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Anodic Oxidation of Anthracene and Related Compounds

Part VII. Stereochemistry of Additions to Anthracenes

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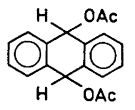
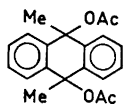
Anodic acetoxylation and methoxylation of anthracene, 9-methylanthracene, and 9,10-dimethylanthracene produces 9,10-disubstituted 9,10-dihydroanthracenes. The major product in every case is the *trans* isomer. The acetates can also be prepared by lead tetraacetate oxidation of the anthracene in benzene.

In a previous paper in this series,[1] the anodic addition of acetate ion to the 9,10-positions of anthracene was reported to produce a 3:1 mixture of the *trans* and *cis* diacetates (Ia and Ib). Addition of acetate had also been observed

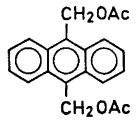


I a *trans*
I b *cis*

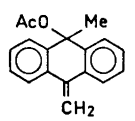


II

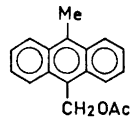
during acetoxylation of 9,10-dimethylanthracene (DMA) to give a diacetate (II) of unknown steric configuration.[2] Lead tetraacetate oxidation of anthracene in benzene [3] was reported many years ago. NMR analysis of the reaction mixture from the latter reaction revealed that a 1:1 mixture of Ia and Ib was formed.[1] Lead tetraacetate oxidation of DMA has been reported to give



III



IV



V

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the diacetate (III),[4] and a mechanism for this reaction has been suggested [5] involving initial formation of II followed by elimination of acetic acid to give IV, and rearrangement of IV to give V as an intermediate.

In this paper, the anodic addition of acetate to 9-methylanthracene (MA), methoxyl to anthracene, MA, and DMA, is reported, and the stereochemistry of addition of nucleophiles to anthracenes is established. A brief investigation of the lead tetraacetate oxidation of MA and DMA in benzene was carried out, and the mechanism proposed [5] for formation of III is strongly supported by the isolation of addition products.

RESULTS

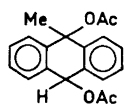
Anodic acetoxylations. Under the conditions employed in this study, the anodic addition of acetate to the 9,10-positions of the anthracene nucleus is a high yield reaction from which the diacetates can readily be isolated. The reactions were carried out in a mixed solvent, acetonitrile-acetic acid (3:1) containing sodium acetate (0.25 M). Constant potential conditions were employed, either by potentiostat or by using the constant current method previously described.[6] The anode potential for the preparative oxidation of MA was +1.2 V, and that for DMA [2] was +1.8 V. (All potentials referred to in this paper are relative to the aqueous saturated calomel electrode.)

Anodic methoxylations. The reactions were carried out in methanol containing sodium methoxide (0.5 M) at a platinum anode at +1.0 V. Co-oxidation of the solvent-electrolyte caused attempts to determine coulometric n values to fail. Current efficiencies of the order of 50 % were observed.

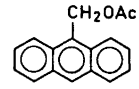
Lead tetraacetate oxidations. The solvent was benzene, and equivalent amounts of oxidant and substrate were used. Reaction was complete in less than 2 h when the substrate was MA or DMA, while about two days was required with anthracene.

Products. In all reactions, the only significant products were the corresponding 9,10-disubstituted derivatives. The isomer distribution could readily be determined by the NMR spectrum of the crude mixture. The integral of ring protons compared to other protons showed the absence of other products. The structure of 9,10-dimethoxy-9,10-dihydroanthracene obtained by anodic methoxylation of anthracene was assigned on the basis of the mass and NMR spectra as was that of 9,10-dimethoxy-9-methyl-9,10-dihydroanthracene from MA. 9,10-Dimethoxy-9,10-dimethylanthracene obtained by anodic methoxylation of DMA was isomerized to the compound previously observed to form during methanolysis of either the *cis* or *trans* diol.[7]

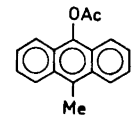
The structures of the diacetates of MA and DMA were assigned on the basis of NMR and mass spectra as well as by converting to known mono-acetates.



VI



VII



VIII

Table 1. Products of oxidative additions to anthracenes.

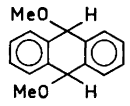
Substrate	Product	Reaction	Distribution *trans*	*cis*
Anthracene	Diacetate	Anodic	75	25
Anthracene	Diacetate	$Pb(OAc)_4$	50	50
Anthracene	Dimethoxy	Anodic	71	29
MA	Dimethoxy	Anodic	74	26
MA	Diacetate	Anodic	One isomer	
MA	Diacetate	$Pb(OAc)_4$	Isomer mixture	
DMA	Dimethoxy	Anodic	83	17
DMA	Diacetate	Anodic	100	0
DMA	Diacetate	$Pb(OAc)_4$	67	33

Heating II in acetic acid resulted in the formation of V in quantitative yield. Under the same conditions, VI gave a mixture of VII and VIII.

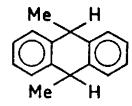
Isomer distributions from all the reactions are summarized in Table 1. NMR and mass spectral data of the products are tabulated in Tables 2 and 3.

DISCUSSION

The stereochemical configuration of the products of the anodic acetoxylation of anthracene was established by comparison with known compounds. The anodic methoxylation products of anthracene, IXa and IXb, have not previously been reported. The steric configurations of these compounds can be assigned on the basis of the relative shifts of the NMR signals for the 9,10-hydrogens. The *trans* configuration of compounds of analogous structure,



IX a *cis*
b *trans*

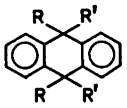


X a *cis*
b *trans*

the diacetates (I) and the dimethyl compounds (X)[8] exhibits an NMR signal for the 9,10-hydrogens downfield from that of the corresponding *cis* isomer (Table 2). The major (71 %) product of anodic methoxylation of anthracene shows a signal for the 9,10-hydrogens at 5.41, while the minor product has this signal at 5.28 ppm. Therefore, the major anodic product can be assigned the *trans* structure, IXb.

The product of acetoxylation of DMA, II, could be converted to the product of anodic methoxylation of DMA (XI) simply by heating a methanolic solution of it at reflux for 1 h. However, in the presence of HCl, XI is isomerized to the isomeric compound, XII, which had previously [7] been observed to form during methanolysis of either the *cis* or *trans* diol (XIIIa or XIIIb)

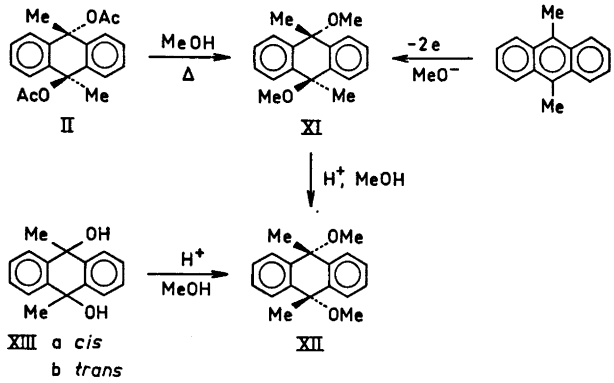
Table 2. Nuclear magnetic resonance data of anthracene derivatives.



Configuration	R	R′	R [a]	R′ [a]
trans	H	AcO	7.10	2.20
cis	H	AcO	6.95	2.10
trans	H	MeO	5.41	3.40
cis	H	MeO	5.28	3.31
trans [b]	Me	H	1.50	3.94
cis [b]	Me	H	1.48	3.87
trans	Me	OH	1.86	—
cis	Me	OH	1.55	—
trans	Me	OMe	1.71	2.78
cis	Me	OMe	1.62	2.78

[a] Measured in $CDCl_3$, expressed in ppm relative to internal TMS standard.
[b] Literature data.[8]

in the presence of HCl. The steric configuration of XI and hence II can be assigned on the basis of the relative chemical shifts of the 9,10-dimethyl protons. In the case of four compounds or known configuration, the diols



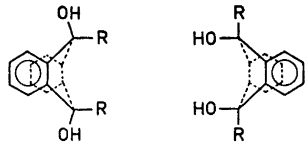
Scheme

(XIIIa, b) and the isomeric dimethyl compounds (Xa, b), the methyl signal for the *trans* isomer appears downfield from that of the *cis* isomer. The major product (83 %) of anodic methoxylation of DMA shows the signal for the 9,10-dimethyls at 1.71, and that for the minor product appears at 1.62 ppm. The

NMR spectrum of the minor product was found to be identical to that of XII. On this basis we can assign the *trans* structure to the major product. Thus, the minor product as well as that obtained from methanolysis of the diols, has the *cis* configuration. Since the diacetate (II) is converted to XI under conditions where isomerization of XI does not occur, it follows that II likewise has the *trans* configuration.

It was not possible to definitely assign stereochemical structures to the products derived from MA due to lack of suitable models for comparison. However, it is reasonable to assume, since the major products in all other cases involve *trans* addition, that this is also the case for the MA derived products.

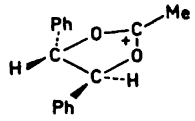
It has been recognized that while two equivalent conformers exist for the *trans* configuration of 9,10-dialkylanthracene-9,10-diols, there are two possible non-equivalent conformers for the *cis* configuration, XIV and XV.[9]



XIV XV

A gradation in the energy barriers between the 9,10-dialkylanthracene-9,10-diols has been postulated.[9] When R is methyl, there is no evidence that isolatable conformers exist; the diethyl analogue has been proposed to exist in stable conformers readily interconvertible by heat, while the dipropyl analogue is believed to form stable conformers which are not effected when heated to 132°C. The NMR spectrum of the product mixture from methoxylation of DMA supports the conclusion [9] that stable conformers do not exist in the dimethyl case. The *trans* (a',e') isomer would be expected to show two methoxyl signals, and the *cis* (a',a') conformer to show a single signal, different from that of the *cis* (e',e') conformer. Thus, the NMR spectrum of a mixture of any two of these components would be expected to show more than one methoxyl signal. The fact that the NMR spectrum of the product mixture has only one methoxyl singlet is strong evidence that stable conformers do not exist.

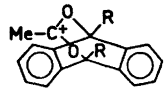
Very few data exist which provide information on the steric course of anodic addition reactions. Mango and Bonner observed stereospecificity during anodic acetoxylation of *trans*-stilbene [10] and interpreted their data to be due to the formation of the cyclic acetoxonium ion (XVI) which reacts with acetate ion to form the *meso* diacetate or with water to form the *threo*-hydroxyacetate in accordance with the observations of Winstein and co-workers.[11,12] We have found that 4,4'-dimethoxystibene undergoes acetoxylation in a manner analogous to *trans*-stilbene,[13] and benzoyloxylation of both *cis* and *trans*-stilbene can be accounted for by the acyloxonium mechanism.[14] Thus the stereochemistry of anodic acetoxylation of stilbenes can be interpreted without invoking a steric influence of the anode. Anodic methoxylation



XVI

of *trans*-stilbene, on the other hand, was found to take place with predominant *cis* addition of methoxyl [15] which could possibly be due to reaction of an adsorbed intermediate from the substrate with methoxide ion.

The predominant isomer formed during anodic addition of acetate ion to anthracene and 9,10-DMA has the *trans* configuration. The fact that *trans* addition is strongly favored again does not require postulating a steric directing effect of the anode, since an intermediate (XVII) analogous to XVI can be drawn to account for *trans* addition. The observation of some *cis* isomer

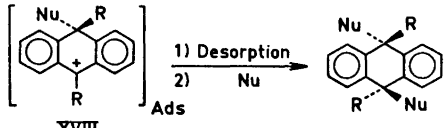


XVII

could be accounted for by attack of water on XVII to form the *cis* hydroxyacetate, which could undergo esterification to the *cis* diacetate. However, since methoxylation, in which case a cyclic ionic intermediate is less likely, also occurs with *trans* addition, it does not seem necessary to propose that *trans* addition of acetoxyl groups is a consequence of acetoxonium ion formation during anodic acetoxylation of anthracenes.

A possible mechanism which accounts for *trans* addition is that the first step is one electron oxidation of the aromatic substrate adsorbed on the electrode, followed by reaction with an adsorbed nucleophile and further oxidation to the cation, XVIII. The aromaticity of the central ring being destroyed, as well as repulsion of the cation from the positive electrode, could contribute to the rapid desorption of XVIII. Attack by a second nucleophilic moiety could then occur from the side not shielded by the electrode to give *trans* addition.

Since there are no direct comparisons with homogeneous reactions available, we cannot definitely assign a steric directing role to the anode. However, the fact that lead tetraacetate oxidation gives lesser amounts of the *trans* isomer, is indicative that the anode does influence the stereochemistry of the



XVIII XIX

products. We hope to be able to present more definitive evidence along this line by studying the stereochemistry of addition to 9,10-diphenylanthracene cation-radical, both at the anode and in homogeneous solution.[16]

Finally, addition products isolated during lead tetraacetate oxidation of anthracenes in benzene strongly support the mechanism proposed [5] for side chain acetoxylation of DMA in acetic acid. This is further supported by the observation that II is transformed to V when heated mildly in acetic acid.

EXPERIMENTAL

The apparatus used for preparative scale electrolysis has been described [6] and the procedure for the isolation of products was the same as used previously.[1] A Varian T-60 spectrometer was used for obtaining NMR spectra in deuterochloroform. Chemical shifts are expressed in ppm relative to tetramethylsilane. Mass spectra were measured with an Atlas Mass Spectrometer CH4. Spectral data of the products are summarized in Tables 2 and 3.

Table 3. Mass spectral data of oxidation products.

Substrate	Product	*m/e* (abundance, %)
Anthracene	Dimethoxy	240 (1.8), 239 (3), 225 (6), 209 (39), 208 (39), 194 (15), 193 (37), 179 (33), 178 (100).
Anthracene	Diacetate	296 (0), 237 (7), 236 (14), 195 (35), 194 (100), 178 (19).
MA	Dimethoxy	254 (5.6), 239 (26), 224 (52), 223 (62), 208 (41), 207 (28), 194 (91), 193 (100), 178 (22).
MA	Diacetate	310 (0), 250 (26), 208 (100), 192 (60).
DMA	Dimethoxy	268 (5), 253 (60), 237 (77), 222 (39), 207 (100), 192 (17), 191 (64), 178 (29).
DMA	Diacetate	324 (4.3), 264 (37), 222 (26), 205 (100), 204 (92).

9-Acetoxymethyl-10-methylanthracene (V). 9,10-Diacetoxy-9,10-dimethylanthracene (100 mg) from anodic acetoxylation of DMA was dissolved in acetic acid and the solution heated at 100°C for 15 min. The solution was allowed to cool, and diluted with methylene chloride. The solution was extracted with several equi-volume portions of water and then with saturated sodium bicarbonate solution. The methylene chloride solution was dried over anhydrous magnesium sulfate and then evaporated to dryness. The residue (89 mg) was recrystallized from ethanol to give V (76 mg), m.p. 146 (lit.[17] 148). The mass spectrum showed a parent ion *m/e* 264 (16 %), and the largest peak at *m/e* 204 (100 %) results from loss of acetic acid from the parent ion. The NMR spectrum had singlets at 2.07 (3H, acetate), 3.11 (3H, methyl), and 6.17 ppm (2H, methylene) and the aromatic protons (8H) centered at about 8.0 ppm.

9-Acetoxymethylanthracene (VII) and *9-acetoxy-10-methylantracene (VIII).* The crude diacetate (VI) (200 mg) obtained from anodic oxidation of MA was dissolved in acetic acid and the solution heated at 100°C for 15 min. After isolation as before, the crude residue (192 mg) was analyzed by NMR, and the spectrum showed the presence of VII (40 %) and VIII (60 %). When the crude mixture was dissolved in a minimum amount

of ethanol, VIII (74 mg) m.p. 166 (lit.[18] 166–167) was obtained. The NMR spectrum of VIII showed singlets at 2.57 (3H, acetate) and 3.06 ppm (3H, methyl), and the aromatic pattern centered at about 7.90 ppm (8H). The mass spectrum had peaks at *m/e* 250 (27 %), 208 (100 %), 192 (56 %), 191 (46 %), and 178 (27 %). Evaporation of the mother liquor and NMR analysis showed that the major component was VII. NMR spectrum of VII is characterized by singlets at 2.05 (3H, acetate) and 6.16 ppm (2H, methylene).

9,10-Dimethoxy-9,10-dimethylanthracene (XI and (XII). The product obtained from anodic methoxylation of DMA was analyzed by NMR (Table 2) and then dissolved in methanol containing a small amount of HCl. After isolation and crystallization from benzene-petroleum ether, the NMR spectrum was identical to that of XII obtained from alcoholysis of either of the diols (XIIIa or b) in the presence of HCl. Assignment of configuration is described in the discussion.

All other products were analyzed as mixtures of isomers by NMR, and mass spectrometry and the spectral data are summarized in Tables 2 and 3.

Lead tetraacetate oxidations were conducted using the same procedure as before.[1]

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