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THE REACTION OF ARYLAZOALKENES WITH DIENOPHILIC COMPOUNDS<sup>(\*)</sup>

By L. Caglioti, G. Rosini, P. Tundo and A. Vigevani<sup>(\*\*)</sup>

Istituto di Chimica Organica e Industriale dell'Università di Bologna

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Azoalkenes are multifunctional compounds whose chemical behaviour is being investigated by our group<sup>(1)</sup> and by others<sup>(2)</sup>. It has been reported by us<sup>(3)</sup> that the conjugated azo-enic system behaves as a typical butadienic system in that it reacts to give 1:4 addition products. The present paper concerns the reaction of arylazoalkenes with dienophilic compounds<sup>(4)</sup>.

As starting materials 1-phenylazocyclohexene (I), 1-p.tolylazocyclohexene (II) and 1-p.methoxyphenylazocyclohexene (III)<sup>(5)</sup> were chosen because of their ready availability from  $\alpha$ -acetoxy cyclohexanone<sup>(6)</sup>; tetracyanoethylene (IV) and N-phenylmaleinimide (V) have been employed as dienophilic systems (Figure 1). The reactions were carried out in benzene solution at room temperature for 24 hours.

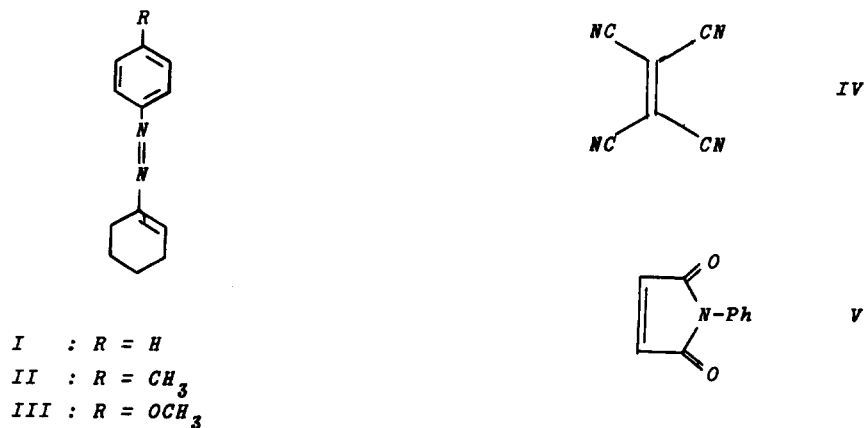
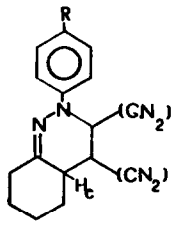
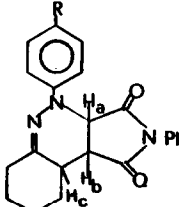


Figure 1

The results we obtained are summarized in Table I.

TABLE I

Start. Mat.	Reagent	Adducts	Yield %	m.p. C.	U.V. (In EtOH) $\lambda_{max}$	
I	IV		VI	47	120-1	235 ( $\epsilon = 7,480$ )
II	IV		VII	72	128-9	230 ( $\epsilon = 9,170$ )
III	IV		VIII	70	144-5	234 ( $\epsilon = 13,550$ )
I	V		IX	75	205-6	234 ( $\epsilon = 10,800$ ) 275 ( $\epsilon = 17,900$ )
II	V		X	73	182-3	235 ( $\epsilon = 8,670$ ) 278 ( $\epsilon = 14,400$ )
III	V		XI	75	164-5	227 ( $\epsilon = 12,600$ ) 278 ( $\epsilon = 16,300$ )

The structures of the compounds have been assigned on the bases of their analysis, N.M.R. spectra in  $CDCl_3$  (Table II and III), I.R. and U.V. spectra

TABLE II

Adducts	Signal	$\delta$ (p.p.m.)	Intensity	Assignment
VI	multiplet pair of doublets singlet	1.1 - 2.9 3.16 $\left\{ \begin{array}{l} J = 12 \text{ Hz} \\ J = 5 \text{ Hz} \end{array} \right.$ 7.50	8 H 1 H 5 H	aliphatic protons $H_c$ aromatic protons
VII	multiplet singlet pair of doublets multiplet	1.1 - 2.9 2.40 3.16 $\left\{ \begin{array}{l} J = 12 \text{ Hz} \\ J = 5 \text{ Hz} \end{array} \right.$ 7.15 - 7.50	8 H 3 H 1 H 4 H	aliphatic protons $CH_3$ $H_c$ aromatic protons
VIII	multiplet pair of doublets singlet multiplet	1.1 - 2.9 3.16 $\left\{ \begin{array}{l} J = 12 \text{ Hz} \\ J = 5 \text{ Hz} \end{array} \right.$ 3.87 6.8 - 7.6	8 H 1 H 3 H 4 H	aliphatic protons $H_c$ $OCH_3$ aromatic protons

TABLE III

Adducts	Signal	$\delta$ (p.p.m.)	Intensity	Assignment
IX	multiplet	1.1 - 2.9	9 H	aliphatic protons
	triplet	3.50 ( $J = 9$ Hz)	1 H	$H_b$
	doublet	4.95 ( $J = 9$ Hz)	1 H	$H_a$
	multiplet	6.7 - 7.9	10 H	aromatic protons
X	multiplet	1.1 - 2.9	9 H	aliphatic protons
	singlet	2.30	3 H	$CH_3$
	triplet	3.50 ( $J = 9$ Hz)	1 H	$H_b$
	doublet	4.92 ( $J = 9$ Hz)	1 H	$H_a$
	multiplet	6.9 - 7.8	9 H	aromatic protons
XI	multiplet	1.2 - 3.0	9 H	aliphatic protons
	triplet	3.53 ( $J = 9$ Hz)	1 H	$H_b$
	singlet	3.80	3 H	$OCH_3$
	doublet	4.88 ( $J = 9$ Hz)	1 H	$H_a$
	multiplet	6.7 - 7.9	9 H	aromatic protons

and are shown in Table I. The stereochemistry of the azoalkene-tetracyanoethylene adducts (VI, VII and VIII) can be inferred from the N.M.R. spectra. The high value (12 Hz) of one of the vicinal coupling constants shows that the hydrogen on the ring junction ( $H_c$  in the Table) is axial<sup>(7)</sup>. Examination of the N.M.R. spectra of the adducts IX, X and XI does not allow us to determine the steric relationship between  $H_a$ ,  $H_b$  and  $H_c$ .

Thus, it can be seen that the arylazoalkenic system reacts with dienophiles in a similar way to carbon dienic systems. The reaction follows a unique course with satisfactory yields and provides a new route to compounds containing the tetrahydropyridazinic ring.

Work is in progress on the generalization of the reaction and on the stereochemical details of the products obtained.

References

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122 (1968)
- (4) The peculiar behaviour of 1-tosylazocyclohexene has been reported :  
W. Barbieri, L. Bernardi, P. Masi, L. Cagliotti, G. Rosini - Tetrah.  
Lett., in press.
- (5) Compound I has been described previously [L. Cagliotti, P. Grasselli,  
G. Rosini - Tetrah. Lett., 50, 4545 (1965)]. Compound II (m.p. 49 -  
- 50 C) furnishes analytical data for  $C_{13}H_{16}N_2$  (U.V.:  $\lambda_{max}$  227 m $\mu$ ,  
 $\epsilon = 10,040$ ; 233 m $\mu$ ,  $\epsilon = 11,200$ ; 240 m $\mu$ ,  $\epsilon = 8,345$ ; 308 m $\mu$ ,  $\epsilon =$   
 $= 22,500$ ; sh at 318 and 330 m $\mu$ ). Compound III (m.p. 67-9 C) furni-  
shes analytical data for  $C_{13}H_{16}N_2O$  (U.V.:  $\lambda_{max}$  229 m $\mu$ ,  $\epsilon = 10,380$ ;  
240 m $\mu$ ,  $\epsilon = 11,100$ ; 246 m $\mu$ ,  $\epsilon = 7,970$ ; 328 m $\mu$ ,  $\epsilon = 23,530$ ; sh at  
340 m $\mu$ ). The I.R. spectra of II and III indicate that no NH is pre-  
sent. The N.M.R. spectra ( $CCl_4$ ) confirm the absence of NH in II and  
III and show the presence of one vinylic hydrogen (multiplet cente-  
red at 6.9 $\delta$ ). The other signals are in agreement with the proposed  
structures.
- (6) Arylazocyclohexenes can be prepared by treatment of the ethereal so-  
lution of the arylhydrazones of  $\alpha$ -acetoxy cyclohexanone with an a-  
queous solution of sodium carbonate at room temperature. Evaporation  
of the ethereal layer affords the azoalkene in good yield.
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