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COPPER(II) IN ORGANIC SYNTHESIS. VI[1] REACTION OF THE COPPER(II) ACETATE COMPLEX OF 1-METHYLISATIN-3-CHLOROPHENYLHYDRAZONE WITH DIMETHYL ACETYLENEDICARBOXYLATE.(°)

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Abstract - The copper(II) complex of 1-methylisatin-3-p-chlorophenyl hydrazone (**2**) reacted with dimethyl acetylenedicarboxylate (DMAD) in accordance to two reaction pathways. Oxidation performed by Cu^{++} gave 1-methyl-3-carbenindolin-2-one (**12**), trapped by DMAD to give products **3-5**, and p-chlorophenylradical (**13**), trapped either by DMAD to give **6**, or by the free ligand **1** to give **7** or by carbenindolinone and DMAD to give **8**. The second pathway involved a [2+2] cycloaddition followed by electrocyclic ring opening and intramolecular cyclization to give 1-methyl-2-indolinone-3-spiro -5'-1'-p-chlorophenyl-3',4'-dimethoxycarbonyl-2'-pyrazoline (**9**) whose structure and configuration were demonstrated by an independent synthesis. The mechanism of the reaction is discussed.

Previous papers of this series have shown that copper(II) complexes of several organic ligands undergo a reaction with dimethyl acetylenedicarboxylate (DMAD) and two main reaction pathways are followed:

a) a Michael reaction;[2,3]

b) an oxidation of the ligand to a ketocarbene which reacted in accordance to a 1,3-dipolar cycloaddition.[4,5]

In the case of isatin-3-phenylhydrazone,[5] besides the oxidation, a [2+2] cycloaddition occurred, followed by electrocyclic ring opening and intramolecular cyclization, which gave a pyridazino [3,4-b] indole (Scheme 1). To give rise to this product, the ligand must have, in position 1, an hydrogen atom or a good leaving group.

To isolate possible intermediates we investigated ligands where the last step of the process was not permitted.

Thus we studied the reaction of the copper(II) complex of 1-methylisatin-3-p-chlorophenyl-hydrazone with DMAD. This copper(II) complex (**2**) was isolated from an ethanolic solution of the free ligand (**1**) in the presence of cupric acetate hydrate and the bright black needles analyzed for two moles of ligand *vs.* one mole of Cu. These analytical data, the absence of the typical green

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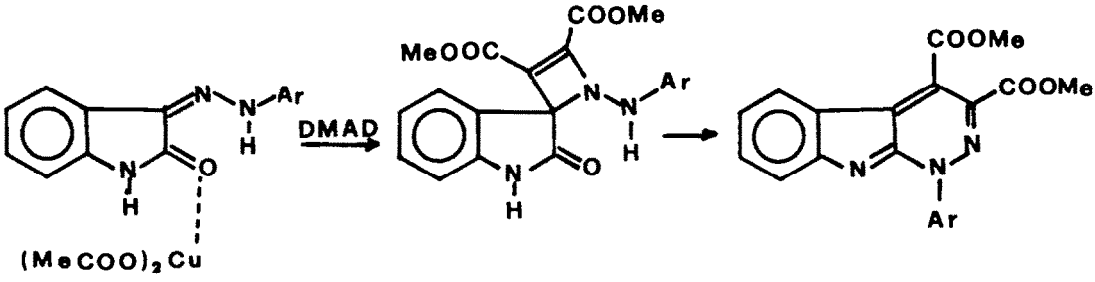
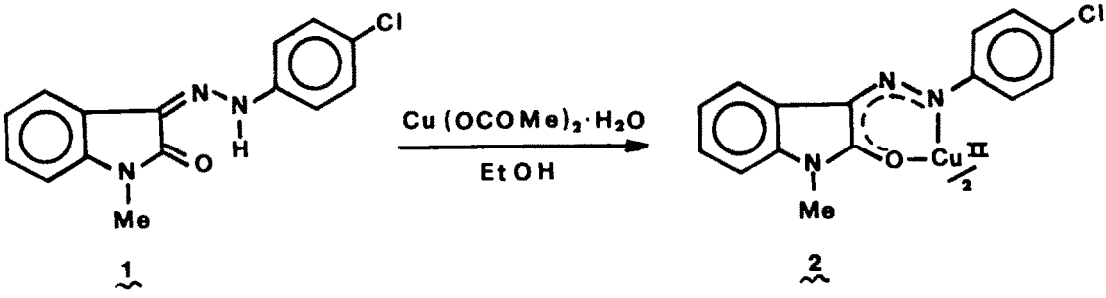
Scheme 1



colour,[1,6] and the IR spectral data (no NH, absence of the ligand carbonyl band at 1675 cm^{-1}) allow to exclude for 2 the structure of tetra-μ-acetato-bis[hydrazonoisatin copper(II)] which we found in 1-unsubstituted isatin derivatives only, when a hydrogen bond occurred between the isatin NH and the oxygen atom of an acetato group.

We propose for 2 a structure of bis-copper(II) complex with a negative charge delocalized onto the ligand (Scheme 2), similar to that of o-quinone monophenylhydrazones,[4] of 1-methyl and 1-acetyl-3-arylaminomethylenoxindoles,[1] and of 4-aminomethylen-Δ^2-pyrazolin-5-ones.[7]

Scheme 2



1 2

The reaction with DMAD occurred either if the copper(II) complex 2 or a mixture of 1 and copper(II) acetate was allowed to react 1 hr in refluxing dioxan.

With the experience of previous work in the field,[5] we assigned, with the aid of elemental analysis and spectral data, the structure to seven main products isolated by column chromatography, after the inorganic copper(I) residue was filtered off.

If copper(II), as pointed out previously,[5] acted as an oxidant, 1-methyl-3-carbenindolin-2-one and p-chlorophenyl radical could be considered as two reacting species giving rise to two main groups of products:

a) compounds containing DMAD and 1-methyl-2-indolinone;

b) compounds deriving from an attack by the p-chlorophenyl radical.

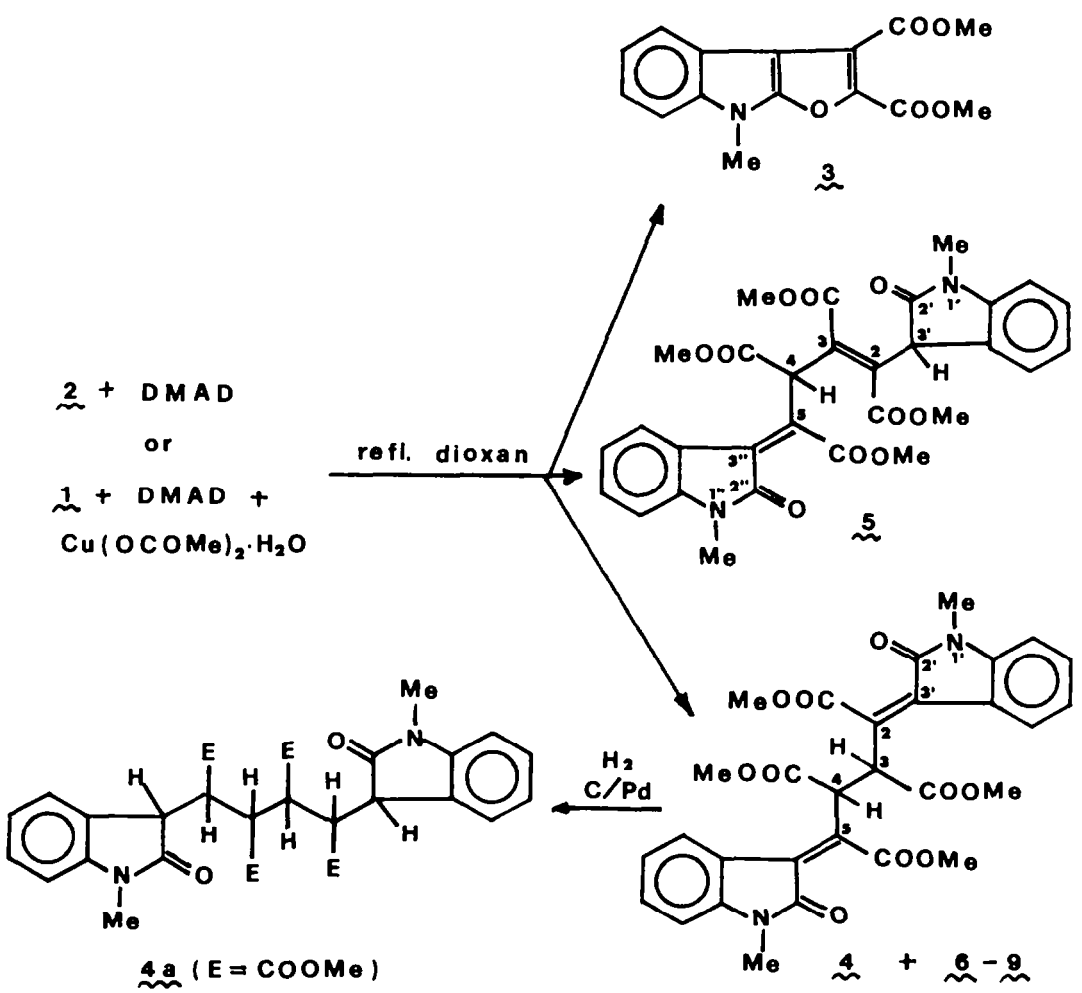
In detail, three products (**3**–**5**), belonging to the first group, were isolated (Scheme 3).

Dimethyl 8-methylfuro[2,3-b]indole-2,3-dicarboxylate (**3**) was the colourless product strictly related to that isolated in previous paper[5] and synthesized by an independent route.

Dimethyl 2,5-bis-1'-methyl-2'-oxindolin-3'-yliden-3,4-dimethoxycarbonylhexanedioate (**4**) was a yellow-orange product with a molecular ion at m/e 576, the lactam band at 1697 cm^{-1} and two ester carbonyls at 1725 and 1740 cm^{-1}. Both ^{1}H- and ^{13}C-NMR spectra were consistent with a symmetric structure: the allylic proton occurred at 6.80 δ moving downfield by addition of $Eu(fod)_3$ and the allylic carbon was a doublet at 42.0 δ. The configuration around the double bond was considered to be Z since the oxindolic H-4 protons were not deshielded at about 8.5 δ as happens when a methoxycarbonyl group is E.[8,9] **4** was reduced in ethanol with H_2 and Pd/C, at room temp. and pressure, giving the hexahydroderivative **4a**, a colourless product with fully consistent spectral data (see Experimental).

Dimethyl 2-1'-methyl-2'-oxindolin-3'-yl-5-1''-methyl-2''-oxindolin-3''-yliden-3,4-dimethoxycarbonyl-2-hexenedioate (**5**) was a yellowish product, an isomer of **4** (the molecular ion being at m/e

Scheme 3

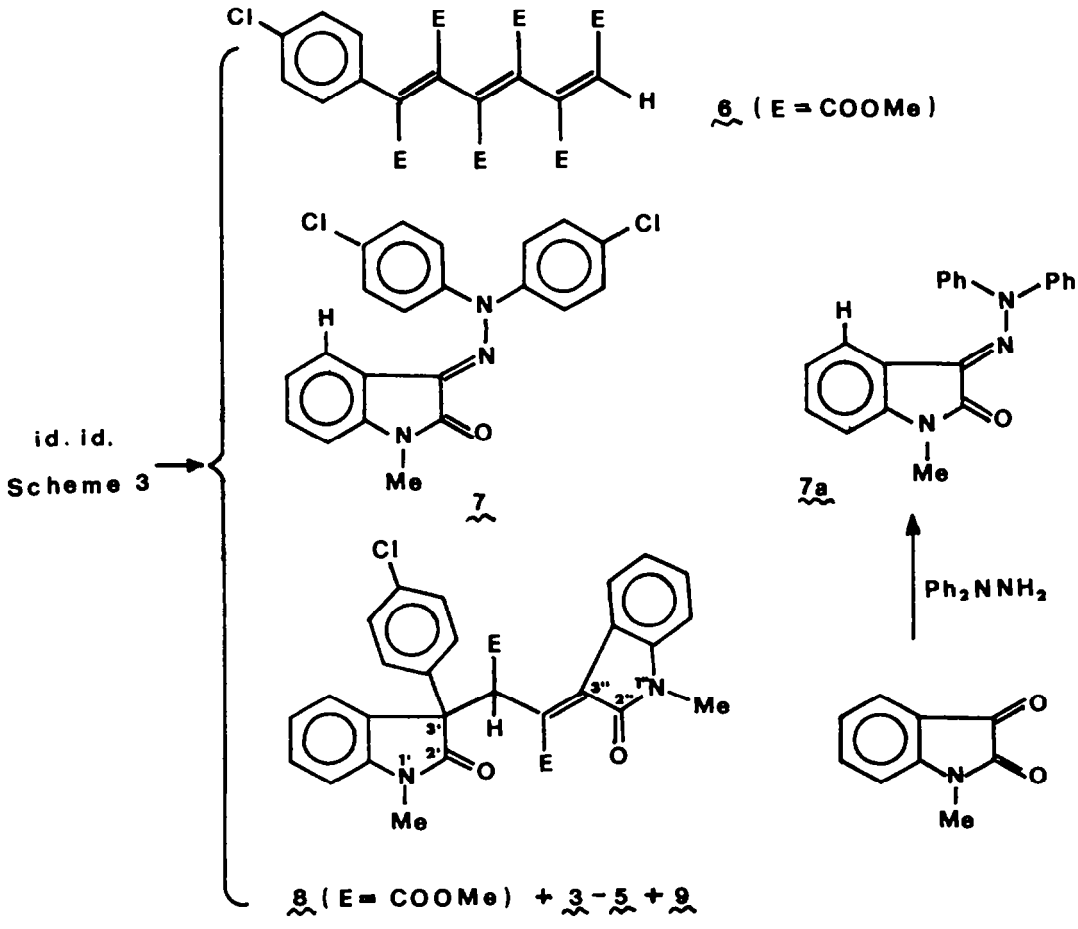


576) showing two lactam bands at 1690 and 1712 cm^{-1} and two ester carbonyls at 1728 and 1745 cm^{-1}. ^{1}H-NMR showed signals consistent with a non-symmetric structure: 4 methoxy groups at 3.47, 3.80, 3.93 and 3.95 δ, two singlets: one at 4.35 δ for the oxindole H-3 proton, one at 6.85 δ for the allylic proton, both shifted downfield by addition of $Eu(fod)_3$. ^{13}C-NMR was again consistent with a non-symmetric structure, the main signals being two N-Me carbons as quartets at 25.9 and 26.2 δ, 4 methoxy at 52.1, 52.4, 52.5 and 52.7 δ, two CH doublets at 46.3 and 54.9 δ for the oxindolic C-3 and the allylic carbon. We considered the configuration around C5 and C3" to be Z, in accordance with existing literature.[8,9] This product, under the conditions experienced for 4 did not reduce, probably for steric reasons.

Three products (6-8) belonged to the second group (Scheme 4).

Dimethyl 2-p-chlorophenyl-3,4,5,6-tetramethoxycarbonyl-2,4,6-octatrienedioate (6) (written in an arbitrary all E configuration) was similar to the product yielded when phenyl radical attacked three DMAD molecules, as isolated in a previous paper.[2]

Scheme 4



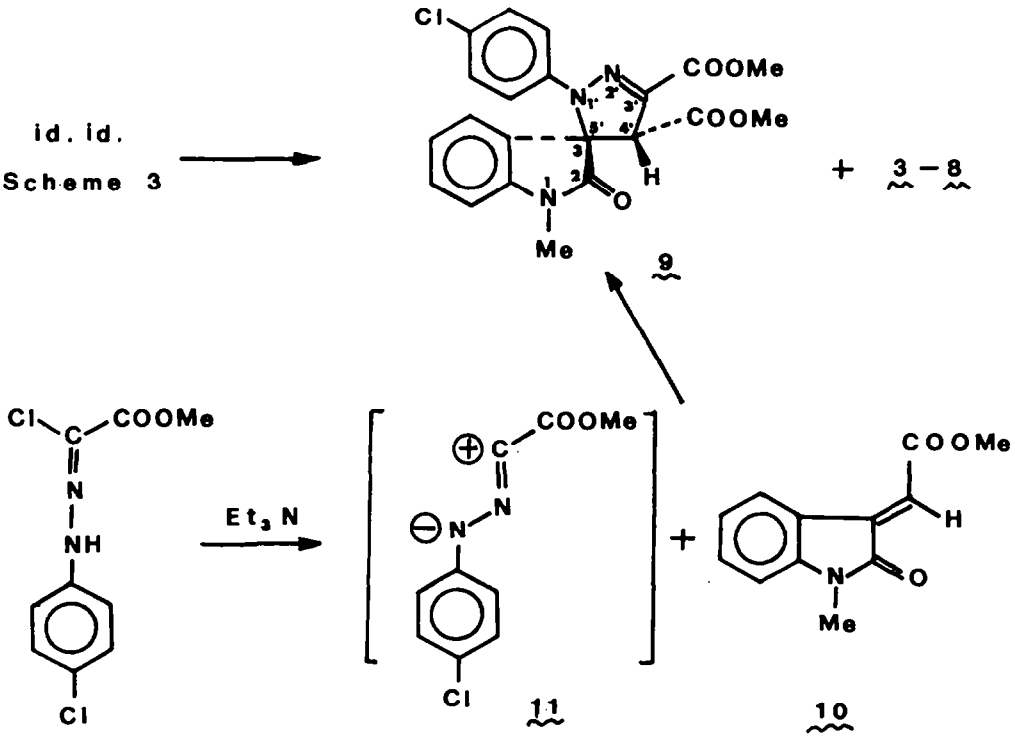
3-Di(p-chlorophenylhydrazono)-1-methylisatin (**7**) was a yellow product with a molecular ion region at m/e 395, 397, 399 in the ratio 9:6:1 and a lactam band at 1715 cm^{-1}. The diphenyl analogue **7a** was synthesized from 1-methylisatin and 1,1-diphenylhydrazine and both NMR spectra had the oxindole H-4 strongly shielded (at 5.80 δ, **7**; at 5.55 δ, **7a**) by one of the hydrazono aryl rings.

Dimethyl 2-3'-p-chlorophenyl-1'-methyl-2'-oxindolin-3'-yl-3-1''-methyl-2''-oxindolin-3''-yliden-butanedioate (**8**). This yellow product had molecular ions at m/e 546, 548, two lactam bands at 1690 and 1712 cm^{-1}, two ester carbonyls at 1728 and 1743 cm^{-1}. Its structure was deduced by its ^{1}H-NMR spectrum: two N-Me groups at 3.15 and 3.29 δ, two methoxy at 3.50 and 3.60 δ, an allylic proton deshielded at 7.85 δ which shifted downfield with addition of Eu(fod)$_3$. The isomer with p-chlorophenyl group in position 2 is unlikely to be consistent either with ^{13}C-NMR (which had an allylic carbon at 47.9 δ) or with the mass spectrum (which had the base peak region at m/e 256, 258).

In addition to these products, which arose from a fragmentation of the ligand, adduct **9** was isolated whose elemental analysis was consistent with a ligand/DMAD ratio 1:1. The molecular ions at m/e 427, 429, the carbonyl absorption at 1720 and 1735 cm^{-1} (no NH absorption), the ^{1}H-NMR spectrum with three methyl signals at 3.30, 3.36 and 3.90 δ and an allylic proton at 4.80 δ, were all consistent with this.

Assuming the mechanism leading to **9** (which we will discuss later) to be correct, we suggested that this adduct was 1-methyl-2-indolinone-3-spiro-5'-1'-p-chlorophenyl-3',4'-dimethoxycarbonyl-2'-pyrazoline (Scheme 5).

Scheme 5



To test this, an independent synthesis was undertaken by allowing methyl 1-methyl-2-oxindolin-3-ylidenacetate (**10**)[9] and N-p-chlorophenylmethoxycarbonylnitrilimine (**11**) (from methyl 2-chloro-2-p-chlorophenylhydrazonoacetate[10]) to react in accordance with a 1,3-dipolar cycloaddition. Since **9** was thus obtained as the only reaction product in 44% yield, its structure was not only confirmed but, given that **10** had an E configuration,[9] the allylic proton of **9** was cis to the lactam group.

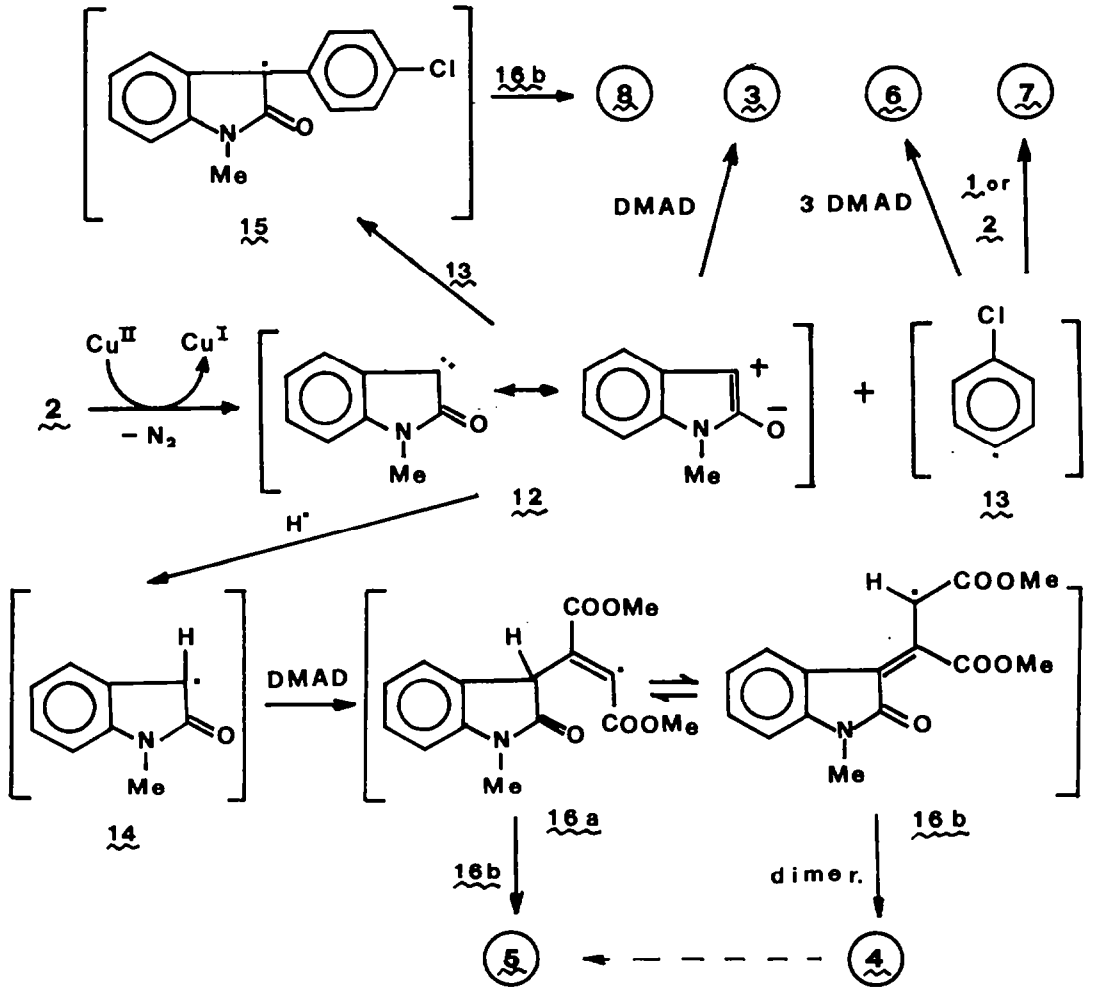
DISCUSSION AND CONCLUSION

The reaction of **2** with DMAD occurred with low chemoselectivity and poor yields, but it was a useful tool to gain further information on the reactivity induced by copper(II) complexation.

Let us first discuss the formation of products obtained by fragmentation of the ligand.

The oxidation of the ligand by copper(II) gave 1-methyl-3-carbenindolin-2-one (**12**) and p-chlorophenyl radical (**13**). An overall scheme with the fate of these intermediates, certainly oversimplified, is here reported (Scheme 6).

Scheme 6



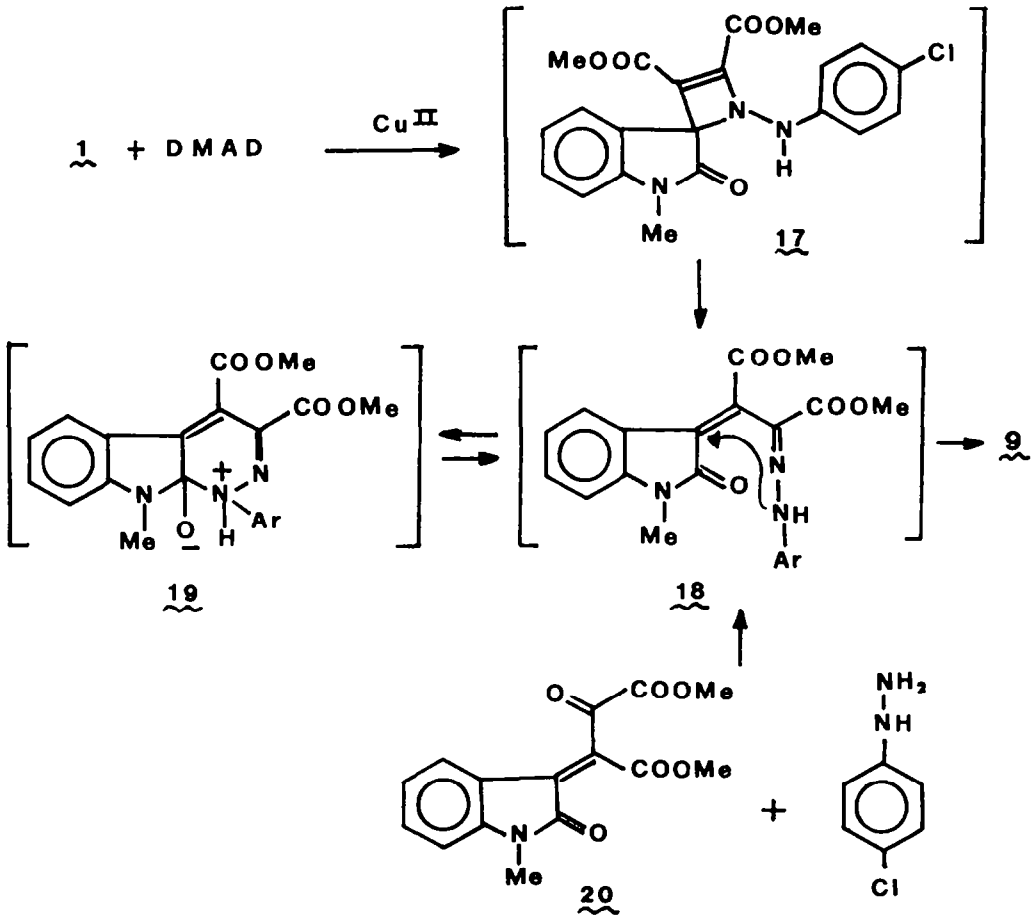
Ketocarbene **12** either behaved as a 1,3-dipole giving **3** (through a 1,3-dipolar cycloaddition), or reacted with a hydrogen radical giving **14**, or reacted with the p-chlorophenyl radical **13** giving **15**. Radical **14**, trapped by DMAD, gave **16a** and **16b** and these were the precursors either of dimers **4** and **5** or of product **8** by reaction with **15**. We cannot exclude the possibility that **5** is a secondary product since, under controlled basic conditions, it was obtained from **4** at room temperature even if a long reaction time was required.

The p-chlorophenyl radical **13** was not only destined to **15**, but either it inserted onto **2** (or **1**) to give **7** or reacted with 3 moles of DMAD to give **6**. This "magic" number of 3 DMAD molecules, already found in a similar reaction,[5] probably derived from the aptitude of copper(II) to cohordinate 3 DMAD which is known to trimerize to hexamethyl mellitate.[11]

If the formation of several "unexpected" products can thus be rationalized, an "expected" product was not found: the Michael adduct of **2** and DMAD. The presence of a negative charge delocalized on the ligand could suggest this reaction pathway, but either different routes are preferred or the adduct is not stable and reverts to the starting reagents.

Only one product did not fit in the above scheme, the adduct **9**. To rationalize its formation we propose a [2+2] cycloaddition of DMAD on the hydrazone exocyclic C=N double bond with formation

Scheme 7



of the spiro-azete **17** which underwent electrocyclic ring opening to **18**. The intramolecular cyclization to pyridazino [3,4-b]indole derivative **19**, even if it occurred, did not gave the final 1,2-elimination,[2] prevented by the presence of a methyl group on the indolinone nitrogen. Thus a cyclization occurred in position 3 of the indolinone ring and **9** was obtained (Scheme 7).

These suggestions are not entirely speculative. Compound **18** (independently from the easily interconverting Z/E configuration) is the p-chlorophenylhydrazone of dimethyl 2-1'-methyl-2'-oxoindolin-3'-yliden-3-oxosuccinate (**20**) which we reported in a previous paper.[1] When a mixture of **20** and p-chlorophenylhydrazine was refluxed in dioxan, 49% yield of **1** and 11% yield of **9** were obtained. If both 4 π-electrocyclic reaction and [2+2] cycloadditions would be equilibria, **1** would be formed in competition with **9**. However we believe that the main pathway to **1** from **20** and p-chlorophenylhydrazine involved a Michael attack of the latter on the 3'-oxindolin position of **20** followed by a retro-Michael elimination of dimethyl oxosuccinate.(*)

The free ligand **1** did not react with DMAD in the absence of copper(II) in blank experiments, hence a mechanism has to be proposed involving the coordination of a reagent with copper(II).

If a planar structure, already found for several 1,5-bidentate bis-copper(II) complexes as salicyclaldehydates,[12,13] N-methyl and N-phenylsalicylaldiminates,[14,15] N,N'-ethylenbis(acetylacetoneininate)[16] and hexafluoroacetylacetonate,[17] can be proposed for **2**, the apical position, which is free for a further ligand,[15-17] can be used to coordinate DMAD.

This coordination with the metal center can involve, with different contributions, the interactions between the filled copper 3xz (or 3yz) with the acetylene LUMO and the empty copper 4s with the acetylene HOMO. The resulting π-complex[18] had the LUMO of its acetylenic ligand lowered and hence activated for a [2+2] cycloaddition.

EXPERIMENTAL

Melting points were determined by the capillary method on a Tottoli apparatus (Büchi). Elemental analyses were made on Erba CHN analyzer mod. 1106. IR spectra (nujol mulls) were recorded on a Perkin-Elmer 983 spectrophotometer and ^{1}H- and ^{13}C-NMR spectra on a Bruker WP80SY spectrometer ($CDCl_3$ was the solvent, chemical shifts are reported in ppm on the δ scale, coupling constants in Hz). Mass spectra were obtained on a Du-Pont 21-492B mass spectrometer.

1-Methylisatin-3-p-chlorophenylhydrazone (**1**). This was obtained from 1-methylisatin[19] and p-chlorophenylhydrazine in boiling ethanol. Yellow crystals (m.p. 193-194° from ethyl acetate, 74% yield). (Found: C, 63.0; H, 4.2; N, 14.6. Calc. for $C_{15}H_{12}ClN_3O$: C, 63.0; H, 4.2; N, 14.7%).

Bis-copper(II) complex of 1-methylisatin-3-p-chlorophenylhydrazone (**2**). Saturated boiling solutions of 2 mmol **1** and $Cu(OCOMe) \cdot H_2O$ in ethanol were mixed and solvent was distilled off until a black solid began to separate. Black needles (45% yield) were filtered off and dried. M.p. 205-206° dec. (Found: C, 57.4; H, 3.4; N, 13.7 Calc. for $C_{30}H_{22}Cl_2CuN_6O_2$: C, 56.9; H, 3.5; N, 13.3%). IR: 1587 cm^{-1}.

Reaction of **2** with DMAD. A mixture of **2** (6.33 g - 10 mmol) and DMAD (5.6 g - 40 mmol) in anhydrous dioxan (300 ml) was refluxed under a N_2 stream for about 2 hrs. The cold reaction mixture was filtered to separate the inorganic material, the solvent was evaporated to dryness and the residue was chromatographed (Silica gel H Merck). Elution started with a mixture of cyclohexane/ethyl acetate 8:2 and through mixtures richer in ethyl acetate, was completed with pure ethyl acetate.

(*) To support this mechanism, dimethyl 1'-methyl-2'-oxoindolin-3'-ylidenmalonate (red plates m.p. 105-106° from benzene/cyclohexane, prepared following the method described for 1'-H analogue[8] but under a longer refluxing, whose elemental analysis and spectral data are fully consistent with its structure) was allowed to react under the same experimental conditions (refluxing dioxan) with p-chlorophenylhydrazine and **1** was obtained in 75% yield.

The first fraction eluted, after DMAD excess, gave 2.44 g of **1** (43% yield).

The second fraction was diarylhydrazone **7** as orange needles (0.16 g, m.p. 179-180° from ethanol, 2% yield). (Found: C, 63.3; H, 3.8; N, 10.6. Calc. for $C_{21}H_{15}Cl_2N_3O$: C, 63.6; H, 3.8; N, 10.6%). IR: 1715 cm^{-1} ($\nu_{C=O}$); ^{1}H-NMR: 3.31 (s, 3H, N-Me), 5.82 (d, J=8.4, 1H, indole H4), 6.50-7.50 (m, 11H, aromatics). Mass spectrum: M^+ 395, 397, 399.

The third fraction was strongly fluorescent (330 nm) and gave **3** (0.36 g, white needles m.p. 185-186° from ethanol, 6% yield). (Found: C, 62.6; H, 4.6; N, 5.0. Calc. for $C_{15}H_{13}NO_5$: C, 62.7; H, 4.6; N, 4.9%). IR: 1747 and 1710 cm^{-1} ($\nu_{C=O}$). ^{1}H-NMR: 3.83 (s, 3H), 3.96 (s, 3H), 4.08 (s, 3H) (1 N-Me and 2 O-Me), 7.2-8.0 (m, 4H, aromatics). Mass spectrum: M^+ 287.

The fourth fraction gave **8** (0.21 g, yellow crystals m.p. 200-201° from ethanol, 3.9% yield). (Found: C, 65.8; H, 4.8; N, 5.1. Calc. for $C_{30}H_{25}ClN_2O$: C, 66.1; H, 4.6; N, 5.1%). IR: 1743, 1728, 1712 and 1690 cm^{-1} ($\nu_{C=O}$). Mass spectrum: M^+ 544, 546. ^{1}H-NMR: 3.15, 3.29 (s+s, 3H+3H, 2 N-Me); 3.50, 3.60 (s+s, 3H+3H, 2 O-Me), 7.22 and 7.59 (4H, p-Cl-C_6H_4), 7.85 (s, 1H, H allylic), 6.7-8.0 (m, 8H, aromatics). ^{13}C-NMR: 26.3 and 26.7 (2 N-Me), 47.9 (allylic CH), 52.3 (2 O-Me nearly overlapped), 108.4, 122.4, 123.9, 128.1, 128.4, 129.2 and 131.0 (aromatics).

The fifth fraction was yellowish fluorescent (330 nm) and gave **9** (0.12 g, yellowish crystals m.p. 170-171° from ethanol, 1.4% yield). (Found: C, 59.0; H, 4.1; N, 10.0. Calc. for $C_{21}H_{18}ClN_3O_5$: C, 58.9; H, 4.2; N, 9.8%). IR: 1735, 1720 cm^{-1} ($\nu_{C=O}$). Mass spectrum: M^+ 427, 429. ^{1}H-NMR: 3.30 (s, 3H, N-Me or O-Me), 3.36 (s, 3H, N-Me or O-Me), 3.92 (s, 3H, O-Me), 4.80 (s, 1H, 4'proton), 6.76 and 7.10 (4H, p-Cl-C_6H_4), 6.8-7.5 (m, 4H, aromatics).

The sixth fraction gave **6** (0.09 g, white crystals m.p. 118-119°, 0.8% yield). (Found: C, 53.5; H, 4.3. Calc. for $C_{24}H_{23}ClO_{12}$: C, 53.5; H, 4.3%). IR: 1730 cm^{-1} ($\nu_{C=O}$). Mass spectrum: M^+538, 540. ^{1}H-NMR: 3.63, 3.76, 3.81, 3.83, 3.86 (ss, 18 H, 6 O-Me), 6.03 (s, 1H, vinyl H), 7.39 (s, 4H, aromatics).

The seventh fraction gave **4** (0.13 g, yellow crystals m.p. 179-180°, 1.1% yield). (Found: C, 62.5; H, 4.8; N, 5.0. Calc. for $C_{30}H_{28}N_2O_{10}$: C, 62.5; H, 4.9; N, 4.9%). IR: 1740, 1725 and 1697 cm^{-1} ($\nu_{C=O}$). Mass spectrum: M^+ 576. ^{1}H-NMR: 3.24 (s, 3H, N-Me), 3.76 and 3.88 (ss, 3H+3H, 2 O-Me), 6.80 (s, 1H, allylic H), 6.7-7.4 (m, 4H, aromatics). ^{13}C-NMR: 25.9 (N-Me), 42.0 (CH allylic), 52.7 (O-Me), 108.0, 122.2, 123.9 and 130.9 (indolinone, C7, C4, C5 and C6 respectively).

The last fraction gave **5** (0.39 g, light yellowish crystals m.p. 224-225° from ethanol, 3.5% yield). (Found: C, 62.3; H, 5.0; N, 4.8. Calc. for $C_{30}H_{28}N_2O_{10}$: C, 62.5; H, 4.9; N, 4.9%). IR: 1745, 1728, 1712 and 1690 cm^{-1} ($\nu_{C=O}$). Mass spectrum: M^+ 576. ^{1}H-NMR: 2.83 (s, 6H, 2 N-Me), 3.47, 3.80, 3.93 and 3.95 (ss, 3H+3H+3H+3H, 4 O-Me), 4.35 (s, 1H, oxindolinyl H3'), 6.85 (s, 1H, diallylic H), 7.68 (dd, 1H, oxindolinyliden H4"), 6.0-7.1 (m, 7H, aromatics). ^{13}C-NMR: 25.9 and 26.2 (2 N-Me), 52.1, 52.4, 52.5 and 52.7 (4 O-Me), 46.3 (oxindolinyl C3'), 54.9 (diallylic C4), 107.2, 107.4, 121.2, 121.5, 125.0, 127.7, 128.1 and 129.4 (indolinones probably in the order C7, C4, C5 and C6).

Catalytic reduction of **4**. **4** (0.08 g, 0.14 mmol) in EtOH (30 ml) was reduced with H_2 at room temperature and pressure in the presence of Pd/C 10% (0.02 g). The theoretical uptake of hydrogen was completed within an hour, the catalyst was filtered, the solvent evaporated and the residue was crystallized from EtOH. **4a** (white crystals) was obtained in nearly quantitative yield, m.p. 204.5-205.5°. (Found: C, 62.0; H, 5.8; N, 5.0. Calc. for $C_{30}H_{32}N_2O_{10}$: C, 62.1; H, 5.6; N, 4.8%). IR: 1725 and 1705 cm^{-1} ($\nu_{C=O}$). Mass spectrum: M^+580. ^{1}H-NMR: 3.16 (s, 3H, N-Me), 3.50 and 3.72 (ss, 3H+3H, 2 O-Me), 3.90 (broad s, 3H, 3 CH-CO), 6.7-7.4 (m, 4H, aromatics).

Isomerization of **4**. **4** (0.05 g., 0.09 mmol) was stirred at room temperature in benzene (10 ml) in the presence of triethylamine (1 ml) for about 1 month. Column chromatography on silicagel (cyclohexane/ethylacetate 6:4 as eluant) gave **5** (0.021 g) identical (m.p., mixed m.p. and IR spectrum) with the previously described product.

Methyl 2-chloro-2-p-chlorophenylhydrazonoacetate. Diazotized p-chloroaniline (from p-chloroaniline, 6.02 g, 47 mmol) was added to an aqueous solution of methyl chloroacetate (8.18 g, 54 mmol) in the presence of sodium acetate following the method reported in the literature. After one night stirring, the product was filtered (6.13 g, 61% yield; m.p. 148-149° from benzene). (Found: C, 44.0; H, 3.2; N, 11.2. Calc. for $C_9H_8Cl_2N_2O_2$: C, 43.7; H, 3.3; N, 11.3%). IR: 1708 cm^{-1} ($\nu_{C=O}$).

Reaction of **11** with **10**. Methyl 1-methyl-2-oxindolin-3-ylidenacetate (**10**) (0.30 g, 1.4 mmol) and methyl 2-chloro-2-p-chlorophenylhydrazonoacetate (0.40 g, 1.6 mmol) were dissolved in benzene (40 ml) and Et_3N (1.5 ml) was added under stirring. After few hrs the solution was washed with water and the solvent distilled off. The residue was chromatographed (cyclohexane/ethyl acetate 7:3 as eluant) and after unreacted **10**, (0.05 g), **9** was isolated (0.26 g, 44% yield), identical in every respect (m.p., mixed m.p. and IR spectrum) with the sample previously described.

Reaction of **20** with p-chlorophenylhydrazine. Dimethyl 2-1'-methyl-2'-oxindolin-3'-yliden-3-oxo-succinate (**20**) (0.39 g, 1.3 mmol) and p-chlorophenylhydrazine (0.20 g, 1.4 mmol) were dissolved

anhydrous dioxan (100 ml) and refluxed under N_2 until tlc showed the disappearance of the starting **20**. The solvent was evaporated and the residue chromatographed on silica gel (eluant cyclohexane/ethyl acetate 7:3). The following products were eluted in the order:
1-methylisatin-3-p-chlorophenylhydrazone (**1**) (0.18 g, 49% yield), identical (m.p., mixed m.p. and IR spectrum) with the previously described product.
1-methyl-2-indolinone-3-spiro-5'-1'-p-chlorophenyl-3',4'-dimethoxycarbonyl-2'-pyrazoline (**9**) (0.06 g, 11% yield), identical (m.p., mixed m.p. and IR spectrum) with the previously described product.

1-Methylisatin-3-diphenylhydrazone (**7a**). A mixture of N-methylisatin (0.8 g, 5 mmol) and 1,1-diphenylhydrazine (1.1 g, 6 mmol) was boiled few minutes in EtOH. **7a** separated as yellow crystals (1.15 g, m.p. 194-195° from EtOH, 72% yield). (Found: C, 76.9; H, 5.2; N, 12.9. Calc. for $C_{21}H_{17}N_3O$: C, 77.0; H, 5.2; N, 12.8%). IR: 1705 cm^{-1} ($\nu_{C=O}$). H-NMR: 3.30 (s, 3H, N-Me), 5.55 (d, J=8.2, 1H, indole H4), 6.4-7.4 (m, 13H, aromatics).

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