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CYCLOADDITIONS OF AZIRIDINES TO AZO COMPOUNDS

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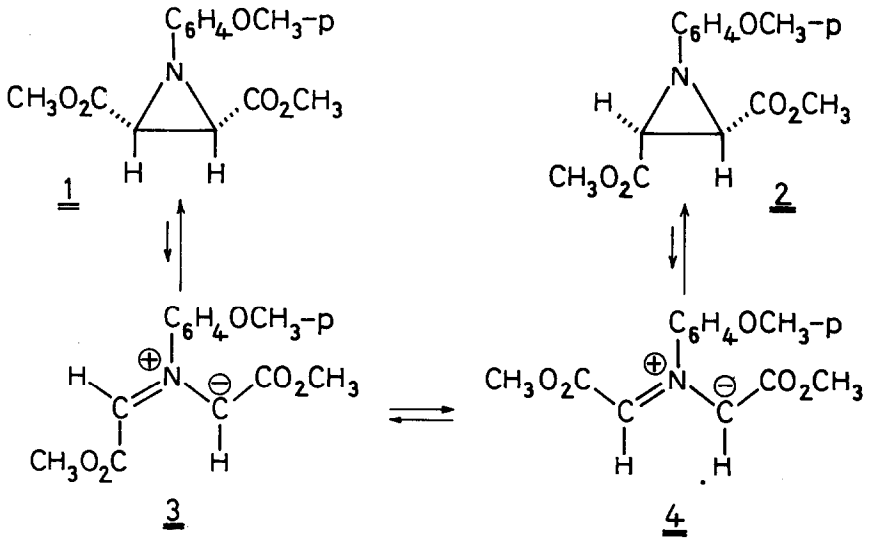
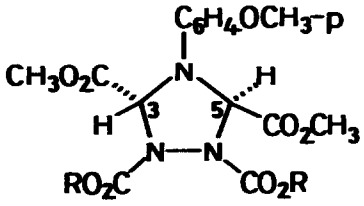
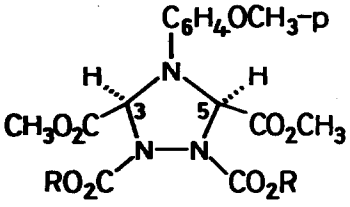
Substituted aziridines like 1 and 2 exist in thermal equilibrium with small concentrations of azomethine ylides as 3 and 4 (1). Ring scission and ring closure are conrotatory electrocyclic processes (2). The azomethine ylides can be intercepted by 1,3-dipolar cycloaddition to a variety of olefinic and acetylenic dipolarophiles (1-7). Also azo compounds turned out to be suitable acceptors.

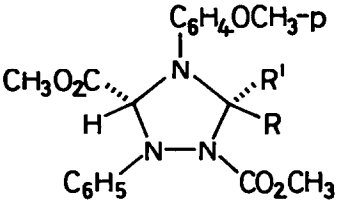


On heating dimethyl 1-(p-methoxyphenyl)-aziridine-2.3(cis)dicarboxylate (1) with diethyl azodicarboxylate in toluene (24 hrs. 100°, N_2), 96% of the triazolidine derivative 5 (m.p. 109-111°) with trans-located ester groups in 3- and 5-position were formed (8). The same high stereospecificity (n.m.r. analytical limit 1%) was observed in the formation of 6 (m.p. 126-128°) from 1 and dimethyl azodicarboxylate. Under the same conditions the trans-2,3-substituted aziridine

2 provided the triazolidine-3,5-cis-diesters 7 (m.p. 89-90.5°) and 8 (m.p. 163-165°), respectively, but with a lower degree of stereospecificity. With dimethyl azodicarboxylate 94% adduct was obtained which consisted of 8 and 6 in a 93:7 ratio. Diethyl azodicarboxylate in toluene at 100° yielded 71% of a 90:10 mixture of 7 and 5; the reaction without solvent furnished 78% 7 + 5 in a 94:6 proportion. We showed earlier that the azomethine ylide 4 undergoes cycloadditions somewhat more slowly than 3 does (9). Thus, part of the intermediate 4 isomerizes to 3 before combining with the azo dipolarophile.







5 R = C_2H_5 7 R = C_2H_5 9 R = H, R' = CO_2CH_3

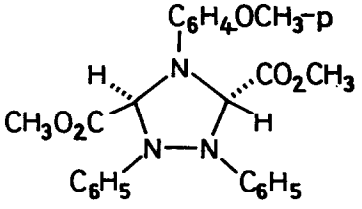
6 R = CH_3 8 R = CH_3 10 R = CO_2CH_3, R' = H

The structures 5 - 8 which are based on n.m.r. evidence, all contain pairs of equivalent ester alkyl groups. The ring protons in 3- and 5-position appear as singlets at τ 3.99 and 3.96 in 5 and 6, respectively (10). The less efficient deshielding by a trans-located ester group on the other side of the ring is responsible for the higher chemical shift of 3-H and 5-H in the trans-2,5-diester: τ 4.29 in 7 and 4.36 in 8.

While the singlet of the ring protons in 5 and 6 is sharp between -40° and + 40°, it is a broad hump in 7 and 8 at 38°, The singlet of 7 at τ 4.29 sharpens on-raising the temperature and separates reversibly into two singlets (one proton each at 3.93 and 4.50) on cooling to -20°. Line shape analysis in the range from 4°-39° and computation by the program GHS (11) disclosed a dynamic process with $\Delta H^{\ddagger}$ 15.5 ± 0.8 kcal/mol and $\Delta S^{\ddagger}$ = 1.6 ± 2 e.u. As the phenomenon is only observable in the 3,5-cis-diesters 7 and 8, hindered rotation is ruled out. The planarity of the carbamate structure makes N-inversion inconceivable. The investigations of Anderson and Lehn (12) on related compounds would suggest a ring inversion. The planes of the two carbamate nitrogens in 7 and 8 are twisted versus each

other; the system flips via a strained coplanar transition state to the mirror image conformation. In the trans-3,5-diesters 5 and 6, both conceivable conformations with respect to the carbamate nitrogen planes - one conformation should be preferred for steric reasons - possess C_2 symmetry; 3-H and 5-H remain equivalent.

A 93:7 mixture of 2 and 1 reacted with 4 equiv. methyl phenylazocarboxylate in toluene (24 hrs. 100°); n.m.r. analysis indicated 97% of the adducts 9 and 10 in a 81:19 mixture. The sing lets for 3-H and 5-H of the 3,5-cis-diester (m.p. 158-160°) showed up at τ 4.37 and 4.40 while the not isolated trans-form 10 possesses one-proton singlets at τ 3.88 and 4.31.



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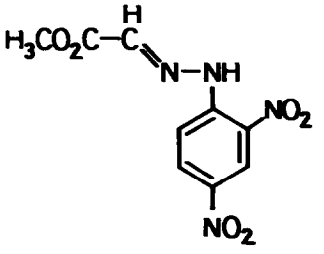

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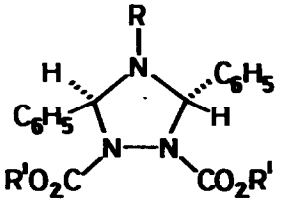

13 R = C_6H_5, R' = C_2H_5

14 R = $C_6H_4OCH_3$-p, R' = CH_3

No 1,3-dipolar cycloadditions to azobenzene seem to have been described. Only ketenes are able to overcome this inertness in their 2+2 cycloadditions (13). It speaks for the 1,3-dipolar activity of the azomethine ylide 3 that the reaction of 2 (via 4 by isomerisation) with azobenzene in toluene (18 hrs. 100°, 6 hrs. 120°) afforded 26% of 11 (m.p. 115.5-117.5°). The trans-3,5-protons give rise to a singlet at τ 4.27. On treatment with 2,4-dinitrophenylhydrazine in alcoholic sulphuric acid, 11 behaved as a cyclic aminal and yielded 56% of 12 besides benzidine sulphate.

Heine et al. (3) have described the formation of 13 from 1,2,3-triphenylaziridine and diethyl azodicarboxylate. Analogously, 2,3(cis)-diphenyl-1(p-methoxyphenyl)aziridine (14) reacted with an excess of dimethyl azodicarboxylate to give a quantitative yield of the adduct 14 (m.p. 149-151°)(15). The ester me-

thyls (s τ 6.51) as well as the ring protons in 3- and 5-positions (s τ 3.12) are equivalent.

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