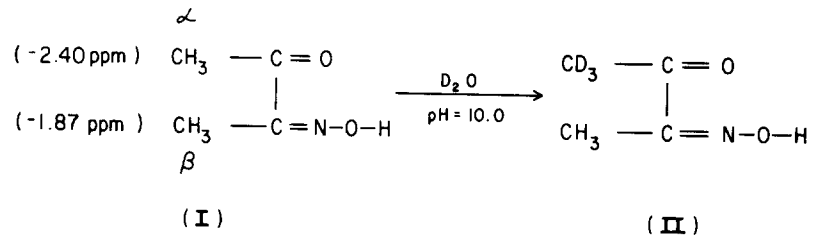
Tetrahedron Letters No. 19, pp 1913 - 1916, 1972. Pergamon Press. Printed in Great Britain.

HYDROGEN-DEUTERIUM EXCHANGE AND NMR SPECTRA OF 2,3-BUTANEDIONE MONOXIME AND BIS(BUTANEDIONE MONOXIME) ETHYLENEDIIMINE

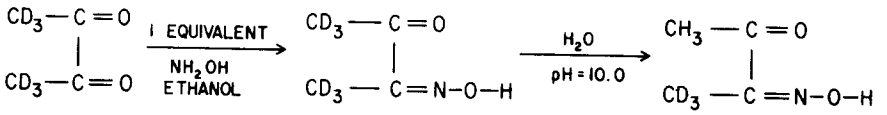
By Richard L. Beach*

Department of Chemistry, Rider College, Trenton, N. J. 08602
(Received in USA 23 February 1972; received in UK for publication 5 April 1972)

The observation that the methyl group α to the carbonyl group of 2,3-butanedione monoxime (δ=-2.40 ppm Figure 1) undergoes hydrogen deuterium-exchange in alkaline D_2O but not in acidic D_2O, while the β-methyl group (δ=-1.87 ppm Figure 1) is totally resistant to exchange in both media presents a route for the preparation of all the deuterated analogs of 2,3-butanedione monoxime as shown on the scheme below:



(I) (II)

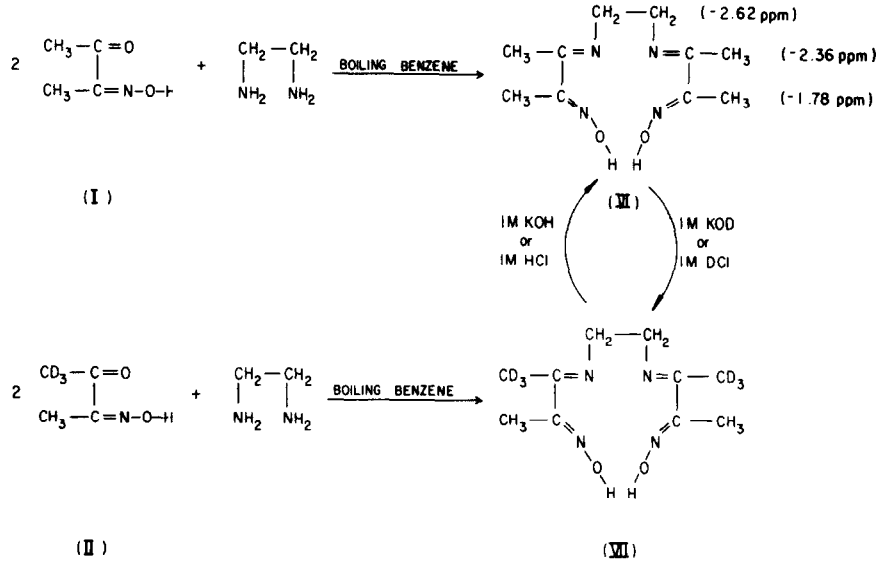


(III) (IV) (V)

By using compound II in the synthesis of bis(butanedione monoxime) ethylenediimine[1] (VII), both the unequivocal assignment of the chemical shifts and conclusive proof that the methyl groups α to the imine groups (δ=-2.36 ppm Figure 2) but not the methyl groups α to the oximino

*Supported by the Rider College Faculty Research Fellowship (Summer, 1971) and the Division of Chemical Education duPont Small Grants Programs.

groups (δ=-1.78 ppm Figure 2) undergo hydrogen-deuterium exchange in both acidic and basic media are established. These data explain why the rate of ligand hydrogen abstraction accompanying the photolytic or pyrolytic bond cleavage of the alkyl cobalt complexes reported by Schrauzer et. al.[2] are most rapid with ethylene- and propylenediimine butanedione monoxime complexes compared to dimethyl glyoxime complexes since the hydrogens α to the imine groups are labile toward hydrogen abstraction; whereas, the hydrogens α to the oximino groups are resistant to removal.



DISCUSSION

Compound II was prepared by allowing 2,3-butanedione monoxime to exchange in alkaline D_2O until approximately 80% of the protium in the α methyl group had been replaced by solvent deuterium as monitored by NMR spectroscopy (Figure 1B). The residual absorption at -2.40 ppm (Figure 1B) due to the 20% unexchanged protium of the α methyl group when left in D_2O buffer continued to decrease until essentially complete exchange and neglible absorption (Figure 1C) was recorded. When compound II is placed in H_2O buffer, the deuterium exchanges with solvent protium re-establishing absorption at -2.40 ppm (Figure 1A), confirming that the loss of absorption is not the result of hydrolysis of the oximino group but is, in fact, due to exchange. Similar increase of absorption at -2.40 ppm is obtained with compound IV when placed in H_2O buffer but no increase in the signal is observed at -1.87 ppm confirming the resistance of the

β-methyl group toward exchange. The chemical shifts of the α and β-methyl groups agree with those previously reported by Guetté et. al.[3].

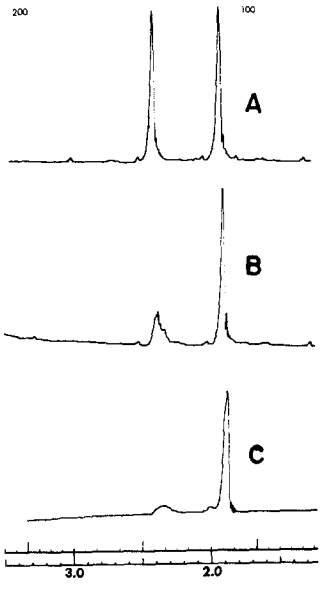


Figure 1

Nuclear Magnetic Resonance Spectra of 2,3-Butanedione Monoxime

(A) Four hours after preparing solution described in (B) in 0.1M phosphate buffer in H_2O rather than in D_2O.
(B) A solution of Compound (II) (20mg) 80% deuterated in 0.50 ml 0.1M phosphate in D_2O pH 10.0.
(C) Solution (B) four hours later.

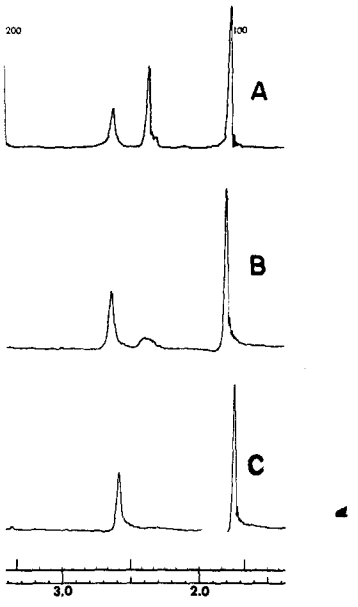


Figure 2

Nuclear Magnetic Resonance Spectra of Bis-(butanedione monoxime) ethylenediimine

(A) Four hours after preparing solution described in (B) in 1N KOH rather than 1N KOD.
(B) A solution of Compound (VII) (30mg) 80% deuterated in 0.50 ml of 1N KOD.
(C) Solution (B) four hours later.

A similar set of experiments were performed with bis(butanedione monoxime) ethylenediimine prepared by condensing compound II, 80% deuterated, with ethylenediamine (Figure 2B). In this case the methyl groups originally α to the carbonyl of 2,3-butanedione monoxime now reside α to the imine groups in bis(butanedione monoxime) ethylenediimine. Consequently, the residual absorption at -2.36 ppm (Figure 2B) results from the unexchanged protium of the methyl groups in compound VII α to the imine while the peak at -1.78 ppm and -2.62 ppm are due to the oximino methyl groups and the equivalent methylene groups, respectively. Allowing compound VII to exchange in 1N KOD caused the protium in the imine methyl groups to be replaced; thus no absorption was recorded at -2.36 ppm (Figure 2C). Alternately, exchanging compound VII in

1N KOH replaces the deuterium and re-establishes absorption at -2.36 ppm (Figure 2A). Note that the methyl groups α to the oximino groups, are resistant to exchange. This exchange, unlike that of 2,3-butanedione monoxime, takes place in both basic and acidic media.

PREPARATION OF COMPOUNDS

Compound II. 2,3-Butanedione monoxime (1.0g) in 25 ml of 1N KOD was allowed to exchange for eight hours. The basic solution was neutralized with 1N HCl and extracted with three 50 ml portions of ether, dried over anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum at 30°C. This treatment resulted in approximately 95% deuterium substitution of the α-methyl group.

Compound III. Prepared by the method of Walters[4] modified by Beach and Plaut[5].

Compound IV. A freshly prepared solution of sodium ethoxide was added to a stirred slurry of hydroxylamine hydrochloride (0.70g) in 10 ml of absolute ethanol containing two drops of phenolphthalein until the pink end point was reached. A small amount of hydroxylamine hydrochloride was then added to dispell the pink color. The hydroxylamine solution was filtered and then added dropwise to a stirred solution containing 0.86 g of deuterated 2,3-butanedione (III) in 10 ml absolute ethanol. The solution was warmed to 65°C for 1.5 hrs. after which the solvent was removed at 30°C under vacuum, leaving a gummy precipitate which was taken up in 10 ml D_2O and extracted with three 25 ml portions of ether, dried over sodium sulfate, filtered and taken to dryness under vacuum at 30°C. A syrupy residue crystalized upon cooling, yielding 0.63 g of product.

Compound V. Prepared from compound IV in a manner analogous to compound II, except 1N KOH was used rather than 1N KOD.

Compound VII. Prepared following the procedure of Mathur and Narang[1] except the deuterated analog (II) of 2,3-butanedione monoxime was used.

(1) N. K. Mathur and D. K. Narang, Talanta 11, 647 (1964).

(2) G. N. Schrauzer, J. W. Sibert, and R. J. Windgassen, J. Am. Chem. Soc., 90, 6681 (1968).

(3) J. P. Guetté, J. Armand and L. Lacombe, C. R. Acad. Sci. Paris, Ser. C, 264(17), 1509 (1967).

(4) D. Herr, M. Matheson, and W. D. Walters, J. Am. Chem. Soc., 63, 1464 (1941).

(5) R. L. Beach and G. W. E. Plaut, Biochemistry, 9, 760 (1970).