

Cycloadditions of 1,2,3-Triphenylaziridine *via* the Azomethine Ylide

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Summary The pyrrolidine derivatives, which were obtained from 1,2,3-triphenylaziridine (configuration unknown) and dialkyl fumarate, dialkyl maleate, or *trans*-dibenzoyl-ethylene, possess 2,5-*trans*-phenyl groups; the *trans*-substituted azomethine ylide must be the intermediate which undergoes the 1,3-dipolar cycloaddition.

HEINE, PEAVY, and DURBETAKI¹ have discovered the cycloadditions of 1,2,3-triphenylaziridine² to alkenes and alkynes. The analogous cycloadditions³ of dimethyl 1-*p*-methoxyphenylaziridine-2,3-*cis*- and -2,3-*trans*-dicarboxylate were shown to be preceded by conrotatory ring opening to *trans,cis*-isomeric azomethine ylides;^{4,5} these heteroallyl anions⁶ undergo 1,3-dipolar cycloadditions.

We were interested in the configuration and *cis,trans*-isomerism of 1,2,3-triphenylaziridine and repeated some of the pioneering work.¹ In our hands, the reaction with *diethyl fumarate* in boiling toluene gave 97% of a mixture of (3) and (5)‡ in an 81:19 ratio; (3) has the properties described earlier.¹ The adducts (3) and (6) show AA'XX' spectra for the pyrrolidine ring protons. Assuming retention of dipolarophile structure during the concerted cycloaddition, the phenyl groups must be *trans* to each other. The chemical shifts and coupling constants (Table) were calculated from the line positions using the iterative program, LAME. The τ -values of 3-H and 4-H are higher in (3) than in (5) (6.42 *vs.* 5.86); it is well documented,⁷ that a ring proton is shielded by *cis-vic*-phenyl, but deshielded by *trans-vic*-phenyl.

Calculated n.m.r. data (CDCl₃, 60 MHz) of the pyrrolidines (3)–(10)

Adduct	τ 2-H	3-H	4-H	5-H	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	3-CO ₂ R		4-CO ₂ R
(3)	4.23	6.42	6.42	4.23	3.74 t	4.00 t	3.74 t	6.03	(CH ₂)	6.03
(4)	4.21	6.39	6.39	4.21	3.69 t	4.78 t	3.69 t	6.28	(CH ₃)	6.28
(5)	4.44	5.86	5.86	4.44	8.35 c	12.63 t	8.35 c	6.17	(CH ₂)	6.17
(6)	4.45	5.85	5.85	4.45	8.45 c	12.52 t	8.45 c	6.57	(CH ₂)	6.57
(7) ^a	4.08	(m 6.2–6.7)		4.36	7.4 t	—	6.9 c	5.92	(CH ₂)	6.18
(8)	4.08	6.58	6.11	4.35	7.42 t	7.35 c	7.28 c	6.38	(CH ₃)	6.80
(9)	4.19	6.19	5.63	4.27	0.81 t	8.96 c	9.84 c	—	—	—
(10)	4.39	5.27	5.27	4.39	7.73	9.25 t	7.73	—	—	—

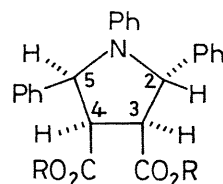
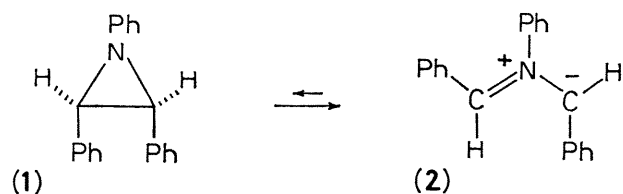
^a Data evaluated from line positions.

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‡ All new adducts described here are crystalline compounds which gave correct C.H.N. analyses.

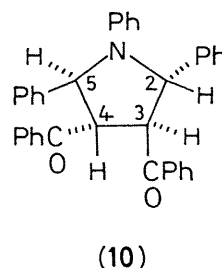
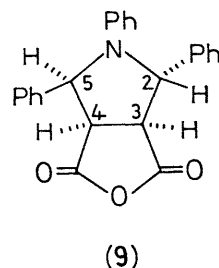
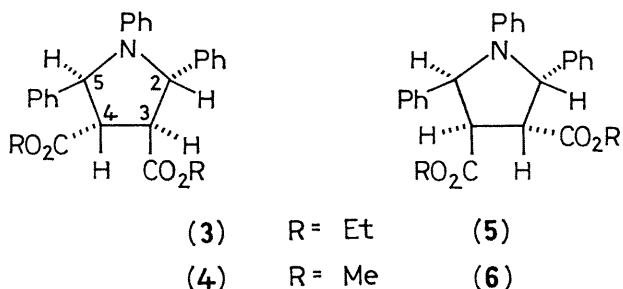
The corresponding adducts (4) and (6) were formed from (1) and *dimethyl fumarate* at 110° and occurred in a 73:27

(7) and (8), the above-mentioned influence of *vic*-phenyl makes the structural assignment possible; 3-H must have



(7) R = Et

(8) R = Me



ratio. An additional argument for the *cis*-relation of phenyl and methoxycarbonyl in (6) is provided by the unusually high τ -value (6.57) for OCH_3 compared with 6.28 in (4).

The *cis*-couplings $J_{2,3} = J_{4,5}$ in (5) and (6) are larger than the *trans*-couplings in (3) and (4) (Table). The vast spread of $J(\text{trans})_{3,4}$, 4.0 and 4.8 Hz for (3) and (4), 12.6 and 12.5 Hz for (5) and (6), demonstrates the conformational flexibility of the pyrrolidine ring and may be taken as a warning not to base structural conclusions on J values alone.

We confirmed the properties described¹ for the adducts of *diethyl maleate* and *maleic anhydride*, (7) and (9), as well as the conversion (9) \rightarrow (7). The American authors assigned structure (5) to their diethyl maleate adduct on the basis of $J_{2,3} = J_{4,5}$ 8 Hz; different chemical shifts for 2-H and 5-H were given ignoring the C_2 symmetry of (5). The ABXY spectrum of the ring protons which we found for the adducts of (1) with *diethyl* and *dimethyl maleate* (Table), establish the chiral structures (7) and (8). Despite the fact that $J(\text{trans})_{2,3}$ is very slightly smaller than $J(\text{cis})_{4,5}$ in

a larger τ -value than 4-H [for (8) 6.58 *vs.* 6.11]. The different τ -values of the ester groups corroborate the lack of symmetry in (7) and (8). The 4- CO_2CH_3 in (8) which is shielded by the *cis-vic-5*-phenyl appears at τ 6.80; 6.38 for 3- CO_2CH_3 is "normal".

Heine *et al.*¹ suggested structure (10) for the adduct obtained in high yield with *trans-dibenzoyl ethylene*; (10) with its twofold axis of symmetry cannot possess different τ -values¹ for four ring protons. The AA'XX' spectrum substantiates the pairwise equivalence of the four ring protons and leads on calculation to the data given in the Table. There is no compelling reason to assign $J_{2,3} = J_{4,5}$ 7.73 Hz to a *trans*-coupling. The preference for the all-*trans*- over the *cis,trans,cis*-structure in the dialkyl fumarate adducts suggests the all-*trans*-configuration for the cycloadduct of *trans-dibenzoyl ethylene* with its bulky substituents.

Thus, all adducts of 1,2,3-triphenylaziridine are derived from the *trans*-disubstituted azomethine ylide (2) which should be interrelated with the *cis*-2,3-disubstituted aziridine (1) by a conrotatory electrocyclic equilibrium. Further evidence is provided in the following communication.

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