with the observed relative rates of acetolysis. Assistance to ionization is presumably provided[2] by a π-electron system oriented *anti* to the leaving group, and **8**-Cl, in which this assistance would have to come from the benzene ring, was the more reactive epimer, a result which might not have been predicted.

The solvolyses described above proceeded cleanly and with complete retention of configuration. Thus **7**-Cl gave **7**-OAc, mp 203.5–204.5°, and **8**-Cl gave **8**-OAc, mp 217–218°, and there appears to be no reason to assume that equilibrating tricyclic cations analogous to **6** but with a fused benzene ring intervene. For the present, therefore, it would appear more reasonable to assume that participation as visualized by Winstein occurs.

Acknowledgments. This work was supported by a Public Health Service Fellowship to G. W. N. (5-F1-GM-33,790) and by Public Health Service Grant GM-12139 from the National Institute of General Medical Sciences. All new compounds had satisfactory elemental analyses (Galbraith Laboratories, Inc.).

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Oxidative Coupling of Phenols

Sir:

The oxidative coupling of phenols to dimeric products is a useful procedure which has found extensive applications in chemical synthesis. Hitherto, however, reactions of this kind have almost invariably been carried out using ferric chloride (Dianin reaction) or ferricyanide. Both these reagents are limited in scope, the former because it is an active Friedel–Crafts catalyst and so is liable to bring about additional unwanted transformations, the latter because it has to be used in alkaline aqueous solution and also tends to oxidize the initially formed biphenol to a quinone. Other oxidizing agents have been tried from time to time[1] but with limited success. Clearly the scope of such reactions would be greatly extended if they could be carried out cleanly in homogeneous solution in an inert organic solvent.

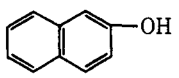
The coupling reaction seems almost certainly to involve oxidation of the phenol by electron transfer, giving rise to an aryloxy radical which then dimerizes. Such intermediate radicals have been detected in a number of cases by esr spectroscopy,[2] and the most successful oxidizing agents are ones which are generally believed to act by electron transfer. Recently we have shown[3] that a wide variety of aromatic derivatives undergo electron-transfer oxidation by manganic or cobaltic acetates in acetic acid; it therefore seemed to us likely that an appropriate Mn^{III} or Co^{III} derivative might act as an effective coupling agent for phenols.

After trying a large variety of such compounds under various conditions, we found the most promising candidate to be manganic tris(acetylacetonate) (MTA); this appears to bring about the coupling of phenols to biphenols in good yield, the reactions being carried out under relatively mild conditions in carbon disulfide or acetonitrile and being easily controlled to give biphenols rather than quinones. Thus, β-naphthol (I) gave 2,2′-dihydroxy-1,1′-binaphthyl (II), and 2,6-di-*t*-butylphenol (III) gave 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butylbiphenyl (IV), in good yield. Similar oxidation of 2,6-xylenol (V) gave mainly the dihydroxybiphenyl (VI) together with a little of the corresponding quinone (VII) and oligomeric products. The conditions and yields are indicated in Table I. The solutions were initially homogeneous; during the reaction a precipitate formed which analysis indicated to be a basic manganous acetylacetonate, with the approximate composition $4MnA_2 \cdot Mn(OH)_2$.

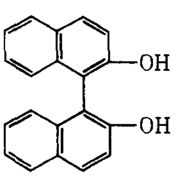
Table I. Oxidative Coupling[a] of Phenols by MTA

Phenol	MTA/ Phenol[b]	Solvent	Time, hr	Product (% yield)
I	1.2	CH_3CN	5	I (69)
I	1.2	CS_2	5	I (60)
III	1	CS_2	3	II (71)
III	2	CS_2	3	II (74)
V	1.3	CS_2	5	VI (48) + VII (3)[c]

[a] All reactions were carried out under nitrogen in gently refluxing solution (*ca.* 0.3 *M* in phenol). [b] Mole ratio. [c] Oligomeric products (23%) were also formed.



I



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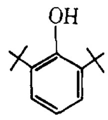

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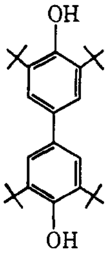

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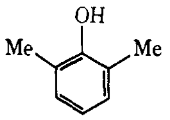

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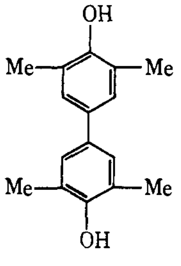
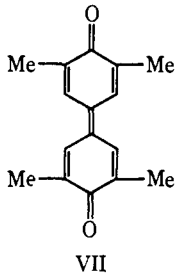


VI



VII

Apart from its solubility in organic solvents, MTA has the advantage of leading first to biphenols which can be isolated in good yield without further oxidation to quinones; thus oxidation of III with ferricyanide

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[1] A. I. Scott, *Quart. Rev.* (London), **19**, 1 (1965); R. G. R. Bacon and A. R. Izzat, *J. Chem. Soc.*, 791 (1966), and papers cited therein.

[2] See, *e.g.*, A. Fairbourn and E. A. C. Lucken, *Proc. Chem. Soc.*, 67 (1960); T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 213 (1964).

[3] P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966); T. Aratani and M. J. S. Dewar, *ibid.*, **88**, 5479 (1966); P. J. Andrulis, Jr., and M. J. S. Dewar, *ibid.*, **88**, 5483 (1966).

gives[4] exclusively the quinone corresponding to IV, whereas MTA gave IV free from the quinone. In order to achieve this result, it is necessary to exclude oxygen and to work in a neutral aprotic solvent; thus, in a recent paper[5] Shono and his collaborators have shown that MTA in a mixture of pyridine and chloroform oxidizes III to polyphenylene oxides, whereas in chloroform alone the quinone corresponding to N was formed.

Further preliminary studies suggest that MTA in carbon disulfide or acetonitrite acts very generally as a coupling agent for phenols and other related compounds; full details will be reported in due course.

Acknowledgment. This work was supported by a grant from the Robert A. Welch Foundation.

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(4) C. D. Cook, E. S. English, and B. J. Wilson, *J. Org. Chem.*, **23**, 755 (1958).

(5) T. Shono, K. Yamanoi, T. Matushita, and K. Shinra, *Kogyo Kagaku Zasshi*, **70**, 2062 (1967); *Chem. Abstr.*, **68**, 114985 (1968).

(6) Robert A. Welch Postdoctoral Fellow; on leave of absence from Osaka City University, Osaka, Japan.

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The Characterization of an Anionic Rhenium Carbonyl Hydride, $[H_2Re_3(CO)_{12}^-]$[1]

Sir:

We wish to report the isolation and crystal structure of $[(C_6H_5)_4As^+][H_2Re_3(CO)_{12}^-]$ (I), the anion of which is obtained in the treatment of $H_3Re_3(CO)_{12}$[2] with base The structure of the anion thus provides some insights into the nature of its conjugate acid, $H_3Re_3(CO)_{12}$, a compound which has thus far proved not to be susceptible to a detailed crystallographic analysis.[3]

To a colorless slurry of 0.5 g of $H_3Re_3(CO)_{12}$[2] in 25 ml of C_2H_5OH an ethanolic solution of 0.1 *M* KOH in slight molar excess is added at room temperature. The solid dissolves to give a bright yellow solution; a precipitate of I is obtained[4] upon addition of $(C_6H_5)_4AsCl$ in ethanol and cooling to −5°.

Conductivity measurements in CH_3CN show that I is a 1:1 electrolyte. The compound is soluble in acetone, tetrahydrofuran, CH_2Cl_2, and CH_3CN and slightly soluble in diethyl ether and ethanol, giving yellow solutions. An H^1 nmr spectrum in acetone shows sharp singlets at τ 2.05 and 27.2 (relative intensity 20.0:2.0 ± 0.1) due, respectively, to $[(C_6H_5)_4As^+]$ protons and hydrogen on rhenium.

Compound I crystallizes from acetone solution as yellow needles in the noncentrosymmetric orthorhombic space group $Pna2_1$ (C_{2v}^9; no. 33) with a = 16.097 Å, b = 28.725 Å, c = 8.145 Å, and V = 3766 Å^3. The observed density ($\rho_{obsd} = 2.255$ g cm^{-3}) is in excellent agreement with the value calculated for M = 1280 and Z = 4 ($\rho_{calcd} = 2.257$ g cm^{-3}). A set of X-ray diffraction data complete to sin θ = 0.42 (Mo Kα radiation) was collected with a Supper-Pace "Buerger" automated diffractometer using a stationary-background, ω-scan, stationary-background counting sequence. All data were corrected for absorption (μ = 118.8 cm^{-1}), and the structure was solved by a combination of Patterson and difference-Fourier techniques. All 52 nonhydrogen atoms have been located. Four cycles of least-squares refinement (in which thermal parameters for rhenium and arsenic atoms were allowed to refine anisotropically) have resulted in a discrepancy index of R_F = 9.6% for the 2393 independent nonzero reflections. Refinement is continuing.

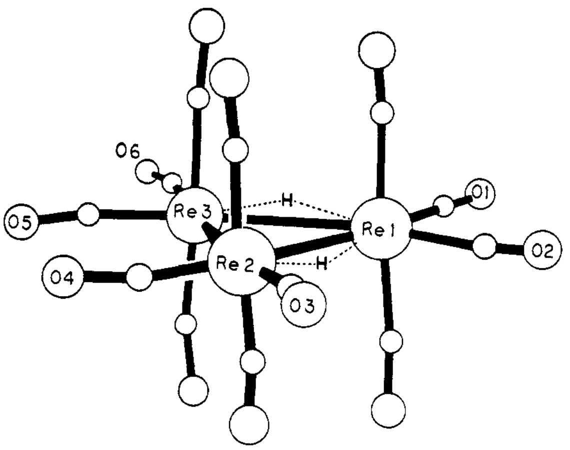

Figure 1. The $[H_2Re_3(CO)_{12}^-]$ ion. Note that the hydride ligands were not located and are drawn in the most sensible chemical positions (see text).

As may be seen in Figure 1, the $[H_2Re_3(CO)_{12}^-]$ anion has approximate C_{2v} symmetry, with the three rhenium atoms defining an isosceles triangle in which Re(1)–Re(2) = 3.173 Å, Re(1)–Re(3) = 3.181 Å, and Re(2)–Re(3) = 3.035 Å, esd 0.007 Å.[5] Four terminal carbonyl groups are bonded to each rhenium atom; two occupy *axial* sites and two occupy *equatorial* sites. Although hydrogen atoms have not been detected directly in the crystallographic investigation, some information on the positions of the hydride ligands may be obtained by a consideration of the Re–Re bond lengths and the angular disposition of carbonyl ligands about each of the rhenium centers. The *axial* carbonyls are more-or-less regularly arranged, but (as may clearly be seen in Figure 2) the *equatorial* carbonyls possess a much less regular arrangement. The *equatorial* OC–Re–CO angles are all in the range 91–93°, and the Re–Re–$(CO)_{eq}$ angles involving the short side of the triangle [*i.e.*, Re(2)–Re(3)–C(5)O(5) and Re(3)–Re(2)–C(4)O(4)] are 91 and 95°. The Re(2)–Re(1)–C(2)O(2) and Re(3)–Re(1)–C(1)O(1) angles are significantly larger (106 and 107°) and the Re(1)–Re(2)–C(3)O(3) and Re(1)–Re(3)–C(6)O(6) angles (112 and 118°) are the largest of all the *cis* angles. This general pattern of bond angles suggests that C(1)O(1)/C(6)-O(6) and C(2)O(2)/C(3)O(3) are each being forced apart, most probably because of the presence of hydrogen atoms somewhere along the two sides Re(1)–Re(3) and Re(1)–Re(2) of the triangle. The only classical valence-bond structure compatible with the structural data and the diamagnetism of the compound is A; however,

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(1) Work supported by NSF Grants GP-8077 (M. R. C.) and GP-6720 (H. D. K.) and ARPA Contract SD-88 (M. R. C.).

(2) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).

(3) H. D. Kaesz, R. Bau, and M. R. Churchill, *ibid.*, **89**, 2775 (1967).

(4) Satisfactory C and H analyses were obtained by Miss Heather King of the UCLA Laboratories. A good oxygen but no satisfactory rhenium analyses could be obtained on this compound by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

(5) Esd includes errors in measurement of the unit cell.