Dehydrogenation at the Ethane Bridge in Transition Metal Chelates of Tetradentate Schiff Bases

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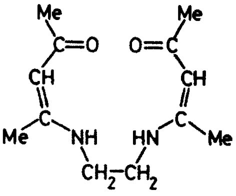
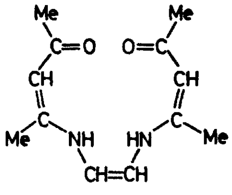
Summary Dehydrogenation has been induced, under mild conditions aided by palladized carbon, in the copper(II), nickel(II), palladium(II), and oxovanadium(IV) chelates of the tetradentate Schiff base 4,4′-(ethane-1,2-diyldi-imino)bis(pent-3-en-2-one); the new compounds are readily distinguished from their parent compounds by column or layer chromatography.

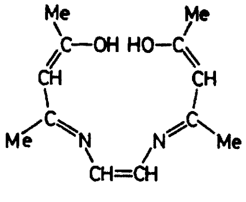
In the preparation of a series of nickel(II) chelates from tetradentate Schiff bases obtained from the higher homologues of pentane-2,4-dione with ethane-1,2-diamine, it was difficult to isolate stable products having satisfactory elemental composition. Examination of these compounds on silica gel layers showed that the chelates consisted of a number of related, nickel-containing species resulting from a complex series of reactions, probably involving aerial oxidation, and leading to the formation of an unsaturated linkage in the ethane-bridge of the ligand unit. As this reaction occurs extensively[1] in numerous nickel(II) chelates (*e.g.*, where R^1 and R^2 in the β-diketone portions $R^1.COCH_2$-$CO.R^2$ of the molecule may be Me, Et, Pr^n, Pr^i, or Bu^t), we have re-examined the copper(II), nickel(II), palladium(II), and oxovanadium(IV) chelates of 4,4′-(ethane-1,2-diyldi-imino)bis(pent-3-en-2-one) (I) and report here the conditions leading to, and the evidence for, their probable conversion into chelates of 4,4′-(ethene-1,2-diyldi-imino)bis(pent-3-en-2-one) (II), or its tautomer (III).



(I)



(II)



(III)

Chelates of (I) were prepared by available methods[2] from the pure ligand. The four chelates of (II) were prepared as crystalline solids, in yields of 30—90%, from the pure chelates of (I) (0·5—1 g), by refluxing for 10—15 h in the minimum volume of mesitylene (*ca.* 30 ml) under nitrogen with an equal weight of palladized carbon (10% palladium by weight on carbon). The corresponding pairs of compounds were readily separated on silica gel (columns or layers) with benzene–ethyl acetate (5—10% in benzene, by volume) when the unsaturated compound moves, in each case, ahead of the parent compound (see Table). The nickel(II) chelate of (I), which is the most reactive compound even at room temperature, shows the presence of appreciable amounts of the dehydrogenated and other species. Indeed, the dehydrogenated species is sufficiently abundant to be recovered directly, by separation on a column of silica gel, without need for actual synthesis.

The dehydrogenation process is supported by elemental, spectroscopic (i.r., mass, and n.m.r.), and chromatographic data. The spectroscopic evidence for the stable, chromatographically discrete derivatives of (II) includes the appearance of parent ions as the most intense ions in the electron-impact mass spectra [with fewer fragments than are observed[3] for the chelates of (I)], and marked downfield movement of the resonance for the remaining two equivalent protons attached to the carbons bridging the diketone units. I.r. spectra reveal two strong bands in the region 1500—1600 cm^{-1}. The C=C stretching vibration occurs at 1560—1570 cm^{-1}, 25—40 cm^{-1} less than is observed[4] for the chelates of (I). The C=N absorption at 1525 cm^{-1} remains unchanged. Furthermore, the easy chromatographic separation of the two related chelates has enabled us to demonstrate that this reaction occurs to some extent in unexpected circumstances such as exist during thermal analysis of the chelates of (I) below 300 °C in a nitrogen stream. In these circumstances, chelates of (II) were also identified in the recovered sublimates although there was no evidence for dehydrogenation from differential thermal analysis of the copper(II), nickel(II), or oxovanadium(IV) chelates. Palladium(II) behaves differently insofar as the chelate of (I) decomposes near its m.p. [to form the chelate of (II)] whereas the chelate of (II) is nearly completely volatile (leaving < 1% residue).

The mechanism involved in these reactions remains obscure. Higher oxidation states of various metals (including Cu, Ni, Fe, and Ru) have been invoked as transition states in other systems,[5] however, strain in the bridging C–C structure,[6] free-radical mechanisms, and thermally induced elimination of hydrogen cannot be excluded.

Isolation of the ligand (II) from either the copper(II) or the nickel(II) complexes has been unsuccessful owing to their greater resistance to the action of hydrogen sulphide (or ethylenediaminetetra-acetate and cyanide ions) than the complexes of (I). This stability is probably associated with an extended conjugation in the chelates of (II). Attempts to dehydrogenate the free ligand by the same experimental procedure have been unsuccessful also.

TABLE

Chelate				Proton resonances (δ)			
Cation	Ligand	Colour (m.p./°C)[a]	R_F[b]	CH_3	=CH (diketone)	CH_2 (bridge)	=CH (bridge)
Cu^{II}	(I)	Violet (140—142)	0·22				
	(II)	Dark brown (180—182)	0·43				
Ni^{II}	(I)	Dark brown (196—198)	0·27	1·85	4·86	3·08	—
	(II)	Orange-red (204—205)	0·52	2·13	5·26	—	6·11
Pd^{II}	(I)	Yellow (225—227)	0·27	1·96, 2·01	4·86	3·44	—
	(II)	Orange (226—228)	0·61	2·22, 2·25	5·27	—	6·30
VO^{IV}	(I)	Grey-green (233—235)	0·16				
	(II)	Yellow-green (227—229)	0·34				

[a] Determined in open capillaries; probably accompanied by decomposition in all cases. [b] Values obtained following simultaneous development of all compounds on a silica gel layer in benzene–ethyl acetate (90 : 10 v/v).

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