OXIDATION BY METAL OXIDES—IX

OXIDATION OF BENZYLIDENEACETONE PHENYLHYDRAZONES WITH NICKEL PEROXIDE

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Abstract—Benzylideneacetone phenylhydrazone on oxidation with nickel peroxide gave a dl-mixture of 1,1', 5,5'tetraphenyl-3,3'-dimethyl-4,4'bipyrazoline, whereas, 2-methylbenzylideneacetone phenylhydrazone under similar conditions gave meso-1,1'-diphenyl-3,3'-dimethyl-5,5'-di-(o-tolyl)-4,4'-bipyrazoline. Similarly, meso-4,4'bipyrazolines were formed in the oxidation of 2-chloro- and 4-methylbenzylideneacetone phenylhydrazones and furfurylideneacetone phenylhydrazone. A mixture of both dl- and meso-forms of 4,4'-bipyrazolines, however, was obtained in the oxidation of 3-chloro-, 4-chloro- and 3-methylbenzylideneacetone phenylhydrazones and piperonylideneacetone phenylhydrazone. The structures of both the dl- and meso-forms of 4,4'-bipyrazolines have been established on the basis of analytical data and spectral evidences. Mass spectral fragmentation of some of these pyrazolines have also been examined.

In earlier communications we have reported the oxidation of several organic substrates such as aldehyde and ketone phenylhydrazones, chalcone phenylhydrazones and pyrazolines with different non-stoichiometric oxides such as manganese dioxide,¹⁻³ and nickel peroxide.^{4.5} Benzophenone phenylhydrazone, for example, on oxidation with manganese dioxide gave a mixture of benzophenone and biphenyl. Under similar conditions, aldehyde phenylhydrazones gave a mixture of several oxidative dimers, triazoles and biphenyl.1 Chalcone phenylhydrazones give rise to pyrazoles when oxidized with manganese dioxide in benzene.² Under similar conditions, pyrazolines give excellent yields of pyrazoles.² The object of the present investigation was to study the oxidation of a few benzylideneacetone phenylhydrazones using nickel peroxide, with a view to examining the nature of the products formed in these reactions.

Treatment of benzylideneacetone phenylhydrazone (1a) with nickel peroxide in benzene solution at room temperature gave a product melting at 310° and identified as an oxidative dimer of 1a, which analysed for C₃₂H₃₀N₄ (Mol. wt., 470 mass spectrometry). Of the four different possible structures 6a, 7, 8 and 9 for the oxidative dimers of 1a, we have assigned structure 6a, representing the dl-form of 1,1',5,5' - tetraphenyl - 3,3' - dimethyl - 4,4' bipyrazoline for our compound on the basis of spectral evidences. The UV spectrum of 6a showed an absorption max at 289 nm with a high extinction coefficient (ϵ , 39,500), which is nearly twice the extinction coefficient for an analogous pyrazoline derivative such as 1,5-diphenyl-3-methyl- Δ^2 -pyrazoline.^{5,6} The IR spectrum of **6a** is also in agreement with that of 1,3,5-trisubstituted pyrazolines.^{7,8} In addition, the oxidative dimer 6a gave a deep violet colouration, on treatment with a mixture of sodium nitrite and sulfuric acid, a test which is characteristic of 1-arylpyrazolines (Knorr pyrazoline test).⁹

It would be expected that the NMR spectral features of **6a** to be quite different from those of the other two oxidative dimers 8 and 9, but similar to that of the

structure 7 (Scheme 1). Although the product that we obtained in the oxidation of 1a was quite insoluble in most of the common organic solvents, its NMR spectrum in trifluoroacetic acid clearly showed chemical shifts at 1.9δ (6H), 4.098 (2H), 5.248 (2H) and 7.288 (20H). Of these the signal at 1.98 was assigned to the two Me protons, whereas the broad, poorly resolved multiplets at 4.09δ and 5.24δ were assigned to the tertiary protons at 4,4'-positions (A, B) and 5,5'-positions (X, Y), respectively. In the NMR spectrum of an analogous oxidative dimer from 3-methylbenzylideneacetone phenylhydrazone (1c; Fig. 1), however, the tertiary proton signals for A and B appeared as two distinct doublets centred around 2.89δ (1H, J = 2.6 Hz, A or B) and 2.91δ (1H, J = 2.6 Hz, A or B). Similarly, the tertiary protons, X and Y also showed two distinct doublets centred around 5.068 (1H, J = 2.6 Hz, X or Y) and 5.08δ (1H, J = 2.6 Hz, X or Y). In addition, the spectrum of 6c showed a singlet at 2.16 δ (6H) due to the Me protons at 3- and 3'-positions, another singlet at 2.27δ (6H) due to the *m*-methyl protons and multiplet at 6.7δ (18H), corresponding to the aromatic protons.

The NMR spectral features of the oxidative dimer are not in agreement with the N-N coupling product 9. Molecular models of 9 show free rotation across the N-N bond and hence the tertiary protons at C_{3-} and C_{3-} positions should be magnetically equivalent. Similarly, the vinylic protons at C₄- and C₄-positions should also be equivalent and hence the spectrum of 9 should show two sets of doublets, one for the tertiary protons and the other for the vinylic protons, resembling an A_2X_2 pattern. It might be mentioned in this connection that the NMR spectrum of a compound such as 1,2,3-trimethyl-5-phenyl- Δ^3 -pyrazoline, (10) which is structurally similar to the pyrazoline fragments in 9, shows a quartat for the C₃-Me group. The vinylic proton and the tertiary proton at C_3 -position appear as multiplets.¹⁰ The appearance of the vinvlic proton at C4- and the tertiary proton at C5- as multiplets, is attributed to the CH₃ protons at C₃-position. If structure 9 were to represent the oxidative dimer, one would expect a spectrum similar to that of 1,2,3-trimethyl-

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Fig. 1. NMR spectrum (100 MHz) of dl-1,1'-diphenyl-3,3'-dimethyl-5,5'-di-(m-tolyl)-4,4'-hipyrozoline (6c).



5-phenyl- Δ^3 -pyrazoline. On similar grounds, we would expect the NMR spectrum of 8 to be quite different from the experimentally observed spectrum. The structure of the oxidative dimer, therefore, has to be represented by either 6c or 7c.

The NMR spectra of pyrazolines have been examined by several workers and it has been shown that the trans-coupling constant in 4,5-disubstituted pyrazolines can vary anywhere between 1.5-9 Hz.11-13 Also, it has been observed that J_{trans} decreases with increasing polarity of the substituent at 4-position. Since the coupling constant for the two tertiary, protons A and X is of the order of 2.6 Hz, these should be trans with respect to each other. With a view to deciding between the structures 6c or 7c for the oxidative dimer of 1c, we have examined the molecular models and found that there is hindrance to free rotation in these molecules due to the Me groups at both 3- and 3'-positions. Further, it was observed that the most favourable conformation for 6c is one in which the two protons A and B are trans to each other with a dihedral angle ranging between 80-100°. The appearance of four distinct doublets for the tertiary protons (A and B) as well as for (X and Y) can be rationalized in terms of the magnetic non-equivalence of A and B, resulting in the coupling of A with X and B with Y, respectively and vice-versa $(J_{AX} = J_{BY} = 2.6 \text{ Hz})$. The absence of any appreciable coupling between the two protons A and B may be due to the fact that the dihedral angle between them is around 90°. In the case of 7c, the hindrance to free rotation across the C_{e} - C_{e} bond is not appreciable and hence both groups of protons A and B as well as X and Y become magnetically equivalent. Accordingly, one would expect two sets of doublets in the NMR spectrum, similar to an A_2X_2 pattern. Thus, on the basis of NMR spectral evidences, we would rule out structure 7c and favour 6c for the oxidative dimer of 1c. Additional support for the structure 6c was derived from a theoretical analysis of the spectrum as an ABXY pattern using LAOCOON III computer program.¹⁴ The theoretically calculated spectrum was in good agreement with the observed spectrum, when the following values of the chemical shifts and coupling constants were used.

$$\delta_A = 2.89, \quad \delta_B = 2.91, \quad \delta_X = 5.06 \quad \text{and} \quad \delta_Y = 5.08$$

$$I_{AB} = J_{AY} = J_{BX} = 0.0 \text{ Hz} \text{ and } J_{AX} = J_{BY} = 2.60 \text{ Hz}.$$

The fact that the vicinal coupling constant, J_{AB} is too small to observe suggests that the dihedral angle H_A -C-C-H_B is close to 90°. Analogously, structure **6a** would represent the oxidation product from **1a**.

Although some examples of 4,5'-bi- Δ^2 -pyrazolines¹⁵ and 3,3'-bipyrazolines¹⁶ have been reported in the literature, no account of 4,4'-bipyrazoline, however, could be found. With a view to confirming the structure of **6a** for the oxidative dimer, we have tried to oxidize this compound further to the corresponding bipyrazole. However, our attempts at oxidizing this compound using reagents like nickel peroxide, sulphur, neutral potassium permanganate and chloranil were unsuccessful. The reason for this inertness of **6a** is not very clear. It may be that the two Me groups at 3- and 3'-positions are shielding the two protons at **4**- and 4'-positions from being attacked by these oxidizing agents.

A probable route to the formation of **6a** in the oxidation of **1a** is shown in Scheme 1. In this scheme, we assume that nickel peroxide abstracts an H atom from benzylideneacetone phenylhydrazone 1 giving rise to a radical intermediate 2. This intermediate 2 can then cyclise to give the pseudo-allylic radical 3 or 4. Further loss of an H atom from either 3 or 4 would lead to the pyrazole derivative 5. Interestingly, this mode of reaction was not observed under our reaction conditions. On the other hand, the dimerization of the radical species 3 through a C-C coupling will result in the formation of both the dl- and meso-forms of 4,4'-bipyrazoline (6 and 7), respectively. If, however, an N-N coupling occurs, then the 2,2'-bipyrazoline derivative 8, would be expected; a C-N coupling on the other hand, would lead to the formation of the bipyrazoline 9 (Scheme 1). In the oxidation of benzylideneacetone phenylhydrazone (1a), we could isolate only the C-C coupling product 6a.

With a view to testing the generality of the oxidation of benzylideneacetone phenylhydrazones for the preparation of bipyrazoline derivatives, we have examined the oxidation of a few representative benzylideneacetone phenvlhvdrazones. of Thus, on treatment 2methylbenzylideneacetone phenylhydrazone (1b) with nickel peroxide gave a 30% yield of a product, identified as meso - 1,1' - diphenyl - 3,3' - dimethyl - 5,5' - di - (o tolyl) - 4,4' - bipyrazoline 7b. The structure of 7b was confirmed on the basis of analytical results and spectral data. The UV spectrum of 7b showed an absorption max at 289 nm with a high extinction coefficient (ϵ , 39,500), characteristic of bipyrazolines. Conclusive evidence for the structure of 7b, however, was derived from its NMR spectrum. The NMR spectrum of 7b showed two sharp singlet at 2.1δ (6H) and 2.26δ (6H) due to the Me groups at the 3-position of the pyrazoline nucleus and the o-Me protons, respectively. In addition, the spectrum showed two sharp doublets at 2.458 (2H, J = 1 Hz) and 5.578 (2H, J = 1 Hz) due to the tertiary protons at 4- and 4'-positions and the benzylic protons, respectively, resembling an A_2X_2 pattern. The aromatic protons appeared as a multiplet centred around 7.07 δ (18H). It was observed from the molecular model of 7b, that there is no free rotation around the $C_{-}C_{4}$, bond and that the most favourable conformation for 7b is one in which the two tertiary protons are trans to each other. Since the molecule is symmetric, the two tertiary protons may become magnetically equivalent. Similarly, the two groups of benzylic protons would also be magnetically equivalent. The small coupling constant between the tertiary proton and the benzylic protons is attributed to the substituents at C_4 - and C_4 -positions. A probable route to the formation of **7b** is shown in Scheme 1.

The oxidation of 2-methylbenzylideneacetone phenylhydrazone (1b) with nickel peroxide gave a 30% yield of meso - 1,1' - diphenyl - 3,3' - dimethyl - 5,5' - di -(o - tolyl) - 4,4' - bipyrazoline (7b), whereas 3methylbenzyldineacetone phenylhydrazone (1c) gave a mixture of both meso - 1,1' - diphenyl - 3,3' - dimethyl -5,5' - di - (m - tolyl) - 4,4' - bipyrazoline (7c, 20%) and dl -1,1' - diphenyl - 3,3' - dimethyl - 5,5' - di - (m - tolyl) - 4,4' bipyrazoline (6c, 8%). Similarly, mixtures of both mesoand dl-forms of 4,4'-bipyrazolines were formed from 3-chlorobenzylideneacetone phenylhydrazone (1f), 4chlorobenzylideneacetone phenylhydrazone (1g), and piperonylideneacetone phenylhydrazone (1i). On the other hand, 4-methylbenzylideneacetone phenylhyd-razone (1d), 2-chlorobenzylideneacetone phenylhydrazone (1e) and furfurylideneacetone phenylhydrazone (1h) gave exclusively the meso-forms of 4,4'-bipyrazoline.

IR spectra of 4,4'-bipyrazolines. In the course of the present investigation, we have examined the IR spectra of few 4,4'-bipyrazolines. The 4,4'-bipyrazolines that we have prepared (6 and 7) show several characteristic absorption bands in the region 4000-700 cm⁻¹ and Table 1 summarizes these data. It has been observed that the spectral features of 4.4'-bipyrazolines are guite similar to those of 1,3,5-trisubstituted Δ^2 -pyrazolines.^{6,7} The most interesting portion of the spectrum is in the range of 1400-1600 cm⁻¹, where one would expect absorption bands due to the C=N, as well as the usual C=C aromatic stretching vibrations. Thus, both the dl- and mesoisomers show a strong absorption band due to the C=N group around 1600 cm⁻¹; the phenyl skeletal vibrations are found between 1425-1450 cm⁻¹. In addition, absorption bands dut o C₆H₃-N and CH-N vibrations are observed around 1300 and 1120 cm⁻¹, respectively. Strong absorption bands due to C-H out-of-plane bending vibrations are also seen in the region, $700-800 \text{ cm}^{-1}$.

4,4'-Bipyrazoline	R	C=N	Skeletal vibrations of phenyl rings		C₅H <u>,</u> –N	CH-N	Substituted benzene C-H out- of-plane bending	
64	C.H.	1595(vs)	1495(vs)	1450(vs)	1320(m)	1140(s)	750(s)	
6c	m-CH ₃ C ₄ H ₄	1600(vs)	1495(vs)	1450(m)	1330(m)	1130(m)	785(s), 765(s)	
61	m-CIC.H.	1590(vs)	1485(vs)	1420(s)	1330(m)	1120(m)	780(s), 750(s), 700(s)	
6g	p-ClC ₆ H₄	1590(vs)	1480(s)	1425(s)	1330(m)	1120(m)	790(s), 735(s)	
61	$\langle \mathbf{x} \rangle$	1600(vs)	1 490 (vs)	1430(s)	1325(w)	1130(w)	815(s)	
7b	o-CH3CaH4	1590(vs)	1485(s)	1450(w)	1315(s)	1140(s)	750(s), 745(s)	
7c	m-CH ₁ C ₄ H ₄	1600(vs)	1495(s)	1430(w)	1300(m)	1135(s)	790(m), 765(s), 715(m)	
7d	p-CH.C.H.	1595(vs)	1495(s)		1320(m)	1140(s)	750(s), 720(s)	
7e	o-CIC.H.	1585(vs)	1490(s)	1425(w)	1325(m)	1150(s)	760(s), 730(m)	
7f	m-CIC.H.	1585(vs)	1485(s)	1410(m)	1300(m)	1140(s)	785(s), 745(s), 715(s)	
7g	p-ClC₄H₄	1585(vs)	1480(s)	1425(m)	1305(m)	1140(s)	740(s), 720(m)	
7h	$\sqrt[]{o}$	1600(vs)	1 495 (s)	1430(w)	1305(m)	1135(m)	780(w), 770(w)	
71		1600(vs)	1500(s)	1 440 (m)	1340(m)	1150(s)	740(s)	

Table 1. IR spectral characteristic of 4,4'-bipyrazolines



Fig. 2. NMR spectrum (100 MHz) of dl-1,1'-diphenyl-3,3'-dimethyl-5,5'-di-(m-tolyl)-4,4'-hipyrozoline (6c) expanded.

NMR spectra of 4,4'-bipyrazolines. The NMR spectra of 4,4'-bipyrazolines are of interest. The proton positions in various dl-4,4'-bipyrazolines (6a, c, f, g, i), have been summarized in Table 2. The spectra of the dl-forms of 4,4'-bipyrazolines are characterized by the presence of a sharp singlet in the range of $1.8-2.3\delta$, due to the Me groups in the 3- and 3'-positions. The tertiary protons at 4and 4'-positions appear as two doublets in the region $2.9-3.0\delta$, as a result of the coupling of these protons with those of 5- and 5'-protons and with a coupling constant $(J_{4,5} = J_{4,5})$ ranging between 2.3 to 2.6 Hz. The small coupling constant is as a result of the conformational restrictions due to the presence of the substituents at positions 4- and 5- and similar observations have been made in the case of 1,3,4,5-tetra-substituted Δ^2 pyrazolines.¹¹⁻¹³ In trifluoroacetic acid, however, the position of this band has been shifted to the region between 4 and 4.18. The benzylic protons at 5- and 5'-positions of these 4,4'-bipyrazolines also show a pair of doublets in the region $4.9-5.4\delta$, with a coupling constant ranging from 2.3 to 2.6 Hz. The aromatic protons appear as multiplets around 7.05δ .

The NMR spectral details of a few meso-4,4'bipyrazolines are listed in Table 3. The Me protons at 3and 3'-positions appear as sharp singlets in the region $1.95 - 2.1\delta$. The tertiary protons at 4- and 4'-positions, as well as the benzylic protons at 5- and 5'-positions appear as two doublets, in the region $2 \cdot 5 - 3 \cdot 0\delta$ and $5 \cdot 4 - 5 \cdot 9\delta$, respectively, and with a coupling constant $(J_{4,5})$ in the range 1 to $1 \cdot 5$ Hz (A₂X₂ pattern). The aromatic protons appear as a multiplet around $7 \cdot 0\delta$.

Mass spectral fragmentation of 4,4'-bipyrazolines. In the present investigation, we have carried out some preliminary studies concerning the mass spectral fragmentation of a few 4,4'-bipyrazolines. It has been observed that the mass spectral fragmentation of both the meso- and the dl-forms of 4,4'-bipyrazolines are identical in almost all details except in the relative intensities of a few peaks. The mass spectrum of a representative 4,4'-bipyrazoline, namely, 6a showed the molecular ion peak at m/e 470. In addition, several peaks at m/e 379, 289, 274, 247, 235, 171, 156, 144, 128 and 115 were observed. A probable fragmentation mode for 6a is shown in Scheme 2. The peak at m/e 379 has been assigned to the ion 6a which may be formed by the loss of phenyl nitrene from the molecular ion. Such a loss of phenyl nitrene is well known in the photolytic and thermal decompositions, as well as under electron impact.¹⁷⁻¹⁹ The peaks at mass units 289, 274 and 247 have been assigned to the fragments 6ab, 6ac and 6ag, respectively, formed by the loss of neutral molecules like Schiff's bases and HCN or radicals like Me, and finally giving a stabilized ion as shown in Scheme 2. The peak at m/e 235 corresponds to half the molecular ion peak and is assigned to the

Table 2. NMR spectra of dl-4,4'-bipyrazolines

Compound	R	Me protons (in ppm)	Me attached to phenyl ring	A or B	A or B	X or Y	X or Y	J _{AX} (Hz)	J _{вү} (Hz)	Aromatic
6a	C,H,°	1.9(s)°	_	4.09; poorly	resolved	5.24; poorly	resolved		_	7·28(m)*
6c	m-CH ₃ C ₆ H ₄ °	2.16(s)	2.27	2.89(d)	2.91(d)°	5-06(d) ^c	5.08(d)°	2.6	2.6	6·7(m)°
6f	m-ClC ₆ H₄ ^b	2.3(s) ^c	_	2-96(d)*	3.05(d)*	5·29(d)°	5-38(d)°	2.5	2.5	7·17(m)°
6g	p-ClC ₆ H ₄ °	1·73(s)°	_	4·05(d)*	4·17(d)*	4·95(d)*	5·05(d)°	2.3	2.3	6·82(m)°
6i*		1.8(s)°		4.02; poorly	resolved	4·87; poorly	resolved	_	-	6·7(m); 7·0(m)

"In trifluoroacetic acid; "In deuterochloroform; 'Singlet; d doublet; m multiplet.

*The dixoymethylene protons in 6i appear as a singlet at 6.1 ppm (2H).



Table 3. NMR spectra of meso-4,4'-bipyrazolines

Compound	R	CH ₃ protons in ppm	CH ₃ attached to phenyl ring	A (ppm)	X (ppm)	J _{ax} (Hz)	Atomatic protons
7ъ	o-CH3CeH4	2·1(s)*	2·26(s)*	2·45(d) ^c	5·57(d)°	1.0	7·07(m) ^c
7c	m-CH₃C₅H₄°	2.0(s)°	2·27(s)*	2.5(d)°	5-42(d)°	1.0	7·03(m) ^c
7d	p-CH₃C₅H₄°	1∙95(s)°	2·3(d)*	2·5(d)°	5·4(d)°	1.5	7·0(m)°
7e	o-ClC ₆ H.ª	$2 \cdot 1(s)^c$	_	2.7(d)°	5-85(d)°	1.0	7·15(m) ^c
7f	m-ClC ₆ H₄ª	1.95(s)°	_	2.45(d) ^c	5·4(d)°	1.5	7·0(m)°
7g	p-ClC ₆ H ₄ °	1.95(s)°	_	2·4(d)*	5·4(d)°	1.5	7·0(m) ^c
7h	$\sqrt[]{o}$	1.95(s)°	-	2·92(d)*	5·52(d)°	1.0	6·02(m)°, 6·3(m),° 7·25(m)°
7i*		2·0(s)*	_	2·55(d)č	5•5(d)°	1.5	6·7(m) ^c

"In CDCl₃; "In CD₃COCD₃; Singlet. d Doublet; m Multiplet.

*The dioxymethylene protons in 7i appear as a singlet at 6.0 ppm (2H).

pyrazoline ion **6ae**. It is interesting to note that in the mass spectra of all 4,4'-bipyrazolines, we could observe this $M/2^+$ ion. The most significant peak is seen at m/e 171 which is the base peak and is assigned the structure **6ad**. This might be due to the pyridazine ion formed from **6ac** or **6ag** by rearrangement and/or loss of some groups. This is the characteristic peak of all 4,4'-bipyrazolines. Other peaks at 156 and 144 mass units would be due to fragments **6ai** and **6af**, respectively. Similarly, the peaks at mass units 206, 128 and 115 could be due to fragments formed from **6ag** or **6ah**.

EXPERIMENTAL

All m.ps are uncorrected and were determined in a Melt-Temp m.p. apparatus. IR spectra were recorded on a Perkin-Elmer 521 Spectrometer and UV spectra were recorded on a Beckmann-DB spectrophotometer. NMR traces were recorded on either a Varian A-60 or HR-100 spectrometer, using TMS as internal standard.

Starting materials. Nickel peroxide (65 g) was prepared by the treatment of nickel sulfate (130 g) with a mixture of 6% NaOCI, (300 ml) and NaOH (42 g), as reported.²⁰ The O₂ content of this sample was found to be of the order of 2.8×10^{-3} g atom per gram of nickel peroxide. Benzylideneacetone phenylhydrazone,²¹ m.p. 157°, 2-chlorobenzylideneacetone phenylhydrazone,²² m.p. 92-93°, 4-chlorobenzylideneacetone phenylhydrazone,²³ 160°, 2methylbenzylideneacetone phenylhydrazone,²⁴ m.p. 138°, 4-methylbenzylideneacetone phenylhydrazone,²⁴ m.p. 154°, furfurylideneacetone phenylhydrazone,25 131-32° m.p. and piperonylideneacetone phenylhydrazone,26 m.p. 163° were prepared from the corresponding benzylideneacetones and phenvlhvdrazine.

3-Methylbenzylideneacetone phenylhydrazone was prepared by refluxing a mixture of 3-methylbenzylideneacetone (1.6 g, 0.01 mol) and phenylhydrazine (1.08 g, 0.1 mol) in EtOH. Removal of the solvent gave a product which was recrystallized from EtOH to give 2.2 g (80%) of 3-methylbenzylideneacetone phenylhydrazone, m.p. 135° (Found: C, 81.68; H, 7.0; N, 11.6. C₁₇H₁₈N₂ requires: C, 81.6; H, 7.20; N, 11.2%). IR spectrum (KBr) ν_{max} :3300 (NH) and 1608 cm⁻¹ (C=N). UV spectrum (cyclohexane) λ_{max} : 218 nm (ϵ , 14,900), 256 (15,000) and 356 (28,700).

Compound II was prepared by stirring a mixture of 3chlorobenzylideneacetone (1.37 g, 7.5 mmol), phenylhydrazine (0.82 g, 7.5 mmol) and AcOH (1 ml) in EtOH (3 ml) for 15 min. The solid which separated out was recrystallized from EtOH to give 1.25 g (63%) of 1f, m.p. 125-26° (Found: C, 70.87; H, 5.63; N, 10.19. C₁₆H₁₅N₂Cl requires: C, 70.98; H, 5.55; N, 10.35%). IR spectrum (KBr) ν_{max} : 3300 (NH) and 1600 cm⁻¹ (C=N). UV spectrum (cyclohexane) λ_{max} : 220 nm (ϵ , 16,000), 254 (15,000) and 350 (30,000). Oxidation of benzylideneacetone phenylhydrazone with nickel peroxide

(A) In benzene at room temperature. A mixture of 1a (2g, 0.0084 mol) and nickel peroxide (4g) was stirred in benzene (200 ml) for 4 hr at room temp. Removal of the inorganic material and of the solvent gave a red viscous liquid which on treatment with EtOH gave 1.4g of a solid product. Recrystallization of this product from a mixture (1:1) of methylene chloride and ether gave 1.2g (70%) of d1-6a, m.p. 310° (Found: C, 81-68; H, 6.54; N, 12.02; Mol. wt., 470 (Mass spectrometry). $C_{32}H_{30}N_4$ requires: C, 81-70; H, 6-38; N, 11-91; Mol. wt., 470.) UV spectrum (dioxan) λ_{max} : 280 nm (ϵ , 35,000).

(B) In refluxing benzene. In a second run, benzylideneacetone phenylhydrazone (1 g, 0.0042 mol) and nickel peroxide (3 g) were refluxed in benzene for 4 hr. Work-up of the mixture as in the previous case gave 0.45 g (45%) of **6a**, m.p. 310° (m.m.p.).

Oxidation of 2-methylbenzylideneacetone phenylhyrazone

Treatment of a mixture of 2-methylbenzylideneacetone phenylhydrazone (1.5 g, 0.006 mol) and nickel peroxide (4.5 g) in benzene (150 ml) for 3 hr at room temp and work-up in the usual manner gave a viscous liquid which was chromatographed over alumina. Elution with light petroleum (b.p. 60-80°) gave 35 mg (4%) of biphenyl, m.p. 70° (m.m.p.).

Further elution of the column with a mixture (1:2) of light petroleum and benzene gave 0.55 (36%) of meso-7b, which melted at 257°, on recrystallization from a mixture (1:1) of benzene and EtOH (Found: C, 81.79; H, 7.28; N, 11.04; Mol. wt., 498 (Mass spectrometry). $C_{34}H_{34}N_{4}$ requires: C, 81.93; H, 6.83; N, 11.24% Mol. wt., 498). UV spectrum (CHCl₃) λ_{max} : 289 nm (ϵ , 39,500).

Oxidation of 3-methylbenzylideneacetone phenylhydrazone

A mixture of 3-methylbenzylideneacetone phenylhydrazone (1 g, 0-004 mol) and nickel peroxide (3.5 g) was stirred in benzene (125) for 3 hr at room temp. Work-up of the mixture as in the previous cases gave a red viscous liquid which was chromato-graphed over alumina. Elution of the column with light petroleum gave 35 mg (6%) of biphenyl, m.p. 70° (m.m.p.). Further elution of the column with light petroleum and benzene mixture (1:1) gave a product, which on recrystallization from a mixture (1:1) of benzene and alcohol gave 0.2 g (20%) of meso-7c, m.p. 189–90° (Found: C, 81-6; H, 6-7; N, 11-5; Mol. wt., 498 (Mass spectrometry). $C_{ss}H_{ss}N_s$ requires: C, 81-93; H, 6-83; N, 11-24%; Mol. wt., 498.) UV spectrum (cyclohexane) λ_{mas} : 220 nm (ϵ , 34,900) and 282 (43,100).

Further elution of the alumina column with a mixture (1:1) of benzene and light petroleum gave a product which was recrystallised from benzene-alcohol mixtures (2:1) to give 75 mg (8%) of dl-6c, m.p. 285-86°. (Found: C, 81.69; H, 6.82; N, 11.21; Mol. wt., 498 (Mass spectrometry). $C_{34}H_{34}N_4$ requires: C, 81-93; H, 6-83; N, 11-24%; Mol. wt., 498). UV spectrum (CHCl₃) λ_{max} : 294 nm (ϵ , 18,400).

Oxidation of 4-methylbenzylideneacetone phenylhydrazone

A mixture of 4-methylbenzylideneacetone phenylhydrazone (1.5 g, 0.006) and nickel peroxide (3.5 g) was stirred in benzene (150 ml) for 4 hr at room temp. Removal of the inorganic material and of the solvent gave a product which was recrystallized from a mixture (1:1) of benzene and EtOH to give 0.55 g (40%) of meso-7d, m.p. 249°. (Found: C, 82-19; H, 6.95; N, 11-23; Mol. wt., 498 (Mass spectrometry). C₃₄H₃₄N₄ requires: C, 81-9; H, 6.8; N, 11-2; Mol. wt., 498). UV spectrum (CHCl₃) λ_{max} : 284 nm (ϵ , 39,700).

Oxidation of 2-chlorobenzylideneacetone phenylhydrazone

2-Chlorobenzylideneacetone phenylhydrazone (1 g, 3.7 mmol) and nickel peroxide (3 g) were stirred in dry benzene (125 ml) for 4 hr at room temp. Work-up of the mixture in the usual manner gave a red viscous liquid which was chromatographed on alumina. Elution with light petroleum gave 35 mg (6%) of biphenyl, m.p. 70° (m.m.p.).

Further elution of the column with a mixture (4:1) of light petroleum and benzene gave a product which was recrystallized from a mixture (1:1) of benzene and EtOH to give 0.18 (18%) of meso-7c, m.p. 233-34° (Found: C, 70.85; H, 5.30; N, 10.16; Mol. wt., 538 (Mass spectrometry). $C_{32}H_{28}N_4Cl_2$ requires: C, 71.24; H, 5.19; N, 10.39; Mol. wt., 538). UV spectrum (cyclohexane) λ_{max} : 279 nm (ϵ , 31,400).

Oxidation of 3-chlorobenzylideneacetone phenylhydrazone

A mixture of 3-chlorobenzylideneacetone phenylhydrazone (1 g, 3-7 mmol) and nickel peroxide (3 g) was stirred in dry benzene (125 ml) for 4 hr at room temp. Work-up of the mixture gave a viscous liquid which on treatment with EtOH yielded a solid product. The ethanolic filtrate was worked up separately Recrystallization of the solid product from a mixture (1:1) of benzene and EtOH gave 75 mg (8%) of dl-6f, m.p. 246-47°. (Found: C, 71·11; H, 4·91; N, 10·19; Mol. wt., 538 (Mass spectrometry). C₃₄H₂₈N₄Cl₂ requires: C, 71·24; H, 5·19; N, 10·39; Mol. wt., 538). UV spectrum (CHCl₃) λ_{mas} : 292 nm (ϵ , 36,000).

The ethanolic filtrate after removal of the crude 6f, was chromatographed on alumina. Elution with light petroleum gave 30 mg (5%) of biphenyl, m.p. 70° (m.m.p.). Further elution of the column with a mixture (4:1) of benzene and light petroleum gave a product which on recrystallization from alcohol-benzene mixture (3:1) gave 0.25 g (25%) of meso-71, m.p. 235-36°. (Found: C, 71·32; H, 5·47; N, 10·47; Mol. wt., 538 (Mass spectrometry). C₃₂H₂₈N₄Cl₂ requires: C, 71·24; H, 5·19; N, 10·39; Mol. wt., 538). UV spectrum (cyclohexane) λ_{mex} : 280 nm (ϵ , 33,300).

Oxidation of 4-chlorobenzylideneacetone phenylhydrazone

Stirring a mixture of 4-chlorobenzylideneacetone phenylhydrazone (1.5 g, 5.5 mmol) and nickel peroxide (4.5 g) in benzene (150 ml) for 4 hr at room temp and work-up of the mixture as in the earlier cases gave a viscous liquid. Treatment of this liquid with EtOH gave a solid product and some EtOH-soluble material. The solid product on recrystallization from EtOAc gave 0.13 g (9%) of *dl*-6g, m.p. 174-75° (Found: C, 71.08; H, 5.50; N, 10.07; Mol. wt., 538 (Mass spectrometry). $C_{32}H_{28}N_aCl_2$ requires: C, 71.24; H, 5.19; N, 10.39%; Mol. wt., 538). UV spectrum (CH₂Cl₂) λ_{max} : 290 nm (e, 19,400).

The EtOH-soluble portion was chromatographed on alumina. Elution with light petroleum gave 30 mg (3%) of biphenyl, m.p. 70° (m.m.p.). Further elution of the column with a mixture (4:1) of benzene and light petroleum gave a product which was recrystallized from a mixture (1:1) of benzene and alcohol to give meso-7g, m.p. 248-49°. (Found: C, 70-98; H, 5:30; N, 10:22; Mol. wt., 538 (Mass spectrometry). $C_{32}H_{2a}N_{4}Cl_{2}$ requires: C, 71-22; H, 5:19; N, 10:39%; Mol. wt., 538). UV spectrum (cyclohexane) λ_{max} : 220 nm (ϵ , 44,900), 230 (sh) (28,800) and (44,200).

Oxidation of furfurylideneacetone phenylhydrazone

Furfurylideneacetone phenylhydrazone (1.5 g, 0.052 mmol) and nickel peroxide (4 g) were stirred in benzene (150 ml) at room temp for 45 min. Work-up of the mixture in the usual manner gave a viscous material which was chromatographed on alumina. Elution with light petroleum gave 40 mg (4%) of biphenyl, m.p. 70° (m.m.p.). Further elution of the column with a mixture (1:2) of light petroleum and benzene gave a product which was recrystallized from alcohol to give 90 mg (6%) of *meso-7h*, m.p. 207-208° (Found: C, 74·49; H, 5·90; N, 12·45; Mol. wt., 450 (Mass spectrometry). C₂₂H₂₆N₄O₂ requires: C, 74·66; H, 5·88; N, 12·44%, Mol. wt., 450). UV spectrum (cyclohexane) λ_{max} : 280 nm (ϵ , 42,500).

Oxidation of piperonylideneacetone phenylhydrazone

Piperonylideneacetone phenylhydrazone (1.5 g, 5.3 mmol) and nickel peroxide (4.5 g) were stirred in benzene (150 ml) at room temp for 5 hr. Work-up of the mixture gave a viscous liquid which was chromatographed on alumina. Elution with light petroleum gave 62 mg (7%) of biphenyl, m.p. 70° (m.m.p.). Further elution of the column with a mixture (1:1) of benzene and light petroleum gave a product which on recrystallization from a mixture (1:1) of benzene and alcohol gave 0.45 g (30%) of meso-71, m.p. 280-81° (Found: C, 73.43; H, 5.61; N, 10-00; Mol. wt., 558 (Mass spectrometry). C_{3.4}H₃₀N₄O₄ requires: C, 73.1; H, 5.4; N, 10-0%; Mol. wt., 558). UV spectrum (CHCl₃) λ_{mas} : 288 nm (e, 40,000).

Further elution of the column with benzene gave a product which on recrystallization from a mixture of EtOAc and EtOH gave 0.2 g (14%) of di-6i, m.p. 270-271° (Found: C, 73-43; H, 5-10; N, 9-93; Mol wt., 558 (Mass spectrometry). $C_{34}H_{30}N_4O_4$ requires: C, 73-1; H, 5-4; N, 10-0%; Mol. wt., 558). UV spectrum (CHCl₃) λ_{max} : 294 nm (ϵ , 28,100).

Attempted oxidation of 1,1',5,5'-tetraphenyl-3,3'-dimethyl-4,4'bipyrazoline

(A) With nickel peroxide. A mixture of 94 mg (0.2 mmol) of **6a** and 0.3 g of nickel peroxide was refluxed in benzene for 3 hr. Work-up of the mixture gave 85 mg (90%) of the unchanged **6a**, m.p. 310° (m.m.p.).

(B) With sulphur. A mixture of 94 mg (0.2 mmol) of **6a** and 0.15 g of S was heated gradually in a test tube to 200°, in an oil-bath. After 2 hr, the mixture was extracted with hot benzene. Removal of the solvent and recrystallization from benzene-alcohol mixture gave 70 mg (75%) of the unchanged **6a**, m.p. 310° (m.m.p.).

(C) With chloranil. A mixture of 94 mg (0.2 mmol) of **6a** with 100 mg of chloranil was refluxed in dry xylene (50 ml) for 10 hr. After removal of the insoluble material, the xylene-soluble portion was washed with a 4% KOH aq and dried over Na₂SO₄. Removal of the solvent under vacuum gave 80 mg (85%) of unchanged starting material, m.p. 310° (m.m.p.), after recrystallization.

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REFERENCES

- ¹I. Bhatnagar and M. V. George, J. Org. Chem. 32, 2252 (1967).
- ²I. Bhatnagar and M. V. George, Tetrahedron 24, 1293 (1968).
- ³I. Bhatnagar and M. V. George, J. Org. Chem. 33, 2407 (1968).
- ⁴K. S. Balachandran, I. Bhatnagar and M. V. George, *Ibid.* 33, 3891 (1968).
- ⁵K. S. Balachandran and M. V. George, *Tetrahedron* 29, 2119 (1973).
- ⁶G. F. Duffon and J. D. Kendall, J. Chem. Soc. 408 (1954).
- ⁷R. H. Wiley, C. H. Jarboe, F. N. Hayes, E. Hansbury, J. T. Nelson, P. X. Callahan and M. C. Sellers, J. Org. Chem. 23, 732 (1958).
- ⁸Por some of the references pertaining to the IR spectral data of pyrazolines, see, ^aJ. A. Moore, J. Org. Chem. 20, 1607 (1955); ^aJ. A. Moore and R. W. Medeiros, J. Am. Chem. Soc. 81, 6026 (1959); ^cG. B. Mueller and B. Riegel, *Ibid.*, 76, 3686 (1954); ^dH. L. Slates and N. L. Wendler, *Ibid.* 81, 5472 (1959); ^aR. Wiechert and E. Kasper, Chem. Ber. 93, 1710 (1960).
- ⁶L. Knorr, Ber. Dtsch. Chem. Ges 26, 100 (1893).

- ¹⁰J. L. Aubagnac, J. Elguero, R. Jacquier and D. Tizane, *Tetrahedran Letters* 3705 (1967).
- ¹¹A. Hassner and M. J. Michelson, J. Org. Chem. 27, 3974 (1962).
- ¹²R. Huisgen, H. Knupfer, R. Sustmann, G. Wallibilich and R. Webendorfer, *Chem. Ber.* 100, 1580 (1967).
- ¹³R. Sustman, R. Huisgen and H. Huber, Ibid. 100, 1802 (1967).
- ¹⁴A. A. Bothner-by, C. Naar-Colin and H. Günther, J. Am. Chem. Soc. 84, 2748 (1962).
- ¹⁵E. F. Baroni and K. A. Kovyrzoici, *Zh. Obsheh. Khim.* 33, 95 (1963); *Chem. Abstr.* 57, 7513 (1964).
- ¹⁶H. R. Snyder, F. Verblanc and D. B. Bright, J. Am. Chem. Soc. 74, 3243 (1952).
- ¹⁷J. S. Splitter and M. Calvin, Tetrahedron Letters 1445 (1968).

- ¹⁶F. P. Lossing, Ann. N. Y. Acad. Sci. 67, 499 (1957).
- ¹⁹K. G. Das, P. S. Kulkarni, V. Kalyanaraman and M. V. George, J. Org. Chem. 35, 2140 (1970).
- ²⁰K. Nakagawa, R. Konaka and T. Nakata, *Ibid.* 27, 1597 (1962).
- ²¹L. Knorr, Ber. Dtsch. Chem. Ges 20, 1099 (1887).
- ²²K. von Anwers and A. Kreuder, *Ibid.* 58, 1984 (1925).
- ²³R. Von Walther and W. Raetze, J. Prakt. Chem. 2, 65, 279 (1902); Brit. Chem. Abstr. 82, 467 (1902).
- ²⁴L. Gattermann, Liebigs Ann. 347, 362 (1906).
- ²³K. von Anwers and H. Voss, Ber. Dtsch. Chem. Ges. 42, 4416 (1909).
- ²⁶F. Haber, *Ibid.* 24, 620 (1891).