> had 80–90% of the H atoms replaced by D atoms. The hydride band at 1934 cm.<sup>-1</sup> almost completely disappears in our deuteride spectra and the band at 1400 cm.<sup>-1</sup> is replaced by a sharper band at 1396 cm.<sup>-1</sup>. In addition a number of new bands were found in the deuteride spectra including ones at 1193, 1691, 1787 and 1850 cm.<sup>-1</sup>.

The following interpretation is placed on these results. The hydride band at 1400 cm.<sup>-1</sup> is the overtone of 703 cm.<sup>-1</sup>. The latter frequency shifts to 600 cm.<sup>-1</sup> in the deuteride where its overtone now gives rise to the band found at 1193 cm.<sup>-1</sup>. The hydride band at 1934 cm.<sup>-1</sup> is reasonably understood as the Co-H stretching frequency! The Co-D stretching vibration is the band at 1396 cm.<sup>-1</sup>. The deuteride bands at 1691, 1787 and 1850 cm.<sup>-1</sup> arise from combinations of the 1396 cm.<sup>-1</sup> fundamental with the previously observed<sup>4</sup> deuteride fundamentals at 296, 393 and 458 cm.<sup>-1</sup>.

These results form a most convincing argument for the presence of a Co-H bond in HCo(CO)<sub>4</sub>. They, together with the earlier spectra,<sup>2-4</sup> are consistent with the C<sub>3v</sub> configuration previously proposed.<sup>2</sup> They show that the C and/or O atoms do not participate significantly in the hydrogen stretching motion and hence the bonding of the hydrogen atom is like that recently found for HMn(CO)<sub>5</sub>.<sup>4,5</sup> It is now possible to give a more advanced discussion of the molecular vibrations and the frequency assignment in HCo(CO)<sub>4</sub> and DCo(CO)<sub>4</sub>. These, as well as the experimental details of this and recent work<sup>4</sup> on these molecules, will be given in a forthcoming paper which will discuss their relation to the various models for the bonding of the hydrogen atom.

The force constant for the Co-H bond is found to be ca. 2.22 md./A. Thus this bond is stronger than the Mn-H bond in HMn(CO)<sub>5</sub><sup>4</sup> despite contrary expectations<sup>5</sup> based on thermal and chemical stabilities.

The fact that the hydrogen vibrations are similar in HCo(CO)<sub>4</sub> and HMn(CO)<sub>5</sub> strengthens the be-

(1) This work was supported by the Atomic Energy Commission under contract AT(11-1)-164.

(2) W. F. Edgell, C. Magee and G. Gallup, *J. Am. Chem. Soc.*, **78**, 4185 (1956).

(3) F. A. Cotton and G. Wilkinson, *Chem. and Ind.*, 1305 (1956).

(4) W. F. Edgell, G. Asato, W. Wilson and C. Angell, *J. Am. Chem. Soc.*, **81**, 2022 (1959).

(5) F. A. Cotton, J. L. Down and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).

lief<sup>4</sup> that a similar situation obtains in other metal carbonyl hydrides. For example, recent infrared<sup>6</sup> and Raman<sup>7,8</sup> spectra of the  $\text{HFe}(\text{CO})_4^-$  ion show bands at 1897, 1937 and 1768, 1835, 1895  $\text{cm}^{-1}$ , respectively. Since only three C-O stretching frequencies are expected for such an ion with  $\text{C}_{3v}$  symmetry, there is a good possibility that one of these four frequencies belongs to the Fe-H stretching mode.

(6) W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell and G. Asato, *J. Am. Chem. Soc.*, **82**, 1254 (1960).

(7) H. Stammreich, K. Kawai, Y. Tavares, P. Krumholz, J. Behmoiras and S. Brill, *J. Chem. Phys.*, **32**, 1482 (1960).

(8) R. A. Friedel, I. Wender, S. L. Shufier and H. W. Sternberg, *J. Am. Chem. Soc.*, **77**, 3951 (1955).

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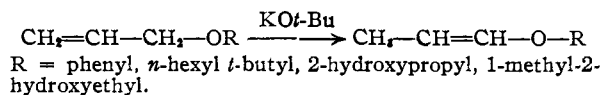
WALTER F. EDGELL  
ROBERT SUMMITT

RECEIVED FEBRUARY 14, 1961

### SOLVENT EFFECTS IN THE BASE-CATALYZED ISOMERIZATION OF ALLYL TO PROPENYL ETHERS

Sir:

In the course of investigating the prototropic rearrangement of allyl ethers to their propenyl analog employing potassium *t*-butoxide as catalyst we have discovered some interesting effects of solvent on the rate of isomerization.



In 1,2-dimethoxyethane 0.66 *M* in potassium *t*-butoxide, 0.68 *M* allyl phenyl ether required about 160 min. for 50% rearrangement to occur at 25°. On the other hand, in dimethyl sulfoxide 0.05 *M* in potassium *t*-butoxide the pseudo-first order half-time was only about 1.5 min. at the same temperature. Taking account of the difference in base concentration the rate is  $1.4 \times 10^8$  faster in dimethyl sulfoxide.

By gas phase chromatography, the phenyl propenyl ether formed in dimethoxyethane was found to be 97% *cis*-isomer, 99% *cis* in dimethyl sulfoxide. This is considerably in excess of the equilibrium concentration of about 65% *cis*.<sup>1</sup> The yield was also virtually quantitative, titrating over 99% propenyl ether by hydroxylamine hydrochloride.<sup>2</sup>

With allyl *n*-hexyl ether there is a very large decrease in rate upon addition of *tert*-butyl alcohol to the system. For instance, in dimethoxyethane 1.72 *M* in ether and potassium *t*-butoxide at 80° the pseudo-first order half-time is about 60 min. In the same solvent 1.6 *M* in the ether, 1.5 *M* in potassium *t*-butoxide but also 2.2 *M* in *t*-butyl alcohol, the pseudo-first order half-time is estimated to be about 15,000 min. at the same temperature. It should be emphasized that this latter half-time is not a true value for homogeneous solution since a white precipitate of *tert*-butyl alcohol potassium *t*-butoxide complex settles out of solution upon addition of the *tert*-butyl alcohol. This complex is still incompletely soluble at 80°. The decrease in rate probably is effected both by

(1) W. H. Snyder, unpublished results.

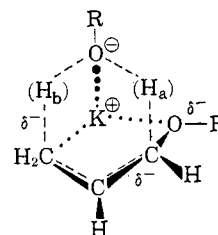
(2) R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. soc. chim. (France)*, 121 (1950).

the insolubility of the catalyst as well as by hydrogen-bonding of the alcohol to the base.

These kinetic results were obtained by following the increase in intensity of the strong 5.98  $\mu$  band of the propenyl ether in the infrared.

Cram, Rickborn and Knox have noted increases as large as factor of  $10^9$  in the rate of deuterium exchange and the rate of racemization of asymmetrically trisubstituted methanes upon going from methanol to *tert*-butyl alcohol to dimethyl sulfoxide.<sup>3</sup> This compares to the factor of *ca.*  $10^8$  which we have observed on going from mixed dimethoxyethane-*tert*-butyl alcohol to dimethyl sulfoxide.

In order to explain the high degree of *cis*-stereospecificity of the rearrangement, and from examination of models, the structure shown seems a likely representation of two intermediate states for the rearrangement.



The  $\alpha$ -hydrogen ( $\text{H}_a$ ) is labilized by attraction to the alkoxide oxygen. By movement of a proton only, the complex with the hydrogen at the position  $\text{H}_b$  results. The dotted lines represent simple electrostatic bonds, the dashed lines those with partial covalent character in the transition complex.

We expect that a study of the deuterium exchange in *t*-butyl alcohol, dimethoxyethane, and dimethyl sulfoxide will shed further light on the mechanism of the rearrangement.

(3) D. J. Cram, Bruce Rickborn, and Graham R. Knox, communication to THIS JOURNAL, not yet published. We are indebted to Professor Cram for sending us a copy of this communication prior to its appearance in print.

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CHARLES C. PRICE  
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### THE RATE OF OXIDATION OF CYTOCHROME c BY FERRICYANIDE IONS<sup>1</sup>

Sir:

Four of the bonds of the octahedrally coordinated iron atoms in ferrohemoglobin and cytochrome c are to the nitrogen atoms of the pyrrole rings of protoporphyrin. The fifth bond is directly to the protein, probably through a nitrogen atom of the imidazole group of histidine.<sup>2,3</sup> The molecules differ, however, in the nature of the sixth group attached to the iron atoms. This sixth group is a water molecule in hemoglobin and another histidine residue in cytochrome c.<sup>2,3</sup> The rate of oxidation of the first heme group in ferrohemoglobin by ferricyanide ions is relatively slow.<sup>4</sup>

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. Theorell and A. Akeson, *J. Am. Chem. Soc.*, **63**, 1084 (1941).

(3) P. George and R. L. J. Lyster, Conference on Haemoglobin (1957), Publication 557, National Academy of Sciences—National Research Council, Washington, D. C., p. 33.

(4) N. Sutin, *Nature*, **186**, in press (1961).