FORMATION OF PYRROLE DERIVATIVES UPON REARRANGEMENT OF 1H-1,2-DIAZEPINES IN THE PRESENCE OF $Fe_2(CO)_9$

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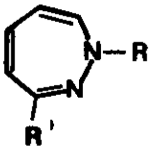
Abstract - On treatment with $Fe_2(CO)_9$ N-arylsulfonyl-1H-1,2-diazepines 1 yield, in addition to iron tricarbonyl complexes 2, isomeric pyrrole derivatives 3. Vinylnitrenes 6, stabilized by iron tricarbonyl moieties, are postulated as the most likely reaction intermediates.

Since our first report of the synthesis of 1-ethoxycarbonyl-1H-1,2-diazepine iron tricarbonyl complex 2a[1], all studies pertaining to the reaction of 1H-1,2-diazepines 1a-d and iron carbonyls have led to [diene]-Fe(CO)$_3$ complexes 2a-d as the only isolated products[2]. That coordination occurs between the butadiene moiety of diazepines and the iron tricarbonyl residue has been shown by X-ray crystallography[3].



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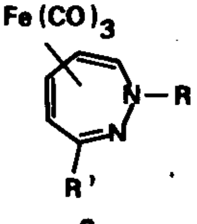

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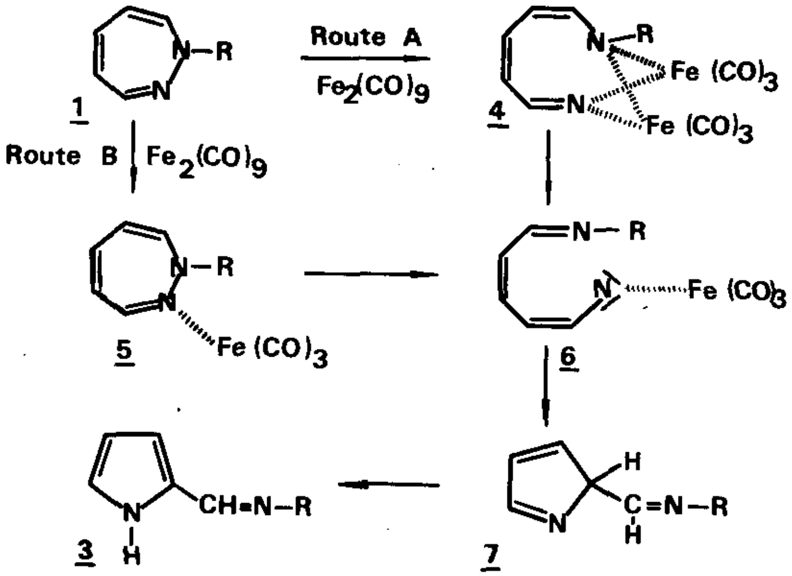
	a	b	c	d	e	f	g
R'	H	H	H	H	H	CH_3	CH_3
R	CO_2Et	$COCH_3$	COPh	Ts	SO_2Ph	Ts	SO_2Ph

We have carefully reinvestigated the synthesis of type 2 complexes and have found a novel type of rearrangement of diazepines 1. Besides the expected complexes 2d-g, which are formed in low yields only, pyrrole derivatives 3d-g are obtained as the main reaction products when diazepines 1d-g are treated with $Fe_2(CO)_9$ (Table 1).

Table 1 - Iron-tricarbonyl complexes 2d-g and pyrrole derivatives 3d-g obtained by treatment of diazepines 1d-g with $Fe_2(CO)_9$

Diazepines 1	Diazepine complexes 2		Pyrrole derivatives 3	
1d	2d	20%	3d	45%
1e	2e	18%	3e	56%
1f	2f	9%	3f	73%
1g	2g	10%	3g	75%

In our opinion two possible mechanistic pathways can be postulated in order to account for the metal carbonyl induced ring contraction of 1,2-diazepines to the isomeric pyrrole derivatives 3.



In route A we suggest formation of the nitrogen bridged complex (diazepine)-$Fe_2(CO)_6$ 4 in which the N-N bond has been cleaved, followed by loss of $Fe(CO)_3$ to yield the coordinated nitrene 6. Such a N-N bond cleavage, with formation of a complex analogous to 4, has been observed upon treatment of 3,5,7-triphenyl-4H-1,2-diazepine with $Fe_2(CO)_9$[4]. The N-N bond of 4,4'-dimethylbenzophenone azine has also been reported to be cleaved by $Fe(CO)_5$ leading to a bridged diiron hexacarbonyl derivative[5].

In route B the first step would give the complex 5 in which the diazepine is bonded to iron via σ lone pair donation from one nitrogen atom [6]. Such coordination would lead to weakening and thence to cleavage of the N-N bond, giving nitrene 6. Ring closure of this last compound followed by [1,5]-hydrogen shift would then yield the final pyrrole 3 [7].

These last steps are quite similar to those which have been proposed to account for the reactions of 2H-azirines with metal carbonyls [8]. As a matter of fact σ or π coordination of the azirine ring with a metal (Fe, Mo, Cr) enhances the propensity of the C-N bond toward cleavage. In some cases a coordinated vinylnitrene is proposed as an intermediate leading to the reaction products [8]. Vinylnitrene 10, which is coordinated to iron or to molybdenum, hes been recently postulated by one of us to account for the rearrangement processes of azirine 8 (Scheme 2).

Although the mechanistic pathways depicted in Scheme 1 seem reasonable, it is not yet clear why iron coordination occurs at nitrogen or with the diene moiety, but never at both sites simultaneously, even if a large excess of $Fe_2(CO)_9$ is used. We are currently investigating the reactivity of other N-N bonds toward metal carbonyls.

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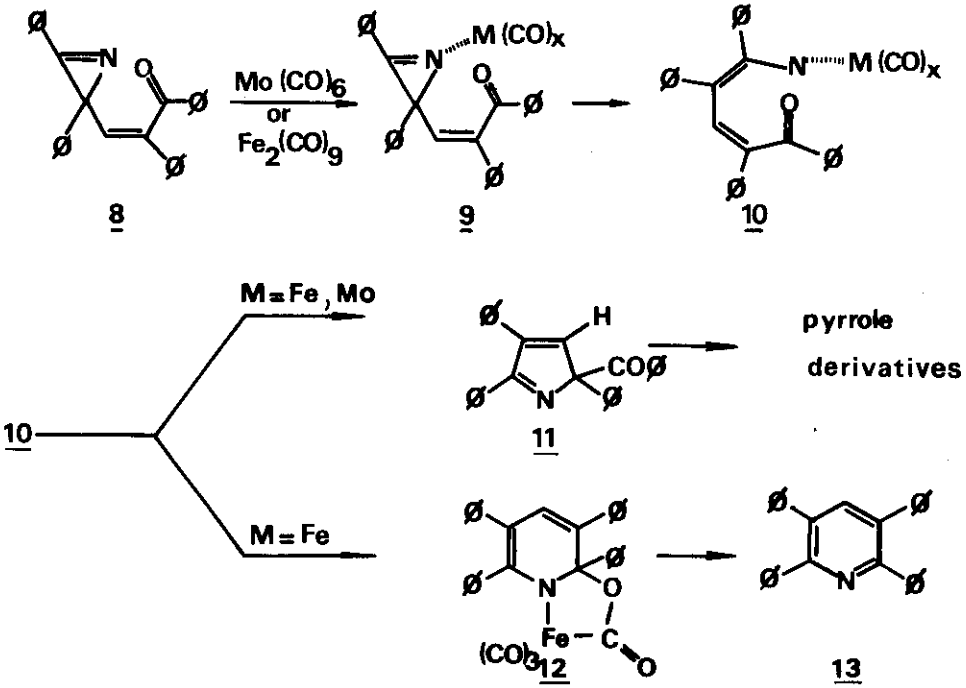

References and Notes

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(6) A square planar complex, in which the 3,5,7-triphenyl-4H-1,2-diazepine is bonded to rhodium via a nitrogen atom is described in reference 4.

(7) Treatment of iron tricarbonyl complex 2d with an excess of $Fe_2(CO)_9$ does not lead to formation of pyrrole 3d; this rules out the intermediacy of 2d in the formation of 3d.

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