

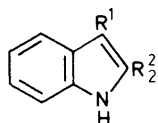
The Chlorination of Indoles by Copper(II) Chloride

Éva Balogh-Hergovich and Gábor Speier*

Research Group for Petrochemistry of the Hungarian Academy of Sciences and Institute of Organic Chemistry, Veszprém University of Chemical Engineering, 8201 Veszprém, Hungary

The reaction of indoles with copper(II) chloride has been studied in acetonitrile. At low copper(II):indole ratios, dimers are formed in the presence of dioxygen, oxygenated products are obtained, and at large copper(II):indole ratios, pyrrole ring-chlorinated products are formed in yields of up to 92%. The reactions are postulated to proceed *via* the radical cations of the indoles formed in an electron-transfer reaction.

The halogenation of a variety of unsaturated organic compounds by copper(II) chloride and bromide has been studied in various solvents. Alkenes are chlorinated by copper(II) chloride particularly when acetonitrile is used as the solvent.¹ Conjugated dienes are brominated to their 1,4-adducts by copper(II) bromide,² carbonyl compounds are easily halogenated in the α -position by copper(II) halides,^{3,4} and phenol is also halogenated by copper(II) chloride.⁴ 9-Alkoxy- and 9-acyloxy-anthracenes undergo reaction with copper(II) halides, under heterogeneous conditions, to give 9,9'-bi-anthracenyl together with smaller amounts of the 10-halogenated product.⁵ 2-Methoxy- and 2-ethoxy-naphthalene undergo halogenation with both copper(II) bromide and chloride in the 1-position.⁶ Indoles react with copper(II) chloride to give various products depending on the reaction conditions. 3-Substituted indoles give oxygenated ring-cleaved and dimerized products^{7,8} in the presence of dioxygen and in its absence, while in the case of excess copper(II) chloride chlorinated products are also formed.⁸



- (1) a; R¹ = Me, R² = H
 b; R¹ = CH₂CO₂Me, R² = H
 c; R¹ = H, R² = Me
 d; R¹ = H, R² = Ph
 e; R¹ = R² = Ph

In the present study the reactions of indoles (**1a**–**e**) with copper(II) chloride in acetonitrile have been investigated. In particular the effect of an excess of copper(II) chloride on the chlorination of indoles has been studied.

Results and Discussion

It has been shown that oxygenated copper(I) chloride in the presence of pyridine reacts with 2- or 3-substituted indoles to give oxidatively cleaved *o*-formyl- or *o*-acyl-amino ketones, a reaction which is relevant to the action of tryptophan 2,3-dioxygenase.^{8–11} Since the structure of the oxygenated copper species could not be established by diffraction methods, chemical and spectroscopic data serve as the basis for speculation as to their structure.^{12–15} Oxygenated copper(II) and/or copper(III) species are believed to effect the oxygenation. The mechanism of these oxygenations is rather obscure and dehydrogenation of the indole ring is assumed to be the first step.

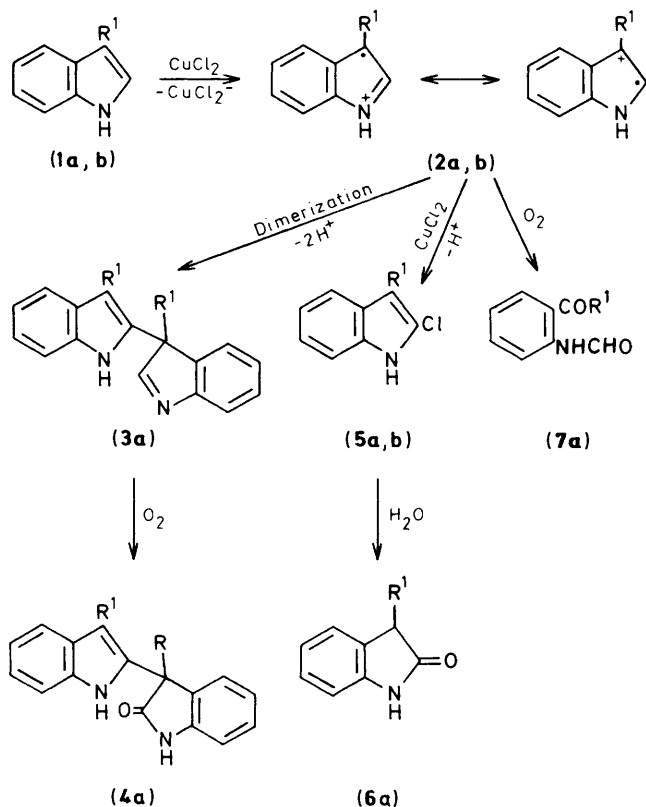
Table. Reaction of indoles with copper(II) chloride

Entry	Indole (mmol)	CuCl ₂ (mmol)	Time (h)	Product	Yield ^a (%)
1	(1a) (7.5)	7.5	4	(4a) (5a) ^b	44 16
2	(1a) (5)	5	4	(7a)	71 ^c
3	(1a) (7.5)	10	8	(5a) ^d	63
4	(1a) (5)	15	8	(5a)	84
5	(1b) (5)	15	8	(5b)	82
6	(1c) (5)	5	4	(9c) (10c)	27 34
7	(1c) (5)	10	8	(9c) (10c)	8 72
8	(1d) (5)	10	10	(10d)	92
9	(1e) (2.5)	7.5	10	(12e) (13e)	66 17 ^c

^a Determined by g.l.c. ^b Other products were (**3a**) (trace), (**6a**) (14%), and (**7a**) (3%). ^c Isolated yield. ^d Other products were (**4a**) (6%), and (**6a**) (4%).

In the dehydrogenation of acyloins,¹⁶ catechols,¹⁷ indolines¹⁸ and in the cyclodehydrogenation of *N*-alkylidene-2-hydroxy-anilines to 2-substituted benzoxazoles¹⁹ by the oxygenated product(s) of [CuClpy]_n, the co-ordinated oxygen-containing ligand(s) *e.g.* hydroxo, μ -oxo and oxo *etc.* serve as basic sites for protons from the substrate. With CuCl₂ and Cu(OMe)Cl the co-ordinated chloride or the methoxide ligands provide the basic sites giving HCl or MeOH besides CuCl and the dehydrogenated products. We were interested to see, whether a similar mechanism could be applied to the oxidative ring cleavage of indoles catalysed by copper(I) chloride in the presence of dioxygen. Therefore, we investigated the reaction of indoles with copper(II) chloride under argon and in the presence of dioxygen in order to elucidate the mechanism of the oxygenation reaction and to disclose whether chlorination of the indole ring can be made to be the main reaction under conditions of excess of copper(II) chloride.

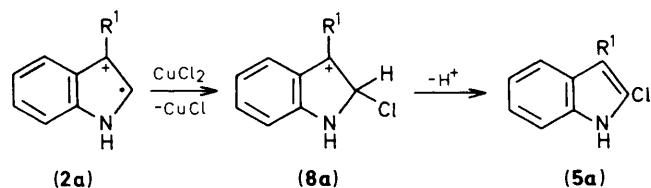
In the reaction of 3-methylindole (**1a**) with copper(II) chloride (stoichiometry 1:1) under argon a variety of compounds were formed as determined by g.l.c.–m.s. methods. Traces of the dimer 3-methyl-3-(3-methylindol-2-yl)-3*H*-indole (**3a**)²⁰ along with 3-methyl-3-(3-methylindol-2-yl)indole-2(3*H*)-one (**4a**), 2-chloro-3-methylindole (**5a**), 3-methylindol-2(3*H*)-one (**6a**), and 2'-formamidoacetophenone (**7a**) are formed (Entry 1 in the Table). The preparative work-up of the reaction mixture gave a somewhat different product composition. Subsequent reactions of the primary products during work-up are probably responsible for this. The possible reactions are shown in Scheme 1. 3-Methylindole (**1a**) reacts with copper(II) chloride by the way of an electron-transfer from the indole to the copper(II) species



Scheme 1.

resulting in a radical cation (**2a**) and CuCl_2^- . The two mesomeric forms of the cation (**2a**) can undergo dimerization to give the very labile dimer 3-methyl-3-(3-methylindol-2-yl)-3H-indole (**3a**),* which is then easily oxygenated during work-up to 3-methyl-3-(3-methylindol-2-yl)indol-2(3H)-one (**4a**). The radical cation (**2a**) can also react directly with dioxygen to give the ring-cleaved product 2'-formamidoacetophenone (**7a**). In addition (**2a**) can also react with copper(II) chloride to give the 2-chlorinated product (**5a**). 2-Chloro-3-methylindole is hygroscopic and is easily transformed to 3-methylindol-2(3H)-one (**6a**) by hydrolysis. The same feature of 2-bromo-3-methylindole toward hydrolysis has been established.²¹ All of these secondary reactions are coupled to a deprotonation reaction with CuCl_2^- leading to the formation of HCl and copper(I) chloride. Two of the three secondary reactions can be suppressed, resulting in the formation of compounds (**5a**) and (**7a**) as the main products. This can be accomplished by (a) the use of a larger concentration of copper(II) chloride, which causes the yield of the chlorinated product (**5a**) to be increased (Entry 3, 4 in the Table), or (b) carrying out the reaction under dioxygen, which then leads exclusively to the oxidatively cleaved product (**7a**). (Entry 2 in the Table). These results shed some light on the mechanism of the reaction and establish the utility of copper(II) chloride for the chlorination of indoles. For the reaction of the radical cation (**2a**) with copper(II) chloride the mechanism illustrated in Scheme 2 is suggested. There is an atom-transfer from the copper(II) chloride to the radical cation (**2a**) yielding copper(I) chloride and (**8a**), and the latter loses a proton to give the chlorinated product (**5a**) and HCl; the

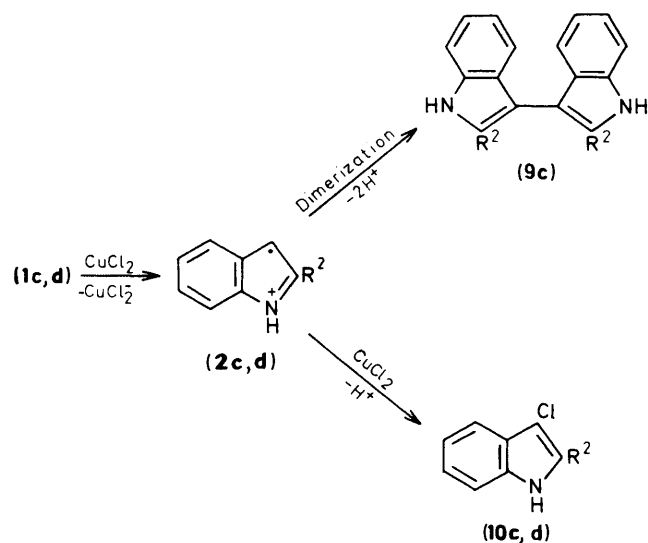
* 3,3'-Dimethyl-3,3'-bi-3H-indole has been suggested without any structure characterization for the radical dimerization of 3-methylindole.^{20a} In other cases^{20b,c} oxygenated dimers could be isolated and characterized by ¹³C n.m.r. and m.s. spectra.



Scheme 2.

chloride coming from CuCl_2^- . A similar pathway has been proposed for the bromination of 2-methoxynaphthalene by copper(II) bromide.⁶ In a similar fashion methyl indol-3-ylacetate (**1b**) can be chlorinated with an excess of copper(II) chloride to methyl 2-chloroindol-3-ylacetate (**5b**) in good yield (Table, entry 5).

The reaction of 2-methylindole (**1c**) with copper(II) chloride shows a somewhat simpler feature. Compound (**1c**) and copper(II) chloride in a stoichiometry of 1:1 gives rise to two products in almost the same yield (Table 1, Entry 6). The dimer, 2,2'-dimethyl-3,3'-bi-indole (**9c**) was isolated and characterized by spectroscopic methods, it being more stable than the dimer (**3a**) formed from 3-methylindole. It is practically inert toward oxygenation. The other product obtained is 3-chloro-2-methylindole (**10c**). This is not susceptible to hydrolysis as found by the 3-methyl analogue.²¹ With a larger excess of copper(II) chloride, the amount of 3-chloro-2-methylindole is enhanced compared to the dimer (**9c**) (Table, Entry 7). Analogously, 2-phenylindole (**1d**) can be chlorinated to 3-chloro-2-phenylindole (**10d**) in good yield when the copper(II) chloride is used in excess (2:1) (Scheme 3 and Entry 8 in the

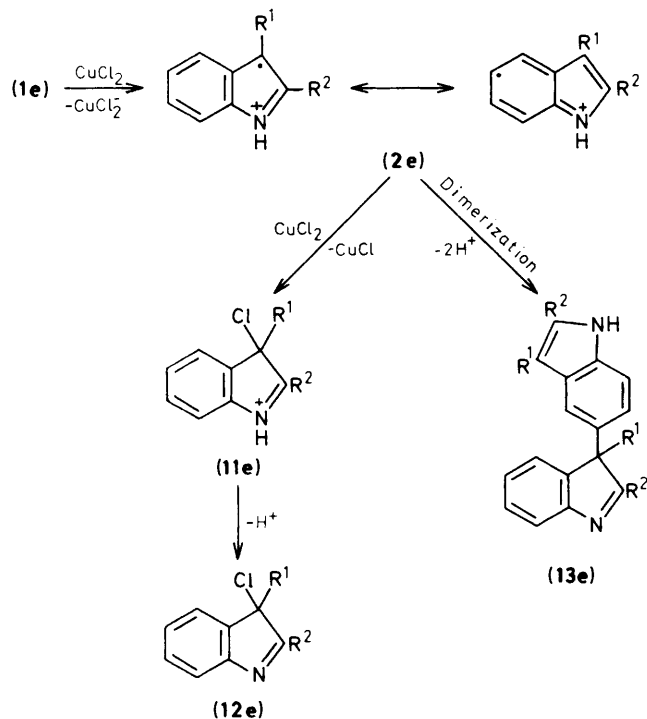


Scheme 3.

Table). In these cases a similar mechanism to that shown in Scheme 1 is assumed. The radical cations (**2c** and **d**), and the dimer (**9c**) are however less reactive towards dioxygen than the corresponding 3-substituted ones. The chlorinated products (**10c** and **d**) have considerable stability, and do not undergo hydrolysis easily.

2,3-Diphenylindole (**1e**) also reacts with an excess of copper(II) chloride (ratio 3:1) to give 3-chloro-2,3-diphenylindole (**12e**) and the dimer (**13e**) (Entry 9 in the Table). This case is also an initial electron-transfer from compound (**1e**) to copper(II) chloride to give the radical cation (**2e**). Here, the

coupling of the two mesomeric forms yields the dimer (**13e**). The mode of the radical-pairing is probably due to steric hindrance of the phenyl groups excluding couplings from 2- and 3-positions only. In the electrochemical oxidation of 2,3-diphenylindole the formation of the same dimer has been substantiated.²² The other route taken by the reaction of the cation (**2e**) with copper(II) chloride leads *via* atom-transfer to (**11e**), which on deprotonation ends up as 3-chloro-2,3-diphenyl-3*H*-indole (**12e**) as shown in Scheme 4.



Scheme 4.

From the reactions of indoles with copper(II) chloride it can be concluded, that the first step is an electron-transfer from the indole to the copper(II) chloride generating a radical cation. These radical cations then undergo competing subsequent reactions such as dimerization, oxygenation, or chlorination depending on the concentration of dioxygen or copper(II) chloride in the reaction. The species so formed are then transformed by deprotonation into the dimeric, oxygenated, and chlorinated products with the concomitant formation of HCl and copper(I) chloride. With a sufficiently large excess of copper(II) chloride this provides a useful preparative method of chlorinated indoles.

Experimental

The starting indoles 3-methylindole (**1a**), 2-methylindole (**1c**), indol-3-ylacetic acid methyl ester (**1b**) (Fluka), and 2-phenylindole (**1d**) (Aldrich) were purchased and used as supplied. 2,3-Diphenylindole (**1e**) was prepared according to the literature.²³ Anhydrous copper(II) chloride was made from $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ (Reanal) by heating at 180°C *in vacuo* for 8 h. Acetonitrile was purified by refluxing it over P_2O_5 followed by distillation from CaH_2 and storage under argon.

G.l.c. analyses were carried out on a Pye Unicam 104 gas chromatograph (Chromosorb-W HP, 80–100 mesh; 3% XE-60; 2 m, inner diameter 2 mm; 200–300 $^\circ\text{C}$; heating rate 6°min^{-1} ; argon carrier gas with 30 ml min^{-1} flow rate). Mass spectra were

taken on a JEOL MS-01-SG-2 mass spectrometer. I.r. and u.v.–vis. spectra were run on Specord IR-75 and Specord M-40 (Carl Zeiss, Jena) spectrophotometers. ^1H N.m.r. spectra were recorded on a Tesla BS-487 spectrometer using $(\text{Me}_3\text{Si})_2\text{O}$ as an internal standard.

Conventional Schlenk-type glassware and inert gas techniques were used throughout the work.

The Reaction of 3-Methylindole (1a) with Copper(II) Chloride under Argon.—To a solution of anhydrous copper(II) chloride (1.0 g, 7.5 mmol) in acetonitrile (15 ml) was added 3-methylindole (0.98 g, 7.5 mmol) in acetonitrile (5 ml), and the reaction was stirred under argon at room temperature for 4 h. G.l.c.–m.s. analysis of the solution revealed the presence of 3-methyl-3-(3-methylindol-2-yl)-3*H*-indole (**3a**), m/z 260 (M^+ , 100%), 259 (38), 245 (28), and 261 (16), 3-methylindole-2(3*H*)-one (**6a**), m/z 147 (M^+ , 100%), 132 (24), 119 (56), 118 (53), and 91 (19) [lit.,²² 147 (100), 132 (28), 119 (56), 118 (52), and 91 (18)], and 2'-formamidoacetophenone (**7a**), m/z 163 (M^+ , 35%), 148 (20), 135 (55), 120 (100), 92 (40), and 65 (37) [lit.,²⁴ 163, 148, and 120 (100)]. Yields are listed in Table (Entry 1).

The solvent was pumped off and the dry residue extracted with ether (200 ml). The ether was then stripped off to give a residue (0.7 g). Chromatography on silica gel with benzene as the eluant yielded 2-chloro-3-methylindole (**5a**) (110 mg, 9%), m.p. 108°C (from light petroleum) (lit.,²⁵ 112°C); λ_{max} (MeOH) 223 (ϵ 24 600 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 274 (6 300), 283 (6 000), and 291 nm (4 700) (lit.,²⁵ 223 (32 400), 274 (7 750), 279 (7 750), and 290 (5 900)); δ_{H} (80 MHz; CDCl_3) 2.22 (3 H, s, Me) and 6.98–8.25 (5 H, m, ArH, NH); ν_{max} (Nujol) 3 370 cm^{-1} (NH); m/z 167 (33%), 166 (37), 165 (M^+ , 100), 164 (95), 130 (82), and 128 (33).

Further chromatography on silica gel using chloroform as eluant gave 3-methyl-3-(3-methylindol-2-yl)indole-2-(3*H*)-one (**4a**) (180 mg, 17%), m.p. (from benzene) 222°C (lit.,²⁶ 224°C); m/z 276 (M^+ , 64%), 261 (100), 233 (37), and 130 (22) [lit.,¹⁰ 276, 261 (100), 233, and 130].

Using the same procedure 3-methylindole (0.98 g, 7.5 mmol) and copper(II) chloride (1.34 g, 10 mmol) after 8 h and subsequent extraction with ether gave compound (**5a**) (700 mg, 57%).

At a higher copper(II) chloride:3-methylindole ratio [copper(II) chloride (2.0 g, 15 mmol) and 3-methylindole (0.65 g, 5 mmol)] but under otherwise identical conditions compound (**5a**) was obtained in even higher yield (550 mg, 67%).

The Reaction of 3-Methylindole (1a) with Copper(II) Chloride in the Presence of Dioxygen.—To a solution of anhydrous copper(II) chloride (0.67 g, 5 mmol) in acetonitrile (10 ml) was added 3-methylindole (0.65 g, 5 mmol) in acetonitrile (5 ml) and stirred under dioxygen for 4 h at room temperature. The solvent was pumped off under reduced pressure and the residue extracted with ether. The extract was evaporated to dryness to yield 2'-formamidoacetophenone (**7a**) (0.58 g, 71%); m.p. 75 – 76°C (from light petroleum) (lit.,²⁷ 75 – 78°C); m/z 163 (M^+ , 35%), 148 (20), 120 (100) [lit.,¹⁰ 163 (M^+), 148, and 120 (100)].

The Reaction of Methyl Indol-3-ylacetate (1b) with Copper(II) Chloride under Argon.—A solution of methyl indol-3-ylacetate (0.95 g, 5 mmol), anhydrous copper(II) chloride (2.0 g, 15 mmol) and acetonitrile (20 ml) was stirred under argon for 8 h. The mixture was evaporated to dryness and extracted with ether. After stripping off the ether a residue (0.9 g) remained which contained starting material (18%) and a new product (82%) as determined by g.l.c. analysis. Chromatography on silica gel with ether as the eluant gave methyl 2-chloroindol-3-ylacetate (0.4 g, 36%) as white hygroscopic crystals, ν_{max} (Nujol) 3 347 (NH) and 1 738 cm^{-1} (CO) [lit.,²⁸ 3 328 cm^{-1} (MeCN)]; δ_{H} (80 MHz; CDCl_3) 3.38 (3 H, s, Me), 3.56 (2 H, s, CH_2), 6.50–

7.50 (4 H, m, ArH), and 9.05 (1 H, br NH); m/z 225 (8%), 223 (M^+ , 23), 166 (31), 165 (10), and 164 (100).

The Reaction of 2-Methylindole (1c) with Copper(II) Chloride under Argon.—A solution of 2-methylindole (0.65 g, 5 mmol), anhydrous copper(II) chloride (0.67 g, 5 mmol), and acetonitrile (20 ml) was stirred under argon at room temperature for 4 h. The solvent was then stripped off and the residue extracted with ether to give a mixture (0.5 g) of 3-chloro-2-methylindole (**10c**) and 2,2'-dimethyl-3,3'-bi-indolyl (**9c**) (Entry 6 in Table 1) as determined by g.l.c. Recrystallization from hexane gave compound (**10c**) (120 mg, 15%), m.p. 98 °C (lit.,²⁶ 98 °C); ν_{\max} (Nujol) 3 385 cm^{-1} (NH) (lit.,²⁶ 3 550 cm^{-1}); δ_{H} (80 MHz; CDCl_3), 2.26 (3 H, s, Me) and 6.80–8.10 (5 H, m, ArH, NH) (lit.,²⁵ δ_{H} 2.26); λ_{\max} (MeOH) 224 (ϵ 28 000 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 282 (28 000), and 290 nm (24 600) [lit.,²⁶ 223 (28 000), 274 (8 500), 281 (930), and 289 nm (8 000)]; m/z 167 (30%), 166 (30), 165 (M^+ , 100), 164 (67), and 130 (62).

Chromatography of the residue on silica gel using chloroform as the eluant gave 2,2'-dimethyl-3,3'-bi-indolyl (**9c**) (80 mg, 12%); m.p. 223 °C (lit.,²⁹ 224 °C); ν_{\max} (Nujol) 3 400 and 3 374 cm^{-1} (NH) (lit.,²⁹ 3 400 cm^{-1}); δ_{H} ($\text{CDCl}_3 + [^2\text{H}_6]\text{Me}_2\text{SO}$), 2.25 (6 H, s, Me), 6.60–7.40 (8 H, m, ArH), and 10.40 (2 H, s, NH) (lit.,³⁰ δ_{H} [$^2\text{H}_6$] Me_2SO) 2.26, 6.60–7.60, and 10.90); λ_{\max} (EtOH) 285 (ϵ 17 800 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 291 nm (17 400) [lit.,²⁹ 285 nm (12 600)]; m/z 261 (18%), 260 (M^+ , 100), 259 (38), 245 (15), and 243 (14).

The Reaction of 2-Phenylindole (1d) with Copper(II) Chloride under Argon.—A solution of 2-phenylindole (0.96 g, 5 mmol), copper(II) chloride (1.34 g, 10 mmol), and acetonitrile (20 ml) was stirred under argon at room temperature for 10 h. The solvent was then stripped off and the residue extracted with ether to give 3-chloro-2-phenylindole (**10d**) (460 mg, 40%); m.p. 88 °C (from light petroleum) (lit.,³¹ 89 °C); ν_{\max} (Nujol) 3 283 cm^{-1} (NH) [lit.,²⁹ (KBr) 3 390 cm^{-1}]; λ_{\max} (MeOH) 246 (ϵ 21 000 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and 306 nm (18 600) [lit.,³¹ (CH_2Cl_2) 238 (20 500) and 305 nm (21 000)]; δ_{H} ($\text{CDCl}_3 + [^2\text{H}_6]\text{Me}_2\text{SO}$), 6.80–8.15 (9 H, m, ArH) and 10.70 (1 H, s, NH); m/z 229 (34%), 228 (18), 227 (M^+ , 100), 192 (13), 165 (12), and 89 (12) [lit.,³¹ 229 (34), 228 (17), 227 (100), 192 (12), 165 (13), 123 (13), and 89 (16)].

The Reaction of 2,3-Diphenylindole (1e) with Copper(II) Chloride under Argon.—A solution of 2,3-diphenylindole (0.67 g, 2.5 mmol), copper(II) chloride (1.0 g, 7.5 mmol), and acetonitrile (20 ml) was stirred under argon at room temperature for 10 h. The solvent was evaporated under reduced pressure to dryness and the residue extracted with ether. G.l.c.–m.s. analysis showed the presence of compounds (**12e**) and (**13e**) in yields as indicated in Table 1 (Entry 8). The ethereal extract was concentrated and the residue dissolved in dichloromethane (20 ml), the addition of ether to which caused the deposition of a yellow compound. Recrystallization from ethanol–ether (5:1) gave the dimer (**13e**) (110 mg, 17%); m.p. 220–222 °C (lit.,²² 225–226 °C); ν_{\max} (KBr) 3 300 cm^{-1} (NH) (lit.,²² 3 400 cm^{-1}); λ_{\max} (MeOH) 257 (ϵ 39 000 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 313 nm (31 500) [lit.,²² 257 (47 000), 314 nm (30 800)]; m/z 536 (M^+ , 100%), 459 (11), 432 (19), 356 (21), and 268 (11) [lit.,²² 536 (100), 459 (14), 432 (21), 356 (25), and 268 (14)].

The filtrate was evaporated to dryness and the residue recrystallized from light petroleum to give 3-chloro-2,3-diphenyl-3H-indole (**12e**) (260 mg, 34%), m.p. 125 °C (lit.,³¹

127–128 °C); ν_{\max} (Nujol) 1 538 cm^{-1} (CN) [lit.,³² (KCl) 1 530 cm^{-1}]; λ_{\max} (CH_2Cl_2) 223 (ϵ 10 200 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and 326 nm (11 500) [lit.,³² 225 (16 600) and 328 nm (7 600)]; m/z 305 (32%), 304 (21), 303 (M^+ , 100), and 268 (24).

Acknowledgements

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References

- W. C. Baird, Z. H. Surridge, and M. Buzi, *J. Org. Chem.*, 1971, **36**, 3324; P. H. Gemlen, M. S. Henty, and F. L. Roberts, *J. Chem. Soc., Dalton Trans.*, 1983, 1373.
- P. R. Stapp, *J. Org. Chem.*, 1979, **44**, 3216.
- J. K. Kochi, *J. Am. Chem. Soc.*, 1955, **77**, 5274; E. M. Kosower and A. S. Wu, *J. Org. Chem.*, 1963, **28**, 633.
- E. M. Kosower, W. J. Cole, G.-S. Wu, D. E. Cardy, and G. Meisters, *J. Org. Chem.*, 1963, **28**, 630.
- D. C. Nonhebel and J. A. Russell, *Tetrahedron*, 1969, **25**, 3493.
- S. R. Bansal, D. C. Nonhebel, and J. M. Mancilla, *Tetrahedron*, 1973, **29**, 993.
- T. Tsuji, H. Keruka, H. Takayanagi, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2369.
- É. Balogh-Hergovich and G. Speier, in 'Progress in Tryptophan and Serotonin Research,' eds. H. G. Schlossberger, W. Kochen, B. Linzen, and H. Steinhart, de Gruyter, Berlin, 1984, p. 669.
- É. Balogh-Hergovich and G. Speier, *Magy. Kém. Foly.*, 1977, **83**, 188.
- É. Balogh-Hergovich and G. Speier, *J. Inorg. Biochem.*, 1980, **13**, 297.
- J. Tsuji and H. Takayanagi, *Chem. Lett.*, 1980, 65.
- G. Davies and M. A. El-Sayed, in 'Copper Co-ordination Chemistry: Biochemical and Inorganic Perspectives,' eds. K. D. Karlin, J. Zubieta, Adenine Press, Guilderland, 1983, p. 281.
- M. M. Rogič, M. D. Swerdloff, and T. R. Demmin, in 'Copper Co-ordination Chemistry: Biochemical and Inorganic Perspectives,' eds. K. D. Karlin, J. Zubieta, Adenine Press, Guilderland, 1983, p. 259.
- G. Speier, Z. Tyeklár, and A. Rockenbauer, *Inorg. Chim. Acta*, 1982, **66**, L69.
- P. Capdevielle and M. Maumy, *Tetrahedron Lett.*, 1982, **23**, 1577.
- G. Speier, *Acta Chim. Acad. Sci. Hung.*, submitted for publication.
- G. Speier, *J. Mol. Catal.*, 1986, **37**, 259.
- É. Balogh-Hergovich and G. Speier, *J. Mol. Catal.*, 1986, **37**, 308.
- G. Speier, *J. Mol. Catal.*, in the press.
- (a) T. Hino and M. Nakagawa in 'Tryptophan, Kagaku-Zokan 85,' eds. K. Narita, F. Sakiyama, and M. Tokushige, Tokyo Kagaku Dojin, Tokyo, 1980, ch. 5; (b) J. Tsuji, H. Kezuka, H. Takayanagi, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2369; (c) H. von Döbeneck and W. Lehnerer, *Chem. Ber.*, 1957, **90**, 161.
- R. C. Hinman and C. P. Bauman, *J. Org. Chem.*, 1964, **29**, 1206.
- G. T. Check and R. F. Nelson, *J. Org. Chem.*, 1978, **43**, 1230.
- S. Bodfors, *Chem. Ber.*, 1925, **58**, 782.
- T. Hino, M. Nakagawa, K. Tsuneoka, S. Misawa, and S. Akaboshi, *Chem. Pharm. Bull.*, 1969, **17**, 1651.
- G. Pappalardo and T. Vitali, *Gazz. Chim. Ital.*, 1958, **83**, 1147.
- G. C. Powers, *J. Org. Chem.*, 1966, **31**, 2627.
- U. Uchino, D. Higashi, and M. Uchida, *Kumamoto. Med. J.*, 1969, **22**, 174.
- W. L. Porter and K. V. Thinmann, *Phytochemistry*, 1965, **4**, 229.
- B. Witkop and J. B. Patrick, *J. Am. Chem. Soc.*, 1951, **73**, 713.
- R. J. Sundberg, *J. Org. Chem.*, 1965, **30**, 3604.
- M. De Rosa, L. Carbognani, and A. Febres, *J. Org. Chem.*, 1981, **46**, 2054.
- M. Ikeda and Y. Tamura, *Heterocycles*, 1925, **58**, 782.