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DIPOLAROPHILIC ACTIVITY OF AROMATIC BONDS TOWARDS AN AZOMETHINE YLIDE

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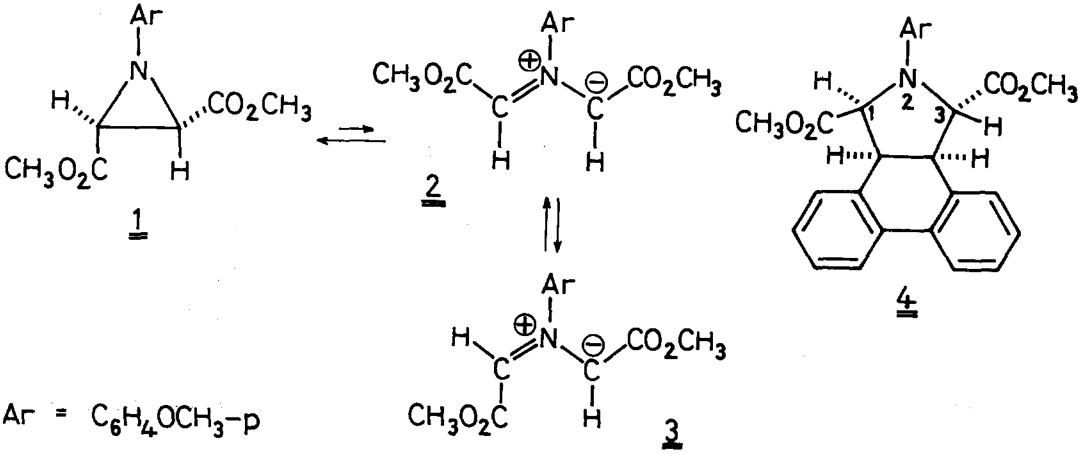
Cycloadditions to aromatic hydrocarbons imply a loss of aromatic resonance. Only few 1,3-dipoles equal ozone in its ability to attack the aromatic bond. The azomethine ylide 3 belongs to these.



1

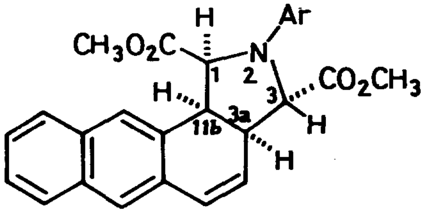
2

3

4

Ar = $C_6H_4OCH_3$-p

The reaction of dimethyl 1-(p-methoxyphenyl)-aziridine-2,3(trans)-dicarboxylate (1) with an excess of phenanthrene (24 hrs. 100°) gave 36% of the adduct 4 (m.p. 167-168°)(1). The protons of the pyrrolidine ring appear as an ABCD spectrum. Ether methyl and 3-CO_2CH_3 show up as singlets at τ 6.17 and 6.31 (2). The methyl group of 1-CO_2CH_3 must be located above the aromatic nucleus because it is highly shielded (τ 7.17). Thus, the structure of the adduct 4 leaves no doubt that the azomethine ylide 3 is the reactive species. The exo,exo-substituted azomethine ylide 2 exists in a conrotatory thermal equilibrium with the 2,3-trans-substituted aziridine 1 (3). That 2 has sufficient time to isomerise to the more active 1,3-dipole 3 (4), demonstrates the low dipolarophilic activity of phenanthrene.



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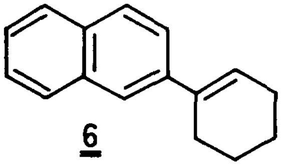

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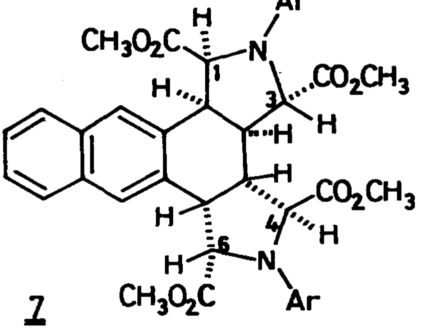

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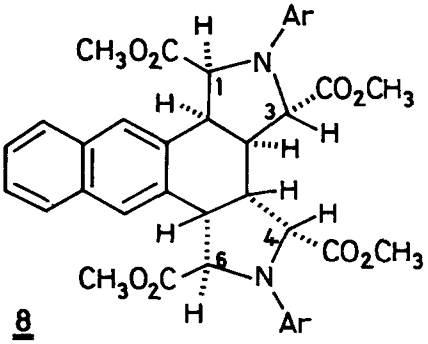

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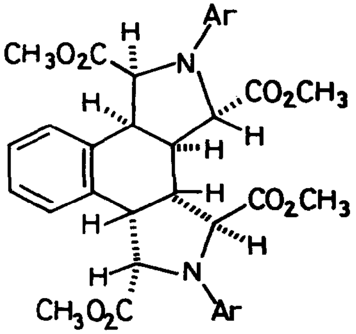
Ar= $C_6H_4OCH_3$-p

On reacting with **1** for 24 hrs. in refluxing chlorobenzene, anthracene combined with the azomethine ylide **3** to give 8% of the 1:1-adduct **5** (m.p. 191-201°) as well as two stereoisomeric 1:2-adducts (m.p. 277-280°, 208-211°) in 22% and 40% yield, respectively. The bis-adduct of m.p. 277-280° crystallised from boiling ethanol; the two other products were obtained pure by thick-layer chromatography.

It is predictable that anthracene would not accept a 1,3-dipole in the 9,10-positions, for a $4\pi + 4\pi$ combination would be forbidden in a concerted thermal reaction. The symmetry-allowed cycloaddition of **3** to the 1,2-positions gave the mono-adduct **5**; the u.v. absorption strikingly resembles that of 2-(1-cyclohexenyl)-naphthalene (**6**). The ester methyls appeared in the n.m.r. spectrum as singlets at τ 6.30 and 7.07. The latter signal probably belongs to the 1-CO_2CH_3 and suggests the configuration shown in **5** where 1-CO_2CH_3 is shielded by the naphthalene system.

Why is the yield of **5** (8%) so low? The monoadduct **5** is endowed with an olefinic double bond of the styrene type. Its activity as dipolarophile exceeds that of the aromatic bond by far. Therefore, most of the monoadduct 5 took up a second molecule of 3 to furnish the diastereoisomeric 1:2-adducts despite anthracene being present in excess. The bis-adducts could be *syn*-*anti*-isomers with respect to the fusion of the two pyrrolidine units to the six-membered ring. We prefer the assumption of the two *anti*-fused structures 7 and 8. While 7 possesses a two-fold axis of symmetry, 8 is without symmetry. In the n.m.r. spectrum of 7 the ring protons of the two $CH_3OC_6H_4$- form a common AA'BB' system, while two such systems are discernible in 8. Two ester groups of 7 (τ 7.18) are shielded by the naphthalene nucleus, namely the ones in 1- and 6-position. In contrast, compound 8 showed only one ester methyl at high field, the 1-CO_2CH_3 at 7.22. The u.v. spectra of both bis-adducts reveal the naphthalene chromophore.



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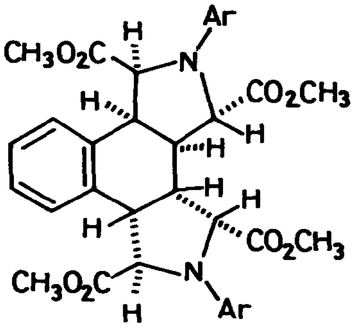

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Ar = $C_6H_4OCH_3$-p

After the reaction of 1 with an excess of *naphthalene* (24 hrs. 120°), no mono-adduct, but the two bis-adducts 9 (m.p. 278-280°) and 10 (m.p. 193-195°) were isolated in 38% yield and separated by thick-layer chromatography on silicagel. The n.m.r.-spectral similarity of 9 with 7 and of 10 with 8 allows to attribute a symmetry element to 9 and none to 10. Instead of the *anti*-fused structure 9 with its C_2 symmetry, also a *cis*-fused system with C_s would be consistent. Again, 9 possesses two shielded ester groups at τ 6.94, 10 only one at 6.94 and all the other OCH_3 in the normal range.

It confirms the structural assignments that the symmetrical bis-adducts 7 and 9 melt higher than the asymmetric compounds 8 and 10 do.

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REFERENCES

(1) All new compounds gave satisfactory C,H,N analyses. Molecular weights were determined with the Mechrolab Osmometer.

(2) N.m.r. spectra were taken in $CDCl_3$ on a Varian A-60 using TMS as internal standard.

(3) R. Huisgen, W. Scheer, and H. Huber, J.Amer.Chem.Soc., **89**, 1753 (1967).

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