

Nitration of Phenanthrene in Acetic Anhydride

D. Malcolm D. Lane,^A Kenneth E. Richards,^A Graeme J. Wright^A and Alfred Fischer^B

^A Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

^B Department of Chemistry, University of Victoria, Victoria, B.C., Canada.

Abstract

Nitration of phenanthrene in acetic anhydride gives 10-acetoxy-10'-nitro-9,9',10,10'-tetrahydro-9,9'-biphenanthryl as major product.

Adduct formation accompanying nitration in acetic anhydride is a normal reaction of appropriately substituted benzene derivatives.¹ In all such adducts the nitro group is *ipso* to another substituent, commonly methyl. Polycyclic aromatic compounds are more prone to undergo addition reactions than benzene, and anthracene has long been known to form a 9-acetoxy-10-nitro adduct on nitration in acetic acid.² Evidently, the loss of resonance energy on forming the adduct from anthracene is sufficiently small that the proton *ipso* to the nitro group is not rapidly lost, with formation of the substitution product, as happens in benzene derivatives in which the nitronium ion is added to an unsubstituted position. Phenanthrene would similarly be expected to undergo an addition reaction at the 9,10-bond. Nitration of phenanthrene in acetic anhydride has been studied by Schmidt and Heinle³ and, more recently, Dewar and coworkers.⁴ They reported only the formation of the various mononitrophenanthrenes.

We have found that reaction of phenanthrene (suspended in acetic anhydride) with nitric acid in acetic anhydride (added dropwise) at 0° gives 10-acetoxy-10'-nitro-9,9',10,10'-tetrahydro-9,9'-biphenanthryl (3) as major product in yields varying from 35 to 45%, together with a complex mixture of other products, including 9-nitrophenanthrene (*c.* 20%). If the reaction is carried out by reverse addition of phenanthrene (completely dissolved in a large volume of acetic anhydride) to the nitric acid-acetic anhydride mixture, very little dimer (3) is formed initially, but it is produced, again as a major product, if the crude reaction mixture is allowed to stand. Dimer is also

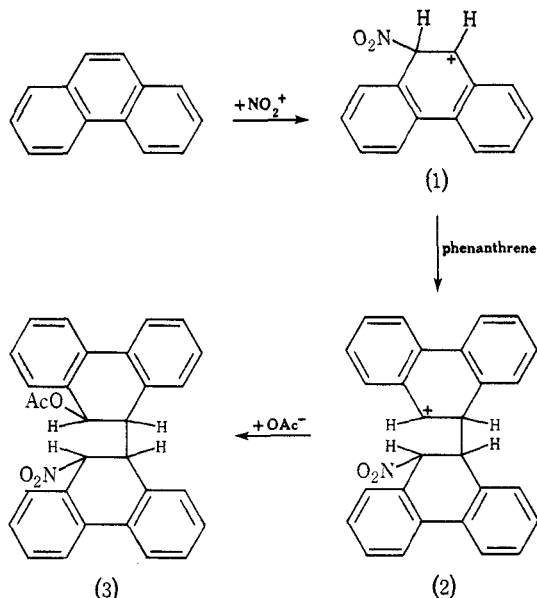
¹ Blackstock, D. J., Fischer, A., Richards, K. E., Vaughan, J., and Wright, G. J., *Chem. Commun.*, 1970, 641; Blackstock, D. J., Cretney, J., Fischer, A., Hartshorn, M. P., Richards, K. E., Vaughan, J., and Wright, G. J., *Tetrahedron Lett.*, 1970, 2793; Galley, M. W., and Hahn, R., *J. Am. Chem. Soc.*, 1974, **96**, 4337; Fischer, A., and Seyan, S. S., *Can. J. Chem.*, 1978, **56**, 1348.

² Dimroth, O., *Ber. Dtsch. Chem. Ges.*, 1901, **34**, 219; Meisenheimer, J., and Connerade, E., *Justus Liebigs Ann. Chem.*, 1904, **330**, 133.

³ Schmidt, J., and Heinle, E., *Ber. Dtsch. Chem. Ges.*, 1911, **44**, 1488.

⁴ Bavin, P. M. G., and Dewar, M. J. S., *J. Chem. Soc.*, 1956, 164; Dewar, M. J. S., and Warford, E. W. T., *J. Chem. Soc.*, 1956, 3570.

produced from reaction product mixtures from which all solvents had been removed by evaporation under reduced pressure at 0°.



Scheme 1

Formation of (3) can be understood in terms of the sequence shown in Scheme 1. The dimerization step in the formation of the biphenanthryl, the addition of carbocation (1) to a second molecule of phenanthrene, has an obvious parallel in the formation of biphenyl derivatives by the acid-catalysed reaction of arene adducts with aromatic substrates.⁵ We suggest that formation of (3), on standing a worked-up reaction mixture for several days, occurs by reaction between an initially formed 9-acetoxy-10-nitro adduct of phenanthrene with unchanged phenanthrene. Loss of the acetate group from the adduct, catalysed by trace amounts of acid likely to be present in the crude product, would give cation (1) which would continue the sequence to give (2) and (3) shown in Scheme 1. 10-Nitrato-10'-nitro-9,9',10,10'-tetrahydro-9,9'-biphenanthryl, a compound closely related to (3), was obtained on reaction of phenanthrene with anhydrous nitric acid in benzene (and also with dinitrogen trioxide or dinitrogen tetroxide in benzene, or fuming nitric acid in chloroform). A radical process was proposed for this reaction.⁶ Analogy with the behaviour of other aromatic substrates in acetic anhydride supports our proposal of an ionic mechanism in this solvent.¹

Experimental

Preparation of Dimer (3)

Phenanthrene (10 g) was suspended in acetic anhydride (40 ml) and stirred in an ice-water bath. Nitric acid (*d* 1.52, 2.3 ml), dissolved in acetic anhydride (5 ml), was added dropwise over 1 h. The mixture was poured into water and allowed to stand for several hours—the crude product mixture

⁵ Fischer, A., and Greig, C. C., *J. Chem. Soc., Chem. Commun.*, 1973, 396.

⁶ Heaney, H., Jones, A. J., and Millar, I. T., *J. Chem. Soc.*, 1965, 2587.

coagulated and the water was decanted. The solid was triturated several times with ether, leaving a white ether-insoluble solid, insoluble in most common solvents. Recrystallization from acetone or from a large volume of ethanol gave 10-acetoxy-10'-nitro-9,9',10,10'-tetrahydro-9,9'-biphenanthryl (3), m.p. 237° (dec.) (Found: C, 77.5; H, 5.1; N, 3.2; O, 14.2. $C_{30}H_{23}NO_4$ requires C, 78.1; H, 5.0; N, 3.0; O, 13.9%). Mass spectrum: m/e 461 (0.2%), 432 (0.4), 414 (0.6), 401 (0.4), 354 (59), 237 (100). δ ($CDCl_3$, 60 MHz) 8.1-7.6, m, 4H, ArH; 7.6-7.1, m, 10H, ArH; 7.1-6.7, m, 2H, ArH; 5.65, d, 1H, $J_{9',10'}$ 2 Hz, H 10'; 5.13, d, 1H, $J_{9,10}$ 2 Hz, H 10; 3.46, dd, 1H, $J_{9,9'}$ 11 Hz, $J_{9',10'}$ 2 Hz, H 9'; 2.77, dd, 1H, $J_{9,9'}$ 11 Hz, $J_{9,10}$ 2 Hz, H 9; 1.58, s, 3H, $OCOCH_3$, ν_{max} (Nujol) 1730, 1620, 1540, 1350, 740 cm^{-1} .

Inverse Addition

Phenanthrene (10 g) dissolved in acetic anhydride (250 ml) was added to nitric acid (d 1.52, 2.5 ml) in acetic anhydride (10 ml) at 0-10° (ice-bath) over 50 min. The reaction was quenched in water (500 ml), washed with ammonia solution (1%) and extracted with ether. Very little dimer had formed at this stage; if the ether solution was allowed to stand for several days, dimer (3) precipitated slowly, and, if the ether was evaporated, dimer formed in the resulting gum over 24 h. The total yield of dimer obtainable by this method was the same as that obtained from preparative nitrations.

Identification of Dimer

The physical properties of the dimer are consistent with the formula (3). In particular, the n.m.r. spectrum is closely similar to the published spectra of the related compounds 10-hydroxy-10'-nitro-9,9',10,10'-tetrahydro-9,9'-biphenanthryl and 10-nitrato-10'-nitro-9,9',10,10'-tetrahydro-9,9'-biphenanthryl.⁷ Furthermore, (3) must have the same stereochemistry as these related compounds since exactly the same arguments (based on the n.m.r. spectra) which were applied to assign the stereochemistry of the 10-nitrato and 10-hydroxy compounds may also be applied to (3). Thus (3) also belongs to the 9,9'-racemic series, the 9,9'-link is formed from pseudo-axial bonds and the acetoxy and nitro substituents are pseudo-axial.⁷

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⁷ Cohen, D., Millar, I. T., Heaney, H., Constantine, P. R., Katritzky, A. R., Semple, B. M., and Sewell, M. J., *J. Chem. Soc. B*, 1967, 1248.