(cyclohex-2-enyl)trimethylsilane, 40934-71-2; (*trans*-5-methylcyclohex-2-enyl)trimethylstannane, 74089-89-7; (*cis*-5-methylcyclohex-2-enyl)trimethylstannane, 74089-88-6; (*cis*-3,5-dimethylcyclohex-2-enyl)trimethylstannane, 83269-39-0; (*trans*-3,5-dimethylcyclohex-2-enyl)trimethylstannane, 83269-40-3; (*cis*-5-methylcyclohex-2-enyl)trimethylgermane, 83269-41-4; (*trans*-5-methylcyclohex-2-enyl)trimethylgermane, 83269-42-5; (5-methylcyclohex-1-enyl)trimethylgermane, 83269-43-6; (*cis*-3,5-dimethylcyclohex-2-enyl)trimethylgermane, 83269-44-7; (*trans*-3,5-dimethylcyclohex-2-enyl)trimethylgermane, 83269-45-8; 5-methylcyclohex-2-enol, 3718-55-6; 3,5-dimethylcyclohex-2-enone, 1123-09-7; *cis*-3,5-dimethylcyclohex-2-enol, 32149-48-7; *trans*-3,5-dimethylcyclohex-2-enol, 83269-48-1.

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# New Aspects in the Chlorination of Indoles with 1-Chlorobenzotriazole and 1-Chloroisatin

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2-Phenyl-, 1-methyl-2-phenyl-, and 2-phenyl-3-methylindole react with 1-chlorobenzotriazole and 1-chloroisatin to form essentially 3-chloroindoles. The composition of the products, which depends on the solvent used, suggests an electron-transfer process for the reactions with 1-chlorobenzotriazole. This is supported by chemical experiments and electrochemical measurements. The reactions with 1-chloroisatin, which do not involve byproduct formation, is interpreted by classical electrophilic substitution. The different reactivities of 1-chlorobenzotriazole and of 1-chloroisatin comes from the different mobility of their chlorine atom.

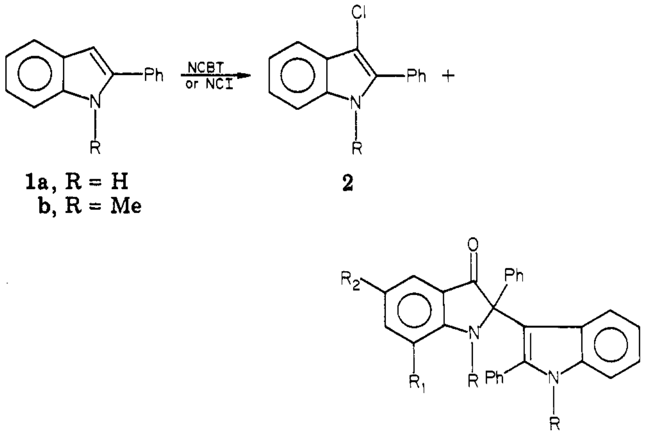
The chlorination of indoles, which normally occurs at C-3 of the indole nucleus, has been extensively studied,[1] and many reagents have been used for this reaction.[2] In 1972 an *N*-chloroindole was suggested as an intermediate in the chlorination of 2,3-dimethylindole with aqueous sodium hypochlorite.[3] More recently the formation and the stability of the *N*-chloroindole intermediate was detected and described by De Rosa.[4]

In the present paper we describe the reactions of 2-phenyl-, 1-methyl-2-phenyl-, and 2-phenyl-3-methylindole with 1-chlorobenzotriazole (NCBT), which has been successfully used in the chlorination of indole alkaloids,[5] and 1-chloroisatin (NCI), which has been recently synthesized by us.[6] Although much has been published in the way of mechanistic speculation, we now propose another possibility, which involves an electron-transfer process and which derives, above all, from the consistency of product composition.

## Results

Each indole was reacted with NCBT and with NCI. All reactions were carried out in benzene, methanol, or aqueous acetonitrile at room temperature with 20% excess reagent.

Scheme I

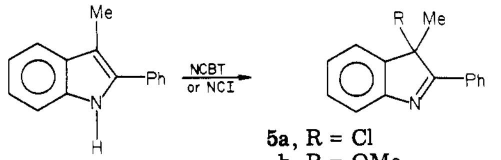


1a, R = H
b, R = Me

2

3a, R = $R_1$ = $R_2$ = H
b, R = Me; $R_1$ = $R_2$ = H
c, R = Me; $R_1$ = H; $R_2$ = Cl
d, R = Me; $R_1$ = $R_2$ = Cl

Scheme II



4

5a, R = Cl
b, R = OMe
c, R = OH
d, R = benzotriazol-1-yl

2-Phenylindole (**1a**) and 1-methyl-2-phenylindole (**1b**) with NCI gave the corresponding 3-chloro derivatives **2a** and **2b** in very good yields, independent of the solvent used (Scheme I, Table I). 2-Phenylindole with NCBT gave the 3-chloro derivative **2a** in benzene and **2a** together with 2-phenyl-2-(2-phenylindol-3-yl)-1,2-dihydro-3*H*-indol-3-one (indoxyl; **3a**) when it was reacted in methanol or aqueous acetonitrile (Scheme I, Table I). 1-Methyl-2-phenylindole (**1b**) with NCBT gave the corresponding 3-chloro derivative **2b** and indoxyls **3b–3d** when the reactions were carried out in methanol and products **2b** and **3b** when benzene was the reaction solvent, whereas when aqueous acetonitrile was the solvent the 3-chloro derivative was not isolated; only indoxyls **3b–3d** were formed (Scheme I, Table I). 2-Phenyl-3-methylindole reacted with NCI, forming

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0022-3263/82/1947-4895$01.25/0

Table I. Reactions of 1a, 1b, and 4 with NCBT and NCI[a]

| compd | reagent | solvent | products (% yields) |
|---|---|---|---|
| 1a | NCBT | $C_6H_6$ | **2a** (92) |
| 1a | NCBT | MeOH | **2a** (64), **3a** (22) |
| 1a | NCBT | $MeCN/H_2O$ | **2a** (60), **3a** (25) |
| 1a | NCI | $C_6H_6$ | **2a** (98) |
| 1a | NCI | MeOH | **2a** (97) |
| 1a | NCI | $MeCN/H_2O$ | **2a** (100) |
| 1b | NCBT | $C_6H_6$ | **2b** (95) |
| 1b | NCBT | MeOH | **2b** (40), **3b** (10), **3c** (15), **3d** (22) |
| 1b | NCBT | $MeCN/H_2O$ | **1b** (35), **3b** (5), **3c** (16), **3d** (15) |
| 1b | NCI | $C_6H_6$ | **2b** (86) |
| 1b | NCI | MeOH | **2b** (77) |
| 1b | NCI | $MeCN/H_2O$ | **2b** (94) |
| 4 | NCBT | $C_6H_6$ | **5a** (50), **5d** (21), **5c** (trace) |
| 4 | NCBT | MeOH | **5b** (75), **5c** (trace) |
| 4 | NCBT | $MeCN/H_2O$ | **5c** (56), **5d** (38) |
| 4 | NCI | $C_6H_6$ | **5a** (85) |
| 4 | NCI | MeOH | **5b** (82) |
| 4 | NCI | $MeCN/H_2O$ | **5c** (87) |

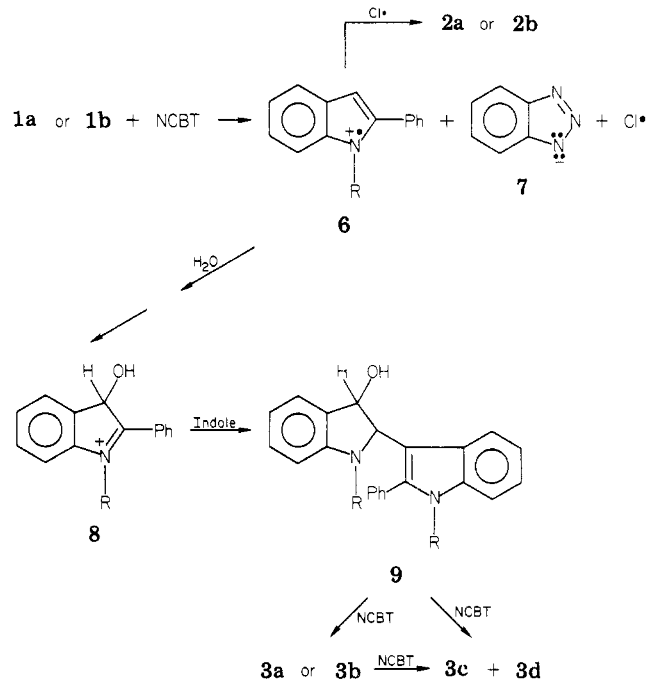
[a] NCBT = *N*-chlorobenzotriazole, NCI = *N*-chloroisatin, indole/reagent ratio = 1:1.2.

products **5a** in benzene, **5b** in methanol, and **5c** in aqueous acetonitrile. However, when it was reacted with NCBT it gave products **5a**, **5c**, and **5d** in benzene, products **5b** and **5c** in methanol, and products **5c** and **5d** in aqueous acetonitrile (Scheme II, Table II).

Compound **5a** underwent methanolysis or hydrolysis, quantitatively forming compounds **5b** and **5c**, respectively, either in acid or alkaline solution, as has been described for the corresponding 3-bromo derivative.[7] Compound **5a** also reacted with benzotriazole, forming product **5d** in good yield.

The 3-chloro derivatives **2a** and **2b** were identified by their analytical data and the absence of the H-3 in the $^1H$ NMR spectra. Products **3a**[8] and **3b**[9] were identified by comparison with authentic samples. Products **3c** and **3d** were identified by the PhNC and >C=O IR absorptions, which were typical for the indoxyls structure.[10] The indolenines **5a–d** were identified by the N=C< group absorption at ca. 1535 cm$^{-1}$ in the IR spectra and the multiplet at $\delta$ 8.4–8.6 corresponding to two ortho hydrogens of the C-2 phenyl group in the $^1H$ NMR spectra. This attribution is in agreement with the literature.[7,11] Compound **5c** was identified by comparison with an authentic sample.[12] Compound **5b** showed spectroscopic data similar to that reported by Gross et al.[7] Analytical and spectroscopic data for all new compounds are reported in Table II.

Scheme III



In the anodic oxidation, carried out in the concentration range [$10^{-4}$–($9 \times 10^{-3}$) M], **1a,b**, **3a,b**, and **4** in acetonitrile (with $Et_4NClO_4$ as supporting electrolyte) exhibit at a pulsed platinum electrode (ppe) an oxidation step at potential between 0.6 and 0.8 V (Table III). A comparison of the parameter value ($i_l/C$) reported in Table III with the one found for the first one-electron reversible anodic step of 3-(arylamino)indoles[13] under identical experimental conditions allowed us to conclude that the electrode process of compounds **1a**, **1b**, **4** and **3a**, **3b** involves one and two electrons, respectively (see $n_{app}$ values, Table III).

The cyclic voltammetric measurements at the scan rates 0.1–250 V s$^{-1}$ showed that the primary oxidation product is rather unstable in every case. In fact, at a stationary platinum electrode the oxidation process of the studied indoles is characterized by the following features: (i) an initial voltage scan from zero toward positive potentials (up to 1.2 V) showed an anodic peak, which corresponds to the oxidation step observed at the ppe; (ii) reversal of the scan showed that the corresponding complementary cathodic peak appears only at scan rates faster than 100 V s$^{-1}$, as expected for a reversible electrol transfer followed by a very rapid chemical reaction.[14] Thus, on increasing scan rates the reaction rate is no longer able to keep up with the electrode polarization rate and the system tends to become reversible. Unfortunately, the normal diagnostic aid,[14] i.e., the variation of peak current with scan rate, was not useful in these studies, since all compounds exhibited both adsorption and product filming.

On addition of increasing quantities of water (molar ratio water/reactant, 0–1000) to the solutions of indoles **1a,b**, **4**, and indoxyls **3a,b** in MeCN–$Et_4NClO_4$, the oxidation step of **3a,b** and **4** was unaffected, whereas that of **1a,b** increased in height until it about doubled the original step recorded in anhydrous acetonitrile (i.e., it became bielectronic, see Table III).

Controlled-potential electrolyses at 0.8 V of indoles **1a** and **1b** in anhydrous or in aqueous acetonitrile involved about 2 faraday/mol of reactant in each case. Nevertheless, it should be noted that in both media (aqueous and nonaqueous) the current was higher that the background current; furthermore, in anhydous acetonitrile it decays

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Table II. Analytical and Spectroscopic Data of New Compounds

| compd[a] | solvent[e] | mp, °C | IR ($\nu$), $cm^{-1}$ [b] | $^1H$ NMR, $\delta$ |
|---|---|---|---|---|
| 2a | A | 80 | 3390[f] | |
| 2b | A | 78 | | 3.62 (1 H, s, NMe), 7.1–7.9 (9 H, m, arom) |
| 3c | B | 235 | 1705[g]<br>1625[h] | 2.76 (3 H, s, NMe, indolinic), 3.44 (3 H, s, NMe, indolic), 6.4–7.4 (17 H, m, arom) |
| 3d | B | 236 | 1705[g]<br>1610[h] | 3.26 (3 H, s, NMe, indolinic), 3.45 (3 H, s, NMe, indolic), 6.4–7.6 (16 H, m, arom) |
| 5a | | oil | 1530[c,i] | 2.02 (3 H, s, Me), 7.3–7.9 (7 H, m, arom), 8.4–8.7 (2 H, m, arom) |
| 5d | A | 160 | 1535[i] | 2.50 (3 H, s, Me), 6.45–6.60 (1 H, d, arom), 7.1–8.1 (12 H, m, arom) |
| 10b | B | 185 | 3340[f]<br>1690[g]<br>1615[h] | 7.1 (1 H, d, H-7, $J$ = 9.7 Hz), 7.3–7.6 (12 H, m, arom)[d] |

[a] Satisfactory analytical data (±0.4% for C, H, N) were obtained for all compounds. [b] In Nujol. [c] In neat. [d] In acetone-$d_6$. [e] A, *n*-heptane; B, ligroin, 100–135 °C. [f] NH. [g] C=O. [h] PhNC. [i] N=C<.

Table III. Electrochemical Data for the Oxidation at a Pulsed Platinum Electrode of Indoles 1a, 1b, 4 and 3a, 3b in Anhydrous and Aqueous MeCN[a]

| compd | $r$ | $E_{1/2}$, V | $i_l$, $\mu A$ | $i_l/C$, $\mu A\ mM^{-1}$ | $n_{app}$ |
|---|---|---|---|---|---|
| 1a | 0 | 0.73 | 2.12 | 1.7 | 1 |
| | 600 | 0.74 | 4.10 | 3.3 | 2 |
| 1b | 0 | 0.64 | 2.20 | 1.8 | 1 |
| | 600 | 0.66 | 4.10 | 3.4 | 2 |
| 4 | 0 | 0.58 | 2.32 | 1.9 | 1 |
| | 620 | 0.56 | 2.32 | 1.9 | 1 |
| 3a | 0 | 0.79 | 4.00 | 3.3 | 2 |
| | 650 | 0.79 | 4.02 | 3.3 | 2 |
| 3b | 0 | 0.69 | 4.05 | 3.4 | 2 |
| | 680 | 0.69 | 4.04 | 3.4 | 2 |

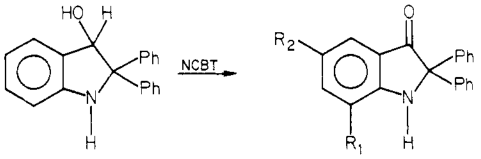
[a] Solutions were MeCN (with or without added $H_2O$)–0.1 M $Et_4NClO_4$–ca. $1.2 \times 10^{-3}$ M reactant; $T$ = 20 °C; electrode pulse time = 2 s; $r$ = molar ratio of $H_2O$ added/reactant; potentials refer to Ag|0.1 M $AgClO_4$ in MeCN; $n_{app}$ = number of electrons involved in the anodic step as determined by comparison of parameter $i_l/C$ with that obtained for the reversible one-electron oxidation step of 3-(arylamino)indoles[13] under identical conditions.

very slowly to the same value, i.e., in anhydrous MeCN also, the primary oxidation product reacted to give species that could be further oxidized at the same potential.

## Discussion and Conclusions

When 2-phenylindole (**1a**) and 1-methyl-2-phenylindole (**1b**) were reacted with NCBT, the product composition varied when the solvent was varied and, in particular, in the case of **1b**, the 3-chloro derivative **2b** did not form at all in aqueous acetonitrile (Table I). These results prompted us to assume the reactions of indoles **1a** and **1b** with NCBT involved the formation of the radical cation **6**. Thus, the mechanism tentatively proposed could be that shown in Scheme III. The radical cation **6** in the presence of an inert solvent, such as dried benzene, yielded essentially 3-chloro derivatives **2a** and **2b**, whereas it might react with nucleophilic reagents such as water, leading to intermediate **8**, in agreement with that described by others.[15-17] The reaction of **8**, with another molecule of starting indole, leads to the intermediate **9**, as supported by other examples described in the literature.[18-20]

Scheme IV



**10**

**11a**, $R_1 = R_2 = H$
**b**, $R_1 = H$; $R_2 = Cl$
**c**, $R_1 = R_2 = Cl$

The anodic oxidations of indoles **1a** and **1b** were carried out in aqueous acetonitrile to explain the proposed mechanism. Unfortunately, indoxyls **3a** and **3b**, which were the expected products, were not isolated owing to their oxidation potential ($E_{1/2}$ = 0.79 and 0.69 V, respectively), which were in the range of the corresponding indoles (Table III). But if the indole **1b** is reacted with $Ce(NH_4)_2(NO_3)_6$ in aqueous acetonitrile, indoxyls **3b** is isolated, albeit in poor yield. These results and the proposed mechanism were also supported by the fact that the oxidation of indole **1b** with NCBT in benzene at low temperature and with Ce(IV) in methanol at room temperature in the ESR cavity gave an intense signal.

We think that indoxyls **3a** and **3b** were formed by NCBT oxidation of the intermediate **9**. In fact, compound **10**, chosen as a model, can be oxidized and chlorinated by NCBT to form compounds **11a–c**. (Scheme IV) This experiment could also explain the formation of the chlorinated indoxyls **3c** and **3d** in the case of **1b** (Table I). Because indoxyl **3c** was also formed by treating indoxyl **3b** with an equimolar quantity of NCBT, it remains difficult to say whether the chlorinated indoxyls **3c** and **3d** were formed by chlorination of **3b** or of intermediate **9**, on the basis of the experiments described above.

For 2-phenyl-3-methylindole (**4**) we had no experimental chemical evidence for the formation of the radical cation intermediate. The reaction of **4** with NCBT, followed by TLC, showed that the first product was the 3-chloroindolenine **5a**, which underwent hydrolysis or methanolysis in the presence of water or methanol. The formation of compound **5d** can be explained by the reaction of **5a** with benzotriazole. This supposition, the hydrolysis and the methanolysis of **5a** were confirmed by independent experiments.

Since the anodic oxidation of **4** in aqueous acetonitrile gave 3-hydroxyindolenine **3c** and since the half-wave oxidation potential of **4** is 0.58 V, i.e., a value lower than those for the indoles **1a** and **1b** (Table III), we assume the for-

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mation of the intermediate radical cation is also involved for the indole 4.

Table I shows that the reactions of indoles **1a** and **1b** with NCI were not affected by the presence or absence of water and that the formation of 3-chloro derivatives **2a** and **2b** took place in good yields. This means that the NCBT and NCI react by different mechanisms, and, furthermore, no signal was recorded when **1b** was oxidized with NCI in the ESR cavity.

The potentials ($E_{1/2}$ vs. satured calomel electrode) of the first irreversible two-electron reduction step measured at a dropping mercury electrode for NCBT (−2.1 V) and NCI (−0.4 V) in DMF with $Bu_4NClO_4$ as supporting electrolyte show a higher mobility of the chlorine atom for NCI compared to NCBT.

On the basis of these observations we deduced that the reactions between indoles and NCI follow the classical mechanism of aromatic electrophilic substitution, involving a positive chlorine.

In summary, the strong oxidation power of NCBT[21] is in agreement with the proposed mechanism, and the oxidation power of NCI[6] is not able to induce the electron-transfer process. Furthermore, NCI can be considered a good chlorinating agent for the synthesis of 3-chloroindoles without the formation of byproducts.

## Experimental Section

Melting points are uncorrected. $^1$H NMR spectra were recorded in deuterated chloroform, if not otherwise specified, with a Varian XL-100 spectrometer with internal tetramethylsilane as the reference. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Compounds **1a**,[22] **4**,[23] **10**,[24] NCBT,[25] and NCI[6] were prepared as described in the literature. **1b** was a commercial Fluka product. Unless otherwise specified, chromatographies were performed on silica gel, eluting with benzene.

**Reaction of 1a, 1b, and 4 with NCBT. a. In Benzene.** A 5-mmol sample of indole in 25 mL of benzene and 6 mmol of NCBT in 25 mL of benzene were mixed at room temperature. After 3 h the precipitated benzotriazole was filtered off and the filtrate was chromatographed.

**b. In Methanol.** Reactions were performed and worked up as described in method a using the same quantities of reagent and solvent.

**c. In Aqueous Acetonitrile.** A 5-mmol sample of indole in 30 mL of 5% aqueous acetonitrile and 6 mmol of NCBT in 10 mL of acetonitrile were mixed at room temperature. After 3 h the solution was evaporated to dryness. The residue, taken up with benzene, gave benzotriazole, which was separated by filtration, and the filtrate was chromatographed.

The isolated compounds and the corresponding yields for each reaction are reported in Table I.

**Reaction of 1a, 1b, and 4 with NCI. a. In Benzene.** A 5-mmol sample of indole in 25 mL of benzene and 6 mmol of NCI in 50 mL of benzene were mixed at room temperature. After 3 h the precipitated isatin was filtered off and the filtrate chromatographed.

**b. In Methanol.** The reaction was performed as described in method a, using 25 mL and 20 mL of methanol to dissolve the indole and NCI, respectively. After 3 h the solution was evaporated to dryness and the residue, taken up with benzene, gave the isatin, which was filtered off, and the filtrate was chromatographed.

**c. In Aqueous Acetonitrile.** A 5-mmol sample of indole in 30 mL of 5% aqueous acetonitrile and 6 mmol of NCI in 20 mL of acetonitrile were mixed at room temperature. After 3 h the solution was evaporated to dryness and the residue, taken up with benzene, gave isatin, which was filtered off, and the filtrate was chromatographed. The isolated compounds and the corresponding yields are reported in Table I for each reaction.

**Methanolysis of 5a. a. In Alkaline Solution.** Compound **5a** (300 mg) was dissolved in 20 mL of 2% sodium methylate. After 2 h the reaction solution was poured into 50 mL of water and extracted with benzene (2 × 25 mL). The benzene layer, separated and dried on $Na_2SO_4$, was chromatographed. Compound **5b** was isolated in quantitative yield.

**b. In Acid Solution.** Compound **5a** (300 mg) was dissolved in 10 mL of 2% hydrochloric acid methanol. After 2 h compound **5b** was isolated in 95% yield, working as described in method a.

**Hydrolysis of 5a. a. In Alkaline Solution.** NaOH (10%, 2 mL) was added to **5a** (300 mg) in 20 mL of acetonitrile. Compound **5c** was isolated in quantitative yield, working as described for the methanolysis.

**b. In Acid Solution.** Concentrated hydrochloric acid (3 mL) was added to a solution of **5a** (300 mg in 10 mL of acetonitrile). After 3 h compound **5c** was isolated in quantitative yield, working as described for the methanolysis.

**Reaction of 5a with Benzotriazole.** Compound **5a** (300 mg in 20 mL of acetonitrile) and benzotriazole (400 mg in 20 mL of acetonitrile) were mixed at room temperature. After 24 h the precipitate, benzotriazole hydrochloride, was filtered off and the filtrate was chromatographed. **5d** (300 mg) was isolated.

**Chlorination of 5b with NCBT.** Indoxyl **5b** (150 mg in 5 mL of benzene) and NCBT (54 mg in 3 mL of benzene) were mixed at room temperature. After 3 h the solution was poured into 10% aqueous $NaHCO_3$ (10 mL). The benzene layer, separated and dried on $Na_2SO_4$, was chromatographed by preparative TLC of silica gel, eluting with benzene; 46 mg of **3c** was isolated.

**Oxidation and Chlorination of 10.** The 3-hydroxyindoline **10** (100 mg in 10 mL of benzene) and NCBT (100 mg in 5 mL of benzene) were mixed at room temperature. After 3 h a mixture of benzotriazole and benzotriazole hydrochloride was filtered off, and the filtrate was chromatographed by preparative TLC of silica gel, eluting with benzene. Compounds **10a**–**10c** were isolated in 40%, 15%, and 35% yields, respectively. Compounds **10a**[12] and **10c**[24] were identified with authentic samples.

Analytical and spectroscopic data of **10b** are reported in Table II.

**Oxidation of 1b with Cerium(IV).** $Ce(NH_4)_2(NO_3)_6$ (300 mg) was added to **1b** (100 mg in 20 mL of 5% aqueous acetonitrile) and the mixture was stirred for 4 h at room temperature. The solution was then poured into water (50 mL) and extracted with benzene. The benzene layer, separated and dried on $Na_2SO_4$, was chromatographed. Compound **3b** was isolated in 7% yield.

**Oxidation of 1b with NCBT, NCI, and Cerium(IV) in the ESR Cavity.** NCBT (1 mL of $10^{-1}$ M benzene solution) was added to a solution frozen with liquid nitrogen of **1b** (1 mL of $10^{-1}$ M benzene solution). The mixture was completely frozen and then transferred to the ESR cavity. An intense and unresolved ESR signal was recorded. No signal was obtained when the experiment was performed with NCI. Equimolar quantities of methanol solution of indole **1b** and $Ce(NH_4)_2(NO_3)_6$ were mixed in the ESR cavity at room temperature; a signal like that described above was recorded.

**Electrochemical Measurements. Apparatus and Procedures.** A three-electrode multifunction assembly (Amel 471) was employed. The working electrode was a pulsed[26] (or stationary in the case of linear sweep voltammetry) platinum disc (Amel 492) of about 1 mm in diameter. Before each experiment the disc was polished with 0.05 μm of polishing alumina, washed with distilled water and acetone and, finally, rubbed gently with a paper towel. The reference electrode assembly was Ag|0.1 M $AgClO_4$–MeCN|fine-porosity fritted glass disk|0.1 M $Et_4NClO_4$–MeCN|fine-porosity fritted glass disk. The counterelectrode was a platinum wire. $Et_4NClO_4$ (Erba RS grade for polagraphy) was used as supporting electrolyte and vacuum dried at 60 °C for 3 days. Argon (99.99%), used to deoxygenate the solutions, was passed through a column of molecular sieves (4-A type), a column of Granusic A (Baker) and, finally, a solution containing the

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supporting electrolyte and reactant at the same concentration as the test solution. During all measurements the temperature was kept constant within ±0.1 °C. Cyclic voltammetric experiments were performed with an oscillopolarograph (Amel 448) using the same cell as for the measurements at low polarization rates. Coulometric determinations and macroscale electrolysis at controlled potentials were carried out with a potentiostat (Amel 552) coupled with an integrator (Amel 721) and a recorder (Amel 867). In a typical run, 50–70 mg of reactant was dissolved in 20–30 mL of MeCN–0.1 M $Et_4NClO_4$. The solution was then electrolyzed at an appropriate potential (0.65–0.85 V), using a platinum-gauze cylinder (1.5-cm diameter) as a working electrode, with a Ag|0.1 M $AgClO_4$–MeCN as reference and a platinum spiral as a counterelectrode separated from the test solution by a fine-porosity fritted glass disks. The solution was magnetically stirred and covered with a continuous argon flow. After the current had fallen to its background value, the solution was evaporated under vacuum and the residue was taken up with benzene (10 mL). The insoluble supporting electrolyte was filtered off, and the filtrate was chromatographed. Only from indole **4**, electrolyzed in aqueous acetonitrile, was the 3-hydroxyindolenine **5c** isolated (10% yield).

**Registry No.** **1a**, 948-65-2; **1b**, 3558-24-5; **2a**, 76794-16-6; **2b**, 82665-92-7; **3a**, 53904-10-2; **3b**, 58863-88-0; **3c**, 82665-93-8; **3d**, 82665-94-9; **4**, 10257-92-8; **5a**, 65837-35-6; **5b**, 78024-78-9; **5c**, 1213-48-5; **5d**, 82665-95-0; **10**, 74441-25-1; **11a**, 1922-77-6; **11b**, 82665-96-1; **11c**, 82665-97-2; 1-chlorobenzotriazole, 21050-95-3; 1-chloroisatin, 2959-03-7.

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# Coal Liquefaction Model Studies: Free Radical Chain Decomposition of Diphenylpropane, Dibenzyl Ether, and Phenyl Ether via β-Scission Reactions

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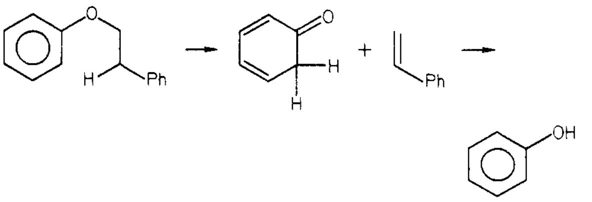
The thermal decompositions of 1,3-diphenylpropane (1), dibenzyl ether (2), and phenethyl phenyl ether (3) have been found to proceed by free radical chain processes. **1** gave toluene and styrene with a reaction order of 1.55, $E_A = 51.4$ kcal/mol, and log $A = 12.5$. The reaction could be initiated by benzyl phenyl ether but not by 1,2-diphenylethane. **2** gave toluene and benzaldehyde with a reaction order of 1.43, $E_A = 48$ kcal/mol, and log $A = 12.6$. The reaction could be initiated with benzyl phenyl ether. **3** gave phenol and styrene with a reaction order of 1.21, $E_A = 50.3$ kcal/mol, and log $A = 12.3$. The reaction could be initiated by benzyl phenyl ether. All of the data are consistent with free radical chain processes with the reaction order determined by the termination reaction. No evidence for concerted reactions has been found.

The thermal conversion of coal into a liquid material has been postulated to involve the formation of free radicals by the homolysis of covalent bonds in short, linear linkages which join the polycyclic clusters of coal into a polymeric network.[1] Prior studies have shown that one-atom links are stable unless substituents on the aromatic rings allow isomerization to more reactive, nonaromatic species.[2,3] Two-atom links are cleaved in a simple bond homolysis which, in most liquefaction studies, is followed by hydrogen abstraction from a hydrogen-donating solvent.[4] Three-atom links have received relatively less attention although the potential chemistry is more complex as simple homolysis reactions, radical chain processes, and concerted unimolecular reactions are all possible. Herein we report the thermal decomposition of 1,3-diphenylpropane (**1**), dibenzyl ether (**2**), and phenethyl phenyl ether (**3**), which serve as models for the thermal chemistry of three-atom linkages in coal and all of which react by free radical chain processes.

Diphenylpropane (**1**) has been reported to give equal amounts of styrene and toluene in a reaction that is 1.6 order in **1**.[5] A free radical chain process has been proposed to explain these observations. This reaction has been reinvestigated here along with studies of initiation by free radical initiators which provide further support for the free radical chain mechanism hypothesis.

Dibenzyl ether (**2**) has previously been reported to give equal amounts of benzaldehyde and toluene in a first-order process with an activation energy of 36 kcal/mol.[6] The formation of benzaldehyde and toluene suggests a free radical process, but the reaction order and activation energy are inconsistent with this explanation. Furthermore, the low activation energy is not consistent with a concerted unimolecular reaction. However, these studies were carried out in tetralin, which is very difficult to purify and raises the possibility of initiation of a free radical process by an impurity in the tetralin. Also these authors did not purify **2** prior to use which might have resulted in peroxide-initiated reactions. Thus, the thermal chemistry of **2** is unclear.

Phenethyl phenyl ether (**3**) has been found to give phenol and styrene (eq 1) in a first-order process with



(1)

activation parameters of log $A = 11$ and $E_A = 45$ kcal/mol.[7]

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