

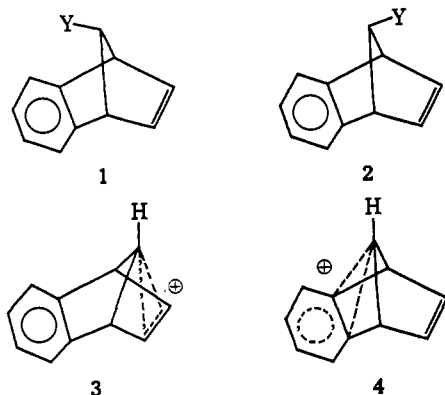
Sciences. All new compounds had satisfactory elemental analyses (Galbraith Laboratories, Inc.).

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Bridged Polycyclic Compounds. LIII. Solvolyses of the Epimeric 7-Chlorobenzonorbornadienes and 5,12-Diphenyl-6,11-dihydro-6,11-(chloromethano)-naphthacenes¹

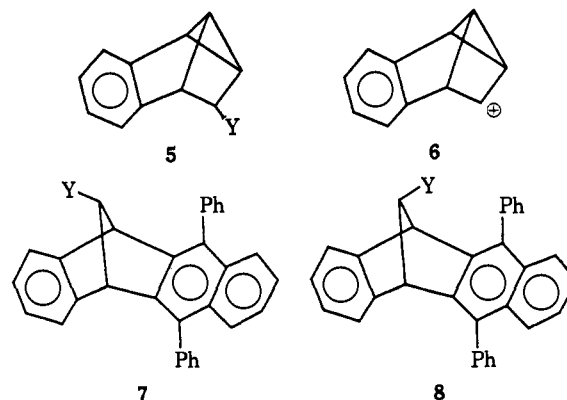
Sir:

The previous communication¹ showed that the cations formed by ionization of *syn*-7-chlorobenzonorbornadiene (1-Cl) and the *anti* epimer (2-Cl) are different and are not interconverted (or lost by Wagner-Meerwein rearrangement) during acetolysis. Instead 1-Cl gives 1-OAc cleanly and 2-Cl gives 2-OAc. These results are consistent with the formulation of the intermediate cations as 3 and 4 from 1 and 2, respectively. Formulations 3 and 4 are derivative of others suggested for analogous species.²



However, just as with the analogous *anti*-7-dehydronorbornyl and 7-norbornadienyl cations,³⁻⁸ tricyclo[4.1.0.0^{4,7}]heptane derivatives are capturable with the cation which we have represented as 3, although not from its presumed epimer 4. Thus, treatment of 1-Cl with 4 *M* sodium methoxide in methanol leads to substantial amounts of 5-OCH₃, along with 1-OCH₃. 5-OCH₃ rearranges completely under acid conditions to 1-OCH₃. The formation of 5-OCH₃ from 1-Cl raises the same question regarding our work that had been raised earlier^{3,9} regarding the 7-norbornadienyl and *anti*-7-dehydronorbornyl cations, namely, that the ion resulting from 1 is a pair of rapidly equilibrating tricyclic ions, *viz.*, 6 and its enantiomorph. Here it might be assumed that 6 leads by direct coordination with nucleophiles to 5 or by geitonodesmic¹⁰ reaction to

1 products, although the argument given by Winstein and his coworkers^{7,8,11} against this suggestion seems equally well applicable to our case.



In view of the Brown-Deno objections and the peculiar kinetics observed¹ in the acetolysis of 1-Cl (but not of 2-Cl), we decided that it was worthwhile to study the acetolysis of an epimeric homobenzylic system where both participating π systems were aromatic rings. It has been shown¹² that 7-dibenzonorbornadienyl *p*-bromobenzenesulfonate solvolyzes without rearrangement, so that substituted analogs seemed likely prospects for stereochemical study. 2-Cl was a particularly resistant dienophile, but use of 1,3-diphenylisobenzofuran¹³ as a diene under conditions (benzene solution; 120–155° for up to 300 hr) which gave Diels-Alder addition followed by dehydration led to 7-Cl, mp 309–310°, from 1-Cl, and 8-Cl, mp 194–195°, from 2-Cl.

Compounds 7-Cl and 8-Cl were subjected to silver ion assisted acetolysis at 150–155° in glacial acetic acid containing 1.2 equiv of silver acetate. In 56 hr the reactions proceeded to the extent of 20% in the case of 7-Cl and to the extent of 75% in the case of 8-Cl, indicating that the compound with the *anti* benzene ring solvolyzes about six times faster than its epimer. The configurations at the 7 position of the chlorides 7 and 8 are known from their modes of formation. Their nmr spectra¹⁴ show a two-proton doublet for the bridgehead protons and a one-proton triplet for the bridge proton ($J \sim 1.7$ Hz in each case). The bridge-proton triplet for 7-Cl occurs at τ 5.42 while that for 8-Cl occurs at τ 5.70, indicating a greater shielding power of the fused benzene ring over that of the fused diphenylnaphthalene system. Consequently, the same relative chemical shift order may be expected for the bridge protons of the acetates 7 and 8, but for their acetoxy methyl groups the shielding effect should be in the opposite order. This is what is observed. The acetate 7 has its H-7 triplet at τ 4.78 and its methyl resonance at τ 8.22, while for the 8-OAc the H-7 triplet occurs at τ 4.96 and the methyl singlet at τ 8.15. It is noteworthy that the relative shielding power of the fused aromatic moieties, supposedly an indication of the strengths of the induced ring currents and therefore a possible measure of electron availability, correlates

(1) Previous paper in this series: S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **90**, 7132 (1968).

(2) See footnotes 5–9, 15, and 16 in ref 1.

(3) H. C. Brown and M. Bell, *J. Amer. Chem. Soc.*, **85**, 2324 (1963).

(4) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(5) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965).

(6) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **88**, 864 (1966).

(7) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).

(8) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).

(9) N. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(10) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **87**, 2879 (1965).

(11) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967).

(12) J. Meinwald and E. G. Miller, *Tetrahedron Letters*, 253 (1961).

(13) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961); M. P. Cava and F. M. Scheel, *ibid.*, **32**, 1304 (1967).

(14) Spectra for compounds 7 and 8 were determined in deuteriochloroform solution on a Varian A-60-A nmr spectrometer.

with the observed relative rates of acetolysis. Assistance to ionization is presumably provided² 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.

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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 time¹ 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 shown³ 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.

(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. Andrusis, 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. Andrusis, Jr., and M. J. S. Dewar, *ibid.*, **88**, 5483 (1966).

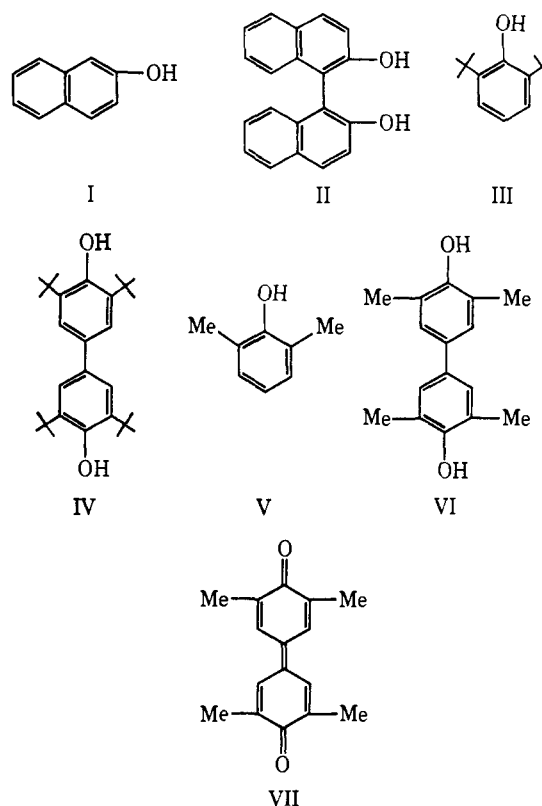
After trying a large variety of such compounds under various conditions, we found the most promising candidate to be manganic tris(acetylacetonate) (MTA); this appears to bring about the coupling of phenols to biphenols in good yield, the reactions being carried out under relatively mild conditions in 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-xylene (**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

Table I. Oxidative Coupling^a of Phenols by MTA

Phenol	MTA/ Phenol ^b	Solvent	Time, hr	Product (% yield)
I	1.2	CH ₃ CN	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.

homogeneous; during the reaction a precipitate formed which analysis indicated to be a basic manganous acetylacetonate, with the approximate composition 4MnA₂·Mn(OH)₂.



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