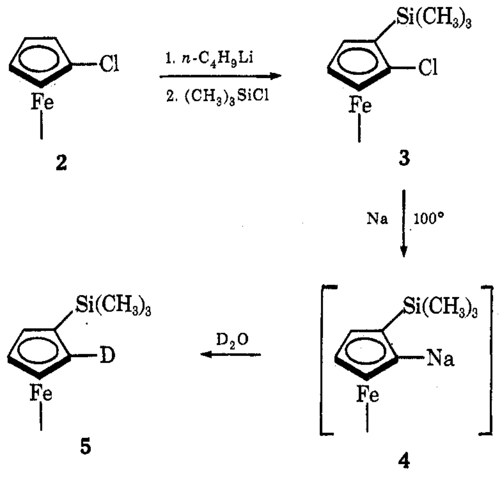
SCHEME I



cene[10] containing a total of 0.88 deuterium atom as analyzed by the falling drop method.

Trimethylsilylferrocene has been the only monosubstituted ferrocene studied to date which exhibits enhanced deshielding of the 3,4-position protons with respect to the 2,5-position protons. Since earlier studies[2] have demonstrated that resonance effects in the ferrocene system detected by pmr spectroscopy are manifested chiefly at the 3,4 positions, the observation of significant deshielding of the $H_{3,4}$ protons in **1** can be attributed to a resonance withdrawal by the d orbitals on silicon from the 3,4 positions.[11]

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[10] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **23**, 900 (1958).

[11] A referee has pointed out that the sequence of chemical shifts in trimethylsilylferrocene is the same as that in the α-ferrocenyl carbonium ion as initially assigned by Cais, *et al.*[12] However, the carbonium ion is a charged intermediate or transition state where charge delocalization would be expected to override secondary ground-state effects as described herein. Interestingly, this ground-state effect in **1** can now be explained as a simple resonance interaction without recourse to arguments involving ring/metal atom movement.[13]

[12] M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Lett.*, 1695 (1966).

[13] For a recent summary and criticism of this concept, *cf.* J. Feinberg and M. Rosenblum, *J. Amer. Chem. Soc.*, **91**, 4324 (1969).

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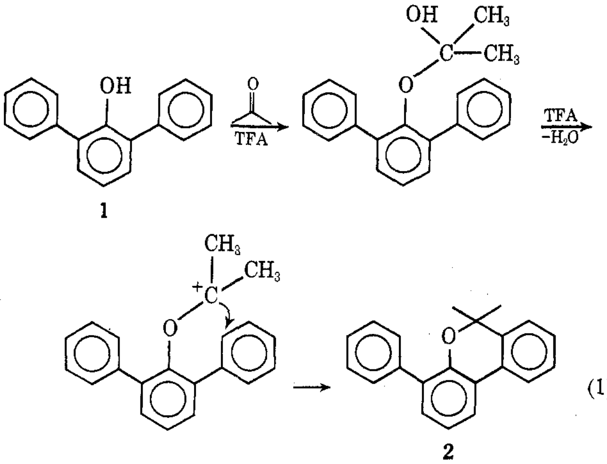
A New Reaction of 2-Phenylphenols with Carbonyl Compounds Yielding Dibenzopyrans

Summary: A new synthesis of dibenzopyrans, fluorenols, and indenofluorenols is described.

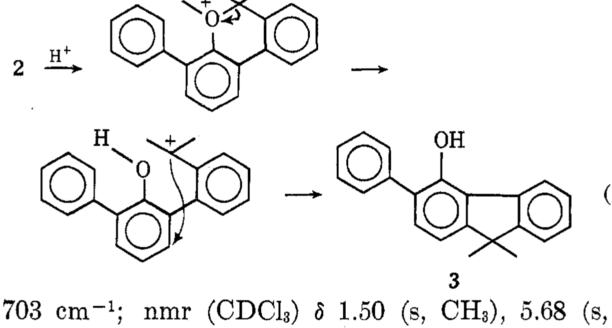
Sir: The acid-catalyzed condensation of carbonyl compounds with phenols to yield bisphenols is a well-known reaction of broad scope.[1] However, it was reported by Kahovec and Pospisil[2] that 2,6-diphenylphenol (**1**) did not react with acetone in the presence of conventional acid catalysts such as hydrogen chloride. This observation was confirmed in our laboratory, but, when **1** was combined with acetone under more strongly acidic conditions, for example, in refluxing trifluoroacetic acid (TFA) (H_0 −3.0),[3] a new condensation reaction occurred yielding 4-phenyl-6,6-dimethyl-6*H*-dibenzo[*b*,*d*]pyran (**2**): mp 79–80°; 64%; *m/e* 286 (M^+), 271 ($M^+ - 15$); nmr ($CDCl_3$) δ 1.55 (s, 6, CH_3), 6.90–7.80 ppm (m, 12, ArH); ir (KBr) 1360 and 1380 (*gem*-dimethyl), 700 cm^{-1} (monosubstituted aryl); satisfactory analysis for $C_{21}H_{18}O$. It is assumed that the reaction proceeds *via* the reversible formation of the phenol hemiacetal of acetone. Protonation and loss of water from the hemiacetal generates a carbonium ion which attacks either of the flanking phenyl groups to form the pyran **2** as shown in eq 1.



(1)

The threshold of acidity (H_0) required for pyran formation was approximately −3.0. No reaction occurred with hydrogen chloride, formic acid (H_0 −2.2),[4] formic-hydrochloric acid, or 50:50 (v/v) formic-trifluoroacetic acid mixtures.

Prolonged refluxing of **2** in TFA rearranged this tertiary benzylic ether to 9,9-dimethyl-3-phenyl-4-fluorenol (**3**) (eq 2): mp 106–107°; ir (KBr) 3540, 703 cm^{-1}; nmr ($CDCl_3$) δ 1.50 (s, CH_3), 5.68 (s, 1, ArOH), 7.00–8.15 ppm (m, 11, Ar H); *m/e* 286 (M^+), 271 ($M^+ - 15$); analyzed for $C_{21}H_{18}O$.



(2)

The rearrangement regenerated an *o*-phenylphenol which in the presence of acetone reacted further to form the indenodibenzopyran (**4**): mp 112–113°; nmr ($CDCl_3$) δ 1.47 (s, 6, CH_3), 1.73 (s, 6, CH_3), 6.93–8.25 (m, 10, Ar H); *m/e* 326 (M^+), 311 ($M^+ - 15$);

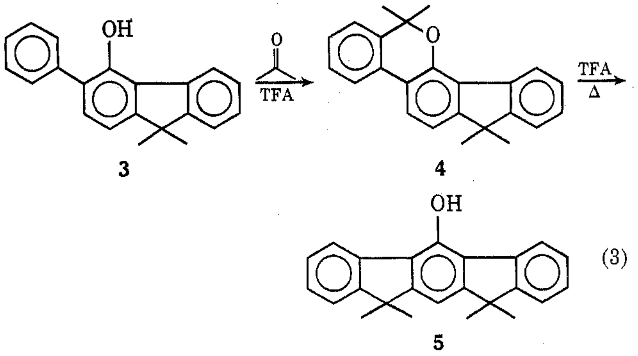
[1] H. Schnell and H. Krimm, *Angew. Chem., Int. Ed. Engl.*, **2**, 373 (1963).

[2] J. Kahovec and J. Pospisil, Collect. *Czech. Chem. Commun.*, **34**, 2843 (1969).

[3] H. H. Hyman and R. A. Garber, *J. Amer. Chem. Soc.*, **81**, 1847 (1959).

[4] R. Stewart and T. Mathews, *Can. J. Chem.*, **38**, 602 (1960).

analyzed for $C_{24}H_{22}O$. **4** in turn rearranged to the indenofluorenol (**5**): mp 210-211°; ir (KBr) 3600 cm^{-1}; nmr ($CDCl_3$) δ 1.41 (s, 12, CH_3), 7.00-8.12 (m, 9, Ar H); *m/e* 326 (M^+), 311 ($M^+ - 15$), 296 ($M^+ - 30$); analyzed for $C_{24}H_{22}O$ (eq 3).



(3)

Each compound (**2**-**5**) has been isolated in pure form by the proper choice of reaction time, acid strength, and stoichiometry.[5] In anhydrous hydrofluoric acid (H_0 -10.2)[6] at 19° with excess acetone all intermediates are cleanly driven to **5** in high yield.

Details and scope of this dibenzopyran synthesis will be reported later.

[5] Complete experimental details on all compounds described in this communication will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D.C. 20036, by referring to code number JOC-73-1621. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

[6] H. H. Hyman, M. Kilpatrick, and J. J. Katz, *J. Amer. Chem. Soc.*, **79**, 3668 (1957).

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