

(1-10) reveal that the signal for the epimer with an equatorial hydrogen appears at higher field than that for the epimer with axial hydrogen.<sup>5</sup> The individual chemical shifts shown by the remaining  $\alpha$ -haloketones (11-17) are also consistent with this "reversal" of the usual axial-equatorial relationship. That this reversal is not primarily due to distant anisotropic effects of the ring system is suggested by the numerous examples of steroidal compounds (alcohols, acetates, etc.) that observe the normal axial-equatorial order<sup>6</sup> and is confirmed by the two pairs of non-ketonic bromo-compounds 18, 19; and 21, 22. In each of these two pairs the axial proton signal adopts its usual position upfield from the equatorial proton signal. The following analysis shows that the anomalous order for the  $\alpha$ -haloketones is caused largely by the presence of a ketone group next to the halogenated carbon.

Aliphatic protons adjacent to a ketone group are ordinarily at lower fields than those in the corresponding non-ketonic analogs. For example, the methylene proton signal is at 1.25 p.p.m. in *n*-pentane and at 2.39 p.p.m. in pentanone-3.<sup>3b</sup> In cyclohexane the signal is at 1.44 p.p.m., and in cyclohexanone the  $\alpha$ -methylenes absorb at 2.25 p.p.m.<sup>3b,7</sup> The chemical shifts for reference cyclohexyl halides with axial hydrogens (23, 25, 27, 29) and for non-ketonic steroid halides with axial hydrogens (18, 20, 21) may be compared to those for steroid  $\alpha$ -haloketones with axial hydrogens (1, 3, 5, 7, 9, 13-17). This comparison shows that the presence of a carbonyl group moves the adjacent axial proton signal downfield. Some specific values for these displacements are 0.64 p.p.m. for 18  $\rightarrow$  5; 0.71 p.p.m. for 21  $\rightarrow$  9; 0.69 p.p.m. for 20  $\rightarrow$  3.

In contrast, an equatorial proton on a halogenated carbon is shifted upfield by introduction of the adjacent carbonyl group (*cf.* 24 with 2; 26 with 4; 22 with 10; 19 with 6; 19 with 12; 30 with 8). Whatever factors are responsible for this net upfield shift, they are of sufficient magnitude to overcome the deshielding normally produced by a carbonyl acting on  $\alpha$ -hydrogens. Furthermore, an equatorial  $\alpha$ -hydrogen is close to the nodal plane of the carbonyl  $\pi$ -system where deshielding might be expected due to the anisotropy of the carbonyl group.<sup>3a,8</sup>

The dependence of vicinal coupling constants ( $J_{HH}$ ) on dihedral angle is well documented, but little is known on how they vary with the nature of attached substituents.<sup>9</sup> The  $J(aa)$  and  $J(ea)$  coupling constants listed in Table II for the set of  $\alpha$ -haloketones 1-8 are

TABLE II  
C<sub>6</sub>-C<sub>5</sub> COUPLING CONSTANTS (C.P.S.)

	Compound number							
	1	2	3	4	5	6	7	8
$J_{HH}(aa)$	10.4 <sup>a</sup>		11.4		11.8		11.9	
$J_{HH}(ea)$		1.2 <sup>a</sup>		2.4		2.8		4.3

<sup>a</sup> The geminal HF coupling constant was 51.2 c.p.s. in 1 and 53.9 c.p.s. in 2.

pertinent. On the assumption that the compounds with equatorial halogens (1, 3, 5, 7) have the same ring geometry, there is a slight increase in  $J_{aa}$  in the series

(5) Another epimeric pair that fits these observations is 2 $\beta$ - and 2 $\alpha$ -fluoroandrostan-3,17-dione, whose C-3 hydrogen signals in deuteriochloroform are at 4.76 and 4.98 p.p.m. ( $\delta$  scale), respectively [N. L. Allinger, M. A. Darroge, M. A. Miller and B. Waegell, *J. Org. Chem.*, **28**, 780 (1963)].

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fluorine  $\rightarrow$  iodine. In the corresponding series with an axial halogen (2, 4, 6, 8) the  $J(ea)$  values show a similar increasing trend. But because of possible steric interaction of a C-6 axial halogen with the angular methyl group at C-10 the  $J(ea)$  values may reflect some ring distortion superposed on a substituent effect.

The chemical shift data in Table I are also of interest in view of disagreement between theoretical predictions<sup>3a,c</sup> and recent experimental findings<sup>10</sup> on the effect of an alkyl group located in a 1:3 diaxial relationship to a proton. Not enough model compounds are available for a full analysis, but the variations in signals (Table I) for protons of a given conformational type (*i.e.*, axial or equatorial) indicate a deshielding effect for the 1:3 diaxial arrangement (or its equivalent).

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### The Photochemical Conversions of Stilbenes to 9,10-Dihydrophenanthrenes

Sir:

Recent speculation<sup>1-4</sup> about the photochemical conversion of *cis*-stilbene (IIa) to phenanthrene (Va) has centered on the formation of a tertiary allylic dihydrophenanthrene (IVa) as intermediate, although this has not been isolated. Stegemeyer<sup>1</sup> found that the initial rate of phenanthrene formation was finite in the case of *cis*-stilbene (IIa) but zero in the case of *trans*-stilbene (Ia). He suggested that the intermediate IIIa was an excited state of *cis*-stilbene which cyclized and dehydrogenated in a concerted process to give phenanthrene.

Both Schaffner<sup>2</sup> and Mallory<sup>3</sup> and their co-workers held the view that the reaction proceeded through the intermediate IVa which was dehydrogenated in a dark reaction by molecular oxygen or by other hydrogen acceptors present. Mallory<sup>3</sup> and Moore<sup>4</sup> have independently shown that phenanthrene is not formed on photolysis of degassed dilute solutions of stilbene. Moore<sup>4</sup> obtained evidence for the intermediate IVa by observing its electronic spectrum and he proposed that this intermediate (IVa) was formed from an excited singlet state of *cis*-stilbene (IIIa) which is not available to *trans*-stilbene.

We have studied the photolysis of two stilbene systems: *trans*- $\alpha\beta$ -dicyanostilbene (Ib) and diphenylmaleinimide (Ic) and have isolated two stable 9,10-dihydrophenanthrenes (VIb and VIc) related to the intermediates (IVa) previously postulated. Both these compounds (VIb and VIc) are unchanged on further irradiation.

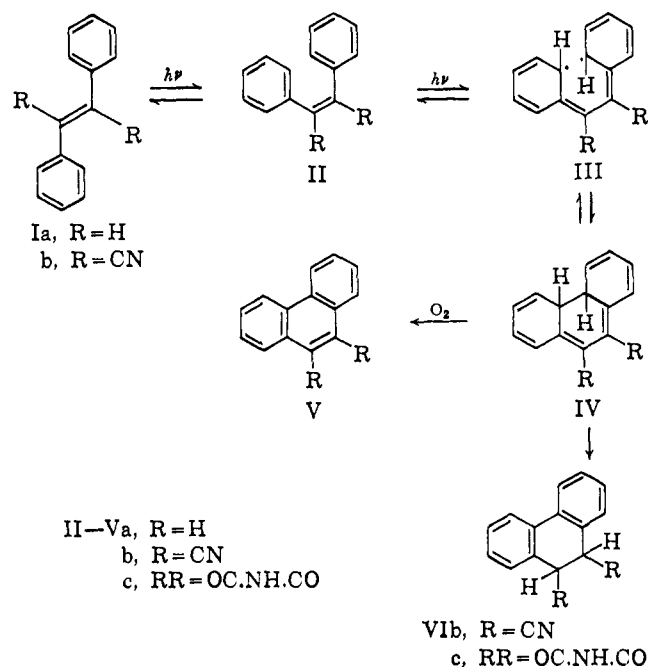
*trans*- $\alpha\beta$ -Dicyanostilbene (Ib,  $3.9 \times 10^{-2} M$ ) was photolyzed in chloroform solution for 15 hr. in a Pyrex vessel surrounding a water-cooled Hanovia 400-w. medium pressure mercury lamp. Fractional crystallization of the product from benzene gave 9,10-phenan-

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threne dicyanonitrile (Vb) and 9,10-dicyano-9,10-dihydrophenanthrene (VIb, 7%).

Compound VIb crystallized as colorless prisms from chloroform (m.p. 199–204°, which varied with the rate of heating). The proton magnetic resonance spectrum exhibited a single peak equivalent to two protons at 5.58  $\tau$  in chloroform and at 4.68  $\tau$  in dimethyl sulfoxide attributed to the protons at the 9 and 10 positions. The infrared spectrum in chloroform had an aliphatic nitrile stretching mode at 2255  $\text{cm}^{-1}$ . *Anal.* Calcd. for  $\text{C}_{16}\text{H}_{10}\text{N}_2$ : C, 83.1; H, 4.4; N, 12.2; mol. wt., 230. Found: C, 83.1; H, 4.4; N, 12.5; mol. wt., 230. Compound VIb had previously been formulated as *cis*- $\alpha\beta$ -dicyanostilbene<sup>6</sup> (IIb). Hydrolysis with methanolic potash gave 9-phenanthrene carboxamide (m.p. 226°<sup>7</sup>; lit. 226°).<sup>8</sup>

Photolysis of *trans*- $\alpha\beta$ -dicyanostilbene in degassed<sup>9</sup> ethanol gave only the dihydro compound (VIb).

Diphenylmaleinimide (IIc,  $7.7 \times 10^{-3}$  M) on photolysis in ethanol for 2.5 hr. gave 9,10-phenanthrene dicarboximide (Vc) and 9,10-dicarboximido-9,10-dihydrophenanthrene (VIc, 40%). The phenanthrene (Vc) crystallized from acetone as yellow needles (m.p. 334–335°). *Anal.* Calcd. for  $\text{C}_{16}\text{H}_9\text{NO}_2$ : C, 77.7; H, 3.7; N, 5.7. Found: C, 77.7; H, 3.8; N, 5.7.

The dihydrophenanthrene (VIc) crystallized from chloroform as colorless prisms (m.p. 245–246° dec.). *Anal.* Calcd. for  $\text{C}_{16}\text{H}_{11}\text{NO}_2$ : C, 77.1; H, 4.45; N, 5.6. Found: C, 76.9; H, 4.6; N, 5.7. Recrystallization from acetone brought about dehydrogenation to the phenanthrene (Vc). Similarly, melting produced the phenanthrene, the m.p. rising to 334–335°. The proton magnetic resonance spectrum showed a single peak equivalent to two protons at 5.18  $\tau$  in dimethyl sulfoxide attributed to the protons at the 9 and 10 positions.

The electronic spectra of compounds VIb and VIc are typical of 9,10-dihydrophenanthrenes (see Table I).

(5) All melting points unless otherwise stated were determined on a Kofler block and are corrected.

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(9) Degassing was performed at  $10^{-6}$  mm. with more than six freezings of the solution.

TABLE I

ELECTRONIC SPECTRA OF 9,10-DISUBSTITUTED 9,10-DIHYDROPHENANTHRENS IN EtOH

Compound	$\lambda_{\text{max}}$ m $\mu$	$\epsilon$	$\lambda_{\text{max}}$ m $\mu$	$\epsilon$	$\lambda_{\text{max}}$ m $\mu$	$\epsilon$
VIb	206	39,000	268	17,500		
	211	41,000				
	223 <sup>a</sup>	8600				
VIc	208	35,000	265 <sup>a</sup>	14,000	303	1200
	230 <sup>a</sup>	10,000	275	16,000		
	240	5800	284 <sup>a</sup>	11,500		
( $\pm$ )- <i>trans</i> -9,10-Di- hydroxy-9,10-di- hydrophenan- threne	211	40,000	269	15,000	298 <sup>a</sup>	2600
	225 <sup>a</sup>	10,000				
<i>cis</i> -9,10-Dihydroxy- 9,10-dihydro- phenanthrene	208	39,500	270	16,500		
	225 <sup>a</sup>	10,000	282 <sup>a</sup>	11,000		
<i>cf.</i> VIa	209	43,500	265	17,500	290 <sup>a</sup>	4400
	220 <sup>a</sup>	10,000			298	4300

<sup>a</sup> Inflection

Proton magnetic resonance measurements on *cis*- and ( $\pm$ )-*trans*-9,10-dihydroxy-9,10-dihydrophenanthrene in dimethyl sulfoxide-deuterium oxide solutions showed single peaks at 5.25 and 5.22  $\tau$ , respectively, supporting the proposed structures for the photolysis products. From the resonance spectra of the aromatic protons it is tentatively suggested that the photolysis products possess the *cis* stereochemistry but this point is being investigated further.

We propose that the dihydrophenanthrenes (VIb and VIc) are rearrangement products of the photolysis intermediates IVb and IVc, the existence of which is thus further confirmed. As a result of these rearrangements the systems become stabilized by the difference in resonance energies of the biphenyl (VI) and the tricyclic hexaene (IV). Other substituted stilbenes are being investigated to see if the rearrangement is dependent on the groups R.

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### The Quinone Oxidation of Ethanol Catalyzed by Chromic Ion

Sir:

The ammonium salt of 2,5-dihydroxy-*p*-benzoquinone (denoted hereafter by  $Q'$ ) reacts with a wide variety of metal ions to form complex salts which are generally insoluble<sup>1</sup>; chloroanilic acid, 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone ( $\text{Cl}_2Q'$ ), has been used extensively in schemes of analysis for metal ions.<sup>2</sup> In the hope of gaining greater insight into the interaction of transition metal ions through conjugated systems, both from the point of view of the activated complex in electron-transfer reactions<sup>3</sup> and of "mixed" valence states, we have undertaken an investigation of the reactions of  $Q'$  and  $\text{Cl}_2Q'$  with chromous ion.

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