Tetrahedron Letters, Vol. 33, No. 17, pp. 2269-2270, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

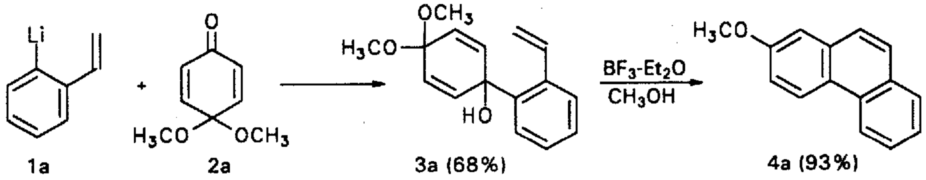
A CONVERGENT APPROACH TO SUBSTITUTED PHENANTHRENES VIA QUINOL KETALS

Tina M. Marks and Gary W. Morrow*, Department of Chemistry
The University of Dayton, 300 College Park, Dayton, Ohio 45469-2357

Summary: *Reaction of 2'-lithiostyrenes with p-benzoquinone monoketals gives p-quinol ketals which undergo Lewis acid-catalyzed cyclization and aromatization, affording 2-methoxyphenanthrenes.*

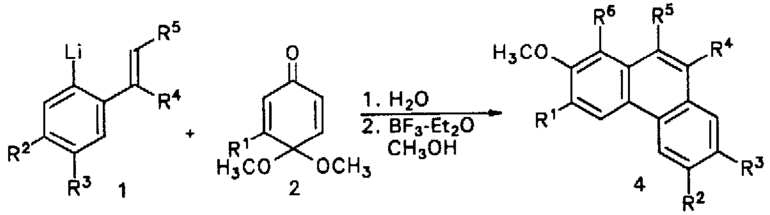
The synthesis of phenanthrenes has been the subject of numerous investigations by organic chemists over the years,[1] due in part to the wide variety of naturally occurring substances which possess the familiar tricyclic skeleton in various patterns of substitution and oxidation state.[2] Our interest in these systems was related to methoxylated phenanthrenes which might be transformed into synthetically exploitable derivatives through application of certain electrooxidation methods. Such methods have been successfully applied to other oxygenated aromatics, affording useful quinone monoketals or quinol ethers.[3a,b] Thus, we report herein a convergent approach to substituted 2-methoxyphenanthrenes via a Lewis acid-catalyzed cyclization of alkenyl-substituted p-quinol ketals.[4]

As shown below, 2'-lithiostyrene **1a** reacts with p-benzoquinone monoketal **2a**, affording p-quinol ketal **3a** as a crystalline solid, m.p. 87-88°C. While the ketal function of **3a** may be readily hydrolyzed in dilute acetic acid/acetone to afford the corresponding p-quinol,[5] we found that addition of catalytic boron trifluoride etherate to a methanol solution of **3a** at room temperature led to rapid formation of 2-methoxyphenanthrene **4a** in excellent yield. Though speculative, a reasonable mechanism would involve ketal ionization followed by carbon-carbon bond formation via trapping of the delocalized carbocationic intermediate by the proximate styrene double bond and aromatization to the phenanthrene via loss of water and a proton.



This convergent approach to the phenanthrene ring system was examined through reaction of substituted 2'-lithiostyrenes with quinone monoketals. Except for **3a** (above), which readily crystallized, the quinol ketals obtained were difficult to purify by chromatography without concurrent decomposition and thus were treated directly in crude form with boron trifluoride etherate in methanol without purification. Note that the yield of **4a** from isolated **3a** was high (93%), but the yield over *both* steps in this case was about 63% whether or not **3a** was isolated and purified. The yields for substituted derivatives (Table) varied somewhat, with methoxyl substitution of the aryllithium component giving a poor yield of phenanthrene (compare entries 2 and 6). Methoxyl substitution of the quinone component also led to a decrease in yield, but an improvement in regioselectivity over a methyl substituent (compare entries 4 and 5). Surprisingly, alkyl substitution on the alkenyl side chain had only a modest effect (compare entries 1, 2 and 3). A poor yield of **4b** (entry 2) via such a cyclization was previously reported during the attempted hydrolysis of the corresponding intermediate quinol ketal.[6]

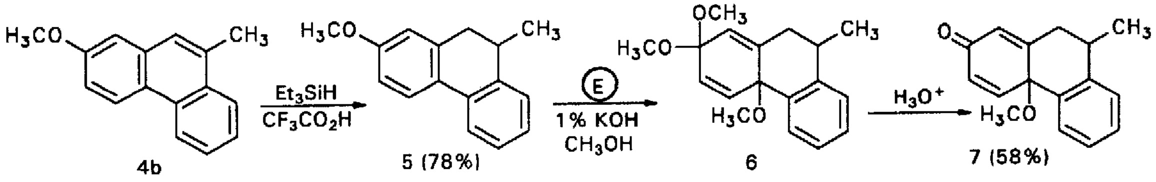
Table. Phenanthrenes via Cyclization of p-Quinol Ketals



Entry	Product **4**	R^1	R^2	R^3	R^4	R^5	R^6	Yield(%)^a	m.p. (^oC)
1	**4a**:	H	H	H	H	H	H	63	96-97
2	**4b**:	H	H	H	CH_3	H	H	72	113-115
3	**4c**:	H	H	H	$-(-CH_2-)_3-$		H	58	125-126
4	**4d/4e**:	H/CH_3	H	H	CH_3	H	CH_3/H	63^b	105-112
5	**4f**:	OCH_3	H	H	CH_3	H	H	40	139-140
6	**4g**:	H	OCH_3	OCH_3	CH_3	H	H	24	164-165

^{a}isolated yields, based on **2**. ^{b}obtained as a 50:50 mixture of regioisomers

Preliminary studies showed that single cell anodic oxidation of **4b** in 1% by weight KOH in methanol using a platinum anode and cathode[3a,b] gave a complex mixture of products. However, reduction of the 9,10 double bond with triethylsilane in CF_3CO_2H[7] to give **5**, followed by anodic oxidation under the above conditions and subsequent hydrolysis of the intermediate quinol ether ketal **6** gave dienone **7** in good overall yield. Further efforts will explore the chemistry of such polyfunctional phenanthrene derivatives.



Acknowledgement: This research was supported by a grant from Research Corporation.

REFERENCES

1. Floyd, A.J.; Dyke, S. F.; Ward, S. E. *Chem. Rev.*, **1976**, *76*, 509.
2. Fieser, L. F. and Fieser, M. "Natural Products Related to Phenanthrene", 3rd ed.; Reinhold: New York, 1949.
3. See: (a) Henton, D. R.; McCreery, R. L.; Swenton, J.S. *J. Org. Chem.* **1980**, *45*, 369 and (b) Swenton, J.S.; DeSchepper, R.E., *Tetrahedron Lett.*, **1985**, 4831.
4. For a related approach, see: Evans, D.A.; Cain, P.A.; Wong, R.Y., *J. Am. Chem. Soc.* **1977**, *99*, 7083.
5. Morrow, G.W.; Chen, Y.; Swenton, J.S., *Tetrahedron*, **1991**, *47*, 655.
6. Stern, A.J.; Swenton, J.S., *J. Org. Chem.*, **1988**, *53*, 2465.
7. For related reductions using these reagents, see: Kursanov, D.N.; Loim, N.M.; Baranova, A.V.; Moiseeva, L.V.; Zalukaev, L.P.; Parnes, Z.N., *Synthesis*, **1973**, 420.

(Received in USA 27 January 1992)