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Thallium in Organic Synthesis. 58. Regiospecific Intermolecular Oxidative Dehydrodimerization of Aromatic Compounds to Biaryls Using Thallium(III) Trifluoroacetate[1a,2]

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Abstract: Treatment of a variety of aromatic substrates with thallium(III) trifluoroacetate (TTFA) in trifluoroacetic acid (TFA), or in carbon tetrachloride or acetonitrile containing boron trifluoride etherate, results in smooth, rapid, and direct regiospecific oxidative dehydrodimerization to give symmetrical biaryls in good to excellent yield. The method is particularly useful when applied to substrates in which the ring substituents are either electron donating or mildly electron withdrawing. Aromatic substrates which contain powerful electron-withdrawing groups (CN, COOR, NO_2) fail to react. The reaction is postulated to proceed via (a) reaction of TTFA with the aromatic substrate and generation of the radical cation $Ar^{+\cdot}$; (b) reaction of this electrophile with the aromatic substrate; (c) oxidative aromatization of the intermediate thus produced by TTFA. Biaryls can be obtained similarly by oxidation of the same substrates with either mercury(II) trifluoroacetate in TFA containing boron trifluoride, lead(IV) acetate in acetonitrile containing boron trifluoride, iron(III) chloride in methylene chloride, or cobalt(III) fluoride in TFA. Yields in the Hg(II) and Fe(III) reactions are generally inferior to those obtained with TTFA, but those obtained in the Pb(IV) and Co(III) oxidations are in many instances comparable to, or even better than, the TTFA results. The oxidations with Hg(II), Pb(IV), Fe(III), and Co(III) are also postulated to proceed via a radical cation mechanism.

The most important and commonly used methods for biaryl synthesis are the Ullmann reaction,[3] the Gomberg reaction,[4] the thermal decomposition of aroyl peroxides,[5] and various Kharasch-type reactions in which an aromatic Grignard reagent is treated with an organic halide in the presence of a metal halide.[6] More recent methods which have not yet been widely utilized include the reaction of aromatic Grignard reagents with thallium(I) bromide,[7] treatment of aryllead(IV) triacetates with trifluoroacetic acid in the presence of activated hydrocarbons,[8] reaction of diaryltellurium(IV) dihalides with Raney nickel at 200 °C,[9] treatment of aryl halides either with zerovalent nickel complexes[10] or with aqueous alkaline sodium formate and palladium on charcoal in the presence of a surfactant catalyst,[11] the coupling of arylmercury(II) salts with either copper metal and a catalytic amount of palladium(II) chloride in the presence of pyridine[12] or $[Cl(Rh(CO))]_2$ and lithium chloride in HMPA,[13] the palladium(II)-catalyzed coupling of arylzinc(II) reagents with aryl halides,[14] the nickel(II)-catalyzed reaction of diaryliodonium salts with methylmagnesium iodide,[15] the oxidative coupling of lithium diarylcuprates,[16] and the reaction of arylboranes with alkaline silver nitrate.[17] The requirement that the starting material possess a substituent group which must eventually be lost in the coupling process is the common denominator in *all* of the above biaryl syntheses. Direct oxidative dehydrodimerization of aromatic compounds to biaryls can be effected with VOF_3,[18a] as well as by some other reagents or reagent combinations[18b-e] other than those used for Scholl-type reactions, but the latter usually give mixtures of isomeric biaryls, and none is known to be general.

We now describe an alternative approach to biaryl synthesis, namely, the regiospecific oxidative dehydrodimerization of electron-rich aromatic compounds by thallium(III) trifluoroacetate (TTFA). This procedure gives good to excellent yields of biaryls and binaphthyls in many cases, and the scope and limitations have been investigated. The present paper deals with intermolecular coupling and presents comparative data on the relative synthetic utility of TTFA, mercury(II) trifluoroacetate, lead(IV) acetate, iron(III) chloride, and cobalt(III) fluoride for this type of reaction. Application of the TTFA procedure to intramolecular coupling and to alkaloid synthesis is described in the accompanying paper.[19]

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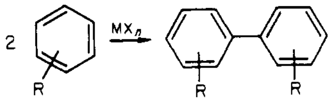
Discussion

Metal salt induced oxidative dehydrodimerization of aromatic compounds (eq 1) has been known for many years and is frequently referred to as the Scholl reaction.[20,21] With few exceptions, however, such processes have been of little synthetic utility, primarily because biaryls are produced in low yields and complex mixtures of products are usually obtained. There has been little detailed mechanistic study of the reactions. They appear to proceed most readily (a) with relatively electron-rich aromatic substrates and (b) when a metal salt is used which can function—at least formally—as a one-electron oxidant. In this latter context, iron(III) chloride and lead(IV) acetate have commonly been employed. Electrochemical oxidation of electron-rich aromatic substrates can also result in dehydrodimerization, and biaryl formation has been reported to occur in excellent yield in a number of instances.[22] The electrochemical method has not, however, been generally adopted for biaryl synthesis.



(1)

Reaction of a wide variety of aromatic substrates with TTFA results in formation of arylthallium di(trifluoroacetates) (eq 2),

$$ArH + Tl(OCOCF_3)_3 \rightarrow ArTl(OCOCF_3)_2 + CF_3COOH \quad (2)$$

the products of formal electrophilic aromatic thallation.[23] In 1973, Elson and Kochi reported that TTFA could also act as an efficient one-electron oxidant for certain aromatic hydrocarbons.[24] ESR examination of the reactions of TTFA with toluene and *o*-xylene, for example, clearly revealed formation of the radical cations of 4,4′-dimethylbiphenyl and 3,3′,4,4′-tetramethylbiphenyl while durene and pentamethyl-, hexamethyl-, and hexaethylbenzene were similarly shown to be cleanly oxidized to the corresponding parent radical cations. As a consequence of this study, Elson and Kochi postulated that "formation of arene cation radicals with TTFA may implicate them as common intermediates in the thallation process", although more recent studies concerned with the determination of partial rate factors for the thallation of toluene have provided strong support for the conventional electrophilic substitution pathway for this substrate.[25] These and other related results[26] proved complementary to those obtained from earlier preparative studies carried out in our laboratory,[27] in which we had found that reaction of anisole and 1-bromo- and 1-iodonaphthalene with TTFA in carbon tetrachloride containing boron trifluoride etherate gave 4,4′-dimethoxybiphenyl and 4,4′-dibromo- and 4,4′-diiodo-1,1′-binaphthyl, respectively, in low (20–30%) yield. Oxidation of 4-bromoveratrole under the same conditions, on the other hand, gave 2,2′-dibromo-4,4′,5,5′-tetramethoxybiphenyl in excellent (~80%) yield.[28]

Subsequent detailed examination of these coupling reactions and optimization of experimental conditions resulted in the development of simple and rapid procedures for the direct dehydrodimerization of a wide variety of relatively basic aromatic compounds to symmetrical biaryls. The oxidations can be carried out using one or more of the following general sets of conditions (for full details see Experimental Section): method A, TTFA, $BF_3 \cdot O(C_2H_5)_2$, and CCl_4 at room temperature; method B, TTFA, $BF_3 \cdot O(C_2H_5)_2$, and CCl_4 at low temperature (−40 to −60 °C); method C, TTFA, $BF_3 \cdot O(C_2H_5)_2$, and CH_3CN at room temperature; method D, TTFA and TFA at room temperature; method E, TTFA, $BF_3 \cdot O(C_2H_5)_2$, and TFA at room temperature. Methods A and B involve oxidation under heterogeneous conditions; methods C–E involve homogeneous conditions. Experimental data for the conversions thus effected are listed in Table I.

These methods constitute simple, effective procedures for the preparation of a variety of highly substituted biaryls in which the ring substituents are either electron donating or mildly electron withdrawing. Aromatic substrates which contain powerful electron-withdrawing groups (COOR, CN, NO_2) fail to couple under the above conditions and are recovered in virtually quantitative yield. Consequently, the TTFA method is complementary to the Ullmann reaction, as the latter procedure usually gives satisfactory yields of biaryls only when the aromatic halides contain powerful electron-withdrawing groups, and is normally an inefficient reaction for the preparation of binaphthyls in particular. Another important aspect of the present procedure is the facility with which 2,2′,6,6′-tetrasubstituted biaryls can be prepared in moderate to good yields. Gibson and Bailey, for example, recently reported that both the Ullmann reaction of the benzyl ether of 2,3,5-trimethyl-4-iodophenol and the Kharasch-type reaction of the corresponding Grignard reagent with copper(II) chloride failed to yield any biaryl.[29] Treatment of the benzyl ether of 2,3,5-trimethylphenol **4** (Table I) with TTFA in acetonitrile containing boron trifluoride, however, gave 2,2′,3,3′,6,6′-hexamethyl-4,4′-dibenzyloxybiphenyl (**15**) in 39% yield in 10 min. Treatment of compounds **3**, **10**, and **11** with TTFA in TFA at room temperature gave the corresponding 2,2′,6,6′-tetrasubstituted biaryls **14**, **21**, and **22** in 74, 99, and 33% yield, respectively.

There are certain other noteworthy aspects of these oxidations. (1) All reactions were carried out using 1 equiv of TTFA to 2 equiv of the aromatic substrate. Under these conditions, starting material was recovered in variable amount from about one-third of the reactions (see Table I for conversion data); in these cases, use of excess TTFA did result in complete oxidation of the starting materials but led to substantially lower yields of biaryls. This is due to competitive reactions in which the starting materials and products are oxidized to highly colored, polymeric materials. Such byproducts were formed in variable amount in almost all of the oxidations, but were easily removed at the isolation/purification stage. (2) Addition of $BF_3 \cdot O(C_2H_5)_2$ is essential for oxidations carried out in CCl_4 or CH_3CN solution. Standard control experiments established that there was no oxidation when $BF_3 \cdot O(C_2H_5)_2$ was omitted. (3) In addition to compounds containing powerful electron-withdrawing groups, the following compounds failed to undergo coupling to biaryls: 4-bromoanisole, 3,5-dimethylanisole, 2,3-dimethoxytoluene, 2,6- and 3,5-dimethoxybromobenzene, 1-cyclopentyl-, 1-benzyl-, 1-bromo-2-methoxy-, 1-iodo-2-methoxy-, 1,6-dibromo-2-methoxy-, 1-methyl-2-methoxy-6-bromo-, and 1-methyl-2-methoxy-3,6-dibromonaphthalene, acenaphthene, anthracene, and phenanthrene. In each of these cases the aromatic substrate was partially or largely oxidized to tarry, unidentifiable materials and starting material was recovered in variable amount (5–95%). (4) Electrophilic aromatic thallation was observed with only two of the substrates studied: 3-bromo- and 3-methylanisole were converted to 2-bromo- and 2-methyl-4-methoxyphenylthallium di(trifluoroacetate), respectively, in good yield.

Secondary reactions were observed to occur in a number of oxidations. Treatment of naphthalene with TTFA in TFA in the presence of $BF_3 \cdot O(C_2H_5)_2$, for example, gave a quantitative yield

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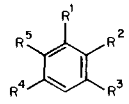
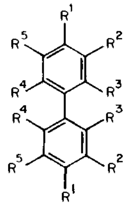
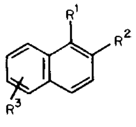
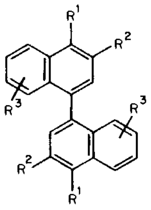
Table I. Oxidative Dehydrodimerization of Aromatic Compounds to Biaryls Using TTFA





compd	aromatic compd R^1	R^2	R^3	R^4	R^5	biaryl compd	method^a	conversion, %^{b}	yield, %^{c}	recrystn solvent	mp, °C	lit. mp, °C
1	CH$_3$O	H	H	H	H	12	D	100	16	ethanol/chloroform	177-178	174^d
2	CH$_3$O	CH$_3$	H	CH$_3$	H	13	D	63	60	toluene/petroleum ether (bp 100-120 °C)	114-116	
3	CH$_3$O	CH$_3$	CH$_3$	CH$_3$	H	14	D	77	74	ethanol	151-153	
4	C$_6$H$_5$CH$_2$O	CH$_3$	CH$_3$	CH$_3$	H	15	C	51	39	ethanol	133-135	
5	CH$_3$O	CH$_3$O	H	CH$_3$	H	16	D	85	74	petroleum ether (bp 100-120 °C)	115-118	115-116^e
6	CH$_3$O	CH$_3$O	H	Br	H	17	D	92	88	toluene/petroleum ether (bp 100-120 °C)	159-160	160^f
7	CH$_3$O	CH$_3$O	H	I	H	18	C	100	89	toluene/petroleum ether (bp 100-120 °C)	181-182	183^f
8	CH$_3$O	CH$_3$O	H	Br	CH$_3$	19	D	61	93	toluene/petroleum ether (bp 100-120 °C)	178-179	
9	CH$_3$O	CH$_3$O	H	I	CH$_3$	20	D	76	83	ethanol	127-129	116-117^g
10	CH$_3$O	CH$_3$O	CH$_3$	Br	H	21	D	85	99	ethanol	210-212	
11	CH$_3$O	CH$_3$O	Br	CH$_3$	H	22	D	58	33	ethanol/methylene chloride	216-217	



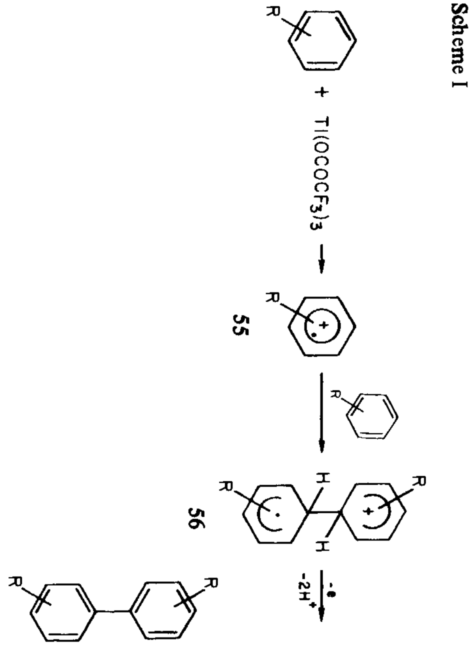


compd	R^1	R^2	R^3	biaryl compd	method^a	conversion, %^{b}	yield, %^{c}	recrystn solvent	mp, °C	lit. mp, °C
23	CH$_3$	H	H	37	A	100	32	acetone/petroleum ether (bp 40-60 °C)	145-147	146-146.5^h
					B	100	93			
					C	100	48			
					D	100	42			
24	(CH$_3$)$_2$CH	H	H	38	C	100	70	ethanol	134-137	
25	CH$_2$COOCH$_3$	H	H	39	C^i	37	53	ethanol/acetone	198-201	
26	C$_6$H$_5$	H	H	40	C^i	70	83	ethanol/chloroform	184-186	

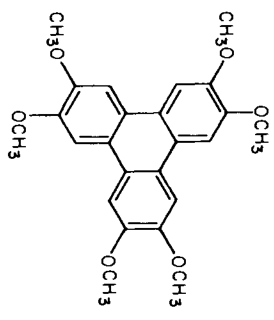
27	CH_3	H	H	41	C	100	88	toluene/petroleum ether (bp 100–120 °C)	259–260	260–261[j]
28	Br	H	H	42	A	100	25	toluene/petroleum ether (bp 100–120 °C)	214–217	217[k]
					D	71	87			
					E	73	55			
29	I	H	H	43	A	100	25	toluene/petroleum ether (bp 100–120 °C)	228–233	232–233[l]
					D	84	94			
30	CH_3	CH_3	H	44	C[i]	52	74	ethanol	160–163	
31	CH_3O	CH_3	H	45	D	82	92	ethanol	172–174	175[m]
32	CH_3O	Cl	H	46	C	37	50	petroleum ether (bp 100–120 °C)	170–171	
					D	89	82			
33	CH_3O	Br	H	47	D	83	81	ethanol/methylene chloride	197–199	
34	Br	CH_3	H	48	D	75	42	toluene/petroleum ether (bp 100–120 °C)	193–195	
35	CH_3O	H	7-CH_3O	49	C[n]	89	60	ethanol	164–166	

[a] A, TTFA/$BF_3 \cdot O(C_2H_5)_2/CCl_4$/room temperature; B, TTFA/$BF_3 \cdot O(C_2H_5)_2/CCl_4$/-40 to -60 °C; C, TTFA/$BF_3 \cdot O(C_2H_5)_2/CH_3CN$/room temperature; D, TTFA/TFA/room temperature; E, TTFA/TFA/$BF_3 \cdot O(C_2H_5)_2$/room temperature. [b] Conversion data are based on the amount of starting material which is recovered, while yield data are based on the amount of starting material which is consumed. [c] Refers to isolated, pure, recrystallized material. [d] Cavill, G. W. K.; Solomon, D. H. *J. Chem. Soc.* 1955, 1404–1407. [e] Cromartie, R. I. T.; Harley-Mason, J.; Wannigama, D. G. P. *Ibid.* 1958, 1982–1985. [f] Baker, W.; Barton, J. W.; McOmie, J. F. W.; Penneck, R. J.; Watts, M. L. *Ibid.* 1961, 3986–3989. [g] Lawson, D. W.; McOmie, J. F. W.; West, D. E. *J. Chem. Soc. C* 1968, 2414–2420. [h] Clar, E.; Sanigök, U.; Zander, M. *Tetrahedron* 1968, *24*, 2817–2823. [i] Reaction carried out at −60 °C. [j] Badder, F. G.; El-Assal, L. S.; Baghos, V. B. *J. Chem. Soc.* 1958, 986–994. [k] Corbellini, A.; Debenedetti, E. *Gazz. Chim. Ital.* 1929, *59*, 391–399. [l] Weitzenböck, R.; Serr, C. *Chem. Ber.* 1913, *46*, 1994–2000. [m] Wolf, G.; Seligman, A. M. *J. Am. Chem. Soc.*, 1951, *73*, 2082–2085. [n] Thallium(III) acetate was used as oxidant.

Scheme I



of a colorless, amorphous, polymeric solid the melting-point range of which varied substantially from experiment to experiment. 1,3- and 1,4-dimethoxybenzene gave similar yellow and red polymeric solids, while 1,2-dimethoxybenzene gave a 29% yield of the dehydro trimer **50**. 9-Methoxyanthracene was smoothly converted to bianthron-9-yl (**51**) in 83% yield, and oxidative conversion of a methoxy substituent to a carbonyl group was also observed with 1-methyl-2-methoxy- and 1,3-dimethyl-2-methoxynaphthalene. Reaction of these substrates with TTFA gave products to which the structures **52a,b** are tentatively assigned on the basis of analytical and spectroscopic data (Experimental Section).



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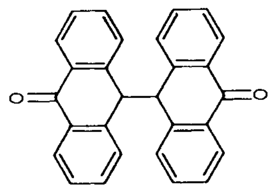

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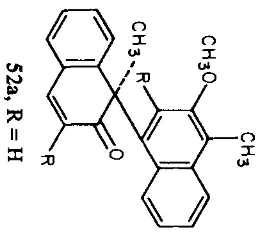
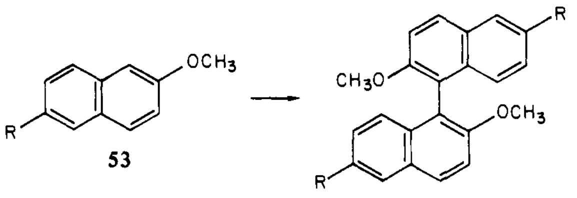


52a, R = H
b, R = CH_3

The utility of the present procedure for the preparation of 2,2′-disubstituted 1,1′-binaphthyls appears to be strictly limited. Treatment of 2-methoxynaphthalene (**53a**) with TTFA, for example, gave only a high-melting, orange-colored, amorphous solid, probably polymeric; when the less powerful oxidant thallium(III) acetate was used, on the other hand, 2,2′-dimethoxy-1,1′-binaphthyl (**54a**) was obtained in 80% yield. 2-Methoxy-6-bromonaphthalene (**53b**), surprisingly, was virtually unaffected by thallium(III) acetate; it was, however, oxidized to the binaphthyl **54b** in 76% yield by TTFA. By contrast, all attempts to couple 2-methyl-, 2-bromo-, 2-methyl-3-methoxy-, and 2-methoxy-3,6-dibromonaphthalene were unsuccessful.

We suggest that these TTFA-induced oxidative dehydrodimerizations are best explained by the sequence of reactions outlined in Scheme I. That is, one-electron transfer from the electron-rich aromatic substrate to Tl(III) results in generation of the corresponding aromatic radical cation **55**. Electrophilic substitution of the aromatic substrate by **55** then leads to **56**, oxidative aro-

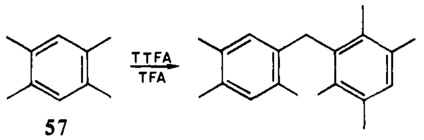


53

54

a, R = H
b, R = Br

matization of which gives the biaryl. This mechanism is consistent with the stoichiometry of the reaction, with the complete regiospecificity of coupling which is observed, and with the results of Elson and Kochi[24] and of others,[26] who have shown that aromatic radical cations are formed in the reactions of various electron-rich aromatic substrates with TTFA. Moreover, treatment of durene (**57**) with TTFA in TFA gives the heptamethyldiphenylmethane **58** (~15% yield), which is also one of the products formed by electrochemical oxidation of durene, a process known to proceed via the radical cation.[30]



57

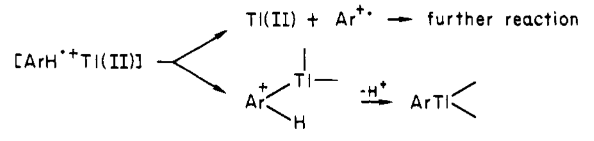
58

One important consequence of the radical cation mechanism is that the oxidation potential of an aromatic substrate is one of the major factors governing the particular reaction course which will be followed when that aromatic substrate is treated with TTFA, i.e., electrophilic aromatic thallation or oxidative dehydrodimerization. Evidence which both supports this hypothesis and also indicates that organothallium intermediates are not involved in the coupling reaction was obtained from a study of the reactions of mesitylene, durene, and naphthalene, and certain mixtures of these compounds, with TTFA. Thus, mesitylene and durene were treated with TTFA in TFA at room temperature, both in the presence and absence of $BF_3{\cdot}O(C_2H_5)_2$, and the reaction mixtures were quenched with aqueous potassium iodide solution to convert arylthallium di(trifluoroacetates) to the corresponding aromatic iodides.[23] The product distributions are shown in Scheme II. As mentioned earlier, naphthalene polymerizes rapidly when treated with TTFA/TFA/$BF_3{\cdot}O(C_2H_5)_2$; in the absence of $BF_3{\cdot}O(C_2H_5)_2$, reaction is slow and after 5 h at room temperature the product distribution was naphthalene (97%), 1-iodonaphthalene (3%), and 1,1′-binaphthyl (<0.1%). Product distribution data from oxidations of mixtures of equivalent amounts of mesitylene and durene and of mesitylene and naphthalene are given in Schemes III and IV, respectively.

The reaction of mesitylene with TTFA in TFA containing $BF_3{\cdot}O(C_2H_5)_2$ results in the formation of bimesityl (**61**) and mesitylthallium di(trifluoroacetate) (analyzed as mesityl iodide **60**). It might be argued, therefore, that the arylthallium compound is an intermediate in the formation of bimesityl. The results shown in Scheme III indicate, however, that this is almost certainly not so. If arylthallium di(trifluoroacetates) were intermediates in biaryl formation, it would be expected that the basicity of an aromatic compound should determine its reactivity with TTFA, whereas, if biaryl formation involves an electron-transfer process, the ionization potential of the aromatic substrate should be the determining factor in the reaction with TTFA. Durene is about 200 times less basic than mesitylene (pK_B = 2.2 vs. 0.4[31]); the durene dehydro dimers **64** and **58** are, however, formed exclusively. This is fully consistent with the ionization potentials (8.39 vs. 8.03 V[32]) and polarographic half-wave oxidation potentials (E_{ox} = 1.85 vs. 1.59 V[33]) of mesitylene and durene, respectively.

The results shown in Scheme IV can be interpreted in a similar manner. The oxidation potential of naphthalene is lower than that of mesitylene (E_{ox} = 1.64 vs. 1.85 V[33]), but mesitylene is more basic than naphthalene (pK_B = 0.4 vs. 4.0[31]). Consequently, naphthalene is oxidized preferentially, and the resulting radical cation reacts with the most basic species in solution, namely, mesitylene, to give 1-mesitylnaphthalene (**67**).[34]

The above results clearly illustrate that oxidation potential and basicity are major factors governing the overall course of reaction of an aromatic substrate with TTFA.[35] They are, moreover, compatible with Elson and Kochi's[35] suggestion that radical cations may be common intermediates in electrophilic aromatic thallation (eq 3).[36] Kochi et al.[37] subsequently postulated a broader interpretation of this suggestion, namely, that electrophilic aromatic substitution in general may contain a sizable electron-transfer component in the transition state, and it is interesting to note in this context that Perrin has recently argued that the nitration of reactive aromatic substrates proceeds via an electron-transfer mechanism.[38]



(3)

A further consequence of the radical cation mechanism is that other reagents besides TTFA should be able to effect oxidative dehydrodimerization of reactive aromatic substrates to biaryls provided that they can (a) participate, at least formally, in one-electron transfer reactions and (b) exist in two valence states, the redox potential between which is sufficiently high that oxidation can occur. Limited evidence in support of this hypothesis was obtained from a study of the oxidation of most of the aromatic substrates listed in Table I with the following reagent systems: (i) mercury(II) trifluoroacetate/TFA/$BF_3{\cdot}O(C_2H_5)_2$;[39] (ii) lead (IV) acetate/CH_3CN/$BF_3{\cdot}O(C_2H_5)_2$;[40] (iii) iron(III) chloride/CH_2Cl_2; (iv) cobalt(III) fluoride/TFA.[41] The results of these studies are listed in Table II.

The mercury(II) and lead(IV) salts were studied primarily

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(30) Nyberg, K. *Acta Chem. Scand.* **1970**, *24*, 1609–1617.

(31) Perkampus, H. H. *Adv. Phys. Org. Chem.* **1966**, *4*.

(32) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916–918.

(33) Neikam, W. C.; Desmond, M. M. *J. Am. Chem. Soc.* **1964**, *86*, 4811–4814.

(34) Similar arguments and interpretations have been used to account for the products formed in the oxidation of (a) mixtures of mesitylene and durene with iron(III) chloride (Nyberg, K. *Chem. Scr.* **1974**, *5*, 115–119) and (b) mixtures of mesitylene and naphthalene with iron(III) chloride (Nyberg, K. *Chem. Scr.* **1974**, *5*, 120–123) and aluminum chloride–copper(II) chloride (Wen, L.-S.; Kovacic, P. *Tetrahedron* **1978**, *34*, 2723–2727).

(35) In principle it should be possible to predict with a fair degree of accuracy whether oxidative dehydrodimerization or aromatic thallation, or both (see ref 36), should occur on treatment of an aromatic compound with TTFA under appropriate conditions, given that either the ionization potential and/or polarographic half-wave oxidation potential of the compound is known. Unfortunately, these data are not available for almost all of the compounds investigated in the present study.

(36) Formation of small amounts of biaryls during electrophilic aromatic thallation using TTFA and other thallium(III) salts has been noted previously: Henry, P. M. *J. Org. Chem.* **1970**, *35*, 3083–3086. Ichikawa, K.; Uemura, S.; Nakano, T.; Uegaki, E. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 545–550.

(37) Kochi, J. K.; Tang, R. T.; Bernath, T. *J. Am. Chem. Soc.* **1973**, *95*, 7114–7123.

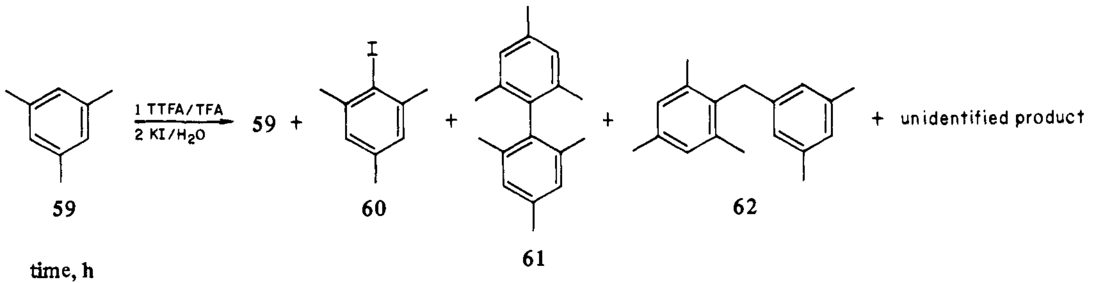
(38) Perrin, C. L. *J. Am. Chem. Soc.* **1977**, *99*, 5516–5518.

(39) Mercury(II) acetate was completely ineffective as a reagent for oxidative dehydrodimerization irrespective of the reaction conditions. $Hg(OCOCF_3)_2$/TFA, $Hg(OCOCF_3)_2$/CH_3CN, and $Hg(OCOCF_3)_2$/CH_3CN/$BF_3{\cdot}O(C_2H_5)_2$ were also almost completely ineffective, and very low (0–15%) conversions to, and yields of, biaryls were obtained using these reagent systems.

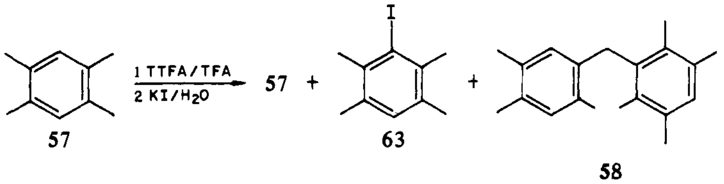
(40) Use of either $Pb(OCOCF_3)_4$ or $Pb(OCOCH_3)_4$/TFA gave biaryls in 20–45% yield, together with highly colored, polymeric materials, and isolation and purification of products were tedious. Use of $Pb(OCOCH_3)_4$/CH_3CN did not result in dehydrodimerization; starting materials were recovered unchanged.

(41) Oxidations using CoF_3/CH_3CN or CoF_3/CH_3CN/$BF_3{\cdot}O(C_2H_5)_2$ were very slow and of little synthetic utility. Strongly coordinated ligands such as acetonitrile are known to significantly reduce the rate of reduction of cobalt(III) salts: Kawai, R.; Kamiya, Y. *Nippon Kagaku Kaishi* **1973**, *8*, 1538–1543; *Chem. Abstr.* **1974**, *79*, 125549.

Scheme II



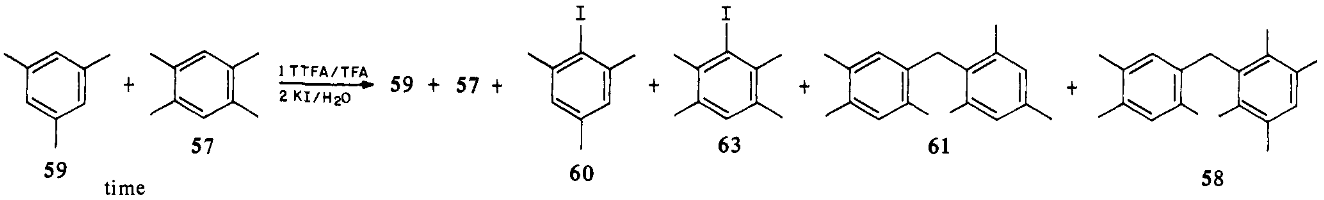
time, h	59	60	61	62	unidentified product
12^a	56.1	43.9	0	0	0
12^b	84.3	0	9.5	<0.1	6.2



time, min	57	63	58
30^a	66.4	0.4	33.2
1^b	92.5	0	7.5

^{a} $BF_3{\cdot}O(C_2H_5)_2$ absent. ^{b} $BF_3{\cdot}O(C_2H_5)_2$ present.

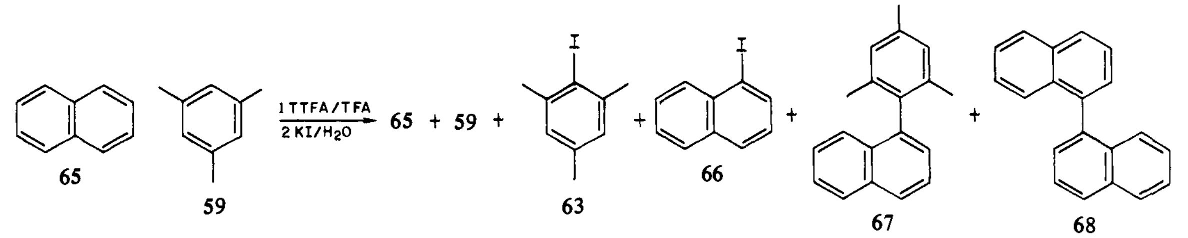
Scheme III



time	59	57	60	63	61	58
2 h^a	25.0	33.5	19.0	8.4	13.5	0.3
1 min^b	38.1	52.0	0.3	0	8.5	<0.1
1 h^b	36.1	52.0	0	0	11.5	<0.1

^{a} $BF_3{\cdot}O(C_2H_5)_2$ absent. ^{b} $BF_3{\cdot}O(C_2H_5)_2$ present.

Scheme IV



	65		59		63		66		67		68	
time, min	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
0.5	50.5	50.3	14.1	37.7	34.4	2.2	<0.1	0	0.7	9.8	<0.1	0
1	49.8	54.6	17.1	35.2	32.0	1.9	<0.1	0	1.1	8.2	<0.1	0
2	48.4	49.0	17.9	41.5	32.3	1.2	<0.1	0	0.8	8.1	<0.1	0
5	49.5	52.6	20.2	40.0	29.3	0.7	<0.1	0	0.9	6.6	<0.1	0
15	48.2	50.9	23.4	42.0	27.5	0.3	<0.1	0	0.9	6.8	<0.1	0
30	46.3	50.3	26.0	44.3	26.5	0	<0.1	0	1.1	5.4	<0.1	0

^{a} $BF_3{\cdot}O(C_2H_5)_2$ absent. ^{b} $BF_3{\cdot}O(C_2H_5)_2$ present.

because the metal ions are isoelectronic with thallium(III), and similar types of reactions are often observed with all three ions. Moreover, while there are examples of oxidative dehydrodimerization of aromatic compounds by lead(IV) acetate,[20,21,26d,42] as far as we are aware no mercury(II) salt has ever been reported to effect such a transformation. Iron(III) chloride and cobalt(III) fluoride were selected as typical one-electron oxidants. The former reagent is known to effect nonphenolic oxidative dehydrodimerization,[22a,26d,34] while reaction of a wide range of aromatic compounds with cobalt(III) salts is known to result in formation of the corresponding radical cations.[26d,37,43] Moreover, Nyberg

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(42) Wessely, F.; Kotlan, J.; Metlesics, W. *Monatsh. Chem.* **1954**, *85*, 69–79. Cavill, G. W. K.; Solomon, D. H. *J. Chem. Soc.* **1955**, 1404–1407. Allara, D. L.; Gilbert, B. C.; Norman, R. O. C. *Chem. Commun.* **1965**, 319–320. Aylward, J. B. *J. Chem. Soc. B* **1967**, 1268–1270. Norman, R. O. C.; Thomas, C. B.; Wilson, J. S. *Ibid.* **1971**, 518–529. Norman, R. O. C.; Thomas, C. B.; Wilson, J. S. *J. Chem. Soc., Perkin Trans. 1* **1973**, 325–332.

(43) Dessau, R. M.; Shih, S.; Heiba, E. I. *J. Am. Chem. Soc.* **1970**, *92*, 412–413.

and Wistrand have recently studied the oxidation of mesitylene, durene, and naphthalene, either alone or in competition experiments, by cobalt(III) salts and obtained various dehydro dimers as the major products.[44]

From Table II it can be seen that oxidative dehydrodimerization is the predominant reaction pathway with all four reagent systems, and we suggest that the mechanism in each case is essentially similar to that with the TTFA reactions, i.e., electron transfer and radical cation formation. From a preparative point of view it is clear that TTFA is a superior reagent to either $Hg(OCOCF_3)_2$ or $FeCl_3$ for biaryl synthesis, but in many instances both $Pb(OCOCH_3)_4$ and CoF_3 are as good as, or better than, TTFA. From a practical point of view, however, the reactions with $Pb(OCOCH_3)_4$ were considerably dirtier than those with TTFA, and the reaction mixtures almost always contained variable amounts of highly colored and/or tarry materials. In contrast, the reactions with CoF_3 generally proceeded smoothly and cleanly and gave exceptionally pure products; very little, if any, overoxidation to polymeric material and/or tars was observed.

Experimental Section

Starting Materials. With the exception of 4-bromo-3-methylveratrole (**8**), 4-iodo-3-methylveratrole (**9**), 5-bromo-2,3-dimethoxytoluene (**10**), 3-bromo-4,5-dimethoxytoluene (**11**), and 1,3-dimethyl-2-methoxynaphthalene, all starting materials were either commercially available or were prepared according to published procedures. Boron trifluoride diethyl etherate was distilled under reduced pressure from calcium hydride prior to use.

4-Bromo-3-methylveratrole (8). 3-Methylveratrole[46] (15.2 g, 0.1 mol) was dissolved in carbon tetrachloride (100 mL), *N*-bromosuccinimide (17.8 g, 0.1 mol) was added, and the mixture was heated under reflux for 12 h and then allowed to cool to room temperature. The succinimide which had separated was collected by filtration and the solvent was removed from the filtrate by distillation under reduced pressure. This gave a yellow oil (20 g), fractional distillation of which under reduced pressure gave 14.5 g (63%) of pure 4-bromo-3-methylveratrole as a very pale yellow oil: bp 134–138 °C (15 Torr); ^1H NMR (CCl_4) δ 7.10 (1 H, d, J = 8.6 Hz), 6.50 (1 H, d, J = 8.6 Hz), 3.76 (3 H, s), 3.71 (3 H, s), 2.29 (3 H, s). Anal. ($C_9H_{11}BrO_2$) C, H, Br.

The spectral data did not unambiguously establish that bromination had taken place in the 4 rather than the 6 position. Consequently, a sample of the above product was converted into the corresponding Grignard reagent in the normal manner and the latter was poured onto powdered solid carbon dioxide. When the reaction was complete, the mixture was hydrolyzed with ice and dilute hydrochloric acid. This gave 2-methyl-3,4-dimethoxybenzoic acid, mp 183–185 °C (lit.[47] mp 184 °C); 2,3-dimethoxy-4-methylbenzoic acid has mp 125 °C.[48]

4-Iodo-3-methylveratrole (9). A finely powdered mixture of iodine (25.3 g, 0.1 mol) and mercuric oxide (16.8 g, 0.05 mol) was added portionwise during 15–20 min to a warm (70 °C) solution of 3-methylveratrole (15.2 g, 0.1 mol) in 95% ethanol (50 mL). Heating was continued for a further 15 min; then the insoluble mercury salts were removed by filtration and washed well with hot ethanol. The ethanolic solution was poured into a solution of potassium iodide (4 g) and sodium thiosulfate (10 g) in water (400 mL) and the resulting mixture was extracted with ether (3 × 100 mL). The ethereal extracts were dried ($MgSO_4$) and the solvent was removed by distillation under reduced pressure to leave an orange solid (22.5 g). Recrystallization of the crude product from 95% ethanol (charcoal) gave 16 g (57%) of pure 4-iodo-3-methylveratrole as colorless plates: mp 82–84 °C; ^1H NMR (CCl_4) δ 7.5 (1 H, d, J = 9.3 Hz), 6.46 (1 H, d, J = 9.3 Hz), 3.8 (3 H, s), 3.73 (3 H, s), 2.36 (3 H, s). Anal. ($C_9H_{11}IO_2$) C, H, I.

As with **8**, the spectral data did not unambiguously establish the position of iodination. A sample of the product was therefore converted into the corresponding benzoic acid as described above; this gave 2-methyl-3,4-dimethoxybenzoic acid, mp 184–185 °C.

5-Bromo-2,3-dimethoxytoluene (10). A mixture of 5-bromo-2,3-dimethoxybenzaldehyde[49] (12.3 g, 0.05 mol), digol (50 mL), and hydrazine hydrate (5 g) was heated on a water bath for 30 min, during which time a pale orange solid separated. The mixture was cooled, potassium hydroxide (4 g) was added, and then the mixture was heated under reflux until evolution of nitrogen ceased (ca. 3 h). The mixture was poured into water (250 mL) and the colorless oil which separated was extracted with ether (3 × 50 mL). The ethereal extracts were dried ($MgSO_4$) and the solvent was removed by distillation under reduced pressure. Fractional distillation of the residual oil (10 g) gave 8 g (70%) of pure 5-bromo-2,3-dimethoxytoluene as a colorless oil: bp 146–150 °C (18 torr); ^1H NMR (CCl_4) δ 6.81 (2 H, s), 3.75 (3 H, s), 3.70 (3 H, s), 2.18 (3 H, s). Anal. ($C_9H_{11}BrO_2$) C, H, Br.

3-Bromo-4,5-dimethoxytoluene (11). This compound was obtained in 45% yield from 3-bromo-4,5-dimethoxybenzaldehyde[50] using exactly the same procedure as described for the preparation of **10**: colorless oil; bp 134–136 °C (5 torr); ^1H NMR (CCl_4) δ 6.86 (1 H, s), 6.58 (1 H, s), 3.73 (6 H, s), 2.2 (3 H, s). Anal. ($C_9H_{11}BrO_2$) C, H, Br.

1,3-Dimethyl-2-methoxynaphthalene. This compound was obtained in 60% yield from 2-methoxy-3-methyl-1-naphthaldehyde using exactly the same procedure as described for the preparation of **10**: almost colorless oil; bp 100–102 °C (6 torr); ^1H NMR (CCl_4) δ 7.85–7.1 (5 H, m), 3.6 (3 H, s), 2.45 (3 H, s), 2.33 (3 H, s). Anal. ($C_{13}H_{14}O$) C, H.

General Methods for the Preparation of Biaryls Using TTFA. Method A. Boron trifluoride diethyl etherate (10 mL) was added to a mixture of TTFA (5.5 g, 0.01 mol) and the aromatic substrate (0.02 mol) in carbon tetrachloride (30 mL). The dark-colored reaction mixtures were stirred at room temperature until a thallium(III) test[52] was negative. Excess of an aqueous solution of potassium iodide was then added and the resulting mixture was stirred at room temperature for 30 min. It was then made basic with aqueous sodium carbonate solution, sodium metabisulfate (5 g) was added, and the thallium(I) iodide was collected by filtration and washed with chloroform (150 mL). The filtrate was extracted with chloroform (2 × 100 mL) and the combined chloroform extracts were dried ($MgSO_4$) and passed through a short column of alumina using chloroform/petroleum ether (bp 40–60 °C) as eluant. Evaporation of the eluant under reduced pressure followed by crystallization of the residual solid thus obtained gave the pure biaryl. Unreacted starting material was recovered by concentration of the mother liquors.

Method B. A mixture of TTFA (5.5 g, 0.01 mol) and boron trifluoride diethyl etherate (10 mL) in carbon tetrachloride (30 mL) was stirred at room temperature until an emulsion formed (ca. 10 min). This mixture was then cooled to the required temperature and the aromatic substrate (0.02 mol) was added. The reaction mixture was allowed to warm up to room temperature and stirred until a thallium(III) test was negative. The biaryl was isolated as described in method A.

Method C. The aromatic substrate (0.02 mol) was added to a solution of TTFA (5.5 g, 0.01 mol) in acetonitrile (25 mL) and then boron trifluoride diethyl etherate (10 mL) was added. A rapid exothermic reaction ensued, and in some cases the biaryl separated from the reaction mixture as a colorless, crystalline solid. The reaction mixture was stirred at room temperature until a thallium(III) test was negative; then it was poured into water (150 mL) and the mixture was extracted with chloroform (2 × 100 mL). The chloroform extracts were dried ($MgSO_4$) and passed through a short column of alumina and the products isolated as described in method A.

Method D. The aromatic substrate (0.02 mol) was added to a solution of TTFA (5.5 g, 0.01 mol) in trifluoroacetic acid (25 mL) and the mixture was stirred until a thallium(III) test was negative. The products were isolated as described in method C.

Method E. The aromatic substrate (0.02 mol) was added to a solution of TTFA (5.5 g, 0.01 mol) and boron trifluoride diethyl etherate (10 mL) in trifluoroacetic acid (25 mL), and the mixture was stirred until a thallium(III) test was negative. The products were isolated as described in method C.

General Method for the Preparation of Biaryls Using $Hg(OCOCF_3)_2$. Boron trifluoride diethyl etherate (5 mL) was added to a mixture of mercury(II) trifluoroacetate (4.26 g, 0.01 mol) and the aromatic substrate (0.02 mol) in trifluoroacetic acid (15 mL) and the mixture was stirred until a mercury(II) test was negative. The reaction mixture was then added to a saturated brine solution (150 mL) and the organic products were extracted with chloroform (2 × 100 mL). Insoluble or-

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(44) Nyberg, K.; Wistrand, L.-G. *Chem. Scr.* **1974**, *6*, 234–238.

(45) Melting points were determined on a Kofler hot-stage microscope melting point apparatus and are uncorrected. Microanalyses were performed by Mr. J. Robinson and Mr. A. R. Saunders of the University of East Anglia. IR spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer using standard Nujol mull and liquid film techniques. ^1H NMR spectra were recorded on a Perkin-Elmer Model R12 60-MHz spectrometer using Me_4Si as internal standard. Gas–liquid chromatograms were measured using a Pye Unicam CCD gas chromatograph with a 2.1 m, 4 mm diameter SE-30 column.

(46) Cain, J. C.; Simonsen, J. L. *J. Chem. Soc.* **1914**, *105*, 156–165.

(47) Perkin, Jr., W. H. *J. Chem. Soc.* **1918**, *113*, 722–765.

(48) Lovie, J. C.; Thomson, R. H. *J. Chem. Soc.* **1961**, 485–487.

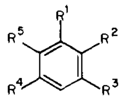
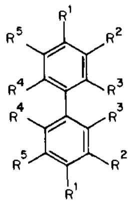
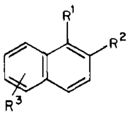
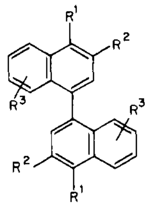
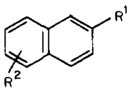
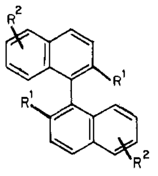
(49) Davies, W. *J. Chem. Soc.* **1923**, *123*, 1575–1593.

(50) Shriner, R. H.; McCutchan, P. *J. Am. Chem. Soc.* **1929**, *51*, 2193–2195.

(51) Buu-Hoi, N. P.; Lavit, D. *J. Chem. Soc.* **1955**, 2776–2779.

(52) An aliquot of the solution was mixed with dilute aqueous sodium hydroxide solution; the presence of thallium(III) is indicated by the precipitation of brown-black thallium(III) oxide.

Table II. Oxidative Dehydrodimerization of Aromatic Compounds to Biaryls Using $Hg(OCOCF_3)_2$, $Pb(OCOCH_3)_4$, $FeCl_3$, and CoF_3[a]

compd	aromatic compd					biaryl compd	$Hg(OCOCF_3)_2$ conversion, %	$Hg(OCOCF_3)_2$ yield, %	$Pb(OCOCH_3)_4$ conversion, %	$Pb(OCOCH_3)_4$ yield, %	$FeCl_3$ conversion, %	$FeCl_3$ yield, %	CoF_3 conversion %	CoF_3 yield, %
														
	R^1	R^2	R^3	R^4	R^5									
3	CH_3O	CH_3	CH_3	CH_3	H	14	0	0	66	53	59	30	35	0
5	CH_3O	CH_3O	H	CH_3	H	16	92	46	70	49	52	56	24	0
6	CH_3O	CH_3O	H	Br	H	17	mercurated product		80	85	52	56	80	81
7	CH_3O	CH_3O	H	I	H	18	unidentified product		83	72	86	*b*	84	86
8	CH_3O	CH_3O	H	Br	CH_3	19	100	46	72	49	13	0	30	77
9	CH_3O	CH_3O	H	I	CH_3	20	tar		71	56	tar		tar	
10	CH_3O	CH_3O	CH_3	Br	H	21	30	42	65	42	60	28	70	92
11	CH_3O	CH_3O	Br	CH_3	H	22	14	96	69	68	50	27	85	84
														
	R^1	R^2	R^3											
23	CH_3	H	H			37	unidentified product		89	85	56	44	42	58
24	$(CH_3)_2CH$	H	H			38	61	34	53	63	35	0	23	0
25	CH_2COOCH_3	H	H			39	0	0	65	95	30	0	tar	
26	C_6H_5	H	H			40	35	55	85	98	48	84	42	72
27	CH_3O	H	H			41	88	81	82	58	100	75	81	88
28	Br	H	H			42	mercurated product		57	84	67	28	78	85
29	I	H	H			43	mercurated product		67	82	62	*c*	70	93
31	CH_3O	CH_3	H			45	88	98	73	24	75	80	89	97
32	CH_3O	Cl	H			46	45	46	49	8	79	62	80	94
33	CH_3O	Br	H			47	0	0	44	19	40	86	36	86
34	Br	CH_3	H			48	mercurated product		42	45	*d*		*e*	
35	CH_3O	H	7-CH_3O			49	83	74	70	69	67	41	85	63
														
	R^1	R^2												
69	CH_3	H				71	4	0	61	54	14	0	21	0
53a	CH_3O	H				54b	83	79	60	72	66	80	84	73
53b	CH_3O	6-Br				54	82	74	70	69	100	55	75	60
70	Br	H				72	9	0	72	55	3	0	12	0

[a] Conversion and yield data were calculated as described in footnote *b*, Table I. Yields refer to isolated, pure, recrystallized material. [b] The only product which was isolated (17%) was hexamethoxytriphenylene (**50**). [c] Product was a colorless solid, probably polymeric (which melted over a wide temperature), and from which no identifiable products could be isolated. [d] Mixture of five products. [e] Mixture of four products.

ganomercurials and metallic mercury were removed at this stage by filtration. The chloroform extracts were dried ($MgSO_4$) and the solvent was removed by distillation under reduced pressure to give the crude product, which was passed down a short column of basic alumina using chloroform/petroleum ether (bp 40–60 °C) as eluant. Evaporation of the eluant under reduced pressure followed by crystallization of the residual solid thus obtained gave the pure biaryl. Unreacted starting material was obtained by concentration of the mother liquors.

General Method for the Preparation of Biaryls Using Pb(OCOCH$_3$)$_4$. Boron trifluoride diethyl etherate (5 mL) was added to a solution of the aromatic substrate (0.02 mol) and lead tetraacetate (4.88 g, 0.011 mol) in acetonitrile (25 mL). The solution immediately turned green or deep blue in color and an exothermic reaction ensued. The reaction mixture was stirred for 3 h, then poured into water, and the products were extracted with chloroform (2 × 100 mL). The chloroform solution was passed through a short column of basic alumina using chloroform/petroleum ether (bp 40–60 °C) mixtures as eluant to remove any highly colored, polymeric materials. Evaporation of the eluant under reduced pressure gave a solid or semisolid residue which contained a mixture of starting material and coupled products. Separation of the crude reaction mixture to give the pure biaryl was accomplished either by recrystallization or, in a few cases, by sublimation. Any unreacted starting material was recovered by concentration of the mother liquors and subsequently analyzed by GLC for impurities.

General Method for the Preparation of Biaryls Using FeCl$_3$. A mixture of the aromatic substrate (0.02 mol) and anhydrous ferric chloride (3.24 g, 0.02 mol) in anhydrous dichloromethane (25 mL) was stirred for 12 h at room temperature. The dark-colored reaction mixture was then poured into water and extracted with chloroform (2 × 100 mL). The chloroform extract was separated, dried (MgSO$_4$), and then boiled with decolorizing charcoal. Removal of the solvent under reduced pressure gave the crude product, which contained a mixture of starting material and product. Isolation of the pure biaryl was accomplished as described above.

General Method for the Preparation of Biaryls Using CoF$_3$. A mixture of the aromatic substrate (0.01 mol) and cobalt(III) fluoride (0.01 mol) in trifluoroacetic acid (25 mL) was heated under reflux for 12 h. The rose-colored reaction mixture was then poured into water and extracted with chloroform (2 × 100 mL). The chloroform extract was dried (MgSO$_4$) and then evaporated under reduced pressure to give a semisolid residue. In most cases, this could then be recrystallized directly to give the pure biaryl, or was otherwise purified by short column chromatography over alumina followed by recrystallization from the appropriate solvent (see Table I).

Oxidation of 1,2-Dimethoxybenzene with TTFA. Oxidation of 1,2-dimethoxybenzene with TTFA using method C gave a 40–50% yield of crude product as a blue-colored solid. Vacuum sublimation gave a 29% yield (100% conversion) of **50** as a colorless solid, mp 303–307 °C with sublimation (lit.[53] mp 297–298 °C), identical with a genuine sample. Low and variable (5–20%) yields of **50** were obtained similarly using methods A, B, D, and E.

Preparation of Bianthron-9-yl (51). 9-Methoxyanthracene was oxidized with TTFA using method C. Addition of water to the reaction mixture gave a cream-colored solid which was collected and recrystallized from toluene. This gave **51** in 83% yield (100% conversion) as pale yellow needles, mp 250–253 °C (lit.[54] mp 245–249 °C). The product was identical with a genuine sample.[55]

Oxidation of 2-Methoxy-1-methylnaphthalene and 1,3-Dimethyl-2-methoxynaphthalene with TTFA. Treatment of 2-methoxy-1-methylnaphthalene with TTFA according to any of the standard methods A–E gave a viscous, orange oil, bp ca. 200 °C (0.5 torr), which could not be crystallized and which (NMR) always contained small amounts of starting material. The structure **52a** is tentatively assigned to this product on the basis of spectroscopic data: $\nu_{C=O}$ 1660–1680 cm^{-1} (br); NMR (CCl$_4$) δ 8.0–6.9 (10 H, complex m), 6.0 (1 H, d, J = 10 Hz), 3.68 (3 H, s), 2.37 (3 H, s), 1.86 (3 H, s).

Oxidation of 1,3-dimethyl-2-methoxynaphthalene with TTFA using any of the standard methods A–E similarly gave a viscous, orange oil which could not be crystallized and which (NMR) always contained small amounts of starting material. The structure **52b** is tentatively assigned to this product on the basis of spectroscopic data: $\nu_{C=O}$ 1665–1685 cm^{-1} (br); NMR (CCl)$_4$ δ 7.9–6.8 (9 H, complex m), 3.6 (3 H, s), 2.48 (3 H, s), 2.32 (6 H, s), 1.86 (3 H, s).

Oxidation of 2-Methoxynaphthalene (53a) with Thallium(III) Acetate. Boron trifluoride diethyl etherate cooled to −40 °C (10 mL) was added to a stirred mixture of thallium(III) acetate (4.08 g, 0.01 mol) and 2-methoxynaphthalene (3.16 g, 0.02 mol) in acetonitrile (25 mL) which was also cooled to −40 °C. The temperature was allowed to rise to ambient, and a thallium(III) test was negative after about 15 min at room temperature. The mixture was poured into water (150 mL), the products were extracted with chloroform (3 × 30 mL), and the chloroform extracts were combined, dried (MgSO$_4$), and passed through a short column of alumina using chloroform as eluant. Concentration of the eluate gave a solid (3.1 g) from which 0.6 g of starting material was recovered by trituration with petroleum ether (bp 40–60 °C). A further 0.3 g of starting material was recovered by vacuum sublimation. Recrystallization of the nonvolatile residue from toluene/petroleum ether (bp 100–120 °C) gave 1.8 g (80% yield, 71% conversion) of pure 2,2′-dimethoxy-1-1′-binaphthyl (**54a**) as colorless prisms, mp 190–195 °C (lit.[56] mp 190–191 °C).

Oxidation of 2-Bromo-6-methoxynaphthalene (53b) with TTFA. 53b was oxidized with TTFA using method C, and the biaryl separated from the reaction mixture as a gray-colored solid after a few minutes. This was collected by filtration and recrystallized from toluene/petroleum ether (bp 100–120 °C) to give pure 6,6′-dibromo-2,2′-dimethoxy-1,1′-binaphthyl (**54b**) in 76% yield (83% conversion) as very pale pink prisms, mp 250–251 °C (lit.[57] mp 239.5 °C). Unreacted starting material (0.8 g) was recovered from the filtrate.

Oxidation of Mesitylene, Durene, Naphthalene and Mixtures Thereof with TTFA. A solution of the aromatic substrate(s) (0.02 mol for single substrates, 0.01 mol of each when two substrates were used) was added to a solution of TTFA (5.5 g, 0.01 mol) in TFA (20 mL) containing boron trifluoride diethyl etherate (10 mL) where appropriate, and the mixture was stirred for the required length of time. Excess of an aqueous solution of potassium iodide was then added and the reaction mixture was stirred for a further 30 min. The orange-yellow thallium(I) iodide was removed by filtration and washed well with chloroform. The filtrate was extracted with chloroform (3 × 25 mL) and the combined extracts were dried (MgSO$_4$). The solvent was removed by distillation under reduced pressure, the residue was passed through a short column of alumina using petroleum ether (bp 40–60 °C) as eluant to remove traces of inorganic salts, and the eluant was concentrated to a volume suitable for GLC analysis. Genuine samples of compounds **58**, **60–64**, and **66–68** were prepared using published procedures.

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[55] We thank Dr. D. C. Nonhebel (Strathclyde University) for supplying a genuine sample of **51**.

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