Evidence for *cis*- and *trans*-1,2,3-Triphenylaziridine from the Ring-opened Azomethine Ylides

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Summary *cis*-1,2,3-Triphenylaziridine equilibrates at 150° with the *trans*-isomer until a 78 : 22 mixture is attained.; the configurational assignments are based on the conrotatory ring-openings to azomethine ylides which were intercepted by suitable dipolarophiles.

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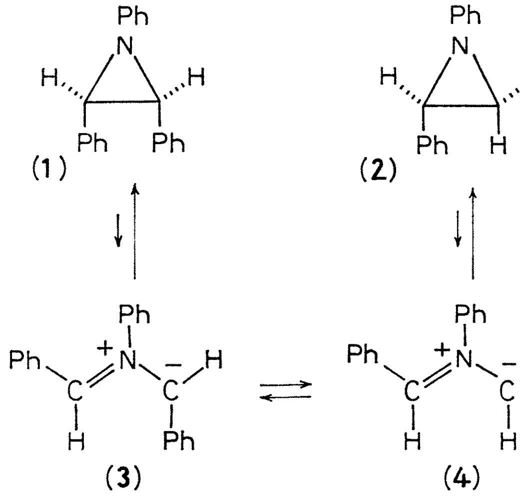
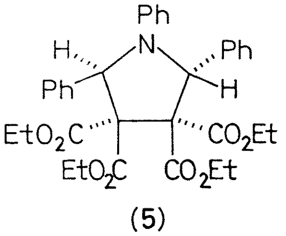
THE assignment of *cis*-configuration[1] to the known 1,2,3-triphenylaziridine[2] (1) is based on the assumption that the electrocyclic ring-opening to an azomethine ylide takes place by conrotation. The cycloadducts formed from (3) and suitable olefinic dipolarophiles at 100—120°, possess phenyls in the 2- and 5-positions which are *trans*-oriented.[1,3] No change in the n.m.r. spectrum of (1) was observed at 100—110°.



On heating (1) to 150°, an equilibrium consisting of 22% of the *trans*-isomer (2) and 78% of (1) was established with a half-life of *ca.* 25 h; after 50 h in mesitylene at 150°, *ca.* 40% of the aziridines had decomposed to other products. On dissolving this mixture in petrol, the bulk of (1) crystallised; the chromatographic separation of (1) and (2) was effected on an alumina column. The *cis*-isomer (1) was eluted by benzene, and subsequently the new *trans*-isomer (2, m.p. 93—94°) by ether. The n.m.r. singlet at τ 6·66 (benzene) which corresponds to the two ring protons of (1) is shifted to τ 6·46 in the *trans*-isomer (2).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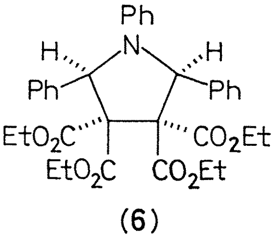
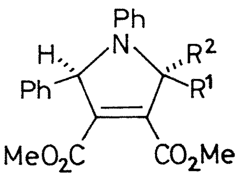
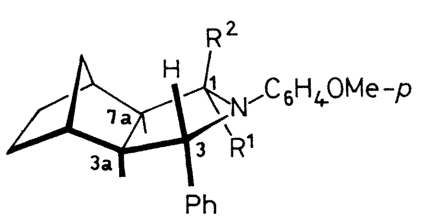

(6)

The cycloadditions of (2) with dipolarophiles occurring at 100° *via* a small equilibrium concentration of the *cis*-substituted azomethine ylide (4) are as highly stereospecific as the reactions of (1).[1] Heating (1) or (2) with an excess of tetraethyl ethylenetetracarboxylate for 60 h at 100° results in quantitative yields of (5) and (6), respectively. The product in each case was formed without contamination by the other isomer. The ring protons of (5) appeared as a singlet at τ 3·40 ($CDCl_3$) and those of (6) at τ 4·35.



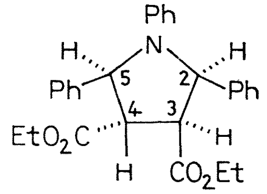


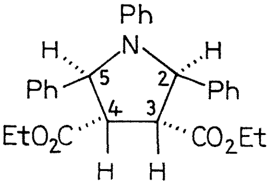
(7) R^1 = H, R^2 = Ph (9)

(8) R^1 = Ph, R^2 = H (10)

The reaction of (1) and (2) with dimethyl acetylenedicarboxylate in boiling toluene also produced virtually quantitative yields of the adducts (7) and (8) stereospecifically. Again the ***trans***- ring protons in (7)[3] were found at lower fields (τ 3·75, $CDCl_3$) than the *cis*-protons in the 2- and 5-positions of (8) (τ 4·17).

Norbornene is a dipolarophile of lower activity[4] and reacts at 150° with the *cis–trans*-mixture of 2,3-diphenyl-1-p-methoxyphenylaziridine, affording the diastereomers (9) and (10), respectively, in 51% and 37% yield. In the n.m.r. spectrum of (9) in $CDCl_3$, 1-H and 3-H appeared as doublets at τ 5·14 and 4·61 with $J_{1,7a}$ 8·5 and $J_{3,3a}$ 3·0 Hz. In (10) the equivalent protons at the 1- and 3-positions corresponded to a doublet at τ 5·75 with $J_{3,3a}=J_{1,7a}$ 3·2 Hz. Thus, a *cis*-phenyl on the other side of the pyrrolidine ring deshields 1-H and 3-H in (9) to a greater extent than the *trans*-phenyl in (10). The stereochemical assignments of (5) — (8) are also based on this principle.


(11)


(12)

The reactions of (2) with diethyl fumarate and diethyl maleate at 100° furnished the adducts (11) and (12), respectively. The ABXY spectrum of the ring protons of (11) indicates chirality; the ester groups are non-equivalent (OCH_2 quadruplets at τ 6·27 and 6·82, $CDCl_3$). The diethyl maleate adduct (12) shows an AA′BB′ spectrum which was calculated from the line positions: 2-H and 5-H τ 4·79, 3-H and 4-H 6·56, $J_{2,3}$ = $J_{4,5}$ 5·81 Hz, $J_{3,4}$ 6·92 Hz. The OCH_2 signal of the equivalent ester groups at τ 5·88 suggests a *trans-vic* relation to the phenyls. Thus, the structures of (11) and (12) confirm that the reacting 1,3-dipole (4) contains *cis*-phenyl groups.

The rates of the cycloaddition of *cis*-2,3-diphenyl-1-*p*-methoxyphenylaziridine (1; N–C_6H_4OMe-*p* instead of NPh) with an excess of diethyl fumarate in ethyl acetate at 90° were measured dilatometrically.[5] The first-order rate constant ($4·8 \times 10^{-5} s^{-1}$) turned out to be ***independent*** of the concentration of diethyl fumarate in the range of 0·3—1·2 *m*. As in the case of dimethyl 1-*p*-methoxyphenylaziridine-2 3-dicarboxylate,[6,7] the fast cycloaddition is preceded by the rate-determining electrocyclic ring-opening to the azomethine ylide The aforementioned aziridine-2,3-dicarboxylate undergoes a *cis–trans*-isomerisation at the same temperature as the cycloaddition[6] However, in the case of the 2,3-diphenyl-1-arylaziridines, this reaction requires a higher temperature A relatively high rotational barrier between (3) and (4) accounts for stereospecific cycloadditions

The *cis*-content of 78% in the equilibrium (1) $\rightleftharpoons$ (2) is surprisingly high, but it has some precedents in other 2,3-disubstituted aziridines[8] We suggest, tentatively, a weak bonding interaction between the lone-pair orbital of the nitrogen and the lowest unoccupied orbital of *cis*-substituents which possess π-bonds

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[4] The 1,3 dipoles which do not possess a double bond in the sextet structure—azomethine ylides belong to this class—do not display the same high reactivity towards angle-strained double bonds as shown by the nitrilium and diazonium betaines, *cf* R Huisgen, *Angew Chem Internat Edn*, 1963, **2**, 633 639

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