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# Ambident Reactivity of Anisole and *p*-Iodoanisole toward Phenylium Cations and Evidence for *ipso*-Attack in Cationic Phenylation

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The phenylation of *p*-iodoanisole from the thermolysis of benzenediazonium tetrafluoroborate affords, among other products, 4-methoxybiphenyl and 4-iododiphenyl ether, providing evidence for the occurrence of *ipso*-attack and attack on oxygen by $C_6H_5^+$. In the case of anisole, the oxygen atom of the methoxy-substituent is also attacked by $C_6H_5^+$ giving rise to diphenyl ether *via* the initial formation of diphenylmethyloxonium ion followed by intermolecular demethylation. We have demonstrated that no intramolecular rearrangement occurs with the oxonium ion. The results are consistent with a mechanism involving kinetically predominant *C*-phenylation of both substrates. Boron trifluoride (a Schiemann reaction product) promotes deiodination of *p*-iodoanisole and its phenylated isomers. This deiodination invalidates the conclusions drawn from isomeric distributions; therefore the presence of $BF_3$ must be carefully controlled in a mechanistic study.

The thermal decomposition of arenediazonium salts in aprotic polar solvents of low nucleophilicity, such as acetonitrile, exclusively generates aryl cations.[1,2] The structure and multiplicity of these aryl cations have been investigated from both theoretical and experimental points of view.[3] A triplet state for arenediazonium cations bearing strongly electron-donating substituents has been predicted [4] and been experimentally observed.[5] On the other hand, molecular orbital calculations indicate the ground state of the phenylium cation to be a singlet.[6] Furthermore, the relative reactivity pattern for arylation of aromatic compounds with various *para*-substituted aryl cations (*e.g.* Me, Cl, $NO_2$) supports a singlet ground state for these species.[2] Therefore, the intermediacy of a spirocyclopropane phenonium ion [7] in the rate-determining step of the cationic phenylation of aromatic compounds seems unlikely. However, Abramovitch's initial proposal of a separate intermediate preceding the formation of the σ-complex might be retained, since $C_6H_5^+$ is highly reactive [6d] and unselective.[7,8] Indeed, in our previous studies of cationic phenylation of methylarenes [9] we have shown that the substrate selectivity reveals a remarkable degree of similarity with that of the nitration by $NO_2^+BF_4^-$.[10] We therefore suggested that cationic phenylation might proceed according to the general scheme of nitration of reactive aromatic compounds.[11,12]

The *ipso*-mechanism is well documented for several electrophiles [13] but has never been demonstrated for $C_6H_5^+$. During studies on cationic phenylation of 1,4-dimethylnaphthalene [9] the 2-position appeared to be the most reactive towards $C_6H_5^+$ as has been observed for other electrophiles.[14,15] Since the protonation of 1,4-dimethylnaphthalene occurs readily at the *ipso*-position [16] we suggested that 2-phenyl-1,4-dimethylnaphthalene results in part from the *ipso*-σ-complex followed by a 1,2-phenyl shift. In order to demonstrate $C_6H_5^+$ attack at a substituted position in an aromatic ring, we chose *p*-iodoanisole as substrate which bears a substituent of high leaving ability ($I^+$) at the 4-position activated by the methoxy-group. Previous studies of the nitration,[17] nitrosation,[18] and sulphonation [19] of *p*-iodoanisole have demonstrated that *ipso*-attack at the carbon bearing the iodine is possible.

The choice of the substrate provides an unexpected dividend as $C_6H_5^+$ attacks not only the carbon atoms but also the oxygen atom of *p*-iodoanisole. *O*-Attack has not been demonstrated in the cationic phenylation of anisole.[7] The electrophilic *O*-alkylation of anisole by alkyl fluoroantimonates in solution,[20,21] as well as by t-butylium ions [22] and dimethylhalogenium ions in the gas phase [23] has been observed. Therefore we reinvestigated the electrophilic phenylation of anisole, looking for products which might arise from the *O*-phenylation of anisole by $C_6H_5^+$.

**Table 1.** Product distribution in the thermal decomposition of benzene tetrafluoroborate and its crown ether complex in anisole[a]

| Experimental conditions | Ratios of phenylanisoles C-2 | C-3 | C-4 | *C*-Phenylation | *O*-Phenylation | Yield |
|---|---|---|---|---|---|---|
| $C_6H_5N_2^+BF_4^-$ in $CH_3CN$ solution | 56 | 12.5 | 31.5 | 82 | 18[b] | 15[c] |
| $C_6H_5N_2^+BF_4^-$ in anisole | 59 | 10 | 31 | 78 | 22 | 5 |
| Crown complex in anisole | 53 | 13.5 | 33.5 | 76.5 | 23.5 | 35 |

[a] 2-Methyl- and 4-methyl-anisole were obtained in variable yields; with the crown ether complex of (I), the ratio of isomeric methylanisoles to diphenyl ether was 0.6. [b] A small amount of diphenyl ether is removed by crystallization together with acetanilide prior the g.l.c. analysis. [c] This yield rose to 20% according to the anisole concentration.

## Results and Discussion

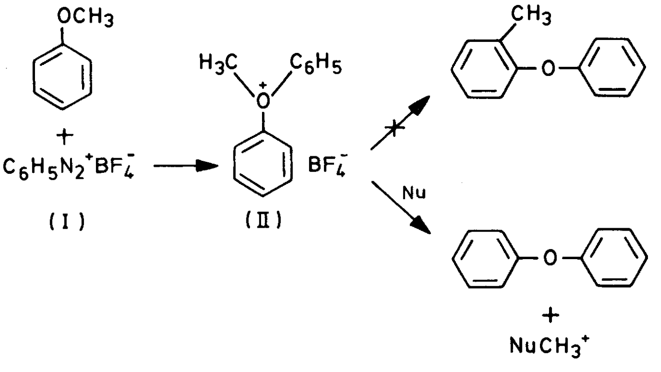
*Phenylation of Anisole.*—The phenylanisole ratios obtained after decomposition of benzenediazonium tetrafluoroborate (I) in acetonitrile–anisole (homogeneous) and anisole (heterogeneous) are in close agreement with those reported by Abramovitch *et al.*[7,24] In the cationic phenylation of anisole (Table 1), the product distributions are not significantly affected by the experimental conditions. Attempts were made to increase the yield of phenylated products by using a crown ether to make the reaction mixture homogeneous.[25] Indeed, a sevenfold increase in the yield of the phenylated products up to 35% resulted from the addition of the crown ether, whereas the maximum yield in acetonitrile is *ca.* 20% .This result can be explained by the absence of a polar co-solvent competing with anisole for $C_6H_5^+$.

In addition to isomeric phenylanisoles, cationic phenylation also produced diphenyl ether and methylanisoles, the form-

**Table 2.** Phenylated product distribution in the thermal decomposition of benzenediazonium tetrafluoroborate in *p*-iodoanisole

| | *O*-Phenylation | *C*-Phenylation | *C*-Phenylation product distribution | | | |
|---|---|---|---|---|---|---|
| Experimental conditions | (IV) | (V) + (VI) + (VIII) | (V) | (VI) | (VIII) | ratio (IX) : (VIII) |
| $C_6H_5N_2^+$ $BF_4^-$ in *p*-iodoanisole | 32.5 | 67.5 | 77.5 | 13 | 9.5 | 10 |
| $C_6H_5N_2^+$ $BF_4^-$ in acetonitrile | 25.5 | 74.5 | 70 | 18 | 12 | 4.2 |
| Crown complex in *p*-iodoanisole | 30 | 70 | 60 | 21.5 | 18.5 | 0.5 |
| $C_6H_5N_2^+$ $BF_4^-$ in *p*-iodoanisole [a] | 25 | 75 | 57.5 | 22 | 20.5 | 1.2 |
| $C_6H_5N_2^+$ $BF_4^-$ in acetonitrile [a] | 28.5 | 71.5 | 58.5 | 22.5 | 19 | 0.3 |
| $C_6H_5N_2^+$ $BF_4^-$ in acetonitrile [b] | 39 | 61 | 83 | 2 | 15 | >25 |

[a] Performed under nitrogen. [b] Thermolysis of (I) in acetonitrile solution under nitrogen stream, was followed by heating with boron trifluoride–ether.



**Scheme 1.**

ation of which has not been reported previously. We have very little alternative but to propose that $C_6H_5^+$ attacks the oxygen atom of anisole giving rise to the diphenylmethyloxonium ion (II) which decomposed to products according to Scheme 1. Several facts support this idea.

(i) In view of the fact that the triphenyloxonium ion has been prepared by thermal decomposition of (I) in diphenyl ether,[26] the formation of (II) from (I) and anisole seems likely.

(ii) Dialkylaryloxonium ions are electrophiles and their alkylating ability is well documented;[20–22] one may assume that (II) should have similar behaviour. The formation of methylanisoles and of diphenyl ether by methyl transfer from (II) to anisole is therefore to be expected. Since the amount of methylanisoles detected is inferior to that of diphenyl ether, a competitive reaction of the methyl group of (II) with $BF_4^-$ [27] is not excluded.

(iii) The presence of an alkylating species is confirmed by the toluene formed when the reaction is carried out in anisole–benzene.

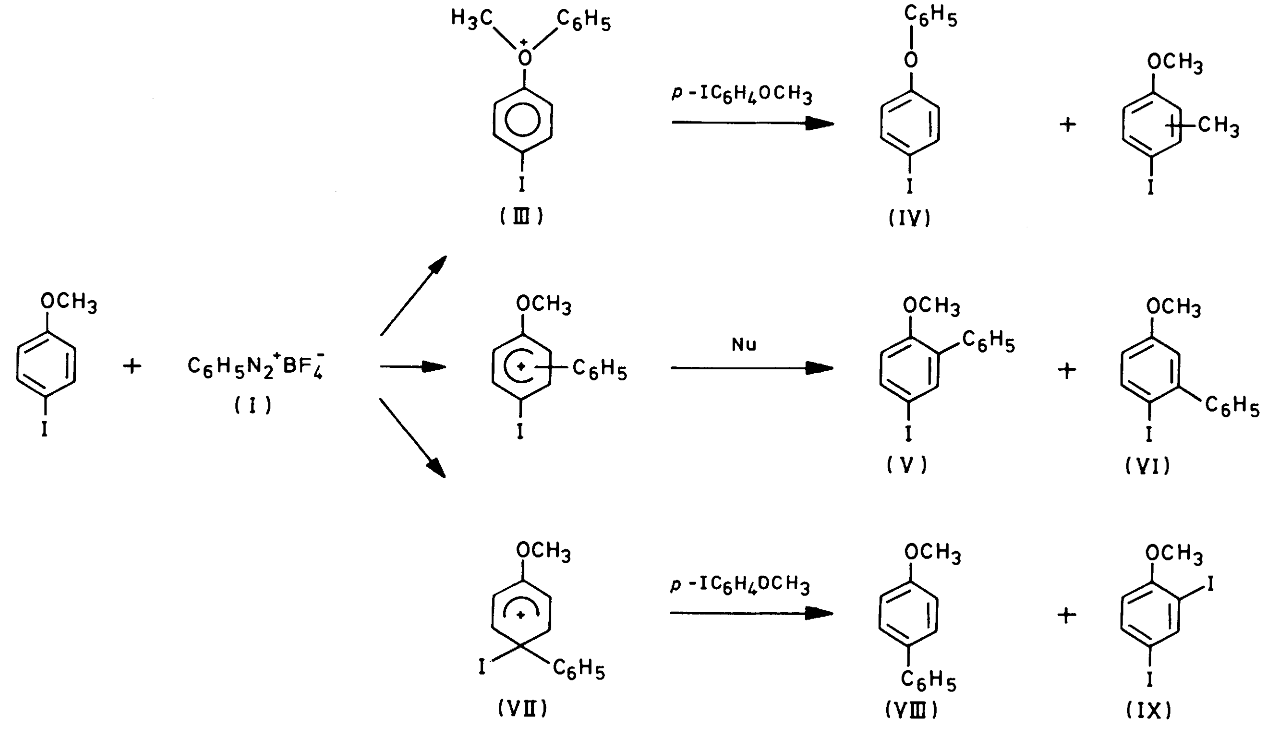
An intramolecular rearrangement of dimethylphenyloxonium ion has been postulated to account for the unusually large amount of *ortho*-isomer obtained in the Friedel–Crafts alkylation of anisole.[28] Dimethylphenyloxonium ion has been prepared and isolated;[20] the authors of this work showed that intramolecular rearrangement is of minor importance but they did not exclude it.[20] Granted that the formation of (II) is accepted, we have a tool for studying the fate of diphenylmethyloxonium ion since intermolecular attack by a nucleophile and intramolecular rearrangement should give two different products, *i.e.* diphenyl ether and phenoxytoluene, respectively. Since we did not detect any phenoxytoluene by g.l.c. analysis, intramolecular methyl migration to the ring can be definitely excluded at least as far as our experimental conditions are concerned.

Although (II) can act as a methylating agent we assume that it cannot act as a $C_6H_5^+$ source, since the solvolysis of methyl trifluoromethanesulphonate generates methyl cations whereas the solvolysis of aryl trifluoromethanesulphonates does not generate aryl cation.[29] Furthermore the triphenyloxonium ion is extremely stable even in aqueous solution [26] and does not seem to act as a phenylating agent. Therefore, the ratio of diphenyl ether to phenylanisoles is kinetically significant, representing the *O*- and *C*-phenylation process. Then, as shown in Table 1, *C*-phenylation is four times greater than *O*-phenylation.

*Phenylation of* p-*Iodoanisole*.—The thermolysis of (I) in *p*-iodoanisole–acetonitrile (homogeneous) and in fused *p*-iodoanisole (heterogeneous) gave complex reaction mixtures as shown in Table 2. Products such as 4-iododiphenyl ether (IV), 4-iodo-2-phenylanisole (V), 4-iodo-3-phenylanisole (VI), and 4-methoxybiphenyl (VIII) presumably resulted from $C_6H_5^+$ attack on *p*-iodoanisole. In addition, fluorobenzene and boron trifluoride (the Schiemann reaction products) and other by-products were obtained, *e.g.* 2,4-di-iodoanisole (IX), the two isomeric methyl-*p*-iodoanisoles, fluorobiphenyls, anisole, and iodine. The relative yields of these by-products were dependent upon the conditions of the reaction.

The isolation of only *p*-phenylanisole without the presence of the *ortho*-isomer is significant since the *ortho*-isomer dominates in the $C_6H_5^+$ phenylation of anisole. This must imply that the *para*-isomer was not formed from a $C_6H_5^+$ attack on anisole formed *in situ*, but from an *ipso*-substitution on *p*-iodoanisole. This provides the first evidence of *ipso*-attack by $C_6H_5^+$. Iodonium ion can be abstracted from the *ipso*-σ-complex by *p*-iodoanisole acting as a nucleophile and giving us (IX) (Scheme 2). Since $I^+$ can be abstracted by other nucleophiles present in the reaction mixture, the ratio (IX) : (VIII) should be smaller than 1. Surprisingly the reverse was observed (Table 2) with the exception of the experiments performed in acetonitrile solution under nitrogen or in the presence of the crown complex of (I). In our opinion the unexpectedly high yields of (IX) can be explained by $BF_3$ attack on *p*-iodoanisole, perhaps at the *ipso*-position, $I^+$ being removed from the intermediate complex by another *p*-iodoanisole molecule and giving us (IX), anisole, and $BF_3$. Several observations support this explanation.

(i) By adding boron trifluoride–ether to fused *p*-iodoanisole under thermolysis conditions we obtained (IX) and anisole with a stoicheiometry of 1 : 1. Therefore it appears that the Lewis acid catalyses the disproportionation of *p*-iodoanisole as is the case with mineral acids.[19,30,31] Heating of boron trifluoride–ether solution in acetonitrile–*p*-iodoanisole also produced (IX) and anisole, but since the amount of (IX) was smaller than that of anisole, acetonitrile might compete with *p*-iodoanisole for the iodinating species. Note that in the thermolysis of (I) the ratio (IX) : (VIII) is smaller in the homogeneous reaction than in the heterogeneous reaction.



Scheme 2.

(ii) By sweeping out $BF_3$ with a nitrogen stream,* the ratio (IX) : (VIII) fell from 4.2 to 0.3 and from 10 to 1.2 in the homogeneous and heterogeneous thermolysis of (I), respectively.

(iii) By subjecting the reaction mixture in which the ratio (IX) : (VIII) was equal to 0.3 to the action of $BF_3$, this ratio became $>25$ and the distribution of the phenylated product was greatly modified (Table 2).

In the presence of $BF_3$, the distribution of the phenylated product was different under homogeneous and heterogeneous conditions. We think that some iodinated phenyl isomers are preferentially attacked by $BF_3$. Indeed with the nitrogen stream (*i.e.* low concentration of $BF_3$), the distributions of the phenylated products in the homogeneous and heterogeneous thermolysis of (I) are almost identical. Likewise, a similar distribution was observed in the presence of a crown ether.† Note that, as observed for anisole, the yields in phenylated products were greatly improved.

In conclusion the isomeric distribution in cationic phenylation of *p*-iodoanisole is strongly dependent on $BF_3$ concentration; the smaller the $BF_3$ concentration the more straightforward the results. Therefore, in the ensuing discussion on reactivity, we shall consider the data from experiments having a (IX) : (VIII) ratio of $<1$. As expected, cationic phenylation occurs to a noticeable extent at a position activated by a methoxy-group giving the ratio *ipso*-substitution to *C*-substitution of 1 : 5. This result lends support to our previous assumption for an *ipso*-attack of 1,4-dimethylnaphthalene since the 1-position of naphthalene, which is four times more reactive than the 2-position,[32] is activated by both methyl substituents.[33]

Cationic phenylation of *p*-iodoanisole exhibits low intramolecular selectivity and comparisons with reactions of other electrophiles, such as nitration and sulphonation, are very difficult. In fact some doubt remains about the importance of nitrosation during nitration of *p*-iodoanisole [18] and the product distribution obtained by its sulphonation has not been reported.[19]

*O*-Phenylation of *p*-iodoanisole occurs readily up to 30% of the total phenylated products, while that for anisole represents *ca.* 22%. This indicates the iodine substituent slightly deactivates the aromatic ring.

## Experimental

*Reagents.*—Anisole was distilled prior to use; *p*-iodoanisole was recrystallized from ethanol and dried under vacuum. Acetonitrile (Fluka, purum) kept over molecular sieves was used without further purification. Benzenediazonium tetrafluoroborate was prepared from freshly purified aniline and sodium tetrafluoroborate. Boron trifluoride–ether (Fluka, prakt.) was distilled under nitrogen before use.

*Analytical Procedure.*—The g.l.c. analyses were performed on a Varian 2400 gas chromatograph equipped with a hydrogen flame ionization detector. The mass spectra were measured on an AEI MS-30 mass spectrometer. For combined g.l.c.–mass spectrometry a Girdel ' série 75 ' gas chromatograph was coupled to the mass spectrometer.

*Product Identification.*—Each product was identified by comparison of its mass spectrum and its retention time in g.l.c. with those of an authentic sample.

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* $BF_3$ cannot be neutralised by addition of base since the presence of base induces the homolytic decomposition of (I).

† The reaction mixture was colourless and the ratio (IX) : (VIII) was low, just as in the thermolysis of (I) under nitrogen, *i.e.* with low $BF_3$ concentration. In all other experiments a dark brown colour is developed due in part to the formation of iodine. Therefore in the presence of a crown ether, the reaction of $BF_3$ with iodinated compounds is of minor importance, the Lewis acid probably being complexed by the macrocyclic polyether.

*General Procedure for Phenylation of Anisole.*—(a) *In acetonitrile solution.* Compound (I) (0.48 g, 2.5 mmol) was added at 60 °C in one portion to a solution of anisole (21.6 g, 200 mmol) in acetonitrile (80 ml). The mixture was stirred until completion of the decomposition, confirmed by absence of coupling with 2-naphthol, washed with water (3 × 100 ml), and dried ($Na_2SO_4$). Anisole was removed by fractional distillation until a residue of 3 ml was left. After precipitation of acetanilide by light petroleum addition, the concentrated filtrate was submitted to g.l.c. analysis. The conditions were: column 10 ft × $\frac{1}{8}$ in packed with 10% QF-1 on 80—100 mesh Chromosorb W, starting temperature 80 °C, programming rate 2 °C $min^{-1}$, nitrogen flow rate 20 ml $min^{-1}$, final temperature 180 °C. The yield in phenylated products was measured with 4-methylbiphenyl as internal standard.

(b) *Without solvent.* The same procedure was used, (I) (1.92 g, 10 mmol) being added to anisole (32.4 g, 300 mmol).

(c) *With the crown complex of* (I). The general procedure was used, (I) (0.096 g, 0.5 mmol) being added to a solution of 18-crown-6 ether (0.528 g, 2 mmol) in anisole (10.8 g, 100 mmol). Solubilization of the diazonium salt required 2 h.

*General Procedure for Phenylation of* p-*Iodoanisole.*—(a) *In acetonitrile solution.* Compound (I) (0.96 g, 5 mmol) was added at 60 °C to a solution of *p*-iodoanisole (5.85 g, 25 mmol) in acetonitrile (20 ml). The procedure described for anisole was used, except the g.l.c. conditions which were: column 10 ft × $\frac{1}{8}$ in packed with 10% silicone rubber SE 52 on 80—100 mesh Chromosorb W, nitrogen flow rate 20 ml $min^{-1}$, isothermal at 200 °C. The retention times were: isomeric methyl-*p*-iodoanisoles 4 and 5.5 min, 4-methoxybiphenyl 10 min, 2,4-di-iodoanisole 12 min, 4-iododiphenyl ether 16 min, 4-iodo-3-phenylanisole 22 min, and 4-iodo-2-phenylanisole 25 min; the retention time of 4-nitrobiphenyl (internal standard) was 18.5 min.

(b) *Without solvent.* The procedure described for anisole was used, (I) (1.92 g, 10 mmol) being added to fused *p*-iodoanisole (70.2 g, 300 mmol). We only modified the temperature conditions of the g.l.c. analysis: starting temperature 170 °C, programming rate 1 °C $min^{-1}$, final temperature 200 °C.

(c) *With the crown complex of* (I). Identical procedure and quantities with those of anisole were used.

(d) *Thermolysis of* (I) *followed by heating with* $Et_2O$–$BF_3$. The thermolysis was performed as described above (a) but with 100 mmol of *p*-iodoanisole and under nitrogen. When the reaction was complete, the yield of phenylated products was 7%, boron trifluoride–ether (100 mmol) was added, and the solution was brought to 60 °C for 120 h. The reaction mixture was then quenched with 5% sodium hydrogencarbonate solution, dried ($MgSO_4$), concentrated, and analysed by g.l.c.

*Reaction of* $Et_2O$–$BF_3$ *with* p-*Iodoanisole.*—Boron trifluoride–ether (50 mmol) was added to a solution of *p*-iodoanisole (10 mmol) in acetonitrile (10 ml). After 23 h at 60 °C the reaction mixture was worked up as described above. The reaction was performed again without acetonitrile.

*Synthesis of Authentic Samples.*—*2-Hydroxy-5-iodobiphenyl.* 2-Hydroxybiphenyl was iodinated with iodine monochloride in glacial acetic acid according to the procedure described by Colbert *et al.*[34] for the iodination of 4-hydroxybiphenyl, b.p. 147—150 °C at 0.1 mmHg (lit.,[35] b.p. 200—205 °C at 15 mmHg, m.p. 35 °C), *m/e* 296 (100%, $M^{+\cdot}$), 295, 169, 168, 141, 140, 139, and 115.

*5-Iodo-2-methoxybiphenyl.* 2-Hydroxy-5-iodobiphenyl was treated with dimethyl sulphate and aqueous hydroxide[36] giving 5-iodo-2-methoxybiphenyl as an *oil* (61%) (Found: C, 50.25; H, 3.45; I, 41.1. $C_{13}H_{11}IO$ requires C, 50.3; H, 3.55; I, 40.95%), $\delta_H$ (100 MHz; $CDCl_3$) 3.78 (3 H, s, $OCH_3$), 6.75 (1 H, X of ABX, $J_{AX}$ 8.7, $J_{BX}$ 0.5 Hz, 3-H), 7.40 (5 H, m, Ph), and 7.60 (2 H, AB of ABX, *J* 2.4, Δν 1.45 Hz, 4- and 6-H), $\nu_{max.}$ (film) 3 070, 3 040, 2 960, 2 940, 2 850, 1 585, 1 500, 1 480, 1 460, 1 440, 1 380, 1 260, 1 240, 1 180, 1 145, 1 030, 885, 805, 770, 700, and 600 $cm^{-1}$, *m/e* 310 (92.5%, $M^{+\cdot}$), 169, 168 [100, $(M - CH_3I)^{+\cdot}$], 165, 140, 139, and 113.

*2-Iodo-5-methoxybiphenyl.* This was prepared as an oil[37] by iodination of 3-methoxybiphenyl with iodine monochloride, $\delta_H$ (100 Hz; $CDCl_3$) 3.81 (3 H, s, $OCH_3$), 6.66 (1 H, dd, *J* 8.7 and 3.2 Hz, 4-H), 6.90 (1 H, d, *J* 3.2 Hz, 6-H), 7.39 (5 H, m, Ph), and 7.82 (1 H, d, *J* 8.7 Hz, 3-H), $\nu_{max.}$ (film) 3 060, 3 030, 3 010, 2 960, 2 940, 2 850, 1 590, 1 565, 1 465, 1 445, 1 390, 1 320, 1 300, 1 225, 1 215, 1 180, 1 040, 1 025, 1 010, 870, 860, 805, 765, and 700 $cm^{-1}$, *m/e* 310 (100%, $M^{+\cdot}$), 267, 168, 152, 140, 139, 114, and 113.

2,4-*Di-iodoanisole.* 4-Iodoanisole was iodinated with iodine monochloride in glacial acetic at 65 °C, m.p. 66—68 °C (lit.,[38] 69 °C), *m/e* 360 (100%, $M^{+\cdot}$), 345, 317, 218, 128, and 127.

4-*Iododiphenyl ether.* Diphenyl ether was iodinated with iodine monochloride[39] in acetic acid, m.p. 47 °C (lit,[39] 48 °C), *m/e* 296 (100%, $M^{+\cdot}$), 268, 220, 169, 168, 141, 139, and 115.

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