

10-Substituted Anthrone Oximes

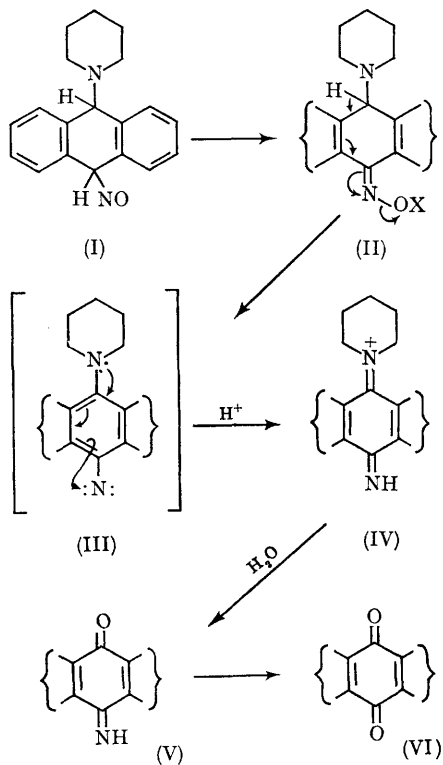
By Y. L. CHOW

(Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada)

No synthesis of an anthrone oxime has been reported as far as we are aware. We report the first synthesis of 10-substituted anthrone oximes and the reactions thereof.

Ready photoaddition of *N*-nitrosamines across a carbon-carbon double bond has been demonstrated.¹ By the same procedure, a 1:1 adduct of *N*-nitrosopiperidine and anthracene was obtained in 52% yield when a methanolic solution of the reactants was irradiated with a Hanovia lamp (54A36). The adduct, m.p. 184–186° (decomp.), shows ν_{\max} (Nujol) 2500–3200, 1620, 1000, and 940 cm^{-1} , and n.m.r. signals [$(\text{CD}_3)_2\text{SO} \cdot (\text{CD}_3)_2\text{CO}$] at τ 2.2, 2.7 (aromatic, 1:7), 4.8 (OH), and 5.33 (benzylic) and is believed to be 10-piperidinoanthrone oxime, (II; X = H), probably formed *via* the *C*-nitroso-compound (I).¹ In agreement with this assignment the proton at τ 4.8 can be exchanged with D_2O and one proton at τ 2.2 may be assigned the *ortho*-aromatic proton *syn* to oximino-group. Under mild conditions, the tosylate (II; X = Ts), m.p. 136–138°, and the acetate (II; X = Ac), m.p. 150–152° (ν_{\max} 1775 cm^{-1}) are prepared by the usual methods. Other 10-dialkylamino-substituted anthrone oximes were also synthesized in the same manner.

The oxime (or tosylate) possesses a rigid structure and, therefore, may have to surmount an



exceedingly high energy barrier to undergo the normal Beckmann rearrangement.² On the other hand the elimination of toluene-*p*-sulphonic acid from the tosylate (II) is greatly facilitated by the driving force for aromatization leading to the anthracenyl-nitrene intermediate (III). Thus, treatment of the tosylate (II) with a dilute methanolic potassium hydroxide solution or with triethylamine gives anthraquinone (VI) and its monoimine* (V), m.p. 243—245° (Calc. for C₁₄H₉NO; *M*⁺, 207·06841. Found: 207·06880)† in good yields. Anthraquinone monoimine is fairly stable in an alkaline solution but is rapidly hydrolysed in an acidic solution.

In order to provide plausible evidence for the

intermediacy of (III), the oxime tosylate was heated under reflux in cyclohexene in a hope that nitrene (III) might be trapped by cyclohexene. From the reaction a basic resin, in addition to a large amount of anthraquinone, was obtained. The resin was shown by mass spectroscopy and n.m.r. to have incorporated a cyclohexene ring. On exposure to air the resin was quickly oxidized to give a complex mixture.³† Working under a nitrogen atmosphere a small amount of a yellow solid was obtained whose molecular formula was shown to be C₂₅H₂₃N₂O (Calc.: *M*⁺, 372·2203. Found: 372·2208).

(Received, February 13th, 1967; Com. 132.)

* Slow hydrolysis to anthraquinone occurs during recrystallization from methanol and the specimen with m.p. 243—245° is analysed to give N, 5·0% (Calc., 6·8%). This compound has been reported to give m.p. 225—226·5° (C. K. Bradsher and D. J. Beavers, *J. Org. Chem.*, 1956, **21**, 824) and 218° (M. L. Stein and H. Euler, *Gazzetta*, 1954, **84**, 290) but no nitrogen analyses were given.

† The *M*⁺-values were measured with an AEI MS-9 mass spectrometer. The Author is very grateful to Professors W. A. Ayer and D. D. Tanner for these results.

‡ The decomposition of tosylate (II) in benzene gave anthraquinone, a black tar, and a green basic fraction, the last of which gradually changed to a black tar during working-up. The n.m.r. spectrum of the basic fraction showed complex signals at τ 3—4 region possibly due to the azepine derivative.

¹ Y. L. Chow, *Canad. J. Chem.*, 1965, **43**, 2711; *J. Amer. Chem. Soc.*, 1965, **87**, 4642.

² P. T. Lansbury and N. R. Mancuso, *J. Amer. Chem. Soc.*, 1966, **88**, 1205.

³ Cf. J. Rigaudy and G. Izoret, *Compt. rend.*, 1954, **238**, 824. As demonstrated here, 9-aminoanthracenes are sensitive to air oxidation.