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REACTION OF IRON CARBONYLS WITH PYRIDAZINE-3,6-DIONES

THE STRUCTURE OF (1,2-DIMETHYL-1,2-DIHYDROPYRIDAZINE-3,6-DIONE)IRON TRICARBONYL

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Summary

Reaction of 1,2-dimethyl- and 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-diones (I) with iron carbonyls gives iron tetracarbonyl complexes (II), which are converted to iron tricarbonyls (III).

The π-olefin structure of II has been confirmed by IR and PMR spectra. X-ray analysis of (1,2-dimethyl-1,2-dihydropyridazine-3,6-dione)iron tricarbonyl (IIIa) showed that the iron atom is bonded to the heterodiene fragment of the cycle including two carbon atoms of the double bond, the ketonic carbon atom and one nitrogen atom.

Introduction

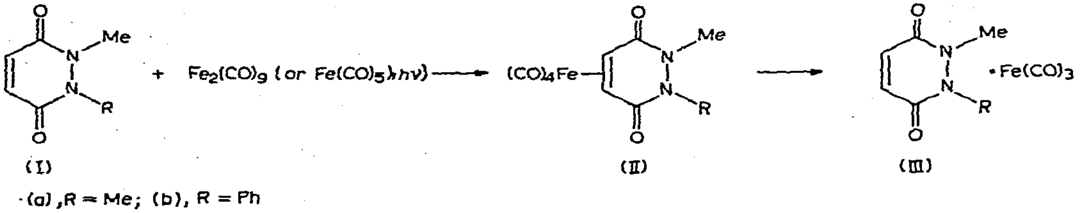
Earlier we showed that the aromatic diazine heterocycles (pyridazines and pyrimidines) react with iron carbonyls to give only σ-complexes [1—3]. The absence of π-complexes in the reaction products could be explained by the break of the aromatic bond system in a heterocycle during the formation of complexes, and also by the free electron pairs at the heteroatoms. The heterocycles act as electron donors, and produce mainly the σ-complexes via such pairs.

One would expect that a decrease in the nitrogen basicity and a passage to non-aromatic heterocycles would stimulate the formation of π-complexes in reactions of the heterocycles with iron carbonyls. Such a decrease in the electron donating ability of the nitrogen in pyridazine heterocycles occurs on going to 1,2-disubstituted 1,2-dihydropyridizine-3,6-diones. The aromaticity is also breaking and the properties of pyridizinediones as ligands should differ essentially from those of the parent pyridazines.

This is believed to be the first report on iron carbonyl complexes of 1,2-dihydropyridazine-2,6-diones, the cyclic hydrazines of maleic acid.

Results and discussion

Reactions of 1,2-dimethyl- (Ia) and 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-diones (Ib) with diiron nonacarbonyls involve two steps. The first affords the iron tetracarbonyl complexes IIa or IIb, which rapidly convert to the iron tricarbonyl compounds IIIa or IIIb. The photochemical reactions with $Fe(CO)_5$ led to IIIa or IIIb. However, employing the IR spectra (in particular the region of CO stretching frequencies) one may easily identify an intermediate formation of the iron tetracarbonyl complexes IIa and IIb.



IIa was isolated in pure form by repeated crystallization of the product mixture generated in reaction of equimolar quantities of the heterocyclic ligand and diiron nonacarbonyl at room or lower temperature. Thin layer chromatography of this mixture on alumina provides no separation of the iron tetra- and tri-carbonyl complexes IIa and IIIa because of their close R_f values.

The iron tetracarbonyl complex of 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-dione (IIIb) could not be isolated in its pure form. According to the NMR data it always had the ligand as an admixture. Crystallization or reprecipitation of the mixture of these compounds lead to decomposition. However, the spectral properties of IIb (Table 1) are quite similar to those of the iron tetracarbonyl complex of 1,2-dimethyl-1,2-dihydropyridazine-3,6-dione and π-monoolefin—iron tetracarbonyl complexes [4, 5]. These data leave no doubt of its intermediate formation in the reaction of iron carbonyls with 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-dione.

The structure of IIa and IIb as π-olefin—iron tetracarbonyl compounds has been confirmed by IR and NMR (Table 1). The signals of olefin protons in the NMR spectra of shift upfield by more than 3 ppm in respect to the starting ligand, evidence of the π-coordinated olefinic bond, whilst the methyl proton chemical shifts were almost unchanged. Thus one may assume that nitrogen atoms or carbonyl groups do not participate in coordination with the iron.

On going from the ligands to iron tetracarbonyl complexes IIa and IIb the IR spectra exhibit a long-wave shift of the C=C stretching frequencies over about 150 cm^{-1} which is specific of olefinic π-complexes. 1,2-Dimethyl-1,2-dihydropyridazine-3,6-dione provides the most clear observation of such a shift.

The presence of four stretching modes of the metal carbonyl groups in their normal region (2100-2000 cm^{-1}) is evidence of an equatorial location of the heterocyclic ligand in the trigonal bipyramidal iron(0) coordination sphere. In this case the $Fe(CO)_4$ fragment has C_{2v} symmetry and should display four IR active modes in this region.

TABLE 1

PMR AND IR SPECTRAL DATA OF 1,2-DISUBSTITUTED 1,2-DIHYDROPYRIDAZINE-3,6-DIONES (Ia, b) AND THEIR IRON TETRA- AND TRICARBONYL COMPLEXES (IIa, IIIb) AND (IIIa, IIIb)

Compound	Chemical shift δ (ppm)			Stretching frequencies (cm^{-1})		
	Solvent	$H_{4,5}$	H_{CH_3}	C=O[a]	C=C[a]	C≡O[b]
Ia	$CDCl_3$	6.86	3.63	1640	1590	
	CCl_4	6.70	3.52			
Ib	$CDCl_3$	6.96	3.18	1640	1590	
IIa	$CDCl_3$	3.73	3.58	1635	1435	2098, 2044, 2038, 2028
	CCl_4	3.79	3.30			
IIb	$CDCl_3$	3.93	3.05	1630		2085, 2043, 2028, 2026
IIIa	$CDCl_3$	3.32[c] 4.80[c]	2.80	1700	1460	2070, 2007, 1998
	CCl_4	3.25[c] 4.65[c]	2.62 2.59			
IIIb	$CDCl_3$	3.45[d] 4.96[d]	2.47	1715	1450	2075, 2020, 2010

[a] In KBr pellets. [b] In cyclohexane. [c] Doublet, *J* 6.0 Hz. [d] Doublet, *J* 6.7 Hz.

Of special interest is the structure of the iron tricarbonyl complexes III. We presume that iron in these compounds obeys the EAN rule, and thus pyridazinediones should act as four-electron bidentate ligands. Spectral data alone (Table 1) provide no unequivocal conclusion.

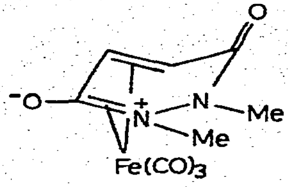
To elucidate the structure of iron tricarbonyl compounds we carried out an X-ray analysis of 1,2-dimethyl-1,2-dihydropyridazine-3,6-dione complex, IIIa.

Crystals of IIIa are monoclinic: *a* 14.412(8), *b* 13.103(7), *c* 6.334(5) Å, γ 112.69(8)°, *V* 1103 Å, mol. wt. 280, D_m 1.73, D_c 1.69 g·cm^{-3} for $Z = 4$, space group $P2_1/b$.

Intensities of reflection with $2\theta \leqslant 40°$ were measured by an automatic Hilger-Watts diffractometer (λ Mo-K_α, graphite monochromator, $\theta/2\theta$ scan). The structure was solved by a heavy-atom technique on 1430 reflections with $F^2 \geqslant 3\sigma(F^2)$. The final *R* factor value is 0.098 after isotropic least-square refinement. Positional and thermal parameters are given in Table 2, bond distances and angles in Table 3.

As is shown by the present X-ray study the iron atom of the molecule IIIa interacts, besides with the three carbonyl groups, also with four neighbouring atoms of a pyridazine cycle including one nitrogen atom (Fig. 1). But the distances Fe···N(2) 2.82(2) and Fe···C(7) 2.81(2) Å are rather long to correspond to an exchange interaction. Thus, the molecule of 1,2-dimethylpyridazine-3,6-dione acts as a π-heterodiene ligand and four-electron donor, and IIIa obeys the noble gas rule.

One may assume that the formation of heterodiene fragment in pyridazinedione ligand is a result of a shift of the nitrogen electron pair producing a system of bonds with positive N atom and negative O. This system is possibly stabilized by coordination with the iron carbonyl group, facilitating charge delocalization.



Only one similar complex with an π-azabutadiene ligand has been investigated by X-ray, namely *N*-cinnamylideneaniline iron tricarbonyl (IV) [6]. As in IV the π-heterodiene ligand N(1)C(4)C(5)C(6) is only approximately planar (Table 4): the N(1) atom is displaced from the three carbons plane by 0.40 Å [0.06 Å in IV]. The dihedral angle between this ligand average plane and that of three carbonyl carbon atoms is 17°, i.e. it is close to the similar angles in other butadiene—$Fe(CO)_3$ complexes: 16.5° in IV, 19° in 1,4-diphenylbutadiene—$Fe(CO)_3$ [7], 18.8° in vitamin A aldehyde—$Fe(CO)_3$ (VI) [8], 21° in octafluorocyclohexa-1,3-diene—$Fe(CO)_3$ (VII) [9]. As in all these complexes the iron atom coordination in IIIa is tetragonal-pyramidal with the C(1)O(1) group in an apical position; two sites of a pyramid base are occupied by the bidentate π-heterodiene, two others by carbonyl groups.

A detailed discussion of bond distances between light atoms is not justified because of the relatively large standard deviations. Still it seems that bond lengths in the heterodiene fragment N(1)—C(4) 1.48(3), C(4)—C(5) 1.44(3), C(5)—C(6) 1.51(3) Å are longer than those observed in IV (1.365, 1.406, 1.423 Å respectively) and the C—C bonds are longer than all those found previously in the π-butadiene complexes the longest of them being 1.46 and 1.45 Å in butadiene—$Fe(CO)_3$ (VIII) [10].

The Fe—N(1) distance 2.05(2) Å is the same as in IV (2.061 Å). The Fe—C(6) distance 2.04(2) Å to the terminal atom of a butadiene system is shorter than the Fe—C(5) distance 2.11(2) Å from its central C(5) atom. Although in other

TABLE 2

ATOMIC COORDINATES AND THEIR ISOTROPIC THERMAL FACTORS

Atom	*X*	*Y*	*Z*	B_j(Å^2)
Fe	0.1892(3)	0.3918(3)	−0.0166(7)	3.80(6)
O(1)	0.1121(10)	0.3140(11)	0.4077(24)	7.6(3)
O(2)	0.1000(10)	0.1687(12)	−0.2069(24)	6.5(3)
O(3)	0.0184(10)	0.4347(11)	−0.2081(24)	6.3(3)
O(4)	0.3181(10)	0.6396(11)	−0.2607(23)	5.8(3)
O(5)	0.4459(10)	0.4138(11)	0.2422(23)	5.8(3)
N(1)	0.2872(13)	0.5462(14)	0.0732(29)	3.8(2)
N(2)	0.3628(13)	0.5310(14)	0.2004(29)	4.1(3)
C(1)	0.1413(16)	0.3416(18)	0.2421(37)	5.5(4)
C(2)	0.1341(16)	0.2576(18)	−0.1312(37)	4.8(4)
C(3)	0.0661(16)	0.4243(17)	−0.1347(38)	4.7(4)
C(4)	0.3127(16)	0.554(18)	−0.1549(37)	4.1(3)
C(5)	0.3174(16)	0.4506(18)	−0.2130(36)	4.1(3)
C(6)	0.3257(15)	0.3785(17)	−0.0346(36)	4.3(3)
C(7)	0.3842(16)	0.4412(18)	0.1391(36)	3.9(3)
C(8)	0.2462(16)	0.6290(18)	0.1588(36)	4.8(4)
C(9)	0.4487(16)	0.6358(17)	0.2774(35)	5.6(3)

TABLE 3

INTERATOMIC DISTANCES AND BOND ANGLES

Bond	*d*(Å)	Angle	ω°	Angle	ω°
Fe—C(1)	1.80(2)	FeC(1)O(1)	177(1)	O(5)C(7)N(2)	120(1)
Fe—C(2)	1.78(2)	FeC(2)O(2)	178(2)	N(2)C(7)C(6)	115(2)
Fe—C(3)	1.85(2)	FeC(3)O(3)	174(1)	C(8)N(1)C(4)	116(2)
Fe—N(1)	2.05(2)	FeN(1)N(2)	107(1)	C(8)N(1)N(2)	115(1)
Fe—C(4)	2.36(2)	FeN(1)C(4)	82(1)	C(4)N(1)N(2)	112(1)
Fe—C(5)	2.11(2)	FeN(1)C(8)	119(1)	C(9)N(2)N(1)	116(1)
Fe—C(6)	2.04(2)	FeC(4)O(4)	139(1)	C(9)N(2)C(7)	119(1)
Fe—O(4)	3.42(2)	FeC(4)N(1)	59(1)	N(1)N(2)C(7)	113(1)
Fe—N(2)	2.82(2)	FeC(4)O(5)	62(1)	C(4)C(5)C(6)	116(2)
Fe—C(7)	2.81(2)	FeC(5)C(4)	80(1)	C(5)C(6)C(7)	112(2)
C(1)—O(1)	1.14(3)	FeC(5)C(6)	66(1)		
C(2)—O(2)	1.18(3)	FeC(6)C(5)	71(1)		
C(3)—O(3)	1.14(3)	FeC(6)C(7)	106(1)		
N(1)—N(2)	1.43(3)	C(1)FeC(2)	92(1)		
N(1)—C(4)	1.48(3)	C(1)FeC(3)	102(1)		
C(4)—C(5)	1.44(3)	C(2)FeC(3)	88(1)		
C(5)—C(6)	1.51(3)	O(4)C(4)N(1)	120(2)		
C(6)—C(7)	1.43(3)	O(4)C(4)C(5)	133(2)		
C(7)—N(2)	1.38(3)	N(1)C(4)C(5)	106(1)		
C(4)—O(4)	1.28(3)	O(5)C(7)C(6)	133(2)		
C(7)—O(5)	1.26(3)				
N(1)—C(8)	1.52(3)				
N(2)—C(9)	1.53(2)				

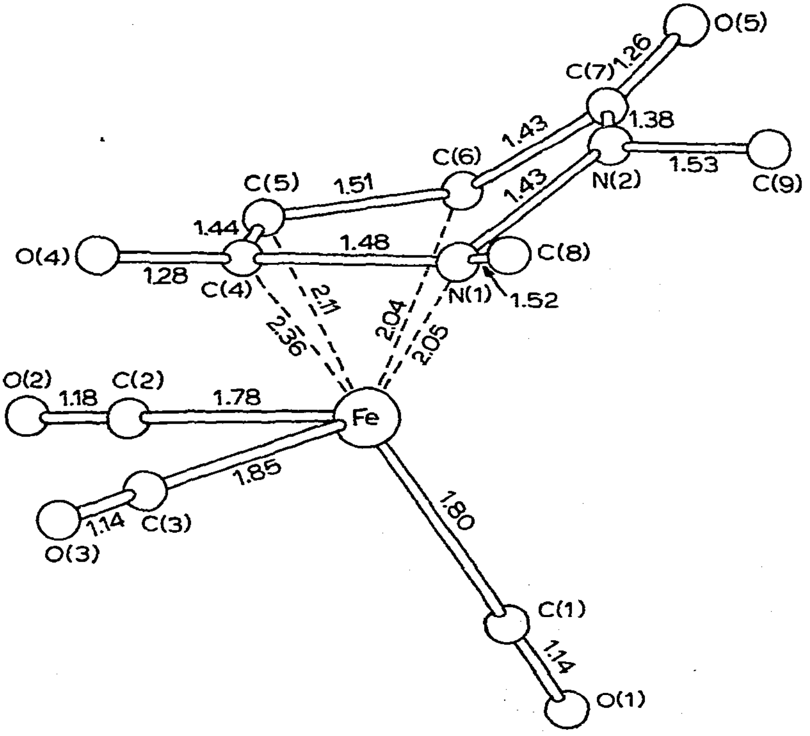


Fig. 1. Scheme of the molecule (1,2 dimethyl-1,2-dihydropyridazine-3,6-dione)iron tricarbonyl and bond lengths.

TABLE 4

COEFFICIENTS OF EQUATIONS $Ax + By + Cz = D$ OF MOLECULE PLANAR FRAGMENTS AND DEVIATIONS (IN Å) OF ATOMS FROM THESE PLANES

Plane	Atoms and their deviations				*A*	*B*	*C*	*D*	Dihedral angle with planes	
									III	IV
I	N(1)	C(4)	C(5)	C(6)	12.3	1.7	0.9	4.6	48.5	17.2
	+0.05	—0.08	+0.09	—0.05						
	C(8)[a]	O(4)[a]								
	0.34	—0.20								
II	C(4)	C(5)	C(6)	N(1)[a]	12.9	0.8	—0.3	4.5		
	0.00	0.00	0.00	0.40						
	C(8)[a]	O(4)[a]								
	0.90	—0.17								
III	N(1)	N(2)	C(7)	C(6)						
	0.00	+0.01	—0.01	0.00	7.6	4.4	4.1	4.3		
	C(8)[a]	C(9)[a]	O(5)[a]							
	0.29	—0.77	—0.01							
IV	C(1)	C(2)	C(3)		11.4	3.3	—1.0	2.5		

[a] Atoms not included in constructing the planes.

butadiene—$Fe(CO)_3$ complexes the first distance is normally longer (2.14 and 2.06 Å in VIII; 2.147, 2.066 and 2.079 Å in VI). The distance Fe—C(4) to other central carbon atom bonded to an electron-attractive O(4) atom is unusually long [2.36(2) Å]. So this Fe—C(4) interaction is rather weak. A bonding with the metal atom results in a shorteningof the N(1)· · ·C(6) distance [2.44(3) Å]

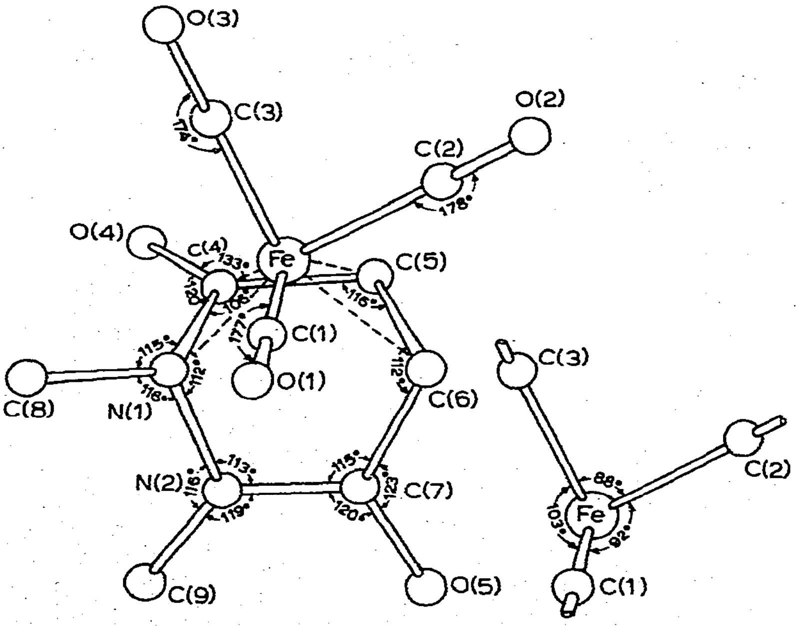


Fig. 2. Projections of the molecule (1,2-dimethyl-1,2-dihydropyridazine-3,6-dione)iron tricarbonyl on the plane of fragment N(1), N(2), C(7), C(6), and bond angles.

which would be equal to ~2.8 Å in the free ligand. A similar shortening of the distance between the terminal atoms of a coordinated butadiene system was found as well in other six-membered cyclic ligands: 2.53 Å in VII, 2.56 Å in π-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium (IX) [11]. In accordance with this contraction the intracyclic angles at the central atoms C(4) and C(5) of the heterodiene fragment are decreased to 106(1) and 116(2)° respectively [114° in VII] in comparison with an ideal value 120° (Fig. 2).

Coordination of the heterodiene fragment results in a loss of the planarity of the pyridazine cycle. This cycle acquires a boat conformation with the dihedral angle N(1)C(4)C(5)C(6)/N(1)N(2)C(7)C(6) 48.5°, which is close to the geometry found in similar systems (47.3° in VII, 48° in IX). Intracyclic angles at N(1) [112(1)°], C(6) [112(2)°] [117° in VII], N(2) [113(1)°] and C(7) [115(2)°] are intermediate between values corresponding to sp^2 and sp^3 hybridizations. The N(1)N(2)C(7)C(6) fragment is strictly (± 0.01 Å) planar including O(5),but the methyl groups are displaced out of this plane by 0.29 [C(8)] and 0.77 Å [C(9)].

Both nitrogen atoms have virtually the same close-to-planar pyramidal configuration (sums of bond angles are equal to 343 and 348° for N(1) and N(2) respectively). The N(1)—N(2) distance 1.43(3) Å corresponds to an ordinary bond (the doubled single-bonded nitrogen radius is 1.40 Å) [12] and is equal to the values found previously in the pyridazine—iron carbonyl complexes with Fe—N σ-bonds [3]. Two other non-coordinated bonds N(2)—C(7) 1.38(3) Å (a sum of single-bonded radii 1.47, that of the double-bonded radii 1.27 Å) [10] and C(6)—C(7) 1.43(3) Å have intermediate lengths and orders.

Both "carbonylic" carbon atoms of the cycle have a planar trigonal configuration: sums of bond angles are 359° for the coordinated C(4) and 358° for the non-coordinated C(5). The bond lengths C(4)—O(4) 1.28(3) and C(7)—O(5) 1.26(3) Å are equal but somewhat greater than the corresponding distances in quinones (1.21 to 1.23 Å) [13, 14].

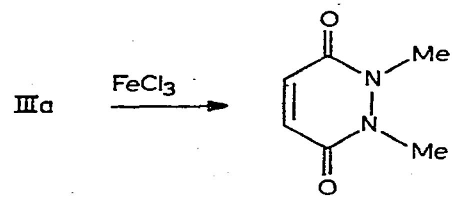
The geometry of the $Fe(CO)_3$ fragment is normal: Fe—C 1.78 to 1.85, C—O 1.14 to 1.18 Å, Fe—C—O 174—173°. The C(2)—Fe—C(3) angle between the carbonyl groups in *trans*-position to π-heterodiene ligand is 88(1)°, i.e. smaller than two other angles C(1)—Fe—C(2) 92(1)° and C(1)—Fe—C(3) 103(1)° as found in other butadiene—$Fe(CO)_3$ complexes.

Knowledge of the exact structures of the iron tricarbonyl—pyridazinedione complexes IIIa and IIIb allows a more detailed analysis of their IR and NMR spectra. As expected, the absorption band in the IR spectra of the carbon—carbon double bond is shifted downfield by ≈ 150 cm^{-1}, which is in good agreement with the essentially greater length of this bond (1.51 Å). In the region of stretching C≡O mode the IR spectra are quite reminescent of those of iron tricarbonyl complexes of the diolefin [15] and α,β-unsaturated ketones [5] and their imines [16]. It is somewhat hard to explain the presence of a broad band at 1720—1700 cm^{-1} in the IR spectra of iron tricarbonyl complexes IIIa and IIIb. One of the possible reasons may be the break of conjugation in a heterocyclic ligand as a result of its coordination, by which the free amide group acquires the character of the saturated amide group.

The olefin proton signals H(4) and H(5) in the NMR spectra of IIIa and IIIb show two doublets with the spin—spin coupling constant $J \sim 6$ Hz and they shift upfield with respect to the starting heterocycle by about 2 and 3.5 ppm; thus the difference in their chemical shifts attains ~ 1.5 ppm (Table 1). Analogously to other iron carbonyl π-complexes of the dienes and heterodienes the upfield doublet may be assigned to the "outer" H(5) protons while the downfield doublet is due to the "inner" H(4) protons.

The methyl proton signals in IIIa and IIIb are shifted over 0.7—0.8 ppm upfield. It is somewhat unexpected that in the NMR spectrum of (1,2-dimethyl-1,2-dihidropyridazine-3,6-dione)iron tricarbonyl the methyl protons at various nitrogen atoms appear in the form of one signal in chloroform or as two close signals ($\Delta\delta$ = 0.03 ppm) in carbon tetrachloride. When the structure of this complex is determined it can be assumed that a coincidence of chemical shifts of methyl protons may be a result of mutual compensation of several effects.

An additional evidence to the structure assumed for complex IIIa was obtained by chemical investigation. An oxidative decomposition of IIIa with Fe^{3+} led quantitatively to the starting 1,2-dimethyl-1,2-dihydropyridazine-3,6-dione.



Experimental

1,2-Dimethyl- and 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-diones (Ia, Ib) were prepared as described in ref. [17].

All the reactions were carried out under argon in absolute solvents. The IR spectra were taken using an UR-10 spectrophotometer in KBr pellets, except the region of stretching frequencies of the carbonyl groups which was measured in cyclohexane—chloroform (4/1). NMR spectra of $CDCl_3$ and CCl_4 solutions were registered on Hitachi-Perkin-Elmer R-20 and Perkin-Elmer R-12 spectrometers. The mercury quartz lamp PRK-4 was used as UV source.

The reaction of 1,2-dimethyl-1,2-dihydropyridazine-3,6-dione (Ia) with $Fe_2(CO)_9$.

(a) 1.82 g of $Fe_2(CO)_9$ was added to a solution of 0.90 g of Ia in 50 ml of acetone. The mixture was stirred for 2 h at room temperature and then filtered. The solvent was evaporated in vacuo from the filtrate. 1.53 g of the residue was precipitated with petroleum ether from chloroform. 0.4 g (19%) of complex IIa was obtained, m.p. 95—100° (dec.). Found: C, 39.31; H, 2.61; Fe, 18.13; N, 9.09; $C_{10}H_8FeN_2O_6$ calcd.: C, 39.04; H, 2.63; Fe, 17.54; N, 8.74%.

(b) 7.28 g of $Fe_2(CO)_9$ was added to a solution of 1.80 g of Ia in 100 ml of acetone. The mixture was stirred at 40—50°. In 3 and 6 h the 1.82 g portions of $Fe_2(CO)_9$ were added to the reaction mixture. After heating for 8 h the mixture was filtered. 2.44 g of the residue was recrystallized from carbon tetrachloride. 2.00 g (55%) of complex IIIa was obtained, m.p. 110—115° (dec.). Found: C, 38.41; H, 2.91; Fe, 19.74; N, 10.36; molecular weight 276 (cryoscopically in bromoform). $C_9H_8FeN_2O_5$ calcd.: C, 38.60; H, 2.87; Fe, 19.94; N, 10.00%, molecular weight 280.

Photochemical transformation of (1,2-dimethyl-1,2-dihydropyridazine-3,6-dione)-iron tetracarbonyl (IIa) into the iron tricarbonyl complex (IIIa)

0.70 g of complex IIa and 9 ml of $Fe(CO)_5$ in 200 ml of THF were irradiated at 20° for 24 h. The mixture was filtered and the filtrate evaporated in vacuo.

Recrystallization of the residue from carbon tetrachloride gave 0.17 g (18%) of iron tricarbonyl complex IIIa. Evaporation of the filtrate to a minimum volume gave additional 0.3 g of IIIa with negligible admixture of IIa (according to the data of IR spectrum).

Reaction of 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-dione (Ib) with $Fe_2(CO)_9$

22.2 g of $Fe_2(CO)_9$ was added to a solution of 6.5 g of Ib in 50 ml of acetone, the mixture was stirred for 4.5 h at room temperature and filtered. The solvent was removed in vacuo from the filtrate. Thin layer chromatography of the residue on alumina (chloroform—heptane 3/1) gave: (a) An upper green band of $Fe_3(CO)_{12}$ identified by its IR spectrum; (b) 1.86 g (17%) of iron tricarbonyl complex IIIb (the second yellow band); (c) 1.55 g of the mixture of iron tetracarbonyl complex IIb and the starting 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-dione (the third light-yellow band).

Complex (IIIb) was purified by precipitation with petroleum ether from benzene. 1.51 g (14%) of IIIb was obtained, m.p. 100—105° (dec.). Found: C, 49.14; H, 2.97; Fe, 16.06; N, 8.50; $C_{14}H_{10}FeN_2O_5$ calcd.: C, 49.43; H, 2.97; Fe, 16.32; N, 8.18%.

We failed to isolate pure complex IIb by repeated chromatography or reprecipitating. It had always on admixture of starting ligand. Complex IIb was characterised by the IR and PMR spectra (Table 1).

Reaction of 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-dione (Ib) with $Fe(CO)_5$

A solution of 0.66 g of (Ia) and 6 ml of $Fe(CO)_5$ in 100 ml of THF was irradiated at 25° at stirring for 28 h. The mixture was filtered and the filtrate evaporated in vacuo. 0.77 g of the residue was chromatographed on alumina (chloroform—petroleum ether 1/1). Two bands corresponded to $Fe_3(CO)_{12}$ and complex IIIb were observed. Recrystallization from benzene with petroleum ether gave 0.35 g (32%) of complex IIIb.

Oxidative decomposition of (1,2-dimethyl-1,2-dihydropyridazine-3,6-dione)iron tricarbonyl (IIIa)

0.56 g of anhydrous $FeCl_3$ was added to 0.53 g of IIIa in 60 ml of benzene. The mixture was stirred for 2.5 h at room temperature and the solvent evaporated in vacuo. The residue was treated with diluted hydrochloric acid and extracted several times with methylene chloride. The extract was dried over calcium chloride and evaporated in vacuo. 0.23 g (82%) of 1,2-dimethyl-1,2-dihydropyridazine-3,6-dione (Ia) was obtained, m.p. 135—137°. A mixture with an authentical sample gave no depression of the melting point. IR and PMR spectra of Ia were similar to those of an authentical sample [17].

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