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Rearrangement Reactions of Bicyclic Systems. Part V.[1] Acid-catalysed Rearrangements of 1,4-Dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene and the Remarkable Effect of Aromatic Methoxy-groups on the Course of the Reaction

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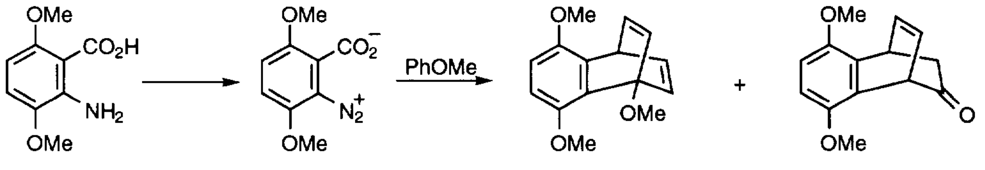
Abstract: *3,6-Dimethoxyanthranilic acid (2) has been prepared by a procedure that is more reliable than our earlier one and used as a 3,6-dimethoxybenzyne precursor in a reaction with anisole to give 1,4-dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene (1,5,8-trimethoxybenzobarrelene) (1). Trifluoroacetic acid-catalysed rearrangement of this benzobarrelene (1) gave as precedented products of bicyclo-rearrangement 3,4-dihydro-5,8-dimethoxy-1,4-ethenonaphthalen-2(1H)-one (5,8-dimethoxybenzobarrelenone) (3) and 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-one (7) along with 2,4',5-trimethoxybiphenyl (6), the product of a remarkable retro-Friedel-Crafts protodealkoxyalkylative fragmentation of the bicyclic system. Similar reactions were observed with perchloric acid. The structure of this unexpected biphenyl was confirmed by its preparation by Gomberg-Bachman-Hey arylation of 1,4-dimethoxybenzene.*

Introduction

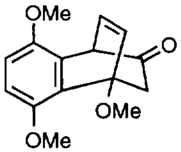
The acid-catalysed rearrangement reactions of benzobarrelenes (1,4-dihydro-1,4-ethenonaphthalenes) follow many paths[1-3] but the primary rearrangement is normally simple: the eventual outcome[2c] depends on whether the benzo- or etheno-bridge migrates to the first-formed carbenium ion. Only in very special circumstances[3e,f] do the rearranged carbenium ions equilibrate. In our initial studies of the rearrangement using tetrahalobenzobarrelenes (5,6,7,8-tetrahalo-1,4-dihydro-1,4-ethenonaphthalenes) we had found[2c] that benzo-migration was an important pathway but not the exclusive one. It was of interest to examine the effect on the course of the rearrangement of replacing the tetrahalobenzo-ring with a more basic one that would migrate more easily. We chose to examine the 5,8-dimethoxy analogue and now report full details[4] of our study of the preparation and acid-catalysed rearrangement reactions of 1,5,8-trimethoxybenzobarrelene (**1**).

Results and Discussion

1,5,8-Trimethoxybenzobarrelene (**1**) (17%) was prepared by aprotic diazotisation[5] of 3,6-dimethoxy-anthranilic acid (**2**) in the presence of an excess of anisole; the minor adduct, isolated as the ketone (**3**) in 5% yield, resulted from 2,5-addition. The comparatively poor yield emphasises the importance of inductively electron-withdrawing aryne-substituents[6] in reactions with even moderately reactive arenes. In a similar reaction with the more nucleophilic 1,3-dimethoxybenzene we obtained the single adduct (**4**) (39%). Our previously reported[2b] yields of adducts with 1,2-dimethoxybenzene (40%) and furan (80%) confirm the trend. In a previous report[2b] we described the preparation of 3,6-dimethoxyanthranilic acid (**2**) from the readily available[7] 3,6-dimethoxy-2-nitro-benzamide (**5**) by hydrolysis and reduction. We found during this study that the hydrolysis as described[2b,7a] (conc. sulphuric acid - excess of sodium nitrite) was somewhat capricious. We suspected that secondary reactions might be occurring in concentrated sulphuric acid; as the amount of water in the system was increased the yield increased reproducibly to a new and improved maximum in excess of 90% at 2:1 v/v sulphuric acid: water. Subsequent reduction (hydrazine hydrate, Pd/C, boiling ethanol)[8a] (95%) also appeared to be better with material prepared in this way. In contrast, catalytic hydrogenation of 3,6-dimethoxy-2-nitrobenzoic acid prepared by direct nitration of 2,5-dimethoxybenzoic acid seems to be less successful.[8b]



(2) **(1)** **(3)**



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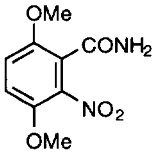

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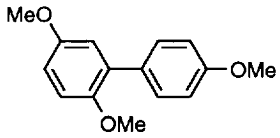
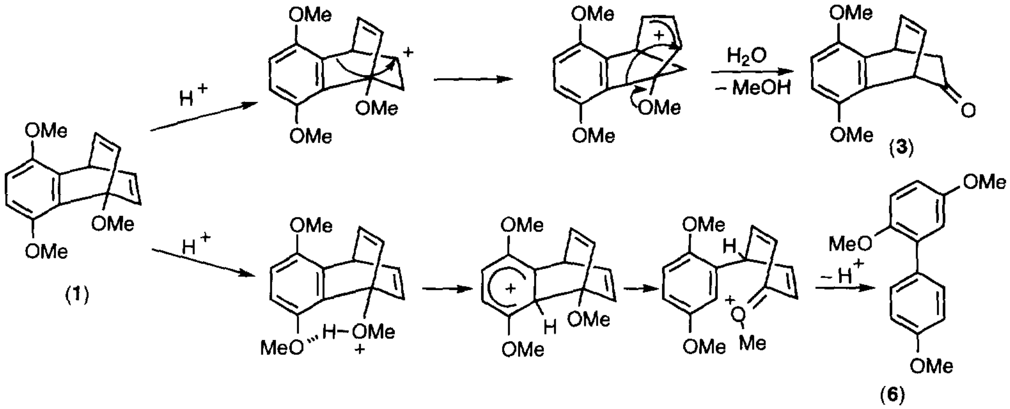


(6)

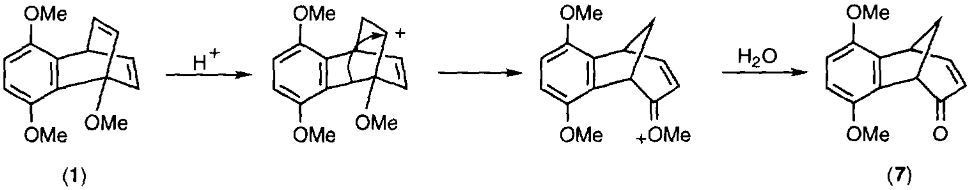
Rearrangement of 1,5,8-trimethoxybenzobarrelene (**1**) at room temperature for 1.5h in aqueous 60%-perchloric acid gave two main products. The more polar was immediately recognisable as 1,2,3,4-tetrahydro-5,8-dimethoxy-1,4-ethenonaphthalen-2(1*H*)-one (5,8-dimethoxybenzobarrelenone) (**3**) (42%), previously isolated as the minor Diels-Alder adduct between anisole and 3,6-dimethoxybenzyne. The less polar product was of a type not previously seen in our studies of these rearrangements. This less polar product was an isomer of the starting material (*m/z* = 244; combustion analysis consistent with $C_{15}H_{16}O_3$) and was thus formed in 21% yield. The 90 MHz ^1H n.m.r. spectrum clearly showed the presence of three methoxy-groups (δ_H 3.72, 3.77, and 3.82 ppm) and a two proton multiplet (δ_H = 7.50 ppm; major coupling constant J = 9.0 Hz) indicative of a 1,4-disubstituted benzene ring; the remaining five proton resonances were a poorly resolved multiplet (δ_H 6.80 - 7.05 ppm). These data strongly suggested that this product was 2,4',5-trimethoxybiphenyl (**6**) - the only remaining ambiguity being the substitution pattern of the trisubstituted ring (Scheme 1).

The structure was confirmed by synthesis: when 4-methoxyaniline was diazotised with pentyl nitrite and catalytic trifluoroacetic acid in the presence of an excess of 1,4-dimethoxybenzene in boiling acetone[9] the known[10] 2,4',5-trimethoxybiphenyl (**6**) (5.5%) was formed; it was indistinguishable from the less polar product of rearrangement.



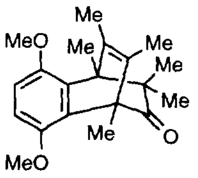
Scheme 1

When a similar rearrangement of the benzobarrelene (**1**) was attempted in anhydrous trifluoroacetic acid the starting material was recovered unchanged. However, 1,5,8-trimethoxybenzobarrelene (**1**) underwent complete rearrangement within 4h in boiling anhydrous trifluoroacetic acid to give 5,8-dimethoxybenzobarrelenone (**3**) (37%) and 2,4',5-trimethoxybiphenyl (**6**) (32%) as previously isolated; in addition a small amount of the known[2b] enone 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-one (**7**) (4%) was isolated (Scheme 2).



Scheme 2

The relative proportions of the products obtained in a 6h reaction were unchanged. Although acid-catalysed rearrangement of the closely related ketone (**8**) has been reported[3f] to give both isomers (**9**) and (**10**), none of our products was unstable under the conditions of its formation.



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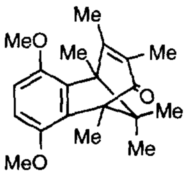

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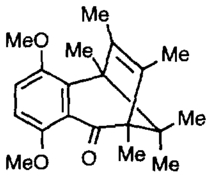
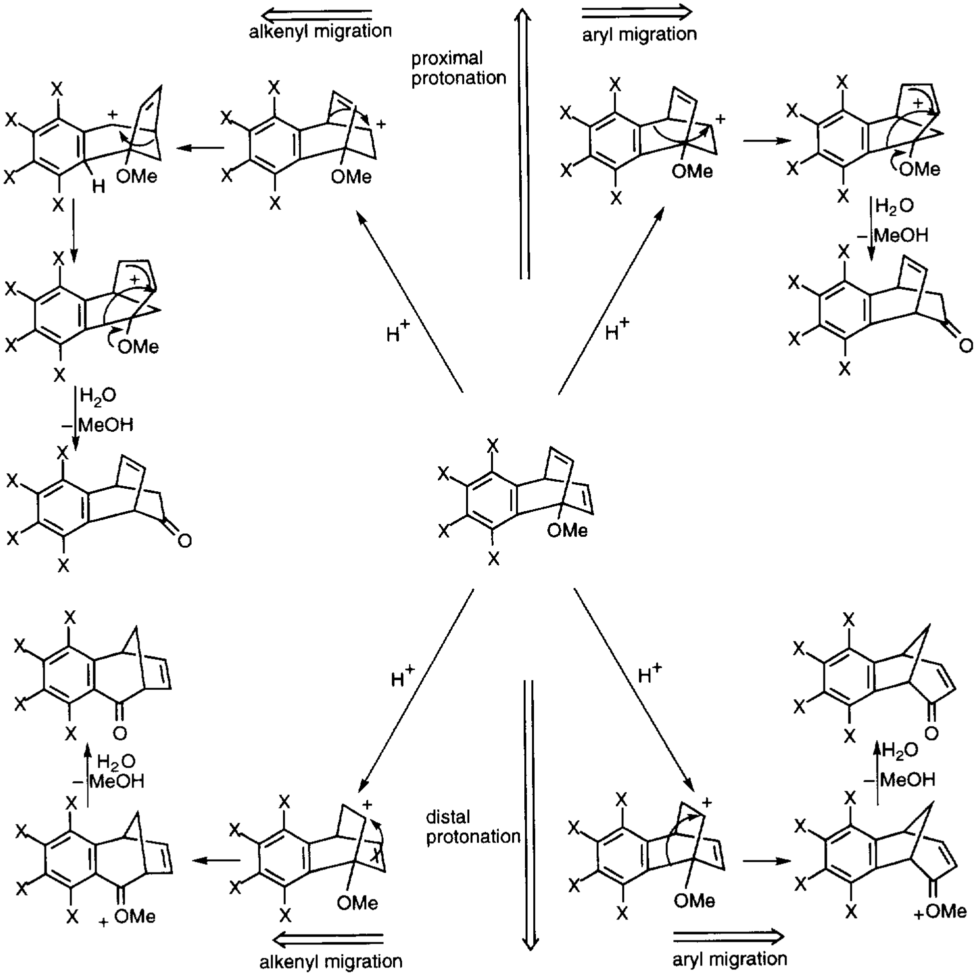


(10)

These rearrangements are only partly explicable within the general mechanism previously advanced. Acid-catalysed rearrangements of 1-methoxybenzobarrelenes normally[2c] follow double-bond protonation and it is the first *C*-protonation that initiates rearrangement. This protonation may occur either proximally or distally to the methoxylated bridgehead and the first migration may be of either the benzo- or the etheno-bridge (Scheme 3). It is clear that in this case, in which the aromatic ring is far more basic than in the other cases that we have studied, the additional process of *ipso* arene-protonation is operating.



Scheme 3

Although acid-catalysed dealkylations are commonplace[11] a highly regioselective dealkyoxyalkylation such as this is unusual. Treatment of a methyl benzyl ether with acid would normally[12] result in *O*- rather than *C*-protonation and lead to *C*-*O* heterolysis. In this case *C*-*O* heterolysis is strongly disfavoured for stereoelectronic reasons and other processes occur. *O*-Protonation is still probably an important factor - the methoxy-group is a good hydrogen bond acceptor[12a] - but only in the sense of controlling *C*- protonation so that a distal carbenium ion is generated. When this distal carbenium ion is generated by proximal protonation of the benzo-bridge it fragments by two consecutive aromatisations, the first of which is a retro-Friedel-Crafts protodealkoxyalkylation, to give the biphenyl (**6**) (Scheme 1). An attempt to label the initial aryl protonation using [^{2}H]trifluoracetic acid was frustrated by extensive deuteriation of the biphenyl (**6**) produced.

The rearrangements that follow the usual olefinic *C*-protonation are also highly regioselective and proceed predominantly by proximal protonation through the distal carbenium ion; fragmentation does not occur without the driving force of re-aromatisation. 5,8-Dimethoxybenzobarrelenone (**3**) can arise from this distal carbenium ion by either[2c] benzo- or etheno-bridge migration. Benzo-bridge migration is favourable even with a tetrachlorobenzo-moiety[2c] and is presumably the overwhelmingly dominant pathway here. However, even though the pathways can be distinguished[2c] by various labelling techniques there is no experimental basis for excluding etheno-bridge migration as a contributory pathway. Although the products isolated from perchloric acid-catalysed rearrangement are derived from regiospecific proximal protonation the products of the trifluoroacetic acid-catalysed rearrangement are only highly regioselective. The tendency to lose regiospecificity as the acid strength is decreased has been noted before[2c] and may reflect a decrease in the proportion of *O*-protonated species. The additional product, 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-one (**7**) arises by distal protonation followed by benzo-bridge migration to the proximal carbenium ion. In this case it is possible to assess the effect on product distribution of increasing the migratory propensity of the benzo-bridge: with a tetrachlorobenzo-bridge there would be a substantial amount[2c] of etheno-bridge migration: none was observed here.

In summary, we see several effects in this study:

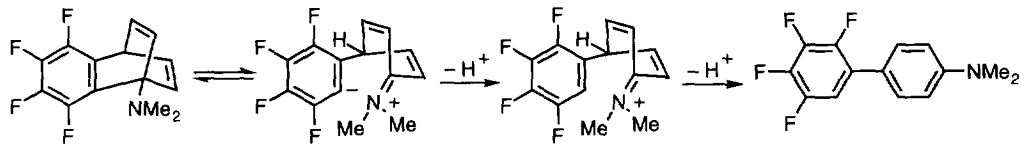
(i) The rearrangements are highly regioselective. This can only be an effect of the bridgehead methoxy-group, which is probably protonated.

(ii) The rearrangements are more stereoselective than those of the analogous 5,6,7,8-tetrahalo-analogues. There is proportionately more of the product arising from benzo-bridge migration, which is the expected result.

(iii) The rearrangements occur under milder conditions than those of the 5,6,7,8-tetrahalo-analogues. This reflects an increase in the π-basicity of the etheno-linkages.

(iv) The increase in the π-basicity of the benzo-bridge itself leads to a most remarkable effect when a regiospecific *ipso*-protonation is followed by retro-Friedel-Crafts fragmentation of the bicyclic system to give, ultimately, the biphenyl (**6**).

Overall, this last reaction has similarities to the solvolysis in hot ethanol of 5,6,7,8-tetrafluoro-1,4-dihydro-*N*,*N*-dimethylamino-1,4-ethenonaphthalene (1-*N*,*N*-dimethylaminotetrafluorobenzobarrelene) (**11**) to give 4'-*N*,*N*-dimethylamino-2,3,4,5-tetrafluorobiphenyl (**13**) (Scheme 4). However, in that case it is heterolysis to the aryl anion (**12**) that precedes protonation[13] whereas we believe that in the present case *ipso*-protonation is the primary step. Thus although solvolytic reactions of benzobarrelenes normally[1-3] lead to rearrangement of the bicyclic skeleton the two possible mechanistic extremes that lead instead to biphenyls have now been observed.



(11) **(12)** **(13)**

Scheme 4

Acknowledgements.

We thank the S.R.C. for studentships (to N.J.H. and J.H.H.) and for a research grant (to H.H.).

Experimental

The spectroscopic data were taken using: i.r., Perkin-Elmer 257; u.v., Unicam SP8000; ^{1}H n.m.r. (in $CDCl_3$ vs tetramethyl-silane) Perkin-Elmer R32; and mass spectra, A.E.I. MS12 instruments. Light petroleum refers to that fraction having b.p. 60-80°C unless otherwise stated. M.p.s. are uncorrected and were determined using a Koffler hot-stage apparatus. Preparative t.l.c. was carried out using silica-gel (Merck PF_{254}).

3,6-Dimethoxy-2-nitrobenzoic Acid

A stirred slurry of 3,6-dimethoxy-2-nitrobenzamide[2b] (76.0 g, 340 mmol) in aqueous sulphuric acid [formed by cautiously adding sulphuric acid (98%; 800 mL) to stirred water (400 mL)] was treated at *ca.* 0°C with small portions of sodium nitrite (33 g, 480 mmol). The solution was allowed to warm to room temperature, stirred at this temperature for 15h and then quenched into an excess of ice/water. The product was isolated by filtration, washed with water, dried, and recrystallised from aqueous ethanol to give 3,6-dimethoxy-2-nitrobenzoic acid (70.6 g, 95%), m.p. 188-191°C (from aqueous ethanol) (lit.,[2b] 192-194°C).

3,6-Dimethoxyanthranilic Acid (2)

A suspension of palladium on charcoal (10%; 400 mg) in a solution of 3,6-dimethoxy-2-nitrobenzoic acid (19.6 g, 860 mmol) in hot ethanol (300 mL) was treated during 0.5h with hydrazine hydrate (30 mL). The mixture was then heated under reflux for 3h, cooled, and filtered. The filtrate was concentrated to a small volume and cooled to give 3,6-dimethoxyanthranilic acid (**2**) (16.2 g, 95%), m.p. 94-96°C (from ethanol) (lit.,[2b] 96-97°C).

1,5,8-Trimethoxybenzobarrelene (1,4-dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene) (1)

A stirred solution of 3,6-dimethoxyanthranilic acid (**2**) (8.1 g, 40 mmol) and trichloroacetic acid (0.080 g) in a mixture of tetrahydrofuran (40 mL) and diethyl ether (40 mL) was treated with pentyl nitrite (10 mL) and then maintained at room temperature for 2h. The dark red precipitate that formed was isolated by decantation and washed with ether (10 mL). **CAUTION:** ***This product may explode violently and unpredictably; it should never be allowed to dry and should never be handled without protective screens.*** A suspension of this dark red solid in 1,2-dichloroethane (50 mL) was added to preheated (60°C) anisole (250 g). The reaction mixture was maintained at this temperature for 4h and then evaporated to leave a dark brown oil that was purified by column chromatography on neutral alumina (Camag; Brockmann activity 1). Elution with diethyl ether: light petroleum (1:2) gave 1,4-dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene (**1**) (1.7 g, 17%), m.p. 78-79°C (from methanol). (Found: C, 74.0; H, 6.6. $C_{15}H_{16}O_3$ requires C, 73.8; H, 6.6%); ν_{max} (KBr) 3 085, 3 000, 2 965, 2 940, 2 915, 2 840, and 1 640 cm^{-1}; δ_H 3.76 (3H, s), 3.80 (3H, s), 3.82 (3H, s), 5.28 (1H, tt, *J* 1.8 and 5.8 Hz), 6.51 (2H, s), and 6.90 (4H, m); *m/z* 244 (M$^+$). Elution with diethyl ether: light petroleum (5:1) gave 3,4-dihydro-5,8-dimethoxy-1,4-ethenonaphthalen-2(1*H*)-one (**3**) (0.46g, 5%), m.p. 104-106°C (from methanol). ν_{max} (KBr) 3 080, 3 010, 2 950, 2 840, and 1 740 cm^{-1}; δ_H 2.04 (2H, d+d, *J* 17 Hz), 3.78 (3H, s), 3.82 (3H, s), 4.65 (1H, m), 4.87 (1H, dd, *J* 2 and 6 Hz), and 6.80 (4H, m); *m/z* 230 (M$^+$) and 188 (M-42$^+$).

3,4-Dihydro-4,5,8-trimethoxy-1,4-ethenonaphthalen-2(1*H*)-one (4)

A stirred solution of 3,6-dimethoxyanthranilic acid (5.4 g, 27 mmol) and trichloroacetic acid (0.050 g) in a mixture of tetrahydrofuran (30 mL) and diethyl ether (30 mL) was treated with pentyl nitrite (7.5 mL) and then maintained at room temperature for 2h. **CAUTION:** ***This product may explode violently and unpredictably; it should never be allowed to dry and should never be handled without protective screens.*** The dark red precipitate that had formed was isolated by decantation and washed with 1,2-dichloroethane (3 x 10 mL) by decantation. A slurry of this dark red solid in 1,2-dichloroethane (10 mL) was added to preheated 1,3-dimethoxy-benzene (200 g). The reaction mixture was maintained at this temperature for 3h and then evaporated to leave a dark brown oil that was purified by column chromatography on neutral alumina (Camag; Brockmann activity 1). Elution with ether: light petroleum (1:1) gave 3,4-dihydro-4,5,8-trimethoxy-1,4-ethenonaphthalen-2(1*H*)-one (**4**) (2.65 g, 39%), m.p. 93°C (from methanol) (Found: C, 69.2; H, 6.1. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.2%); ν_{max} (KBr) 2 930, 2 830, and 1 730 cm^{-1}; δ_H 2.39 (2H, s), 3.69 (3H, s), 3.78 (3H, s), 3.83 (3H, s), 4.88 (1H, dd, *J* 2 and 6 Hz), and 6.7 (4H, m); *m/z* 260.

Acid-catalysed rearrangements of 1,4-dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene (1,5,8-trimethoxybenzobarrelene) (1)

(a) In Perchloric acid

1,4-Dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene (**1**) (0.60 g, 2.46 mmol) was stirred with aqueous perchloric acid (60%; 50 mL) at room temperature for 1.5h. The reaction mixture was poured into ice (200 g) and extracted with chloroform (3 x 50 mL). The extracts were combined, washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to leave an oil. The oil was purified by preparative t.l.c. using diethyl ether: light petroleum (1:1) as eluant to give two main bands: a) at solvent front; 2,4',5-trimethoxybiphenyl (**6**) (0.127 g, 21%), m.p. 62-64°C (from light-petroleum) (lit.,[10] 62-64°C). (Found: C, 73.9; H, 6.7 Calc. for $C_{15}H_{16}O_3$ C, 73.8; H, 6.6%); ν_{max} (KBr) 3 000, 2 945, 2 915, 2 840, 1 618, 882, 835, 798, and 745 cm^{-1}; λ_{max}(cyclohexane) 325 (logε 3.11), 310 (3.77), 302 (3.83), 290 (3.72), 255 (4.11), 222 (4.22), and 211 (4.33)nm; δ_H 3.72 (3H, s), 3.77 (3H, s), 3.82 (3H, s), 6.8-7.05 (5H, m), and 7.50 (2H, d, *J* 9 Hz); *m/z* 244. b) 3,4-dihydro-5,8-dimethoxy-1,4-ethenonaphthalen-2(1*H*)-one (**3**) (0.225 g, 42%) m.p. and mixed m.p. 104°C; spectroscopically indistinguishable from an authentic sample (above).

(b) In Trifluoroacetic acid

A solution of 1,4-dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene (**1**) (0.935 g, 3.83 mmol in boiling trifluoroacetic acid (15 mL) was heated under reflux for 4h. The reaction mixture was poured onto ice and extracted with diethyl ether. The extract was dried ($MgSO_4$) and evaporated to leave an oil. The oil was purified by preparative t.l.c. as above to give 3 main bands: a) 2,4',5-trimethoxybiphenyl (**6**) (0.298 g, 32%);

b) 3,4-dihydro-5,8-dimethoxy-1,4-ethenonaphthalen-2(1*H*)-one (**3**) (0.327 g, 37%); and c) 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-one (**7**) (0.038 g, 4.3%), m.p. 137-141°C (from ethanol) (lit.,[2b] 140-141°C); spectroscopically indistinguishable from our authentic sample.

2,4',5-Trimethoxybiphenyl (6) by arylation of 1,4-dimethoxybenzene

1,4-Dimethoxybenzene (6.9 g, 50 mmol), 4-methoxyaniline (1.23 g, 10 mmol), trifluoroacetic acid (2 drops), and pentyl nitrite (1.3 g, 11.1 mmol) were heated under reflux for 2h in sufficient acetone to form a homogeneous solution. The reaction mixture was evaporated under reduced pressure and the residue was purified initially by column chromatography on neutral alumina (Camag, Brockmann activity 1) using diethyl ether: light-petroleum (b.p. 40-60°C) (3:7) and finally by preparative t.l.c. as above to give 2,4',5-trimethoxybiphenyl (**6**) (0.120 g, 5.3%) m.p. 62-64°C [from light petroleum (b.p. 40-60°C)] (lit.,[10] 62-64°C).

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