Tetrahedron Letters, Vol.29, No.2, pp 225-226, 1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A FACILE ROUTE TO PERYLENEQUINONE

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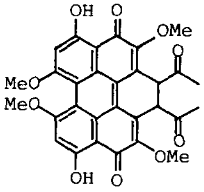
Summary Two-stage Ullmann and phenol coupling were effected in a single operation on methyl 5-bromo-1,2-dihydroxy-6,8-dimethoxynaphthalene-3-acetate to give dimethyl 5,8-dihydroxy-1,3,10,12-tetramethoxy-4,9-perylenequinone-6,7-diacetate with ferric chloride as oxidant

A limited group of natural products possessing a common perylenequinone nucleus has been isolated from certain fungi[1] as well as from aphid,[2] such as elsinochrome A (1),[3] hypocrellin (2),[4] and erythroaphin fb (3)[5] There are a few synthetic approaches to perylenequinones[6,7,8]



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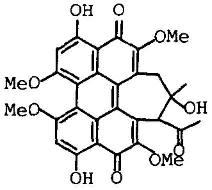

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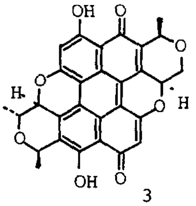

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and one synthesis[9] was later shown[10] that, instead of the presumed perylenequinone, a binaphthalene derivative was actually obtained We like to report a facile synthesis of a perylenequinone, which is amenable to ready modification to give related natural products

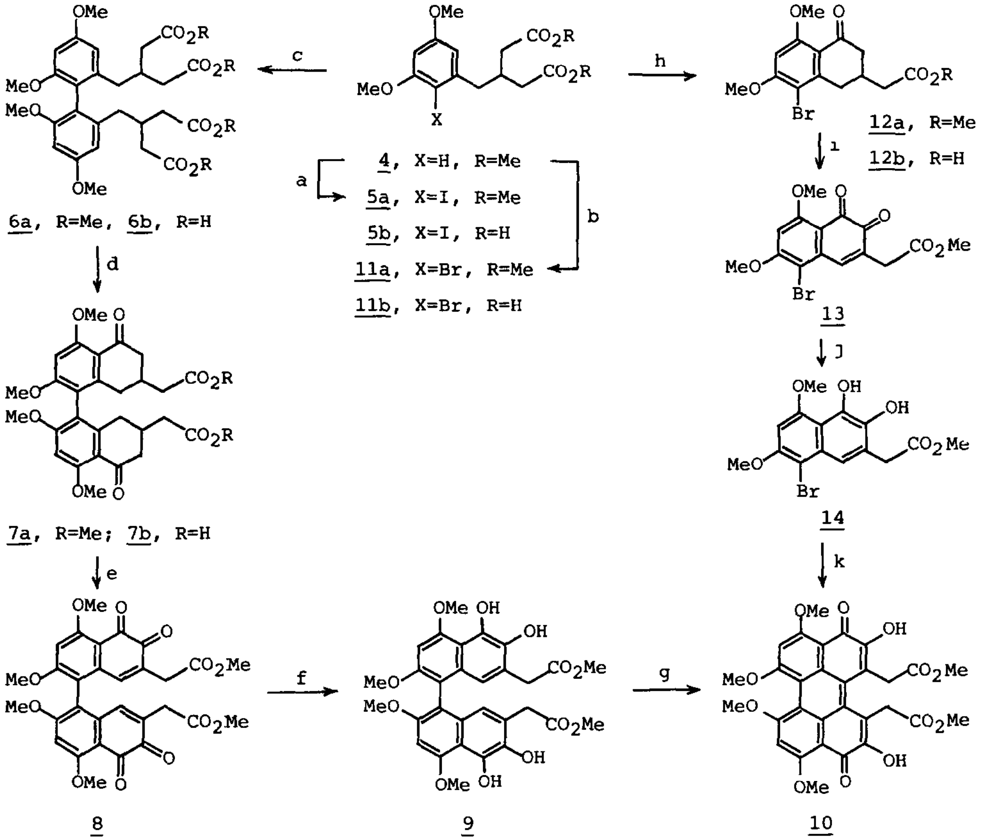
The synthesis consisted of union of two appropriately substituted phenyl or naphthalene parts as shown in the scheme and was started with dimethyl 3-(3,5-dimethoxybenzyl)glutarate (4),[11] followed by iodination (to 5a),[12] Ullmann coupling (to 6a),[13] cyclization of acid (6b) with PPA (to 7b),[8] and oxidation of dimethyl ester (7a) with selenium dioxide[14] to give bi-o-naphthalene-5,6-quinone (8) which was then reduced with sulfur dioxide[15] to the unstable tetramethoxy-bi-o-naphthalene-3,4-diol (9) Ultimate oxidative coupling of 9 by ferric chloride[16] led to perylenequinone (10) Ferric chloride failed to cyclize 8

A more efficient route was found with the bromo analogue (11a) obtained by bromination of 4 [17] The dibasic acid (11b) (95% yield from 11a) was cyclized with PPA to the ketoacid (12b) and its methyl ester (12a) (85% yield from 12b) was oxidized (to 13) and reduced similarly to give the bromodimethoxynaphthalenediol (14). Both 11 and 12 did not undergo Ullmann reaction, but 14 on oxidative coupling with ferric chloride led unexpectedly to a double coupling to give the same perylenequinone (10)

Perylenequinone (10) bears all necessary functional groups amenable to conversion to some of the perylenequinone natural products and the double coupling reaction is worthwhile for further studies of its scope and mechanism, both of which are now under way

References and Note

1. D Merlini and C Nasini, Natural Perylenequinones from Moulds, 2nd Intern. Conf , Chemistry and Biotechnology of Biologically Active Natural Products, Budapest, 1983
2 R H. Thomson, Naturally Occurring Quinones, 2nd ed., Academic Press, New York, 1971,p 576.
3 R. J J Lousbery, C A Salemink, U Weiss, and T. J Batterham, J. Chem. Soc., (C), 1219



a. I_2, CF_3CO_2Ag, MeOH, RT, 3.5h (82%). b. Br_2, $CHCl_3$, RT, 3h (71%). c Cu, 240°C, 20min (48%). d. PPA, 100°C, 1h (83%). e. SeO_2, HOAc, 70°C, 1h (60%). d (97%). i. as e, 3h (98%). j. as f (94%). k. as g, 17h (32.9%).

(1969).
4. S. Y. Wan and Y. T. Chen, Kexue Tongbao, 25, 1148 (1980); W. S. Chen, Y. T. Chen, X. Y. Wan, E. Friedrichs, H. Puff, and E Breitmaier, Liebigs Ann. Chem., 1981, 1880.
5. D. W. Cameron, R. I. T. Cromartie, and Lord Todd, J. Chem Soc., 62, 72, 90, 94 (1964).
6. A. Zincke, W. Hirsch, and E. Brozek, Monatsh., 51, 205 (1929), 52, 13 (1929); A. Calderbank, A. W. Johnson, and A. R. Todd, J Chem. Soc , 1285 (1954).
7. D. C. Allrop and J. D. Bu'Lock, J Chem. Soc., 4090 (1958).
8. F. Dallacker and H. Leidig, Chem. Ber , 112, 2672 (1979).
9. K. H. Weisgraber and U. Weiss, J. Chem. Soc., Perkin Trans I, 83 (1972)
10. U. Weiss, H M. Fales, and K. H. Weisgraber, Liebigs Ann. Chem., 1979, 914.
11. R. P. Hatch, J. Shringarpure, and S. M. Weinreb, J. Org. Chem., 43, 4172 (1978).
12. E. Brown, J. P. Robin, and R. Dhal, Tetrahedron, 38, 2569 (1982). All yields correspond to isolated products. All new compounds have been fully characterized by NMR and IR spectroscopy and possess satisfactory elemental analyses or exact mass.
13. P. H. Gore and G. K. Hughes, J. Chem. Soc., 1615 (1959).
14. V. Viswanatha and G. S K. Rao. Tetrahedron Letters, 247 (1974).
15. N. G. Kundu, J. Org. Chem., 44, 3086 (1979).
16. R. G. R. Bacon and A R. Izzat, J. Chem. Soc., (C), 791 (1966).
17 A. Chatterjee and B. G. Hazra, Tetrahedron, 36, 2513 (1980).

Acknowledgements: Committee of Education and Natural Science Fundation are indebted for financial supprots and Professor Hui-tong Tang for advices on spectroscopic matters.

(Received in Japan 7 August 1987)