upon reacting alcohol VI (Scheme III) with 1,3-cyclohexanedione in the presence of $Pd(PhCN)_2Cl_2$. An alternative step, involving the initial aromatization of I to catechol followed by etherification to dioxane, may be excluded since no reaction of catechol with both 1,2-cyclohexandiols is promoted by $Pd(PhCN)_2Cl_2$ in the reported conditions. Furthermore, we observed that the benzodioxanes IV and V are obtained in the same way in the absence of dione I by the reaction of *trans*- and *cis*-1,2-cyclohexanediols, respectively, with $Pd(PhCN)_2Cl_2$. This reaction proceeds via an initial oxidation, to dione I, of a certain amount of diol by the Pd^{2+} salt as reported for the oxidation of simple alcohols.[4]

1,4-Benzodioxanes are a class of heterocyclic compounds with hypnotic and sedative activity.[5] The novel synthetic route reported appears of some interest when compared with alternative syntheses requiring more severe reaction conditions or generally giving low yields.[6] From these results, and others reproted previously,[1] dichlorobis(benzonitrile)palladium(II) appears to be a versatile activating agent, under unusually mild conditions, for the alcoholic and epoxidic functions.

Experimental Section

General. $Pd(PhCN)_2Cl_2$ was prepared by the method of Kharasch.[7] Benzene was distilled over sodium metal. Melting points were determined with a Kofler apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 257 Infracord and NMR spectra with a Perkin-Elmer apparatus (90 MHz) in $CDCl_3$; for TLC, Kieselgel G from Merck was used. GLC analyses were carried out with a "Carlo Erba" Fractovap G-1 using a 60-m capillary column with 5% Carbowax as the stationary phase.

Synthesis of Dioxanes II-V. The following procedure for the preparation of V is representative. Dione I (1 mmol), 1 mmol of *cis*-1,2-cyclohexanediol, and 2 mmol of $Pd(PhCN)_2Cl_2$ were made to react by refluxing in 3 mL of benzene overnight in a dry nitrogen atmosphere. The reaction mixture was then hydrolyzed with water and extracted with ethyl ether. The aqueous phase was evaporated to dryness to recover the palladium salt. The ether extracts were dried (anhydrous Na_2SO_4) and evaporated. The reaction mixture was chromatographed on a silica gel column. By elution with 90:10 hexane–ethyl ether, V was obtained (65% yield) as microcrystals, mp 43–44 °C, from methanol: IR 1260 and 1050 cm^{-1} (aromatic ether), 1590 and 1490 cm^{-1} (phenyl group), 2860 cm^{-1} (aliphatic carbons); NMR 3.7 (1 H, m), 4.20 (1 H, m), 6.82 (4 H, s) ppm.

In the same way, from I and *trans*-1,2-cyclohexanediol, IV is obtained (50% yield) as an uncrystallizable compound; in the IR spectrum the same typical bands as for V were found; in the NMR spectrum V is different from IV in a single multiplet (2 H) centered at 3.7 ppm in the ethereal region. By further elution of the reaction mixture, a minor compound (15% yield) that is under examination was obtained.

The benzodioxanes II and III were identified by GLC comparison with authentic samples. The respective yields were 50% and 52%. In these reported reactions the residual yields are attributable to starting compounds as well as to a variable amount of catechol derived from the aromatization of I by Pd^{2+} salts.

Preparation of VII and VIII by Reaction of 1,3-Cyclohexanedione with Alcohol VI and $Pd(PhCN)_2Cl_2$. We utilized the same ratio of reagents and conditions reported above. The crude reaction mixture was chromatographed on a silica gel column by eluting with 50:40:20 benzene–hexane–ethyl ether. We obtained VII (22% yield) as a liquid; in the IR spectrum there was no absorbance in the carbonyl region. In the NMR spectrum a complex signal in the aromatic region (4 H) centered at 6.40 ppm, a single triplet (4 H) centered at 3.90 ppm (attributable to four ethereal protons), and a strong singlet centered at 1.3 ppm (attributable to the alcoholic aliphatic chain) were found. By further elution, we obtained a small amount of starting compound and then VIII (60% yield) as an uncrystallizable compound. In the IR spectrum two strong bands at 1660 and 1615 cm^{-1} typical of an O=C–C=C–OR system were found. In the NMR spectrum characteristic signals at 5.25 (1 H, s, olefinic proton) and 3.75 ppm (2 H, t, ethereal protons) were found.

Registry No. I, 765-87-7; II, 493-09-4; III, 75768-16-0; IV, 75768-17-1; V, 75459-45-9; VI, 36653-82-4; VII, 75768-18-2; VIII, 75768-19-3; *cis*-1,2-cyclohexanediol, 1792-81-0; *trans*-1,2-cyclohexanediol, 1460-57-7; dichlorobis(benzonitrile)palladium(II), 14220-64-5; 1,3-cyclohexanedione, 504-02-9; 1,2-ethanediol, 107-21-1; 2,3-dimethyl-2,3-butanediol, 76-09-5.

(3) Dunn, T. M. In "Modern Coordination Chemistry"; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, pp 266–267.
(4) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. II, p 119.
(5) Nelson, W. L.; Wennerstrom, J. E.; Dyer, D. C.; Engel, M. *J. Med. Chem.* **1977**, 881. Hoppe, J. O.; Pribyl, E. D.; Wheeler, K. W. In *Med. Chem. (Academic)* **1963**, *6*, 123.
(6) (a) Elderfield, E. C. *Heterocycl. Compd.* **1957**, *6*, 71. (b) Goosen, A.; McCleland, C. W. *J. Chem. Soc., Chem. Commun.* **1975**, 655.
(7) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 884.

Synthesis of Aryl Ortho Esters from Benzanilide Acetals

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The recent report[1] of a new method for the preparation of aryl ortho esters[2] prompts us to describe a procedure which we have recently found successful. Our approach involves the intermediate preparation of a benzanilide acetal (1, Scheme I), this being produced easily from the corresponding benzanilide by using standard amide acetal synthetic procedures.[3] The benzanilide acetal is not purified but simply treated for 5–10 min with excess acetic acid in methanol. After neutralization of the acid, standard workup produces a 1:1 mixture of the desired ortho ester and *N*-methylaniline. These can be easily separated by fractional distillation or, in the case of the 4-nitrobenzoate, by recrystallization of the ortho ester. The approach produces good yields of pure ortho ester. We have used it now in three cases: Ar = 4-MeOC_6H_4 (58% yield after separation from *N*-methylaniline, based on initial benzanilide), Ar = 4-MeC_6H_4 (67% yield), and Ar = $4\text{-NO}_2C_6H_4$ (40% yield). The procedure appears capable of extension to aliphatic ortho esters and, by using a different alcohol in the final step, should also be able to produce a mixed ortho ester.

The method owes its success to the very labile nature of the C–N bond of the anilide acetal in an acid solution.[4] Mechanistically, the final step in the synthesis must be proceeding with protonation on nitrogen and loss of *N*-methylaniline, followed by reaction of the so-formed dialkoxycarbonium ion with solvent. This same ion is also formed as an intermediate in the Pinner ortho ester synthesis.[2] The advantage of the anilide acetal procedure comes from the very mild acid conditions and short re-

(1) Breslow, R.; Pandey, P. S. *J. Org. Chem.* **1980**, *45*, 740.
(2) (a) The standard procedure starting from a nitrile, the Pinner synthesis,[2b] usually results in a mixture which is difficult to separate[1] when applied to the preparation of an aryl ortho ester. (b) DeWolfe, R. "Carboxylic Ortho Acid Derivatives"; Academic Press: New York, 1970; pp 2–11.
(3) Reference 2b, pp 422–424.
(4) McClelland, R. A.; Somani, R. *J. Chem. Soc., Chem. Commun.* **1979**, 407.

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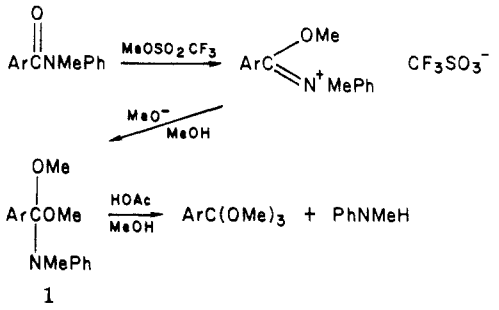
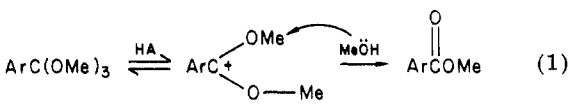
Scheme I

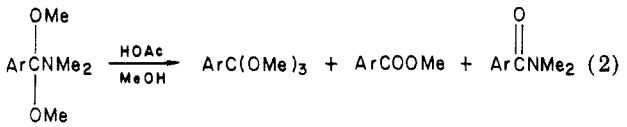


action times which are involved. This minimizes the possibility of the ortho ester reverting back to dialkoxycarbonium ion and eventually being dealkylated to form a simple benzoate ester[1] (eq 1).



(1)

Interestingly, attempts to prepare ortho esters by using amide acetals derived from dimethylamine lead to a mixture of products (eq 2). The difference here is that C–O



(2)

bond cleavage competes with C–N cleavage in acid.[5] The former reaction produces an imidatonium ion, the same type of species which is involved in the Pinner reaction.

Experimental Section

Trimethyl 4-Methylorthobenzoate. *N*,4-Dimethylbenzanilide (15.0 g, 0.067 mol) and methyl trifluoromethanesulfonate (13.0 g, 0.080 mol) were stirred in dry CH_2Cl_2 (30 mL) overnight. Dry ether (100 mL) was added, resulting in the precipitation of the imidatonium salt. This was filtered, washed with ether, redissolved in CH_2Cl_2 (30 mL) and added over a period of 30 min to a cooled (0 °C) stirred solution made by the addition of sodium (3.0 g) to dry methanol (50 mL). The solvents were removed on a rotary evaporator, and hexane (200 mL) was added. This dissolved the anilide acetal, and the remaining solid consisting of sodium trifluoromethanesulfonate and excess sodium methoxide was filtered. Evaporation of the hexane produced the crude anilide acetal.

This was taken up in dry methanol (50 mL) and 5 mL of glacial acetic acid added. After the mixture was stirred for 10 min, 10 g of potassium carbonate was added and the methanol removed on the rotary evaporator. Ether (100 mL) and water (50 mL) were added, the ether layer was dried (K_2CO_3), and the ether was removed. Fractional distillation at 0.1 mm produced *N*-methylaniline at 20–30 °C followed at 90 °C by the ortho ester: 8.8 g (67%, based on initial benzanilide); NMR ($CDCl_3$) δ 7.47 (d, 2 H), 7.13 (d, 2 H), 3.13 (s, 9 H), 2.35 (s, 3 H).

Trimethyl 4-methoxyorthobenzoate was prepared in a similar way by starting from 19.8 g of anilide; yield 10.1 g (58%).

Trimethyl 4-nitroorthobenzoate was prepared in a similar way by starting from 6.0 g of anilide. The majority of the *N*-methylaniline was removed by distillation at 0.1 mm, and the ortho ester recrystallized from ethanol–H_2O; yield 2.0 g (40%).

Reaction of Amide Acetal. *N*,*N*,4-Trimethylbenzamide dimethyl acetal (1.0 g) was stirred in dry MeOH (20 mL) containing acetic acid (1 mL) for 2 h. The solution was worked up as described above. The NMR of the crude product showed peaks attributable to the ortho ester, the benzamide, and the ester; no separation was attempted.

(5) McClelland, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 1844.

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Registry No. Trimethyl 4-methylorthobenzoate, 22911-22-4; trimethyl 4-methoxyorthobenzoate, 4316-33-0; trimethyl 4-nitroorthobenzoate, 27689-97-0; *N*,4-dimethylbenzanilide, 40669-49-6; methyl trifluoromethanesulfonate, 333-27-7.

^1H and ^{13}C CIDNP Study of the Radical Rearrangement Involved in the Reaction of *tert*-Butylsulfinyl Chloride with *N*-Hydroxysulfonamides

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Alkyl- and arylsulfinyl chlorides have been found to react with several types of *N*-hydroxy compounds, including hydroxylamines,[1] *N*-hydroxyureas,[2] *N*-hydroxycarbamates,[3] *N*-phenylhydroxamic acids,[4] and oximes.[5] These reactions predominantly occur via the formation of O-sulfinylated intermediates which subsequently undergo thermal rearrangement involving radical cage processes. Herein we report a study of the reaction of *tert*-butylsulfinyl chloride (**1**) with *N*-hydroxymethane- (**2a**) and *N*-hydroxybenzenesulfonamide (**2c**) and their *N*-methyl-substituted derivatives (**2b** and **2d**, respectively) in the presence of at least 1 equiv of pyridine.[6] ^1H and ^{13}C CIDNP effects provide clear evidence for a homolytic rearrangement of a transient *N*-[(*tert*-butylsulfinyl)oxy]-sulfonamide intermediate via rather persistent sulfonamidyl radicals.

Results and Discussion

The products obtained from the reactions of **1** with **2a–d** are listed in Table I and their formation is rationalized in terms of the mechanism depicted in Scheme I. The first step involves nucleophilic displacement of chloride at the tricoordinate sulfur atom[7] of **1** by the hydroxyl oxygen atom of **2a–d** (α-effect nucleophile). This substitution is strongly accelerated by the presence of pyridine acting as a base.[6] Despite many attempts, the proposed intermediate *N*-[(*tert*-butylsulfinyl)oxy]sulfonamides (**3a–d**) could not be isolated or adequately characterized by NMR spectroscopy. However, their formation is quite plausible in view of the evidence discussed below. For several related reactions[2-4] the corresponding intermediates also decomposed rapidly; only *O*-sulfinylated oximes (formed from oximes with sulfinyl chlorides) were found to be sufficiently stable to allow their isolation before thermal rearrangement.[5,8]

(1) Hovius, K., Engberts, J. B. F. N. *Tetrahedron Lett.* **1972**, 181.
(2) Bleeker, I. P.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 120.
(3) Bouma, W. J.; Engberts, J. B. F. N. *J. Org. Chem.* **1976**, *41*, 143.
(4) Heesing, A.; Homann, W. K.; Müllers, W. *Chem. Ber.* **1980**, *113*, 152.
(5) Brown, C.; Hudson, R. F.; Record, K. A. F. *J. Chem. Soc., Perkin Trans. 2* **1978**, 822.
(6) The presence of pyridine is essential.[2,3] Since the pK_a of *N*-hydroxysulfonamides is ca. 10 (Brink, K.; Gombler, W.; Bliefert, C. *Z. Anorg. Allg. Chem.* **1977**, *429*, 255) and that of $pyrH^+$ 5.25, it is not likely that the reaction proceeds via the anions of **2a–d**.
(7) For a review of nucleophilic attack at tricoordinate sulfur, see: Tillett, J. G. *Chem. Rev.* **1976**, *76*, 747.

0022-3263/81/1946-1012$01.00/0