phosphine (expt 14) and increasing rate with decreasing ligand strength[8] (expt 9, 11, and 12) in the order PPh_3 < $AsPh_3$ < $SbPh_3$. However, related hydridoruthenium complexes[9] may also be involved here, and recovered catalyst samples often contain ruthenium carbonyl species (ν(C≡O) 1950 cm^{-1}) as a result of ethanol decarbonylation.[6] Samples may also show new maxima at 1580 cm^{-1} assignable to NO_2 vibrations of the coordinated $RR'CNO_2^-$ anion.[10] The dependence of the hydrogenation rate upon applied H_2 pressure and substrate concentration indicates (6) to include the rate-determining step. Deoxygenation of the coordinated nitroalkane anion[1b] (eq 5) might proceed *via* a nitrene-like intermediate,[4] but this seems unlikely in view of the lack of evidence for coupling products. A more detailed examination of C–NO_2 reduction by solubilized ruthenium complexes, embodying both selective and sequential hydrogenation, has been found possible with nitroaromatic substrates.[11]

A variety of ruthenium complexes with π-bonding ligands, capable of forming hydrido species of differing lability, have been screened and found active for hydrogenation of nitroalkanes[12] (expt 9–16). Bis(triphenylphosphine)iron tricarbonyl and iron pentacarbonyl both yielded some amine[4] but were generally less effective and showed lower stability in the alkali media.

Experimental Section

Hydrogenation (prepurified) was purchased from Matheson Co., dichlorotris(triphenylphosphine)ruthenium(II) was supplied by Strem Chemical Co., and other ruthenium complexes were prepared by published methods.[13] Nitrododecane (a mixture of 2 through 6 isomers) was synthesized by liquid–vapor phase nitration of *n*-dodecane.

Synthesis Procedure. A known weight of ruthenium complex (0.1–2 mmol) was dissolved, with stirring, in 100 ml of predried, N_2-saturated, equivolume benzene–ethanol, alkali metal hydroxide was added as required, and the mixture was heated to 120° in a glass-lined pressure reactor. Nitrododecane (1–100 mmol) was injected into the reaction mixture from a side ampoule, and the H_2 pressure was adjusted (1–90 atm). The course of the reduction may be monitored by withdrawing small (1–2 ml), clear liquid samples at regular time intervals and analyzing these by glpc or ir.

On cooling, the product liquid was concentrated under reduced pressure, and the amine product was isolated by solvent extraction. Dodecylamines were identified by ir, nmr, elemental analyses, and comparison with authentic samples.

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Registry No.—2-Nitrododecane, 53119-34-9; 3-nitrododecane, 53608-64-3; 4-nitrododecane, 53608-65-4; 5-nitrododecane, 53608-66-5; 6-nitrododecane, 53199-35-0; 2-dodecylamine, 13865-46-8; 3-dodecylamine, 53608-67-6; 4-dodecylamine, 19031-73-3; 5-dodecylamine, 53608-68-7; 6-dodecylamine, 53608-69-8; $RuCl_2(PPh_3)_3$, 15529-49-4; $RuHCl(PPh_3)_3$, 19631-00-6; $RuCl_3(AsPh_3)_2$, 41685-48-7; $RuCl_2(SbPh_3)_3$, 15709-80-5; $RuCl_2$(diphos)$_2$, 53608-63-2; $RuCl_2(CO)_2(PPh_3)_2$, 14564-35-3; $[Ru(CO)_3Cl_2]_2$, 22594-69-0; $Fe(CO)_5$, 13463-40-6; $Fe(CO)_3(PPh_3)_2$, 21255-52-7.

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(4) See for example (a) F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, **9**, 342 (1970); (b) J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965); (c) H. Alper, *Inorg. Chem.*, **11**, 976 (1972).
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A Short Route to Functionalized Naphthalenes

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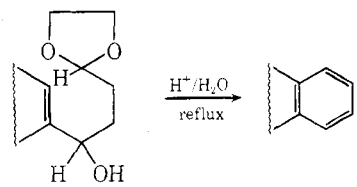
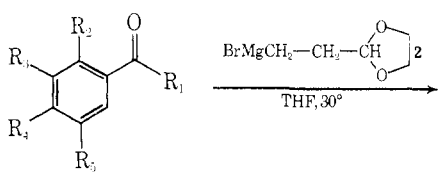
In recent work the synthesis of benzothiophenes and benzimidazoles from thiophenes and imidazoles, respectively, was presented.[1,2] Typical was the introduction of a suitably functionalized four-carbon atom fragment on the heterocyclic system, followed by acid-catalyzed formation of the benzene moiety as indicated below. This type of

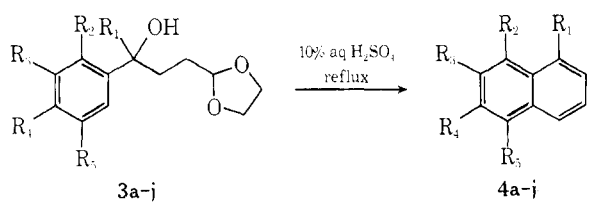


reaction seemed to be extendible to ring systems which are susceptible toward electrophilic substitution reactions.

This approach applied in the synthesis of naphthalenes proved to be successful. Reaction of the strongly activated 3,4,5-trimethoxybenzaldehyde (**1a**) with Grignard derivative **2**[3] gave alcohol **3a**, which upon treatment with refluxing 10% aqueous sulfuric acid for 1 hr afforded 2,3,4-trimethoxynaphthalene (**4a**) nearly quantitatively.[4]



1a–j



3a–j 4a–j

In the same way products **4b–f** were obtained in excellent yields. Naphthols **4g** and **h** could be obtained under the same conditions on allowing hydroxybenzaldehydes **1g** and **h** to react with 2 equiv of **2** and following this with cyclization. Formation of the less activated products **3i** and **j** leading to 2-methylnaphthalene and naphthalene required prolonged reaction times (6 and 16 hr, respectively). It should be mentioned that in the cases where cyclization could take place at two different positions (**3c, 3e, 3f, 3h,** and **3i**) more than 90% regiospecificity was observed, leading to the least hindered products.

A particular case is presented by the synthesis of naphthol **6.** Treatment of **3a** with manganese dioxide[5] in refluxing benzene gave ketone **5.** Under the assumption that the deactivation of the keto group on the benzene ring was

Table I
Naphthalenes

Compd	Yield, %	Mp, °C	Bp, °C	Empirical Formula
4a[a]	95		154–156 (5)	$C_{13}H_{14}O_3$
4b[b]	75	115–118		$C_{12}H_{12}O_2$
4c[c]	84	69–70		$C_{11}H_{10}O$
4d[d]	62		128–132 (1)	$C_{12}H_{12}O_2$
4e[e]	91	95–97		$C_{11}H_8O_2$
4f[f]	84			$C_{12}H_{12}O$
4g[g]	54	48–51		$C_{11}H_{10}O_2$
4h[h]	52	118–120		$C_{10}H_8O$
4i[i]	84		115–120 (1)	$C_{11}H_{10}$
4j[j]	31	78–80		$C_{10}H_8$
6[k]	30	92–95	175–185 (0.05)	$C_{13}H_{14}O_4$

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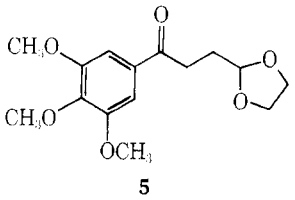
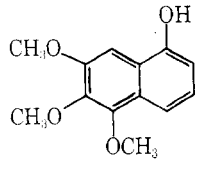
compensated by the methoxy groups, compound **5** in 10% sulfuric acid was converted to naphthol **6** in moderate



5



6

a, $R_1 = R_2 = H$; $R_3 = R_4 = R_5 = OCH_3$
b, $R_1 = R_2 = R_5 = H$; $R_3 = R_4 = OCH_3$
c, $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OCH_3$
d, $R_1 = R_2 = R_4 = H$; $R_3 = R_5 = OCH_3$
e, $R_1 = R_2 = R_5 = H$; $R_3, R_4 = O\text{-}CH_2\text{-}O$
f, $R_1 = CH_3$; $R_2 = R_4 = R_5 = H$; $R_3 = OCH_3$
g, $R_1 = R_4 = R_5 = H$; $R_2 = OH$; $R_3 = OCH_3$
h, $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = OH$
i, $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = CH_3$
j, $R_1 = R_2 = R_3 = R_4 = R_5 = H$

yield. The results are summarized in Table I. Attempts made in our laboratories to achieve a facile entry into indoles and benzofurans in this particular way failed because of the instability of the pyrrole and furan ring under the cyclization conditions.

Experimental Section

General. Melting points were determined on a Mettler apparatus and are uncorrected. Nmr data were consistent with the assigned structures (Varian T-60, TMS as an internal standard). The intermediates were characterized by means of nmr and converted as is to the products offered in Table I. All starting materials were commercially available. Grignard derivative **2** was prepared according to a known procedure.[3] The preparation of the naphthalenes is illustrated by the synthesis of **4a**.

1-(1,3-Dioxolan-2-yl)-3-hydroxy-3-(3,4,5-trimethoxyphenyl)propane (3a). To a solution of **2**, prepared from 1.6 g (0.065 g-atom) of magnesium and 12.3 g (0.065 mol) of 2-(2-bromoethyl)-1,3-dioxolane in 50 ml of THF, was added dropwise with stirring a solution of 8.5 g (0.045 mol) of 3,4,5-trimethoxybenzaldehyde (**1a**) in 20 ml of THF. After additional stirring for 4 hr the reaction mixture was poured in 500 ml of a 10% NH_4Cl solution and extracted twice with $CHCl_3$. Washing, drying, and evaporation of the organic phase left a viscous oil, which upon treatment with (*i*-Pr)$_2$O afforded 10.6 g of **3a** as a solid; mp [benzene–petroleum ether] 86–87°. *Anal.* Calcd for $C_{15}H_{22}O_6$: C, 60.40; H, 7.38. Found: C, 60.44; H, 7.57. Nmr ($CDCl_3$) δ 1.75 (m, 4, $-CH_2CH_2-$), 3.24 (s, 1, OH), 4.57 (m, 1, ArC*H*(OH)), 4.84 (m, 1, -OCH(R)O-), 6.60 (s, 2, Ar*H*).

1-(1,3-Dioxolan-2-yl)-3-oxo-3-(3,4,5-trimethoxyphenyl)-propane (5). To a solution of 5 g (0.017 mol) of **3a** in 75 ml of benzene was added 20 g of MnO_2. The mixture was refluxed with stirring for 2 hr. Filtration of the reaction mixture and evaporation of the solvent left 4.2 g (87%) of **5** as a white crystalline solid; mp 57–59° [(*i*-Pr$_2$)O–petroleum ether]. *Anal.* Calcd for $C_{15}H_{20}O_6$: C, 60.81; H, 6.76. Found: C, 60,83; H, 6.93. Nmr ($CDCl_3$) δ 2.14 (m, 2, ArCOCH_2), 3.01 (m, 2, ArCOCH$_2$CH_2), 4.49 (t, 1, OC(R)*H*O), 7.22 (s, 2, Ar*H*).

1,2,3-Trimethoxynaphthalene (4a). A solution of 5.96 g (0.02 mol) of **3a** in 10 ml of methanol was added in 5 min to 100 ml of stirred refluxing 10% sulfuric acid. After 1 hr the reaction mixture was cooled and extracted twice with $CHCl_3$. Washing with 5% $NaHCO_3$ solution, drying, and evaporating of the solvent left an oil, which upon distillation yielded 4.0 g (95%) of **4a**; bp 154–156° (5).

Registry No.—**1a**, 86-81-7; **1b**, 120-14-9; **1c**, 591-31-1; **1d**, 7311-34-4; **1e**, 120-57-0; **1f**, 586-37-8; **1g**, 148-53-8; **1h**, 100-83-4; **1i**, 620-23-5; **1j**, 100-52-7; **3a**, 53579-08-3; **3b**, 53597-09-4; **3c**, 53597-10-7; **3d**, 53597-11-8; **3e**, 53597-12-9; **3f**, 53597-13-0; **3g**, 53597-14-1; **3h**, 53597-15-2; **3i**, 53597-16-3; **3j**, 53597-17-4; **4a**, 5892-02-4; **4b**, 10103-06-7; **4c**, 93-04-9; **4d**, 10075-61-3; **4e**, 269-43-2; **4f**, 2825-01-6; **4g**, 1888-41-1; **4h**, 135-19-3; **4i**, 91-57-6; **4j**, 91-20-3; **5**, 53597-18-5; **6**, 53597-19-6; 2-(2-bromoethyl)-1,3-dioxolane, 18742-02-4.

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Synthesis of Prostaglandins Containing the Sulfo Group

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It is a matter of interest to evaluate the biological and pharmacological activities of prostaglandin analogs containing the sulfo group in place of the carboxy function (C-1). We now report the synthesis of prostaglandin sulfonic acids by the Wittig reaction with a phosphorous ylide having the sulfo group.

(4-Sodium sulfonato-*n*-butyl)triphenylphosphonium bromide (**1**) was obtained as colorless crystals, mp 268–270°, from sodium 4-bromo-*n*-butanesulfonate and triphenylphosphine in *N,N*-dimethylformamide on heating. Reaction of the corresponding ylide, prepared from **1** and a solution of sodium methylsulfinyl carbanide in dimethyl sulfoxide, with 2-oxa-3-hydroxy-6-*syn*-(3α-tetrahydropyranyloxy-1-*trans*-octenyl)-7-*anti*-tetrahydropyranyloxy-*cis*-bicyclo[3.3.0]octane[1] (**2**), an intermediate for the Corey synthesis of prostaglandins, in dimethyl sulfoxide at 30° for 3 hr afforded the sulfonic acid **3** as yellow-brown crystals in 48% yield.

According to the procedures of Corey[1,2] and Pike,[3] the sulfonic acid **3** was converted to the corresponding $F_{2\alpha}$ (**4**), $F_{1\alpha}$ (**5**), E_2 (**6**), E_1 (**7**) and A_2 (**8**).