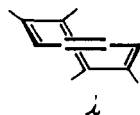


7465 (1974); R. E. Wingard, Jr., R. K. Russell, and L. A. Paquette, *ibid.*, **96**, 7474 (1974).

- (11) J. M. Photis, unpublished results.  
 (12) J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organomet. Chem.*, **39**, 330 (1972); G. Scholes, C. R. Graham, and M. Brookhart, *J. Am. Chem. Soc.*, **96**, 5665 (1974).  
 (13) Isomer **4** is much less reactive toward this reagent. Heating with 5 mol equiv of the ligand transfer reagent is required for formation of the 1,6,7,8-tetramethylbicyclo[4.2.0]octatriene-Fe(CO)<sub>3</sub> complex.  
 (14) Trans isomer **i** has the same C<sub>2</sub> symmetry as **5a** and might also be in equilibrium with bicyclic isomer **5b** as the result of a thermally allowed conrotatory butadiene-cyclobutene isomerization. The <sup>1</sup>H and <sup>13</sup>C NMR spectra, together with formation of adduct **7** and complex **8**, could therefore be construed as evidence for this species. While these data are most assuredly compatible with either **5a** or **i**, it is more difficult to



reconcile reversible conversion to dianion **9** on the basis of the trans isomer. Also, the trans double bond in **i** should be highly reactive toward peracids. Yet, we find that treatment of the polyolefin with monopero-phthalic acid affords exclusively the C<sub>7</sub>C<sub>8</sub> epoxide of **5b**, the likely (but not necessary) result of disrotatory closure of epoxy-**5a**. No evidence was found for oxygenation between the central methyl groups as expected for **i**.

- (15) L. B. Anderson and D. Taggart, private communication.  
 (16) N. L. Allinger, private communication. The entropy difference between the two isomers is 0.  
 (17) L. A. Paquette, S. V. Ley, R. H. Meisinger, R. K. Russell, and M. Oku, *J. Am. Chem. Soc.*, **96**, 5806 (1974).  
 (18) S. W. Staley, G. M. Camer, and A. W. Orvedal, *J. Am. Chem. Soc.*, **96**, 7433 (1974). We thank Professor Staley for experimental directions in advance of publication.  
 (19) Compare L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **94**, 9224 (1972); L. A. Paquette and M. Oku, *ibid.*, **96**, 1219 (1972); L. A. Paquette, M. Oku, W. E. Heyd, and R. H. Meisinger, *ibid.*, **96**, 5815 (1974).  
 (20) Compare the behavior of bicyclo[4.2.0]octatrienes: ref 9.  
 (21) E. H. White, E. W. Friend, Jr., R. L. Stern, and H. Maskill, *J. Am. Chem. Soc.*, **91**, 523 (1969).  
 (22) The financial support of the National Science Foundation, National Cancer Institute, and Eli Lilly Company is gratefully acknowledged.

Leo A. Paquette,\* James M. Photis, Gary D. Ewing

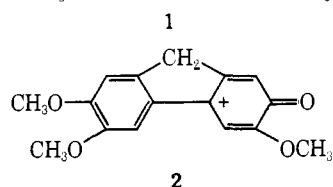
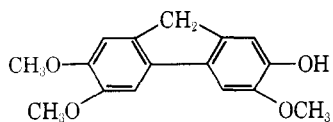
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Received January 10, 1975

### Effect of Forced Coplanarity of Biphenyl Rings on the Ease of Formation and Stability of Phenolic Cations

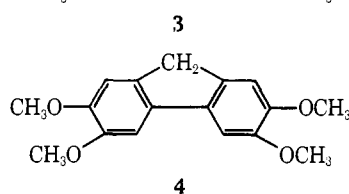
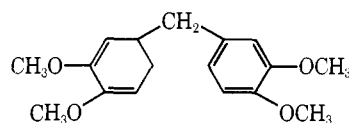
Sir:

The methylene bridge in the phenolic biphenyl (**1**) forces the two rings to be coplanar which has a profound effect upon the ease of oxidation and the stability of the resulting cations. Here we report the direct observation of the cation radical of **1** and the corresponding phenoxonium ion (**2**). The phenoxonium ion shows limited stability in acetonitrile while the cation radical is indefinitely stable in media containing trifluoroacetic acid (TFA).



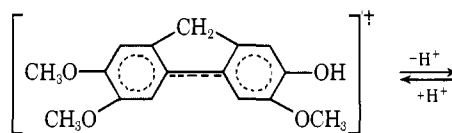
Anodic oxidation of the tetramethoxydiphenylmethane (**3**) in dichloromethane-TFA (3:1) containing the nucleo-

phile scavenger, trifluoroacetic acid anhydride<sup>1</sup> (TFAn), proceeds in the normal manner<sup>2</sup> giving the bridged biphenyl (**4**) in high yield. However, in the presence of 1% H<sub>2</sub>O, oxidation was accompanied by first cyclization to **4** and then

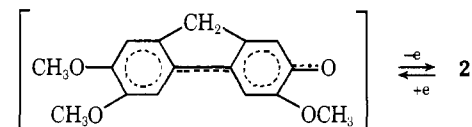


anodic cleavage of the ether group<sup>3</sup> giving **1** in high yield. Neither the corresponding ethane nor the propane underwent demethylation under the latter conditions.<sup>4</sup> When **4** was subjected to the same electrolysis conditions, the yield of **1** was nearly quantitative.

The cyclic voltammogram of **1** in acetonitrile consisted of a quasi-reversible 2e oxidation peak at +0.70 V<sup>5</sup> and the corresponding reduction peak at +0.66 V (voltage sweep rate 40 mV/sec). The peak separation increased with increasing voltage sweep rate indicating that the electron transfers are coupled with a chemical step, i.e., deprotonation of the initial cation radical (**5**) to **6** which is further ox-

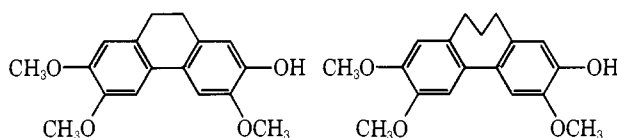


**5**



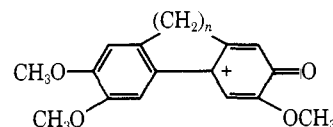
**6**

idized to **2**. Voltammograms of **7** and **8** under identical conditions showed oxidation peaks at +0.85 and +1.01 V, re-



**7**

**8**

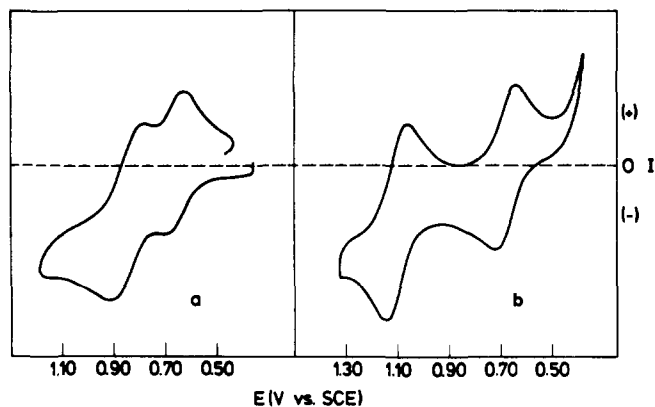


**9a**, n = 2

**9b**, n = 3

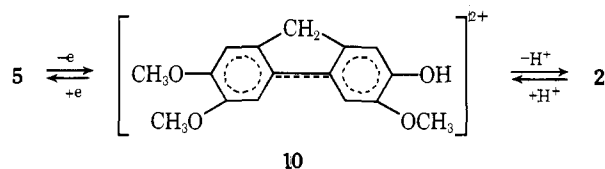
spectively. The phenoxonium ion (**9a**) from the dimethylene bridge compound could be observed by cyclic voltammetry at slow sweep rates while **9b** was much less stable. The lifetime of **2** in acetonitrile was estimated to be an order of magnitude greater than **9a** under comparable conditions. In fact, two-electron oxidation of **1** in acetonitrile at room temperature gave a solution of **2** (~25% yield) which had a half-life of about 5 min.

The cyclic voltammogram of **1** in dichloromethane-TFA (3:1) is illustrated in Figure 1a. The voltammogram consists of two consecutive one-electron redox couples, the first

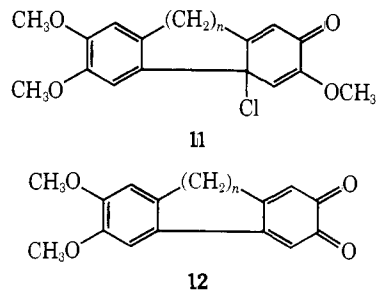


**Figure 1.** Cyclic voltammograms of **1** in (a) dichloromethane-TFA (3:1) and (b) dichloromethane-TFA- $\text{CF}_3\text{SO}_3\text{H}$  (45:3:2). Supporting electrolyte is  $n\text{-Bu}_4\text{NBF}_4$  (0.2 M). Voltage sweep rate is 150 mV/sec.

being reversible and the second quasi-reversible indicating a coupled chemical step. In the same medium, one-electron coulometric oxidation of **1** gave the cation radical (**5**) which could also be prepared by adding small amounts of  $\text{CF}_3\text{SO}_3\text{H}$  to solutions of **1** in TFA. The ESR spectra of **5** produced electrochemically and chemically were identical. Solutions of **5** prepared electrochemically could be quantitatively converted back to **1** by cathodic reduction. One-electron oxidation of **5** gave **2** which is stable in dichloromethane-TFA (3:1). The cyclic voltammogram of **1** in dichloromethane-TFA- $\text{CF}_3\text{SO}_3\text{H}$  (45:3:2) is shown in Figure 1b. In this case, at low voltage sweep rates (40 mV/sec) both redox couples appear to be reversible. However, at higher sweep rates the peak separation of the second couple became greater, once again implicating a coupled chemical reaction. Thus we can conclude that the second couple corresponds to oxidation of **5** to the dication (**10**) which is in equilibrium with **2**. This is also indicated by the fact that solutions of **2** prepared by two-electron oxidation of **1** in the latter medium are not stable, presumably because of the greater reactivity of **10**.



Examination of molecular models of the bridged biphenyls, **1**, **7**, and **8**, showed that the aromatic rings of **1** are forced to lie in the same plane while the preferred conformations of **7** and **8** are such that planes of the rings are  $\sim 20^\circ$  and  $\sim 60^\circ$  to one another. Since the most stable conformation of the cation radicals is one in which both rings lie in the same plane,<sup>6</sup> the greater the interplanar angle between the biphenyl rings in the substrates the greater the energy difference between cation radical and substrate. The latter is clearly reflected by the ease of oxidation: **1** (+0.70 V), **7** (+0.85 V), and **8** (+1.01 V). A further manifestation of forced planarity in the ions derived from **1** is the reactivity of **2** as compared to **9a** and **9b**. Chloride ion is oxidized by **2** while chlorination of **9a** and **9b** is observed to give cyclohexadienones **11**. Reaction of **2** or **9b** with water is accompanied by demethylation to give the orthoquinones **12** while  $\text{H}_2\text{O}$  acts as a base toward **9a** producing the phenanthrene.<sup>7</sup> Thus, the increased conjugation in **2** makes the aromatic system far less susceptible to nucleophilic attack. One might ask why **2** is less reactive toward nucleophiles but still undergoes an electron transfer reaction with  $\text{Cl}^-$ . If we consider the respective transition states we see that nucleophilic



attack on the phenoxonium ion involves considerable change in geometry while planar **2** reverts to planar **1** after electron transfer which is accompanied by a minimal change in geometry. Preliminary results also indicate that **5** is much less acidic than the cation radicals derived from **7** and **8**.

The only previous report of stable phenolic cation radicals and phenoxonium ions concerned those derived from the  $\alpha$ -tocopherol model compound.<sup>8</sup> The ions from **1** appear to be far less reactive. Further work is in progress on these unusual systems.

## References and Notes

- (1) O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).
- (2) A. Ronlán, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **95**, 7132 (1973).
- (3) V. D. Parker, *Chem. Commun.*, 610 (1969).
- (4) The propane gave only the bridged biphenyl while the ethane gave a mixture of the corresponding phenanthrene and dihydrophenanthrene.
- (5) All potentials are for oxidation or reduction at a platinum electrode and are referred to the saturated calomel electrode.
- (6) A. Ronlán, J. Coleman, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 845 (1974). In order to have the most effective overlap of orbitals on the carbons where the rings join, the ions must assume a planar conformation.
- (7) Details of the product studies will appear later.
- (8) U. Svanholm, K. Bechgaard, and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 2409 (1974).

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## Group 6 Metal Carbonyl Induced Dimerization of Azirines

Sir:

There has been considerable recent interest in metal carbonyl effected ring-cleavage reactions of small ring systems such as 2-vinylloxiranes<sup>1</sup> and benzvalene.<sup>2,3</sup> In addition, diiron enneacarbonyl [ $\text{Fe}_2(\text{CO})_9$ ] can induce photolytic-type rearrangement of santonin using nonphotolytic conditions.<sup>4</sup> These results led to a study of the effect of metal carbonyls on 2-aryl azirines, a three-membered ring heterocycle which has been extensively investigated in terms of thermal<sup>5</sup> and photolytic<sup>6</sup> ring cleavage. We now wish to report that group 6 metal hexacarbonyls,  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ), causes dimerization of 2-aryl azirines to dihydropyrazines and pyrazines under very mild conditions.

Reaction of 2-phenylazirine (**1**,  $\text{R} = \text{H}$ )<sup>7</sup> with an equimolar amount of molybdenum hexacarbonyl (**2**,  $\text{M} = \text{Mo}$ ) in anhydrous tetrahydrofuran (THF) at room temperature for 24 hr ( $\text{N}_2$  atmosphere) gave<sup>8</sup> 2,5-diphenylpyrazine (**3**,  $\text{R} =$