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The Reaction Of Dimethyldioxirane With Chrysene: Formation Of A Trioxide[1]

Robert W. Murray*, Megh Singh, and Nigam Rath

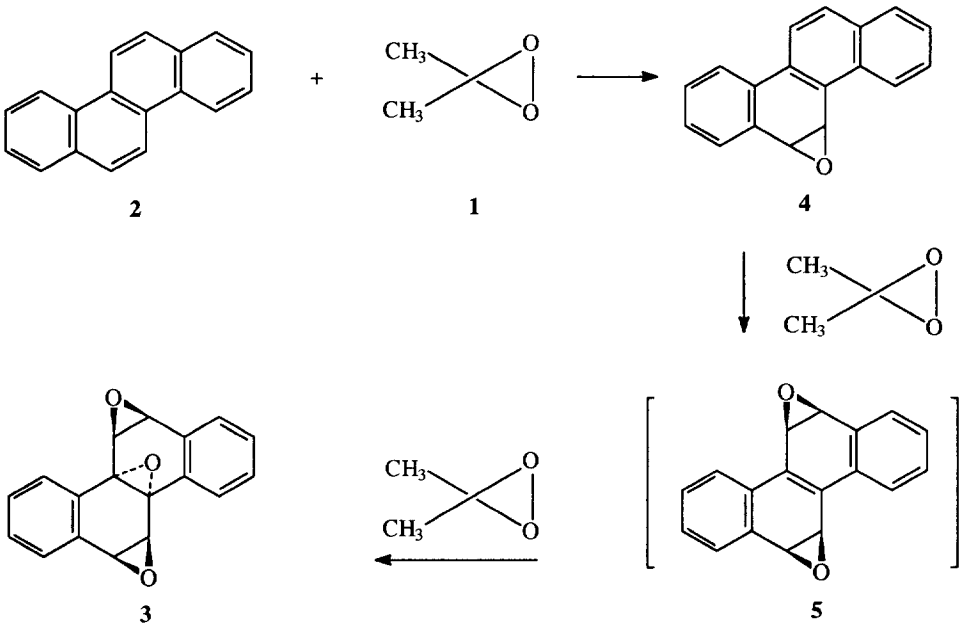
Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO, 63121, USA

Abstract: Oxidation of chrysene with dimethyldioxirane gives a number of products including the interesting trioxide, chrysene-5,6:4b,10b:11,12-trioxide, **3**. The x-ray crystallographic stucture of **3** indicates that it is a non-planar system. Copyright © 1996 Elsevier Science Ltd

The carcinogenicity of certain polycyclic aromatic hydrocarbons (PAH) is known[2] to be related to their metabolic activation. The metabolites which are critical for the binding of the oxidized PAH to important biological molecules, including DNA, contain the arene oxide moiety.[3] This observation has led to a great interest in the synthesis of arene oxides. While the arene oxides receiving the most attention have been monooxides or dioxides there are only a few examples of the formation of trioxides. Three stereoisomeric trioxides of benzene were described some time ago.[4] Likewise isomeric tri- and higher polyoxides of naphthalene have been reported.[4] A trioxide of a cyclohexatriene derivative also has been prepared.[5] Triphenylene has been oxidized to a trioxide by *m*-chloroperbenzoic acid.[6]

Since we first reported[7] the isolation of dimethyldioxirane in acetone solution the chemistry of this remarkable O atom transfer reagent and related dioxiranes has received a growing amount of attention.[8] In an earlier report[9] we described the synthesis of arene oxides using *in situ* generated dimethyldioxirane. Since that report we and others have synthesized additional examples if arene monooxides using dimethyldioxirane.[8] In 1989 Boyd and coworkers described[10] the first use of dimethyldioxirane to synthesize arene dioxides. We now report that dimethyldioxirane **1** reacts with chrysene **2**[11] to give the interesting trioxide **3** (Scheme 1). The trioxide is accompanied by the monoxide **4.** We believe that **4** reacts further with **1** to give the ***cis*** dioxide **5** which is not isolated. Examination of the structure of the trioxide reveals that formation of the dioxide involves reaction at the two K-regions of **2.** The dioxide so formed then contains a double bond at the C_{4b}-C_{10b} position which is no longer aromatic. This double bond is then rapidly epoxidized by **1** with the oxygen being installed *trans* to the two K-region oxides. This rapid epoxidation consumes the dioxide preventing its observation.[14]

Scheme 1



The structure of **3** was determined by X-ray diffraction. This structure (Figure 1) shows clearly the *cis* relationship of the two K-region oxides as well as the *trans* positioning of the third oxide relative to the first two. The two K-region oxides confer a non-planarity to the overall structure which is not compensated by the presence of the third, *trans* oxide. A similar non-planarity has been observed[15] in 7,12-dimethylbenz[*a*]anthracene-5,6-oxide.

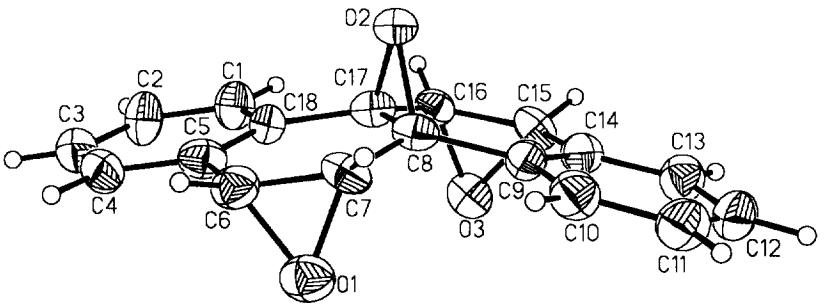


Figure 1. X-ray Crystal Structure of **3**.

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11. Sample procedure: To a magnetically stirred solution of **2** (0.071 g, 0.311 mmol) in 5 mL of acetone was added 28 mL of an 0.068 M solution of $1^{7,8}$ (1.87 mmol) in acetone. The reaction mixture was stirred in the

dark at room temperature for 72 h to give an orange colored solution. ^{1}H NMR analysis of the residue indicated the presence of chrysene-5,6-oxide[12] (δ 4.70, d, *J* = 4.20 Hz, 1 H; 5.34, d, *J* = 4.20 Hz, 1 H), chrysene-5,6-dione[12] (δ 9.37, d, J = 8.80 Hz) and a minor product which was identified as chrysene trioxide **3** (δ 3.95, d, *J* = 4.15 Hz, 4.60, d, *J* = 4.15 Hz). Solvent was removed on a rotary evaporator to give a dark orange-red residue (0.0934 g). GC/MS and ^{1}H NMR analysis of the residue indicated the presence of the products described above and two other minor products. One of these was identified as 6-hydroxychrysene on the basis of its ^{1}H and mass spectra[13]. A second minor product which shows a set of doublets at δ 4.10 (d, J = 3.86 Hz) and 4.25 (d, J = 3.86 Hz) has not yet been identified. The residue was subjected to preparative TLC (Analtech 1000 μ Kieselgel 60 PF_{254} coated plates) using methylene chloride as eluent. The UV active band at R_f 0.5 was removed and extracted with methylene chloride. Filtration and evaporation of the solvent gave a cream-colored residue (0.01 g, 8 %). Recrystallization of the residue from CH_2Cl_2/hexane afforded trioxide **3** as colorless needles; mp 245-248° C(dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (d, *J* = 4.15 Hz, 2H), 4.60 (d, *J* = 4.15 Hz, 2H), 7.35-7.65 (m, 6H, Ar H), 7.94 (d, *J* = 7.38 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.73, 53,60, 61.19, 127.94, 129.61, 131.41, 131.45, 131.97; MS (EI, 70 eV): m/z (rel. intensity) 277 (M+1, 2), 247 (100). Calcd for $C_{18}H_{12}O_3$: 276.29. Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found C, 77.57; H, 4.48.

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14. The *cis* strereochemistry in **5** may be due to an attractive dipole interaction between the strong dipole in **1** and the dipole in the first oxide. Trioxide **3** may be accompanied by a strereoisomeric trioxide. The reaction mixture contains trace quantities of other materials which have not yet been identified.
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