HETEROCYCLES, Vol 22, No 6, 1984

REACTIONS OF 3-DICYANOMETHYL-1-ETHYLBENZOTRIAZOLIUM YLIDE WITH ACETYLENIC ESTERS

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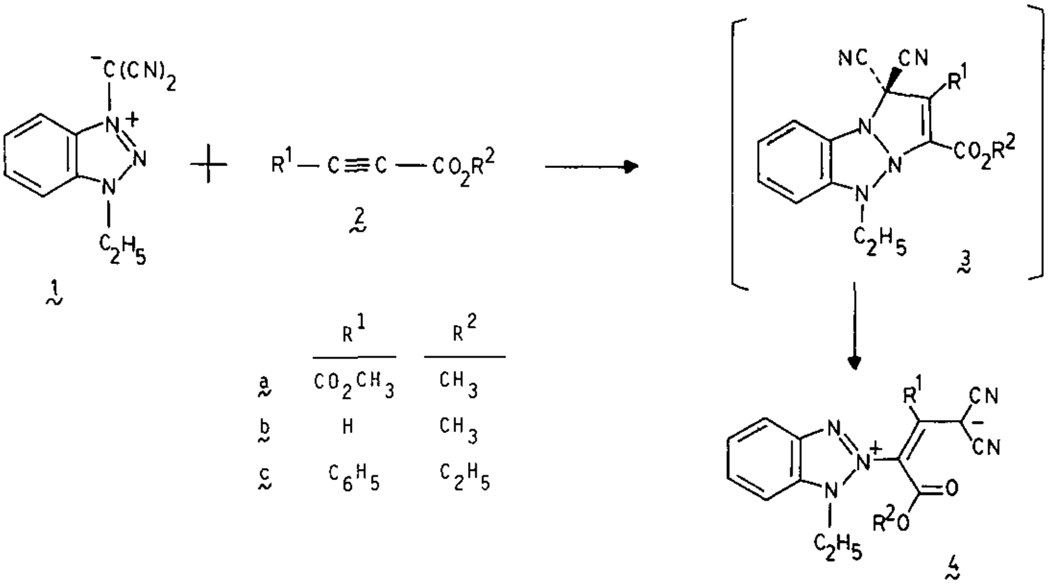
Abstract- The titled compound (1) reacts with acetylenic esters (2) giving 1:1 adducts (4), *via* 1,3-dipolar cycloaddition. Concerning the regioselectivity of the reaction, experimental results are in agreement with theoretical calculations and correspond to an inverted polarization of the azomethineimine moiety with regard to most known examples.

3-Dicyanomethyl-1-ethylbenzotriazolium ylide (1),[1] an azomethineimine, reacts with acetylenic esters (2) in refluxing toluene yielding 1:1 adducts (4) isolated by cooling and by addition of n-hexane (Table 1). Compounds (4) are originated by opening of the initial cycloadducts (3):



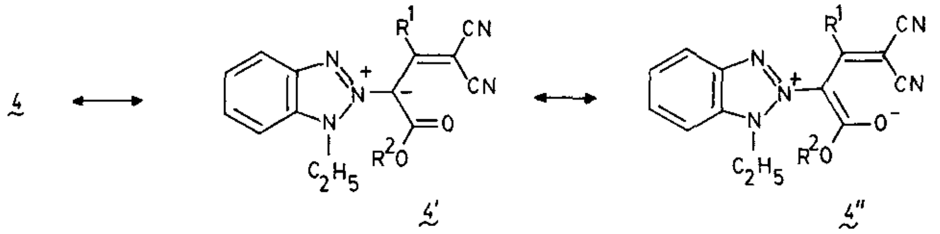
	R^1	R^2
a	CO_2CH_3	CH_3
b	H	CH_3
c	C_6H_5	C_2H_5

The structure of compounds (4) has been established on the basis of spectroscopic data. The i.r. spectra of the adducts (4) show a strong double νCN band at 2180-

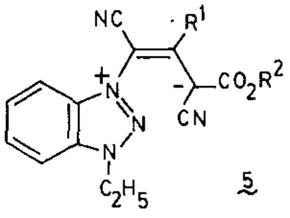
Table 1

Compound	Reaction time	Yield(%)	Mp(ethanol)	Analysis			
4a	15 h	34	203-204°C	Calc.: Found.:	C,57.79 57.51	N,19.83 19.80	H,4.25 4.32
4b	15 h	37	196-198°C	Calc.: Found.:	C,61.00 60.76	N,23.71 23.70	H,4.43 4.50
4c	480 h	14	179-180°C	Calc.: Found.:	C,68.47 68.25	N,17.62 17.96	H,4.74 4.75

2190 and 2200-2210 cm^{-1}, similar to the one observed in the starting ylide (1),[1] which is characteristic of a high degree of ionic character. Compound 4a shows two very different νCO absorptions at 1730 and 1690 cm^{-1}. while the νCO absorption of compounds 4b and 4c appears at 1680 cm^{-1}. The near 1685 cm^{-1} band can be assigned to the ester group at position C1' and its low frequency shift is attributed to canonical structure 4". *The band at 1730 cm^{-1} in compound 4a corresponds to the* ester group ($R^1 = CO_2CH_3$) at position C2'. Thus the i.r. spectra prove the position of the CO_2R^2 group in 4b and 4c and, consequently, its position in the non isolated cycloadducts 3b and 3c.



In the ^{13}C n.m.r. spectra of compounds (4), the cyano substituents at C3' are anisochronous (4a: 115.8 and 116.5; 4b: 116.8 and 118.8; 4c: 117.5 and 118.3 ppm) due to the restricted rotation around C2'-C3' bond (canonical structures 4' and 4"). C1' carbon atoms are upfield shifted (4a: 94.5; 4b: 99.0; 4c: 97.5 ppm) because *they bear a high density of negative charge*, while carbon atoms C2' are downfield shifted (4a: 155.8; 4b: 148.6; 4c: 162.8 or 164.4 ppm). C3' carbon atoms appear at similar frecuencies (4a: 48.7; 4b: 45.2; 4c: 51.9 ppm) to that of the corresponding carbon atom in the stranting ylide (1).[2] Chemical shifts of the aromatic carbons of the benzotriazolium ring (mean values: C4: 122; C5: 130; C6: 135; C7: 111; C3a: 143; C7a: 133.5 ppm) are similar to those of 1,2-dimethylbenzotriazolium iodide.[3]



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An alternative ylidic structure **5** arising through a (2+2) type cycloaddition mechanism involving the exocyclic dicyanomethyl carbanionic moiety[4] (see also reference 5) can be ruled out since the ^{13}C n.m.r. spectra are clearly incompatible with an 1,3-disubstituted benzotriazolium structure.[2,3] The observed regioselectivity in the first step (**1** + **2**→**3**) is in good agreement with the theoretical predictions obtained from a second order perturbational treatment.[5] Both experimental and theoretical results show that the negative extreme of the dipole **1** is on the exocyclic carbon atom and not on the endocyclic N2 atom, as in most examples described in the literature [7,8] (see however reference 9). A ring opening similar to **3**→**4** has been described by Burger *at al.*[10] but concerning a non aromatic azomethineimine

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Received, 2nd March, 1984