Tetrahedron Letters No. 6, pp 495 - 496, 1974. Pergamon Press. Printed in Great Britain.

THE UNUSUAL FORMATION OF PHENANTHRENE DURING THE METHYLATION OF BENZO[h]QUINOLINE 1-OXIDE WITH METHYLSULFINYL CARBANION.

Y.HAMADA and I.TAKEUCHI
Pharmaceutical Faculty, Meijo University,
Tempaku-cho, showa-ku, Nagoya, Japan

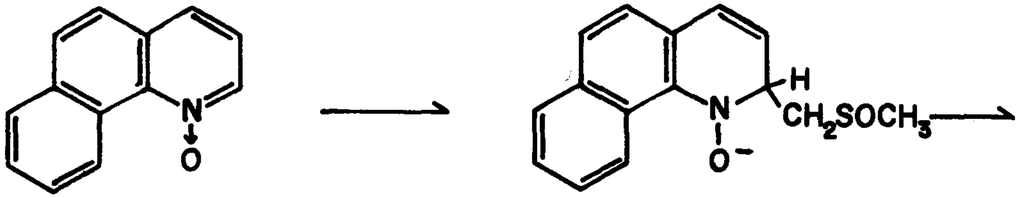
M.HIROTA
Department of Applied Chemistry, Faculty of Engineering,
Yokohama National University, Minami-ku, Yokohama, Japan

(Received in Japan 10 November 1973; received in UK for publication 28 December 1973)

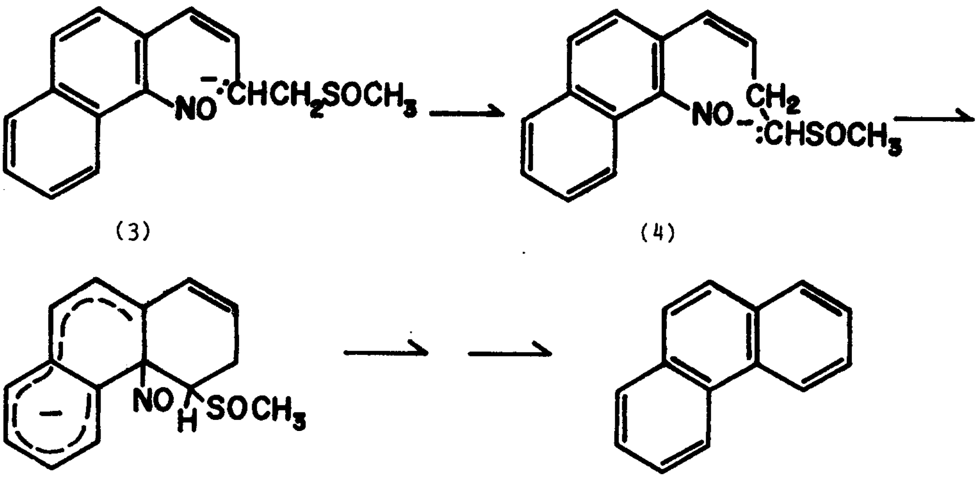
The methylsulfinyl carbanion has been recognized as an efficient methylating agent, and used to methylate several heteroaromatic compounds successfully.1) The present authors have also studied on the nucleophilic substitution of some nitrogen heterocycles and determined the orientation of the methylation of naphthyridines.2) On the other hand, the methylation of quinoline and related heterocyclic N-oxides was carried out and shown to produce the expected methyl derivatives in most instances.3) However, when benzo[h]quinoline 1-oxide was submitted to the reaction with methylsulfinyl carbanion in the usual procedure, an unusal reaction took place to produce phenanthrene in an excellent yield.

Thus, under the nitrogen atmosphere, 1.56g(0.008mole) of benzo[h]quinoline 1-oxide dissolved in 40ml of DMSO was added to the sodium hydride solution in DMSO kept at 70°C, and the reaction mixture was stirred for about 4 hrs. After the reaction was completed, the reaction mixture was poured into an excess of water and extracted with chloroform. The organic layer was separated and dried over anhydous magnesium sulfate. The solvent was distilled off, and then purified by column chromatography. Phenanthrene was obtained as colorless leaflets. Yield:1.22g(86%). The product was indentified by mixed melting point,elementary analysis, infrared, n.m.r. and mass spectra [m/e 178(M^+)].

The reaction to produce phenanthrene might be interpreted by the following scheme.



(1) (2)



(3) (4) (5) (6)

Initial nucleophilic attack by methylsulfinyl carbanion to benzo[h]quinoline N-oxide induces the fission of C-N bond of the N-oxide group, and the produced carbanion(3) isomerizes rapidly to the more stable carbanion(4). Then, the anion performs the intramolecular nucleophilic attack to produce the carbocyclic product(5), and the subsequent elimination reactions might give phenanthrene as the final product. The scope and the mechanistic details of this reaction are now under investigation, however, a kind of steric effect might play an important role, since the same reactions with quinoline and benzo[f]quinoline N-oxides give the normal methyl-derivatives.

References

1) G.A.Russell and S.A.Weiner, J.Org.Chem., 31, 248(1966)
2) Y.Hamada, I.Takeuchi and M.Hirota, Chem.Pharm.Bull.(Tokyo), 1751(1971)
3) Y.Kobayashi, I.Kumadaki, H.Sato, C.Yokoo and T.Mimura, Chem.Pharm.Bull.(Tokyo), 21, 2066(1973)