

ISOMERIC DIENE INTERMEDIATES AND AN ACETATE REARRANGEMENT  
IN AROMATIC ACETOXYLATION

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Recently we reported<sup>1</sup> the isolation of a diene addition intermediate (1a) from the reaction of *o*-xylene with nitric acid-acetic anhydride. We now report that the analogous reaction of hemimellitene and *p*-xylene yields in each case a cis-trans pair of 1,4-diene intermediates. These intermediates have all been isolated. The dienes give aryl acetates on decomposition, and those from *p*-xylene do so through a rearrangement which appears to be intramolecular.

Mixtures from which the intermediates could be isolated were obtained for both hydrocarbons by quenching the crude reaction products in carbon tetrachloride and washing with water. The hemimellitene adducts (2a and 2b, cis-trans isomers), isolated by chromatography on 10% deactivated alumina and subsequent fractional crystallisation, were identified by their spectroscopic data. Adduct (2a) was markedly more stable than (2b), but both decomposed in acetic acid at 60° (and on g.l.c.) to give 5-acetoxihemimellitene, the major ring acetylation product reported earlier<sup>2</sup>. Chromatography of the *p*-xylene extract on 10% deactivated alumina allowed the separation of two 1,4-adducts (3a, 3b; ca. 2:1). These cis-trans isomers were assigned the 1-nitro-4-acetoxy-1,4-dimethyl structure on the basis of their n.m.r. spectra, each of which revealed a signal due to four olefinic protons but no protons geminal to a nitro or acetoxy group. Decomposition of each diene in acetic acid at 60° (and on g.l.c.) gave the expected<sup>2</sup> 2-acetoxy-*p*-xylene. Similar decomposition in propionic acid-

sodium propionate did not lead to incorporation of propionate; the breakdown is therefore likely to involve an intramolecular 1,2-acetate shift.

The 1,4-diene from *o*-xylene previously reported<sup>1</sup> had been isolated by chromatography of the crude reaction mixture on 5% deactivated alumina. At that time the presence of a second isomeric adduct in the reaction mixture was established and this compound was tentatively assigned a 3-nitro-4-acetoxy structure. We have now isolated this adduct by column chromatography on 10% deactivated alumina, and spectroscopic data for this pure adduct allow a 1,4-diene (1b) structure to be assigned unequivocally. The two isolable *o*-xylene adducts are therefore cis-trans isomers, and the pattern is similar to that found for the other two hydrocarbons.

In order to relate acetoxyarene product to diene intermediate, an examination was made of product distributions for hemimellitene before and after decomposition of the intermediate dienes. The data in Table I indicate that intermediate diene formation accounts satisfactorily for acetoxyarene products provided that two assumptions are made; first, that the small amount of 5-acetoxyhemimellitene in the crude mixture is the result of diene breakdown prior to quenching and second, that the 4-acetoxyhemimellitene - which is not a breakdown product of adducts (2a) and (2b)- arises from corresponding but much less stable 1,4-dienes. We consider these assumptions to be reasonable.

Table I. Product distributions from reaction of hemimellitene with nitric acid-acetic anhydride

	<u>before decomposition</u> (%)		<u>after decomposition</u> (%)	
	(a)	(a)	(a)	(b)
4-nitro	46	47	47	46
5-nitro	8	9	9	8
4-acetoxy	8	8	8	11
5-acetoxy	5	36	36	35
total diene (2a + 2b)	33	0	0	-

(a) n.m.r. analysis

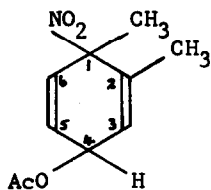
(b) g.l.c. analysis

Hemimellitene adducts. (2a). m.p. 60°,  $\nu_{\max}$  1740, 1540, 1370, 1225  $\text{cm}^{-1}$ ,  
 $\lambda_{\max}$  204 nm, ( $\epsilon$  7300), n.m.r. (60MHz,  $\text{CCl}_4$ )  $\delta$  1.68 (singlet;  $\text{C}^1\text{H}_3$ ), 1.76  
(triplet;  $J_{\text{C}^2\text{H}_3, \text{H}^3}^{\text{app}}$ ,  $J_{\text{C}^6\text{H}_3, \text{H}^5}^{\text{app}}$  ca. 0.5Hz,  $J_{\text{C}^2\text{H}_3, \text{H}^4}^{\text{app}}$ ,  $J_{\text{C}^6\text{H}_3, \text{H}^4}^{\text{app}}$  1.5Hz; 6H;  
 $\text{C}^2\text{H}_3$ ,  $\text{C}^6\text{H}_3$ ), 2.06 (singlet; OAc), 5.53 (multiplet;  $J_{\text{H}^4, \text{C}^2\text{H}_3}^{\text{app}}$ ,  $J_{\text{H}^4, \text{C}^6\text{H}_3}^{\text{app}}$  1.5Hz;  
 $J_{\text{H}^4, \text{H}^3}^{\text{app}}$ ,  $J_{\text{H}^4, \text{H}^5}^{\text{app}}$  2.5Hz;  $\text{H}^4$ ), 5.79 ppm (multiplet;  $J_{\text{H}^3, \text{C}^2\text{H}_3}^{\text{app}}$ ,  $J_{\text{H}^5, \text{C}^6\text{H}_3}^{\text{app}}$  ca. 0.5Hz;  
 $J_{\text{H}^3, \text{H}^4}^{\text{app}}$ ,  $J_{\text{H}^5, \text{H}^4}^{\text{app}}$  2.5Hz; 2H;  $\text{H}^3, \text{H}^5$ ). (2b).  $\nu_{\max}$  1730, 1540, 1375, 1225  $\text{cm}^{-1}$ ,  
 $\lambda_{\max}$  203.5 nm, ( $\epsilon$  11200), n.m.r.  $\delta$  1.77 (singlet;  $\text{C}^1\text{H}_3$ ), 1.79 (triplet;  
 $J_{\text{C}^2\text{H}_3, \text{H}^3}^{\text{app}}$ ,  $J_{\text{C}^6\text{H}_3, \text{H}^5}^{\text{app}}$  ca. 0.5Hz,  $J_{\text{C}^2\text{H}_3, \text{H}^4}^{\text{app}}$ ,  $J_{\text{C}^6\text{H}_3, \text{H}^4}^{\text{app}}$  1.0Hz; 6H;  $\text{C}^2\text{H}_3, \text{C}^6\text{H}_3$ ),  
2.01 (singlet; OAc), 5.65 (multiplet;  $J_{\text{H}^4, \text{C}^2\text{H}_3}^{\text{app}}$ ,  $J_{\text{H}^4, \text{C}^6\text{H}_3}^{\text{app}}$  1.0Hz;  $J_{\text{H}^4, \text{H}^3}^{\text{app}}$ ,  
 $J_{\text{H}^4, \text{H}^5}^{\text{app}}$  4.0Hz;  $\text{H}^4$ ), 5.82 ppm (multiplet;  $J_{\text{H}^3, \text{C}^2\text{H}_3}^{\text{app}}$ ,  $J_{\text{H}^5, \text{C}^6\text{H}_3}^{\text{app}}$  1.0Hz;  
 $J_{\text{H}^3, \text{H}^4}^{\text{app}}$ ,  $J_{\text{H}^5, \text{H}^4}^{\text{app}}$  4.0Hz; 2H;  $\text{H}^3, \text{H}^5$ ).

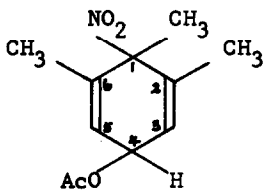
p-Xylene adducts. (3a).  $\nu_{\max}$  1742, 1545, 1365, 1240  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  196.5 nm,  
( $\epsilon$  15800), n.m.r.  $\delta$  1.45 (singlet; 3H;  $\text{C}^1\text{H}_3$  or  $\text{C}^4\text{H}_3$ ), 1.76 (singlet; 3H;  
 $\text{C}^4\text{H}_3$  or  $\text{C}^1\text{H}_3$ ), 1.93 (singlet; OAc), 6.03 ppm (singlet; 4H; olefinic protons).  
(3b).  $\nu_{\max}$  1742, 1545, 1372, 1240  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  196.5 nm, ( $\epsilon$  16900), n.m.r.  
 $\delta$  1.53 (singlet; 3H;  $\text{C}^1\text{H}_3$  or  $\text{C}^4\text{H}_3$ ), 1.67 (singlet; 3H;  $\text{C}^4\text{H}_3$  or  $\text{C}^1\text{H}_3$ ),  
1.94 (singlet; OAc), 6.21 ppm (singlet; 4H; olefinic protons).

o-Xylene second adduct. (1b).  $\nu_{\max}$  1730, 1540, 1365, 1215,  $\text{cm}^{-1}$ ,  
 $\lambda_{\max}$  208.5 nm, ( $\epsilon$  12600), n.m.r.  $\delta$  1.78 (singlet;  $\text{C}^1\text{H}_3$ ), 1.83 (triplet;  
 $J_{\text{C}^2\text{H}_3, \text{H}^3}^{\text{app}}$  0.8Hz,  $J_{\text{C}^2\text{H}_3, \text{H}^4}^{\text{app}}$  1.0Hz;  $\text{C}^2\text{H}_3$ ), 2.03 (singlet; OAc), 5.72  
(multiplet;  $J_{\text{H}^4, \text{C}^2\text{H}_3}^{\text{app}}$  1.0Hz,  $J_{\text{H}^4, \text{H}^3}^{\text{app}}$  2.5Hz,  $J_{\text{H}^4, \text{H}^5}^{\text{app}}$  2.5Hz;  $\text{H}^4$ ), 5.87

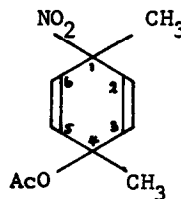
(multiplet;  $J_{H^3, C^2H_3}^{app}$  0.8 Hz;  $J_{H^3, H^4}^{app}$  2.5 Hz;  $H^3$ ), 6.03 (doublet;  $J_{H^5, H^4}^{app}$  2.5 Hz;  $H^5$ ), 6.03 ppm (singlet;  $H^6$ ).



(1)



(2)



(3)

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#### References

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