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SYNTHESIS AND PHOTOREARRANGEMENT OF SUBSTITUTED K-REGION ARENE OXIDES

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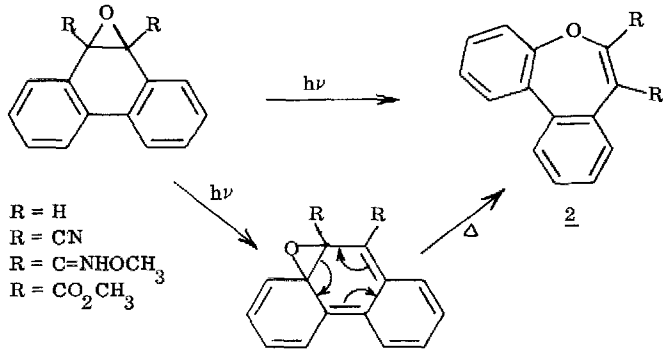
Since our initial report of the photorearrangement of 9,10-epoxy-9,10-dihydrophenanthrene (1a) to 2,3:4,5-dibenzoxepin (2a)[2] several publications have appeared which substantiate our contention that the photointerconversion of K-region arene oxides to oxepins is general in nature.[3,4,5] Additional examples have also been observed in our laboratories which we wish to disclose at this time.

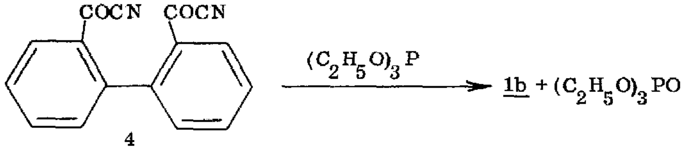


1a, R = H
b, R = CN
c, R = $C{=}NHOCH_3$
d, R = CO_2CH_3

2

3

9,10-Dicyano-9,10-epoxyphenanthrene (1b), mp 191-193°, was synthesized (70%) by application of the method of Mukaiyama previously utilized to condense aroyl cyanides to 2,3-dicyanostilbene oxides.[6] 2,2'-Dicyanoformylbiphenyl (4), mp 96-98°, ir (KBr) 2220 cm^{-1} (m, -CN), 1680 cm^{-1} (s, -CO) is prepared (79%) in turn by treating diphenic acid chloride with cuprous cyanide under conditions (190-200°; 0.2 mm) where the yellow product 4 sublimes. Addition of triethylphosphite to a stirred benzene solution of 4 at low temperature gives the dicyanoarene oxide 1b which precipitates from solution upon standing overnight.[7]



4

$$4 \xrightarrow{(C_2H_5O)_3P} 1b + (C_2H_5O)_3PO$$

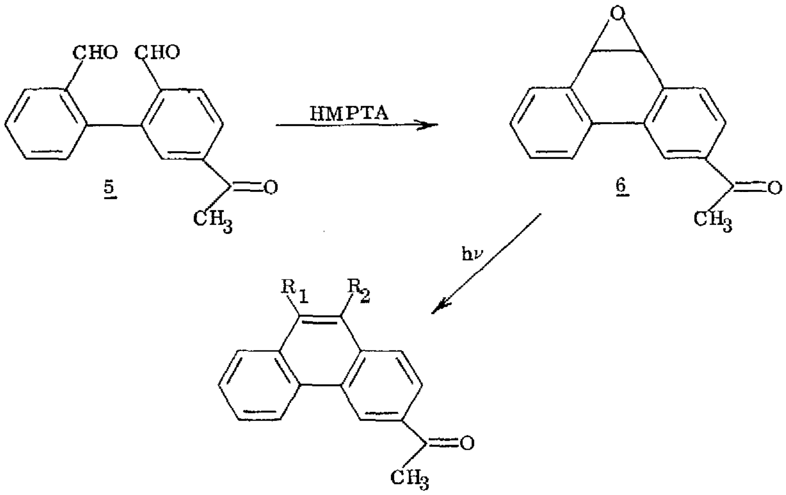
The structure of 1b was confirmed by deoxygenation of the oxirane with tri-n-butylphosphine[6] to 9,10-dicyanophenanthrene identical in all respects to an authentic sample.[8] Furthermore hydrolysis of 1b to phenanthrenequinone may be achieved by heating the oxirane under reflux in aqueous tetrahydrofuran containing added surfuric acid. Conversion of the dinitrile 1b to the corresponding diester 1d, mp 164-166° [$(C_2H_5)_2O$] ir (Nujol) 1740 cm^{-1} (s, -CO); nmr ($CDCl_3$) δ 3.85 (s, 6H, $-OCH_3$), was accomplished (47%) by hydrolysis (10% sulfuric acid in methanol; 25°) of the bis-imino ether 1c which was prepared in essentially quantitative yield by treating 1b with 0.18 M sodium methoxide in methanol.

The nitrile 1b, like the parent oxide 1a, was found to be photolabile and to rearrange (73%) upon irradiation (254 nm)[9] in degassed benzene to an isomeric colorless solid, mp 186-188° (C_6H_6-C_6H_{12}). This photoproduct was identified as 6,7-dicyano-2,3:4,5-dibenzoxepin (2b) by mass spectrometry as well as 300 MHz, nmr, and 25.2 MHz, cmr spectral data.[10] Examination of the cmr spectrum of this product (obtained under proton-noise-decoupled and signal frequency off-center-resonance decoupled conditions) reveals that the molecule possesses 16 aromatic carbon atoms of which 8 are proton-bearing. Signals for two nonequivalent vinylic carbon atoms and two nonequivalent cyano group carbon atoms complete the spectrum. The cyano group signals in the cmr spectrum of 2b show signal enhancement upon addition of the shift relaxation agent tris(acetylacetonato)chromium (III).[11] Also consistent with assignment 2b in the 300 MHz spectrum of 2b is the appearance of 8 assignable resonance signals in the δ 7.25 to 7.70 ppm region characteristic of the aromatic protons.

The diester 1d like the parent system 1a and dinitrile 1b also undergoes photorearrangement (254 nm)[9] to the dibenzoxepin 2d, mp 97-99° (CH_3OH-H_2O), ir (Nujol) 1700 cm^{-1}; nmr ($CDCl_3$) δ 3.81 and 3.83 (d, 3H-OCH_3). This is evident from the appearance of nonequivalent methoxy protons in the nmr spectrum of the photorearrangement product and the disappearance of the low-field 2 H multiplet characteristic of the deshielded 4,5-protons characteristic of phenanthrenes and their 9,10-dihydro derivatives.

By-products formed upon direct irradiation of 1a include 9-phenanthrol and fluorene. The former in contrast to 2a is believed formed in a triplet process.[12] This view is supported by the capacity to quench phenanthrol formation with trans-1,3-pentadiene and to circumvent the rearrangement to 2a by utilization of sensitizers such as benzophenone or triphenylene.

In an attempt to confirm that the chemically significant excited state in the conversion of 1a to 1b is singlet in character the photochemistry of 3-acetyl-9,10-epoxy-9,10-dihydrophenanthrene (6) was studied. 5-Acetyl-2,2'-diformylbiphenyl (5), nmr ($CDCl_3$) δ 2.63 (s, 3H, $-CH_3$), 9.05 (s, 2H, -CHO); mp of tris-oxime 197-198° (C_2H_5OH-H_2O) was prepared (77%) by ozonolysis of 3-acetylphenanthrene[14] according to the procedure utilized by Bailey and Erickson to oxidize phenanthrene.[15] Cyclization of 5 to 3-acetyl-9,10-epoxy-9,10-dihydrophenanthrene (6), mp 148-150° (C_6H_{14}); nmr ($CDCl_3$) δ 2.25 (s, 3H, $-CH_3$), 4.50 (s, 2H, HCO), 8.50 (s, 2H, ArCH); ir ($CDCl_3$) 1685 (s, -CO) was achieved (64%) using hexamethylphosphorus triamide according to the procedure described by Newman and Blum for the synthesis of 1a.[16]



7a, R_1 = OH; R_2 = H
b, R_1 = H; R_2 = OH

Direct irradiation of 6 at 254 or 350 nm (in benzene or acetone) gives a single base soluble phenanthrol 7, mp 196-198° (C_2H_5OH) in essentially quantitative yield. It is noteworthy that thermolysis of 6 at 200° provides an alternate isomeric phenanthrol. The structure 7a, 3-acetyl-9-phenanthrol, is assigned to the photoproduct obtained from 6 on the basis of its proton-decoupled 100 MHz, nmr spectrum in which long range coupling of the protons on positions 4 and 10 is apparent. The thermolysis product was assigned the alternate structure 7b, 3-acetyl-10-phenanthrol, on the basis of the faint coupling observed between the protons in the 1- and 9-positions. That two isomers 7a and 7b are formed was confirmed by admixture of the photo- and thermochemical products whereby the nmr signals which have very similar chemical shifts are distinguishable.

The absence of oxepin(s) among the photolysis products of 6 corroborates our conclusion that rearrangements of the type 1 to 2 are singlet in character and proceed by an "oxygen walk" mechanism involving intermediates of the type 3. By analogy with acetophenone ($\Phi_{isc} = 0.99$)[17] the incorporation of the acetyl group in 6 should ensure that population of the triplet state through intersystem crossing should be efficient.

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10) We are grateful to Dr. Felix Wehrli, Varian A. G./Steinhauserstrasse, 6300 Zug/ Switzerland for determination of 300 MHz nmr and 25.2 MHz cmr spectra.

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