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REACTIONS OF DIPHENYLBUTADIYNE WITH CARBODIIMIDES IN THE PRESENCE OF IRON CARBONYLS

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SUMMARY

Reactions of diphenylbutadiyne with diarylcarbodiimides in the presence of iron carbonyls produce three types of pyrroline derivative, 1-aryl-3-phenyl-4-phenylethynyl-5-aryliminopyrrolin-2-one, 1-aryl-4-phenyl-3-phenylethynyl-2,5-bis(arylimino)pyrroline and 1,1′-diaryl-3,3′-diphenyl-2′,5,5′-tris(arylimino)-4,4′-bipyrrolin-2-one (Ar = phenyl, *p*-tolyl and *p*-chlorophenyl). A similar reaction using dicyclohexylcarbodiimide gives 1-cyclohexyl-3-phenyl-4-phenylethynyl-5-cyclohexyliminopyrrolin-2-one as the sole product. Acid hydrolysis of the above phenylethynyl-pyrrolinones and -pyrrolines affords the corresponding phenylethynylpyrroline-2,5-diones. The bipyrrolines have been similarly hydrolyzed to the bipyrroline-2,2′,5,5′-tetrone derivatives. The reaction of the phenylethynylpyrrolinone (Ar = phenyl) with diphenyl or di-*p*-tolyl carbodiimide in the presence of $Fe(CO)_5$ gives the bipyrroline derivative as the isocyanide insertion product. The arylisocyanide iron carbonyl complexes $Fe(CO)_{5-m}(CNAr)_m$ are considered to be the active species for the formation of phenylethynyl bis(imino)pyrrolines and bis(imino)pyrroline rings in bipyrrolines.

The carbonylation[1] and oligomerization[2] reactions of acetylenes with transition metal catalysts have been studied by several workers and a variety of acetylene–metal complexes has been suggested as reactive intermediates. However, little is known about the reaction between acetylenes and heterocumulenes catalyzed by transition metal complexes, although in previous papers[3,4] we have reported that the reactions of acetylenic compounds, such as phenylacetylene and diphenylacetylene, with heterocumulenes in the presence of metal carbonyls afford interesting five-membered ring compounds through the involvement of acetylene–metal complexes as intermediates. Of particular interest are the carbonylation and addition reactions of disubstituted acetylenes via the "doubly σ-bonded" iron complex. The reaction of diphenylbutadiyne (I) with heterocumulenes is reported in this paper.

Reactions between I and diarylcarbodiimide IIa–IIc in the presence of iron carbonyls give three types of pyrroline derivatives, which are difficult to prepare by other methods, *i.e.* 4-phenylethynyl-5-iminopyrrolin-2-ones IIIa–IIIc, 3-phenylethynyl-2,5-bis(imino)pyrrolines IVa–IVc and 2′,5,5′-tris(imino)-4,4′-bipyrrolin-2-ones Va–Vc. It should be noted that the further reaction of the phenylethynylpyrrolinones IIIa–IIIc formed in the first step with carbodiimides IIa–IIc and iron carbonyls afford the corresponding bipyrrolines Va-Vc.

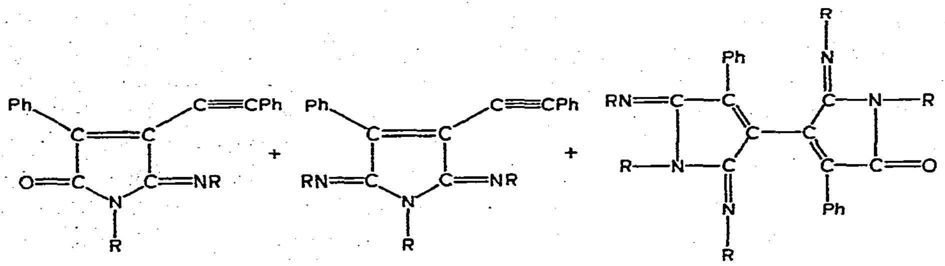
We suggest that arylisocyanide derivatives of iron carbonyls, such as $Fe(CO)_{5-m}(CNAr)_m$, play a significant role as the reactive intermediates in the formation of the bis(imino)pyrroline ring compounds IVa–IVc and Va–Vc.

RESULTS AND DISCUSSION

Reactions of diphenylbutadiyne (I) with carbodiimides

The reaction of I with diphenylcarbodiimide (IIa) in the presence of $Fe(CO)_5$ at 160° produces 1,3-diphenyl-4-phenylethynyl-5-phenyliminopyrrolin-2-one (IIIa), 1,4-diphenyl-3-phenylethynyl-2,5-bis(phenylimino)pyrroline (IVa) and 1,1′,3,3′-tetraphenyl-2′,5,5′-tris(phenylimino)-4,4′-bipyrrolin-2-one (Va) in yields of 28, 1 and 14%, respectively.

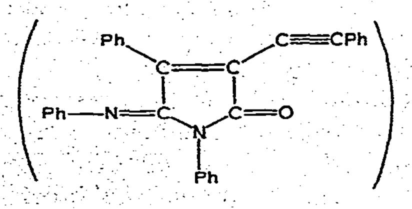
$$\underset{(I)}{Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph} + \underset{(IIa\text{–}IId)}{R{-}N{=}C{=}N{-}R} + Fe(CO)_5 \xrightarrow{155-210^\circ}$$



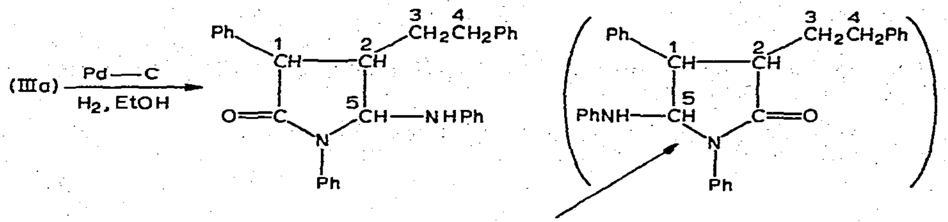
(IIIa–IIId) (IVa–IVc) (Va–Vc)

(a: R = phenyl, b: R = *p*-tolyl, c: R = *p*-chlorophenyl, d: R = cyclohexyl)

The phenylethynylpyrrolinone IIIa is formed by CO insertion into the equimolar adduct of I and IIa, its structure having been determined from the following spectral data and, in addition, from the NMR spectral data for the hydrogenation product VI. The IR spectrum of IIIa exhibits absorption maxima corresponding to the C≡C, C=O and C=N groups at 2220, 1725 and 1660 cm^{-1}, respectively while the mass spectrum exhibits a molecular ion at m/e 424 ($C_{30}H_{20}ON_2$ calcd.: 424). Two forms, IIIa and IIIa′, are possible for the structure of this compound and hence in order to confirm whether the Ph–N=C or the C=O group is attached to the C-1 position of I, hydrogenation of III has been carried out in the presence of palladium on carbon as a



(IIIa′)

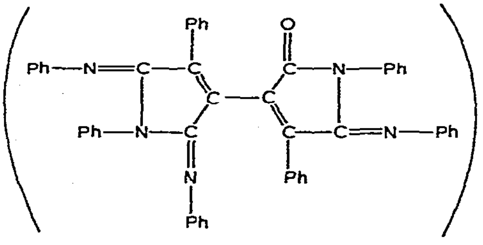


(VI) (IIIa') (VI')

catalyst. 5-Anilino-1,3-diphenyl-4-phenethylpyrrolidin-2-one (VI) was the sole product and was isolated in 25 % yield. The NMR spectrum of VI exhibits two protons as a complex multiplet centered at δ 1.50, assigned to the hydrogen at C-3, a triplet at 2.48 assigned to the C-4 methylene protons, a single-proton complex multiplet centered at 2.95* assigned to the hydrogen at C-2, a single-proton doublet at 3.93 assigned to the hydrogen at C-1, a single proton as a broad peak centered at 4.10 assigned to N–H and a single proton as a broad doublet centered at 5.64 assigned to the hydrogen at C-5. The δ 4.10 peak disappeared upon addition of D_2O and the broad doublet at 5.64 changed to a sharp doublet. The presence of the doublet due to the C-1 proton of VI provides strong evidence in favour of the structure, since the hydrogen at C-1 would not appear as a doublet in the corresponding spectrum of VI'. Thus the NMR data for the hydrogenated compound are consistent with structure IIIa.

The bis(phenylimino)pyrroline IVa was formed as the adduct from the reaction of one mole of I and two moles of IIa through the elimination of one N–Ph group, the structural assignment being based on IR analysis (C≡C at 2220, C=N at 1660 and 1630 cm^{-1}) and mass spectra (M^+ m/e at 499) and on elemental analysis.

The spectral data for bipyrroline Va [IR 1730 (C=O), 1660 and 1630 cm^{-1} (C=N); mass spectrum m/e at 721 (M^+)] indicate that Va contains two types of pyrroline rings similar to those in phenyliminopyrrolinone IIIa or bis(phenylimino)-pyrroline IVa. It is therefore not unreasonable to assume that subsequent reaction of



(Va')

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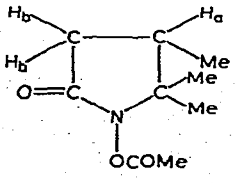
* The NMR spectrum of the 4-substituted pyrrolidin-2-one shown below exhibits a H_a proton signal at high field similar to that of the C-2 proton of VI[15].



τ 7.3—8.1 (H_a and $2H_b$, multiplet)

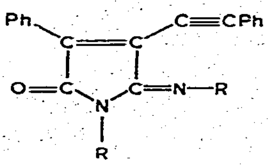
TABLE 1.

REACTIONS OF DIPHENYLBUTADIYNE (I) WITH CARBODIIMIDES (IIa–d) IN THE PRESENCE OF IRON CARBONYLS

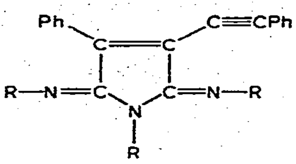
a: R = phenyl, b: R = *p*-tolyl, c: R = *p*-chlorophenyl, d: R = cyclohexyl.

Expt No.	*R*	*Reactant (mole)*			*Temp. (°C)*	*Time (h)*
		I	*RN=C=NR*	*Fe(CO)$_5$*		
1	Phenyl	0.04	0.08	0.08	160	4.5
2	Phenyl	0.028	0.03	0.028	160	3.0
3	Phenyl	0.025	0.05	0.025	185	1.5
4	Phenyl	0.03	0.06	0.06	210	5.5
5[c]	Phenyl	0.015	0.03	[d]	110	5.0
6[e]	Phenyl	0.01	0.02	[f]	164	6.0
7[e,h]	Phenyl	0.005	0.01	[g]	164	6.5
8[i]	Phenyl	0.02	0.04	0.04	155	4.0
9	Phenyl	0.01	0.01	[j]	160	1.0
10	*p*-Tolyl	0.008	0.016	0.016	155	5.0
11	*p*-Chlorophenyl	0.02	0.03	0.02	180	4.0
12	Cyclohexyl	0.015	0.03	0.03	180	4.0
13[c]	Cyclohexyl	0.025	0.05	[k]	110	5.0

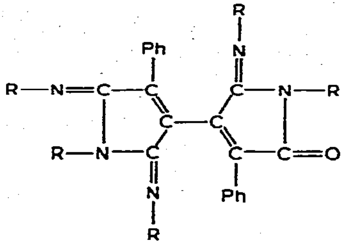
Product, yield[a] (%)



(IIIa – IIId)



(IVa-IVc)



(Va-Vc)

(IIIa – IIId)	(IVa-IVc)	(Va-Vc)
28	1	14 (21)[b]
28	1 (2)[b]	10 (29)[b]
15	2	34 (51)[b]
4	1	37 (56)[b]
16	3	7 (11)[b]
12	10	3 (5)[b]
50	2	7 (11)[b]
	20	
11	1	13 (20)[b]
20	4 (6)[b]	4 (8)[b]
14		
14		

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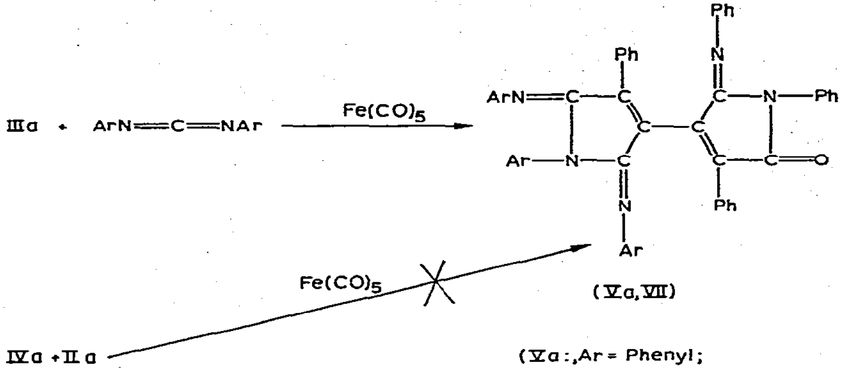
[a] Based on I. [b] Based on carbodiimide. [c] Toluene used as solvent. [d] $Fe_3(CO)_{12}$ (0.005 mole) used instead of $Fe(CO)_5$. [e] Mesitylene used as solvent. [f] $Fe(CO)_4PPh_3$ (0.01 mole) used. [g] $Fe(CO)_3(PPh_3)$ (0.005 mole) used. [h] Compound VIII was obtained in 29% yield. [i] PPh_3 (0.004 mole) added to the reaction mixture. [j] $Fe(CO)_4$-(CN–Ph) (0.01 mole) used. [k] $Fe_3(CO)_{12}$ (0.008 mole) used.

IIIa or IVa, formed *in situ* in the first step, with IIa in the presence of Fe$(CO)_5$ would result in the formation of bipyrroline Va. Two isomeric structures, Va and Va′, may also be visualized for this compound. In order to clarify the formation pathway and the structure of the product, the following experiments were performed. Reaction of IIIa, isolated from the above reaction, with IIa in the presence of Fe$(CO)_5$ was undertaken under similar conditions to those used above to give the bipyrroline Va in 29% yield. However, the same reaction using IVa instead of IIIa gave neither bipyrroline Va nor any other significant products. These results indicate that the bipyrroline Va is derived from IIIa and has a structure as shown above. In addition, the pyrrolinone IIIa also gave the corresponding bipyrroline VII when reacted with di-*p*-tolylcarbodiimide (IIb) in the presence of Fe$(CO)_5$ (34% yield).



(Va, VII)

(Va: Ar = Phenyl;
VII: Ar = *p*-Tolyl)

The results of the reaction between I and IIa under varying conditions are summarized in Table 1. In the reaction using Fe$(CO)_5$ at 160°, the phenylethynylpyrrolinone IIIa was obtained in good yield (28%). The same reaction at higher temperatures (185 and 210°) resulted in lower yields of IIIa (15 and 4%, respectively). In contrast, the yield of bipyrroline Va was improved as the temperature increased (Expts. 1–4). These results suggest that the pyrrolinone IIIa, formed in the first step, reacts further with IIa and Fe$(CO)_5$ more readily at a higher temperature to afford the bipyrroline Va in good yield.

A similar reaction using $Fe_3(CO)_{12}$ instead of Fe$(CO)_5$ gave the pyrrolines IIIa and Va in 16 and 7% yield, respectively.

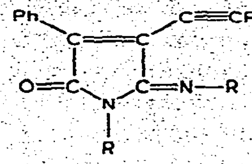
Although the pyrroline IVa could only be isolated in relatively low yields from reactions similar to those above using Fe$(CO)_5$ or $Fe_3(CO)_{12}$ (Expts. 1–5), the yield of IVa was increased to 10% when tetracarbonyl triphenylphosphine iron was employed. In this case, the pyrrolines IIIa and Va were also obtained in 12 and 3% yield, respectively. The same reaction using tricarbonyl bis(triphenylphosphine)iron gave a 29% yield of compound VIII instead of the above pyrrolines. Compound VIII was shown to be the 1/1 adduct of IIIa and IIa on the basis of its mass spectrum and elemental analysis, and could be obtained independently from the uncatalyzed reaction of IIIa with IIa at 185° (67% yield). The structure of this compound has yet to be determined.

When triphenylphosphine is added to a reaction mixture consisting of I, IIa

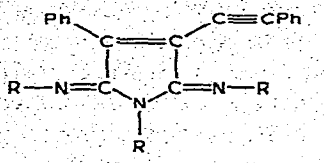
TABLE 2

CHARACTERIZATION OF PYROLINE DERIVATIVES

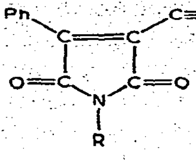
Phenylethynylpyrroline



(IIIa–IIId)



(IVa–IVc)



(IXa–IXd)

Compound		*R'*	*Recrystallisation solvent*[a]	*M.p. (°C)*
No.	*R*			
IIIa	Phenyl		A,B,C	170–171
IIIb	*p*-Tolyl		A,B,C	190–191
IIIc	*p*-Chlorophenyl		A,C	167–168
IIId	Cyclohexyl		D	147–148
IVa	Phenyl		A,C	237–238
IVb	*p*-Tolyl		A,B,C	184–185
IVc	*p*-Chlorophenyl		A,C	177–178
IXa	Phenyl		A,C	172–173
IXb	*p*-Tolyl		A,C	169–170
IXc	*p*-Chlorophenyl		A,C	203
IXd	Cyclohexyl		B	78
Va	Phenyl	Phenyl	A,C	231–232
Vb	*p*-Tolyl	*p*-Tolyl	A,C	241
Vc	*p*-Chlorophenyl	*p*-Chlorophenyl	A,C	274
VII	Phenyl	*p*-Tolyl	A,C	241–242
Xa	Phenyl	Phenyl	A,C	229–230
Xb	*p*-Tolyl	*p*-Tolyl	A,C	130
Xc	*p*-Chlorophenyl	*p*-Chlorophenyl	A,C	245–246
XI	Phenyl	*p*-Tolyl	A,C	159–162

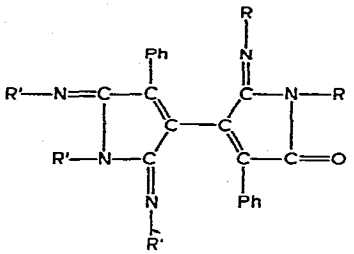
Formula	*Analyses*					
	Found (%)			*Calcd. (%)*		
	C	*H*	*N*	*C*	*H*	*N*
$C_{30}H_{20}ON_2$	84.93	4.68	6.54	84.88	4.75	6.60
$C_{32}H_{24}ON_2$	84.90	5.15	6.19	84.93	5.35	6.19
$C_{30}H_{18}ON_2Cl_2$	73.12	3.49	5.85	73.03	3.68	5.68
$C_{30}H_{32}ON_2$	82.66	7.34	6.25	82.53	7.39	6.42
$C_{36}H_{25}N_3$	86.65	5.38	8.22	86.54	5.04	8.41
$C_{39}H_{31}N_3$	86.36	5.62	8.06	86.47	5.77	7.76
$C_{36}H_{22}N_3Cl_3$	71.52	3.43	7.14	71.71	3.68	6.97
$C_{24}H_{15}O_2N$	82.68	4.37	4.07	82.50	4.33	4.01
$C_{25}H_{17}O_2N$	82.61	4.54	3.96	82.62	4.72	3.85
$C_{24}H_{14}O_2NCl$	75.26	3.48	3.74	75.10	3.68	3.65
$C_{24}H_{21}O_2N$	81.20	6.00	3.66	81.10	5.96	3.94

(*continued*)

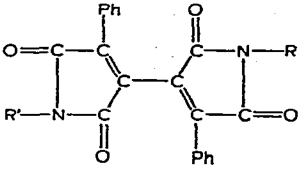
TABLE 2 (*contd.*)

Formula	*Analyses*					
	Found (%)			*Calcd. (%)*		
	C	*H*	*N*	*C*	*H*	*N*
$C_{50}H_{35}ON_5$	83.34	4.75	9.55	83.19	4.89	9.70
$C_{55}H_{45}ON_5$	83.48	5.45	8.73	83.41	5.73	8.84
$C_{50}H_{30}ON_5Cl_5$	67.41	3.31	7.87	67.17	3.38	7.83
$C_{53}H_{41}ON_5$	83.20	5.23	9.44	83.33	5.41	9.17
$C_{32}H_{20}O_4N_2$	77.29	3.98	5.78	77.40	4.06	5.64
$C_{34}H_{24}O_4N_2$	77.72	4.71	5.48	77.85	4.61	5.34
$C_{32}H_{18}O_4N_2Cl_2$	68.07	3.00	5.01	67.97	3.21	4.96
$C_{33}H_{22}O_4N_2$	77.90	4.43	5.36	77.63	4.34	5.49

Bipyrroline



(Va–Vc, VII)



(Xa–Xc, XI)

Colour	*IR*[b] *(Nujol)(cm*$^{-1}$*)*		
	C≡C	*C=O*	*C=N*
Orange needles	2220 m	1725 s	1660 s
Orange needles	2210 m	1730 s	1650 s
Orange needles	2220 m	1730 s	1660 s
Yellow crystals	2190 m	1710 s	1640 s
Red needles	2220 m		1660 m, 1635 s
Red needles	2210 m		1660 m, 1630 s
Orange needles	2220 m		1660 m, 1630 s
Yellow needles	2210 m	1770 m, 1710 s	
Yellow needles	2210 m	1770 m, 1715 s	
Yellow needles	2220 m	1765 m, 1715 s	
Yellow needles	2190 m	1765 m, 1700 s	
Orange needles		1730 s	1660 s, 1630 s
Orange needles		1725 s	1655 s, 1625 s
Orange needles		1730 s	1660 s, 1630 s
Orange needles		1725 s	1655 s, 1625 s
Yellow needles		1770 m, 1710 s	
Yellow needles		1770 m, 1710 s	
Yellow needles		1770 m, 1710 s	
Yellow needles		1770 m, 1710 s	

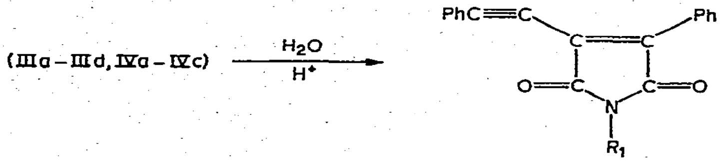
[a] A = benzene–hexane, B = EtOH, C = benzene–EtOH, D = hexane. [b] A rough indication of the absorption intensity is given by the symbols s, strong; m, medium.

and $Fe(CO)_5$ at 155° (using a $PPh_3/Fe(CO)_5$ molar ratio of 0.1/1), the pyrrolinone IIIa is the main product (50% yield), the yield of bipyrroline Va being poor (7%) (Expt. 8). The reason for this is not obvious and further studies are necessary to clarify this point.

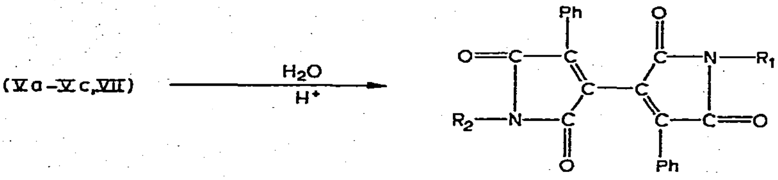
The reaction of I with di-*p*-tolyl or di-*p*-chlorophenyl carbodiimide (IIb or IIc) affords three types of pyrroline derivative (IIIb, IIIc, IVb, IVc, Vb and Vc, respectively) corresponding to those obtained with IIa, as shown in Table 1. In a similar reaction using dicyclohexylcarbodiimide (IId), the phenylethynylpyrrolinone IIId was obtained in 14% yield, but pyrrolines corresponding to IVa or Va were not observed (Table 1).

The acid hydrolysis of phenylethynylpyrrolines IIIa–IIId and IVa–IVc gave phenylethynylpyrroline-2,5-dione derivatives IXa–IXd quantitatively. The bipyrrolines Va–Vc and VII were similarly hydrolyzed to the corresponding bipyrroline-2,2′,5,5′-tetrones Xa–Xc and XI.

Data relating to the characterization of these various pyrrolines are given in Table 2.



(IXa – IXd)

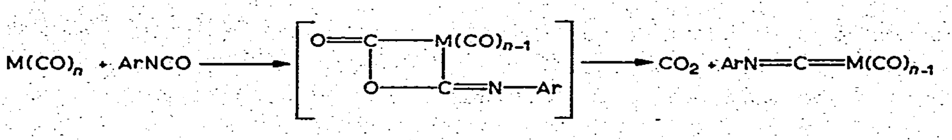


(Xa – Xc, XI)

(a: $R_1=R_2=$phenyl, b: $R_1=R_2=p$-tolyl, c: $R_1=R_2=p$-chlorophenyl, d: $R_1=$ cyclohexyl, XI: $R_1=$phenyl, $R_2=p$-tolyl)

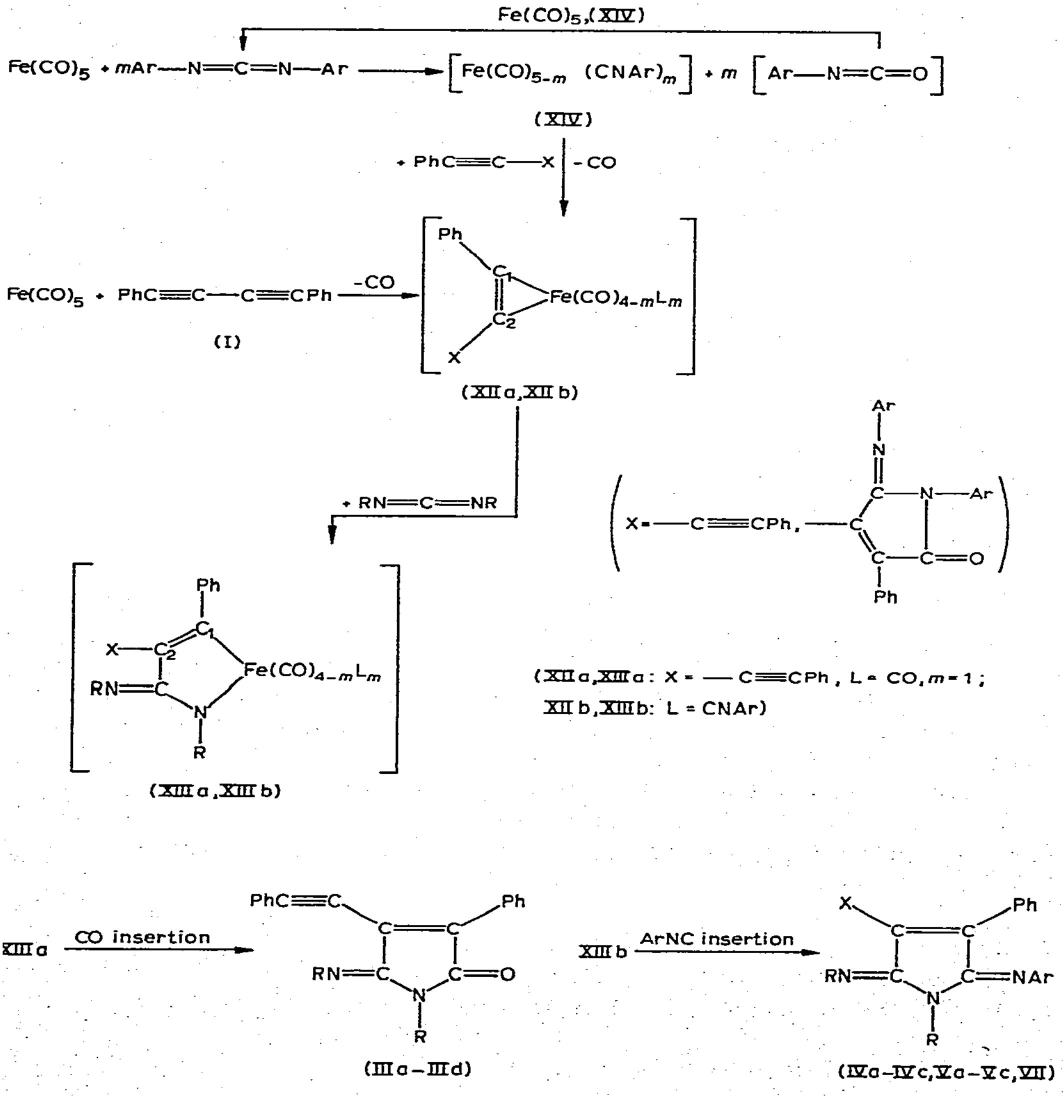
Mechanisms for the formation of pyrrolines IIIa–IIId, IVa-IVc, Va–Vc and VII

It is well known[5] that the reaction of acetylenic compounds (including diyne I which was used in this study[6]) with metal carbonyls affords a variety of stable organometal carbonyls and cyclic organic products, and it is generally considered[5] that the first step in the reaction is the substitution of carbon monoxide ligands by one mole of acetylene. In this case, it is assumed that the "doubly σ-bonded" iron complex[3,4] XIIa, initially formed in the substitution reaction of I with $Fe(CO)_5$, plays an important role in the formation of the various carbonylation products, *i.e.* phenylethynylpyrrolinones IIIa–IIId, the most probable reaction path being that depicted in Scheme 1. Insertion of the carbodiimides (IIa–IId) into the C_2–Fe bond of complex XIIa gave complex XIIIa, which was converted to the pyrrolinones (IIIa–IIId) by CO insertion followed by ring closure.

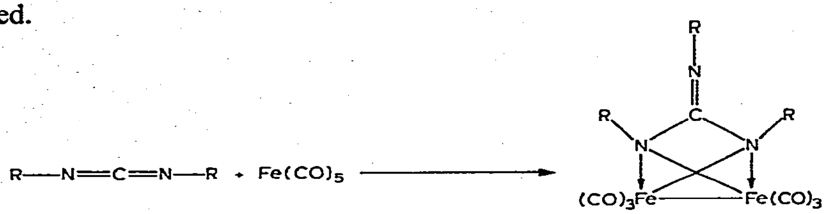


On the other hand, it has been reported[7] that the reaction of aryl isocyanates with various metal carbonyls gives CO_2 and isocyanide metal carbonyl complexes (albeit in poor yield). It is therefore possible that the reaction of diaryl carbodiimides with $Fe(CO)_5$ follows the same route, yielding aryl isocyanates (which are subsequently

SCHEME 1



reconverted to the carbodiimides by catalysis with $Fe(CO)_5$[7]) and aryl isocyanide derivatives of iron carbonyl, *i.e.* $Fe(CO)_{5-m}(CNAr)_m$, XIV. On the basis of this scheme, it may be suggested that the isocyanide ligand rather than CO is incorporated into the products to give the bis(arylimino)pyrroline ring compounds IVa–IVc, Va–Vc and VII. To test this suggestion, reaction of diacetylene I* or pyrrolinone IIIa with carbodiimide IIa in the presence of the isocyanide complex $Fe(CO)_4(CN{-}Ph)$ has been studied when the expected products, phenylethynylpyrroline IVa and bipyrroline Va, were obtained in good yield, *i.e.* 20 and 35%, respectively (Table 1). Hence, the pyrrolines mentioned above are apparently produced by an isocyanide insertion pathway similar to that shown in Scheme 1 and involving the formation of the intermediate complexes XIIb and XIIIb from the isocyanide complexes XIV as depicted.



(R = isopropyl, cyclohexyl)

(XV)

In addition, it has been reported[8] that dialkyl carbodiimide reacts with $Fe(CO)_5$ to give the guanidino-diiron carbonyl complex XV. In the reaction of diphenylcarbodiimide (IIa) with $Fe(CO)_5$ studied in this work, complexes of type XV were not isolated although the isocyanide complex $Fe(CO)_4(CNPh)$ was obtained in poor yield (see experimental section).

The reaction of phenylisocyanate[3] or diphenylketene[4] with diacetylene I has been attempted in the presence of $Fe(CO)_5$, but the expected carbonylation products or any well-defined adducts were not obtained.

EXPERIMENTAL SECTION

All melting points were determined on a Yanagimoto micro melting point apparatus and are reported uncorrected.

Infrared spectra were measured using a JASCO IR-E spectrometer. Proton magnetic resonance spectra were measured using a JEOL LNM-3H-60 spectrometer with $CDCl_3$ as the solvent and using TMS as the internal standard. Mass spectra were measured using a Hitachi RMU-6E spectrometer.

All reactions were carried out under a nitrogen atmosphere using a 50 ml four-necked flask equipped with a mechanical stirrer, reflux condenser, dropping funnel and nitrogen inlet. Chromatographic separations were carried out using activated neutral alumina columns.

Materials

$Fe(CO)_5$ and dicyclohexylcarbodiimide were purchased from a commercial source. Diphenylbutadiyne[9], diaryl carbodiimides[7], $Fe_3(CO)_{12}$[10], $Fe(CO)_4PPh_3$[11],

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* In this reaction, IIIa or Va was not isolated.

$Fe(CO)_3(PPh_3)_2$[11] and $Fe(CO)_4(CNPh)$[12] were prepared according to previously outlined procedures. Mesitylene and toluene were dried by refluxing over sodium and fractionated.

Reactions of diphenylbutadiyne (I) with diphenylcarbodiimide (IIa)

A mixture of I (0.04 mole), IIa (0.08 mole) and $Fe(CO)_5$ (0.08 mole) was stirred at 160° for 4.5 h. After removal of the remaining carbon monoxide under reduced pressure, the reaction mixture was extracted with 200 ml of benzene, concentrated *in vacuo* and the residue chromatographed. The first fraction (1/1 hexane–benzene eluent) was concentrated *in vacuo* and recrystallized from benzene–hexane to afford 0.2 g of IVa: mass spectrum (70 eV) *m/e* 499 (M^+), 422, 407, 396, 305, 202. The filtrate was concentrated and the residue was recrystallized (ethanol–hexane) giving trace amounts of an orange-coloured crystalline diacetylene iron carbonyl complex having the formula $Fe_2(CO)_6(PhC_4Ph)_2$. This complex had m.p. and IR in agreement with the literature value[6]: m.p. 181–183° (dec.); IR (Nujol) 2225, 2190 (C≡C), 2075, 2050, 2000 and 1950 cm^{-1} (C≡O). The second fraction (1/3 hexane–benzene eluent) upon concentration and recrystallization from benzene–hexane gave 4.7 g of IIIa: mass spectrum (70 eV) *m/e* 424 (M^+), 396, 347, 305, 230, 202. The third fraction (benzene and ether eluent) upon concentration and recrystallization from benzene–hexane afforded 4.4 g of Va: mass spectrum (70 eV) *m/e* 721 (M^+), 602, 527, 499, 424, 408, 396, 202. The fourth fraction (ethanol eluent) was concentrated and recrystallized from ethanol to give 5.9 g of *N,N'*-diphenylurea (35% yield): a mixed melting point with an authentic sample showed no depression[13].

Reactions involving I, IIa and iron carbonyls using different experimental conditions, as shown in Table 1, were carried out in a similar manner (*vide supra*).

Reactions using di-*p*-tolyl-, di-*p*-chlorophenyl- and dicyclohexyl-carbodiimide were also undertaken as described above. After similar treatment, the following products were isolated by means of chromatographic separation and recrystallization (Table 1, 2): 1-*p*-tolyl-3-phenyl-4-phenylethynyl-5-*p*-tolyliminopyrrolin-2-one (IIIb); 1-*p*-tolyl-4-phenyl-3-phenylethynyl-2,5-bis(*p*-tolylimino)pyrroline (IVb), 1,1'-di-*p*-tolyl-3,3'-diphenyl-2',5,5'-tris(*p*-tolylimino)-4,4'-bipyrrolin-2-one (Vb), 1-*p*-chlorophenyl-3-phenyl-4-phenylethynyl-5-*p*-chlorophenyliminopyrrolin-2-one (IIIc), 1-*p*-chlorophenyl-4-phenyl-3-phenylethynyl-2,5-bis(*p*-chlorophenylimino)pyrroline (IVc), 1,1'-di-*p*-chlorophenyl-3,3'-diphenyl-2',5,5'-tris(*p*-chlorophenylimino)-4,4'-bipyrrolin-2-one (Vc), 1-cyclohexyl-3-phenyl-4-phenylethynyl-5-cyclohexyliminopyrrolin-2-one (IIId).

Reactions of phenylethynylpyrrolinone IIIa with diphenylcarbodiimide (IIa) in the presence of iron carbonyls

A mixture of IIIa (0.001 mole), IIa (0.002 mole) and $Fe(CO)_4(CNPh)$ (0.0015 mole) in 2 ml of mesitylene was magnetically stirred at 185° for 2 h. After removal of the solvent, the reaction mixture was dissolved in 10 ml of benzene and the solution was chromatographed. The fraction (benzene eluent) upon concentration and recrystallization from benzene–hexane gave 0.25 g of Va (35% yield). Compound Va was also obtained in 29% yield (0.2 g) from the reaction between IIIa (0.001 mole), IIa (0.002 mole) and $Fe(CO)_5$ (0.001 mole) at 180° for 3.5 h.

The attempted reaction of IVa (0.001 mole) with IIa (0.002 mole) in the presence of Fe(CO)$_5$ (0.0015 mole) in 5 ml of mesitylene at 170° for 5 h gave no significant products.

1,3,3′-*Triphenyl*-1′-*p*-*tolyl*-2′,5′-*bis*(*p*-*tolylimino*)-5-*phenylimino*-4,4′-*bipyrrolin*-2-*one* (*VII*)

A mixture of IIIa (0.002 mole), di-*p*-tolylcarbodiimide (0.004 mole) and Fe(CO)$_5$ (0.002 mole) in mesitylene (6 ml) was magnetically stirred at 164° for 6 h. After similar treatment as above, 0.5 g of VII was isolated by chromatographic separation (34% yield): mass spectrum (70 eV) *m*/*e* 763 (M$^+$).

5-*Anilino*-1,3-*diphenyl*-4-*phenethylpyrrolidin*-2-*one* (*VI*)

The hydrogenation of IIIa (0.6 g) in 300 ml of absolute ethanol over 5% of palladium on carbon (10 g) at 6 atm hydrogen pressure was undertaken at room temperature over a period of 24 h. After filtering off the catalyst, the solution was evaporated and the residue recrystallized from benzene–hexane to afford 0.15 g of VI (25% yield): white needles, m.p. 176–177°; IR (Nujol) 3320 (N–H), 1690 cm^{-1} (C=O); mass spectrum (70 eV) *m*/*e* 432 (M$^+$), 340, 326, 248, 234, 220, 208, 206, 143, 129, 117, 115; NMR (CDCl$_3$) δ 1.50 (m, 2, PhCH$_2$CH$_2$CH), 2.48 (t, 2, *J* 7.5 Hz, PhCH$_2$–), 2.95 (m, 1, –CH$_2$CH$<$), 3.93 (d, 1, *J* 9.0 Hz, PhCHCO), 4.10 (broad, 1, N–H), 5.64 (broad d, 1, N$>$CH), 6.30–7.45 (m, 20, C$_6$H$_5$). Upon addition of D$_2$O, the broad peak at δ 4.10 disappeared and the broad doublet at 5.64 became a sharp doublet (*J* 6.0 Hz). Anal.: Found: C, 83.37; H, 6.27; N, 6.35%. C$_{30}$H$_{28}$ON$_2$ calcd.: C, 83.30; H, 6.53; N, 6.48%.

No other compound was isolated from the filtrate.

Acid hydrolysis of the pyrrolines IIIa–IIId, IVa–IVc, Va–Vc and *VII*

Either IIIa–IIId, IVa–IVc, Va–Vc, or VII (0.3–0.5 g) was dissolved in 30–50 ml of ethanol and 10 ml of concentrated hydrochloric acid added. After refluxing for 1–2 h on a steam bath, the reaction mixture was cooled, extracted (benzene and ether), dried (MgSO$_4$), concentrated and recrystallized (benzene–hexane) giving IXa–IXc (from IIIa–IIIc and IVa–IVc), IXd (from IIId), Xa–Xc (from Va–Vc), or XI (from VII). Hydrolyses were quantitative. The nomenclature of the products obtained is given below: 1,4-diphenyl-3-phenylethynylpyrroline-2,5-dione (IXa), 1-*p*-tolyl-4-phenyl-3-phenylethynylpyrroline-2,5-dione (IXb), 1-*p*-chlorophenyl-4-phenyl-3-phenylethynylpyrroline-2,5-dione (IXc), 1-cyclohexyl-4-phenyl-3-phenylethynylpyrroline-2,5-dione (IXd), 1,1′,4,4′-tetraphenyl-3,3′-bipyrroline-2,2′,5,5′-tetrone (Xa), 1,1′-di-*p*-tolyl-4,4′-diphenyl-3,3′-bipyrroline-2,2′5,5′-tetrone (Xb), 1,1′-di-*p*-chlorophenyl-4,4′-diphenyl-3,3′-bipyrroline-2,2′,5,5′-tetrone (Xc), 1-*p*-tolyl-1′,4,4′-triphenyl-3,3′-bipyrroline-2,2′,-5,5′-tetrone (XI).

The 1/1 *adduct between IIIa and IIa* (*VIII*)

A mixture of IIIa (0.4 g) and IIa (0.5 g) was magnetically stirred at 185° for 10 h. The mixture was cooled, dissolved in 10 ml of benzene and the solution chromatographed. The fraction (using a mixture of benzene and ether as eluent) upon concentration and recrystallization from benzene–hexane gave 0.4 g of VIII (67% yield) as orange needles, m.p. 284–286°; IR (Nujol) 1715 (C=O) and 1655 cm^{-1} (C=N); mass spectrum (70 eV) *m*/*e* 618 (M$^+$), 590 (M$-$CO), 541 (M$-$Ph), 499 (M$-$PhNCO), 424

(M−PhNCNPh), 396 (424−CO) or (499−PhNC), 321 (424−PhNC), 305 (424−PhNCO), 293 (321−CO), 216 (293−Ph), 202 (PhC_4Ph), 180 (PhC=NPh). Anal.: Found: C, 83.22; H, 4.91; N, 9.12%. $C_{43}H_{30}N_4O$ calcd.: C, 83.47; H, 4.89; N, 9.05%.

Reaction of diphenylcarbodiimide (IIa) with $Fe(CO)_5$

A mixture of IIa (0.02 mole) and $Fe(CO)_5$ (0.02 mole) was stirred at 160° for 5 h. After removal of the remaining $Fe(CO)_5$, the reaction mixture was extracted with 100 ml of benzene. The solid material (1.6 g) was removed by filtration. The IR spectrum of this solid showed a strong band at 1645 cm^{-1} but the structure was not investigated further.

The filtrate was concentrated *in vacuo* and the residue, whose IR spectrum showed strong bands at 2140 (due to carbodiimide IIa) and near 2000 cm^{-1}, was chromatographed. The first fraction (hexane eluent) upon concentration *in vacuo* and recrystallization from hexane afforded 0.1 g of $Fe(CO)_4(CNPh)$ as yellow crystals (2% yield). The complex had m.p. and IR in agreement with those of an authentic sample[12]. The second fraction (benzene eluent) upon concentration and recrystallization from benzene–hexane gave 0.4 g of the β-trimer of diphenylcarbodiimide as white crystals (10% yield): a mixed m.p. with an authentic sample showed no depression[14]. The third fraction (ethanol eluent) upon concentration and recrystallization from ethanol gave 1.3 g of *N,N'*-diphenylurea (31% yield).

A guanidino complex of type XV could not be prepared by a similar reaction.

When the reaction was undertaken at 190° for 2 h, similar results to those described above were obtained.

Reaction in refluxing heptane over a period of 24 h was also tried using the method described for dialkyl carbodiimide[8]. No complexes were isolated and IIa was subsequently recovered by distillation (77% yield).

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