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CYCLOADDITION REACTION OF 1,2,4-TRIAZOLIUM PHENACYLIDES WITH CINNAMIC ESTERS

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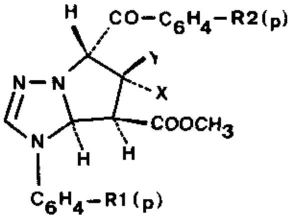
Abstract - 1,2,4-Triazolium phenacylides generated in situ from the corresponding 1,2,4-triazolium salts reacted with cinnamic esters to afford tetrahydropyrrolotriazole derivatives. These [3+2] dipolar cycloaddition reactions occur stereo- and regiospecific, giving only derivatives of the type (4a-d). The stereo- and regiochemistry of these products was mainly elucidated by ^{1}H-NMR, ^{13}C-NMR and DEPT analysis.

In previous works, we have mainly studied the stereochemistry of the cycloaddition reactions of 1,2,4-triazolium phenacylides (3) with cis and trans symmetric olefinic dipolarophiles. Thus the reaction of (3) with methyl fumarate and methyl maleate afforded only one isomer of 1:1 adduct in each case, (5a) and (5b) respectively.

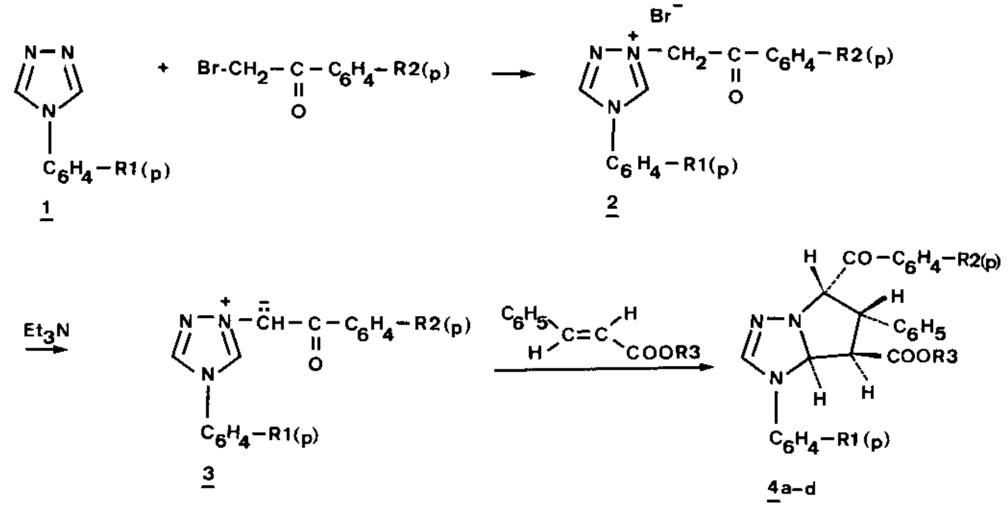


5a X = $COOCH_3$; Y = H

5b X = H ; Y = $COOCH_3$

The structure of the isomers (5a,b) was elucidated by ^{1}H-NMR (60 MHz)[1,2] and theoretical studies showing a stereospecific [3+2] cycloaddition in compliance with a concerted mechanism. Similar results have been obtained in the cycloaddition of xanthinium ylides with trans olefinic dipolarophiles.[3] Ylides (3) were also used in cycloaddition with monosubstituted olefins also affording one isomer of 1:1 adduct.[4,5] To our knowledge no study has been carried out in stereo and regioselectivity of 1,3-dipolar cycloadditions of cycloimmonium ylides with unsymmetrically 1,2-disubstituted olefins.

So in this paper we wish to report the cycloaddition reactions of 1,2,4-triazolium phenacylides with methyl and ethyl cinnamates. The phenacylides (3a-c) were generated in situ without isolation from the bromides (2a-c) by the deprotonation with triethylamine and allowed to react with cinnamic esters (Scheme 1, Table 1).[5,6,7] In all cases the cycloaddition afforded one isomer (4a-d). The elucidation of the structure of these adducts is important in the determination of the stereo and mainly the regioselectivity of the cycloaddition.



Scheme 1.

The structure of the constructed tetrahydropyrrole moiety was elucidated by ^{13}C-NMR (100.62 MHz)[8], ^{1}H-NMR (400.13 MHz)[8] and 2D-NMR heteronuclear correlation[9] of chemical shifts ^{13}C-^{1}H for (4d) (Figure 1). The chemical shifts of the four carbon atoms of this cycle are very similar in adducts (4a,c,d) (Table 2). The most deshielded is assigned to be 7a-C, located between two N-atoms,[10,11] followed by 5-C (bearing keto group), 7-C (bearing ester group), 6-C (bearing phenyl group). The assignment of ^{1}H-NMR spectra were made on the basis of chemical shifts and spin-spin decoupling (Table 2). 7a-H is only coupled to the adjacent 7-H and 5-H only to 6-H. The 2D-NMR heteronuclear correlation of chemical shifts ^{13}C-^{1}H for (4d) allows to verify that the most deshielded 7a-H is bound to the most deshielded 7a-C and the more shielded 5-H to the more shielded 5-C. This relation is not verified in the case of 6- and 7- atoms. Considering the coupling constants J-7,7a (6.75 - 7 Hz) J-5,6 (7.45 - 7.7 Hz) and J-6,7 (11.65 - 11.9 Hz), the structure of the 1:1 adducts is assigned to be the H7a, H7 - cis - H7, H6 - trans - H6, H5-cis configuration as in the case of the previously obtained adduct (5a).[12,13]

These results allow to notice that the cycloaddition reactions of 1,2,4-triazolium phenacylides with cinnamates are regio and stereospecific. They also show that the sense of the addition of the dipole on the dipolarophile is that indicated by the electronic factors.

Table 1. Tetrahydropyrrolo[1,2-b]triazoles 4a-d

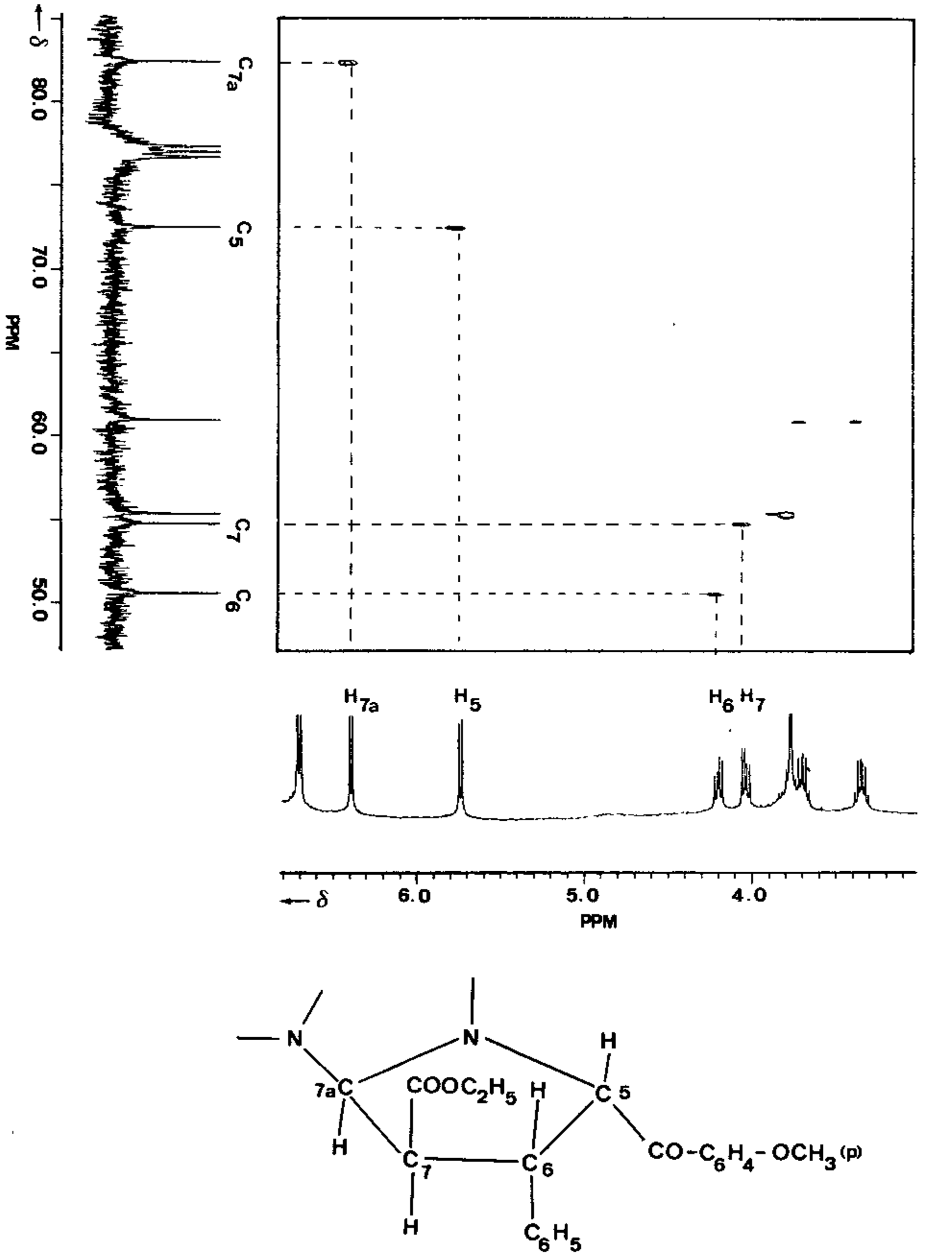
Comp.[a]	R1	R2	R3	Yield (%)	mp (°C) (solvent)	I.R. (cm^{-1}) (KBr)	MS[b] m/z
4a	CH_3	NO_2	CH_3	40	161-162 (CH_3CN/CH_3OH)	1730(CO) 1685(CO)	322 ; 162
4b	H	H	C_2H_5	32	173-174 (CH_3OH)	1730(CO) 1665(CO)	263 ; 176
4c	CH_3	OCH_3	CH_3	37	165-166 (CH_3CN/CH_3OH)	1730(CO) 1660(CO)	307 ; 162
4d	CH_3	OCH_3	C_2H_5	34	150-151 (CH_3OH)	1720(CO) 1655(CO)	307 ; 176

a - all compounds gave satisfactory elemental analysis. b - Ylide and ester fragments.

Table 2. ^{1}H and ^{13}C-NMR data (tetrahydropyrrole moiety)

	^{13}C - NMR (ppm)				^{1}H-NMR (ppm)				J (Hz)		
	5-C	6-C	7-C	7a-C	5-H	6-H	7-H	7a-H	J-5,6	J-6,7	J-7,7a
4a	73.69	50.29	54.01	82.22	5.74 d	4.25 dd	4.00 dd	6.36 d	7.70	11.65	6.75
4b	-	-	-	-	5.80 d	4.23 dd	4.05 dd	6.42 d	7.45	11.65	7.00
4c	72.59	50.45	54.51	82.40	5.73 d	4.19 dd	4.06 dd	6.41 d	7.45	11.90	6.75
4d	72.52	50.57	54.76	82.43	5.74 d	4.20 dd	4.03 dd	6.39 d	7.45	11.65	6.75

Figure 1 - 2D-NMR heteronuclear correlation ^{13}C - ^{1}H for 4d.



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