

SECONDARY  $\alpha$ -DEUTERIUM ISOTOPE EFFECTS IN THE DIAZETIDINE FORMATION  
FROM AZODICARBOXYLATES AND VINYL ETHERS

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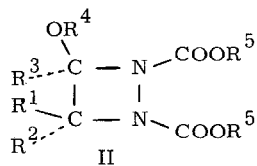
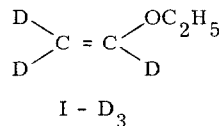
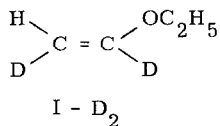
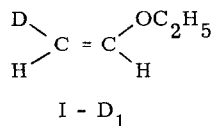
(Received in UK 21 May 1969; accepted for publication 26 June 1969)

It is an empirical fact that  $\alpha$ -substitution in olefins of protium by deuterium increases the rate of addition reactions ( $sp^2 \rightarrow sp^3$ ) by  $\sim 10\%$  per deuterium<sup>4)</sup>. In  $4\pi + 2\pi$  cycloaddition reactions the rates increase with the increasing number of deuterium atoms incorporated, independently whether the deuterium is located in the  $4\pi$  and/or  $2\pi$  system at one or both carbons undergoing change in hybridization from  $sp^2$  to  $sp^3$  in the course of adduct formation<sup>5)</sup>. It has been concluded from this that simultaneous change of hybridization at all involved centers occurs in the transition state, demonstrating the concerted nature of this type of cycloaddition reaction, which is allowed according to the selection rules of Woodward and Hoffmann<sup>6)</sup>.

The same rules require a two step process for suprafacial / suprafacial  $2\pi + 2\pi$  cycloaddition reactions. It is known, that diphenyl ketene adds to 1-deuterio-cyclohexene (yielding a cyclobutanone) preferentially with the carbonyl group to the deuterio-substituted carbon ( $k_D/k_H = 1.13 \pm 0.03$ )<sup>7)</sup> suggesting that a primary attack occurs between these two centers.

In the terminating step of the addition of acrylonitrile to 1,1-dideuterio-allene =  $CH_2$  has been found to be preferred over =  $CD_2$  ( $k_D/k_H = \text{min. } 0.83 \pm 0.02$ )<sup>8)</sup>. Studies on 1,2-dideuterio-olefins in 1,2-cycloaddition reactions are missing as yet.

Azodicarboxylates yield diazetidines (II) with vinyl ethers<sup>9), 10), 11)</sup>. We have investigated the secondary  $\alpha$ -deuterium isotope effects on this  $2\pi + 2\pi$  cycloaddition reaction in order to gain further insight into its mechanism.



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>
II - D <sub>0</sub>	H	H	H	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>
II - D <sub>1</sub>	D	H	H	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>
II - D <sub>2</sub>	H	D	D	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>
II - D <sub>3</sub>	D	D	D	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>

I-D<sub>1</sub> and I-D<sub>3</sub> were prepared from ethoxy-deuterio-acetylene<sup>12)</sup> with H<sub>2</sub> or D<sub>2</sub> over aged Raney Nickel, I-D<sub>2</sub> from ethoxy-acetylene with D<sub>2</sub>.<sup>13)</sup> I-D<sub>1</sub>, I-D<sub>2</sub> or I-D<sub>3</sub>, respectively, were mixed with undeuterated ethyl vinyl ether (I-D<sub>0</sub>), and the composition of these mixtures was determined mass spectrometrically.<sup>14)</sup> The reaction of these mixtures with max. 8 mole % of dimethyl azodicarboxylate (DMAD) took 2 days for completion. After removal of excess vinyl ether the composition of the diazetidines formed was determined mass spectrometrically. The deuterium effects were calculated as follows:

$$\frac{[\text{I-D}_0]}{[\text{I-D}_n]} \times \frac{[\text{II-D}_n]}{[\text{II-D}_0]} = \frac{k_{\text{D}_n}}{k_{\text{H}}} \quad n = 1, 2, 3$$

The experimental data (table) show:

$$k_{\text{D}_1} / k_{\text{H}} = 1.21 \pm 0.02$$

$$k_{\text{D}_2} / k_{\text{H}} = 1.08 \pm 0.02$$

$$k_{\text{D}_3} / k_{\text{H}} = 1.30 \pm 0.06$$

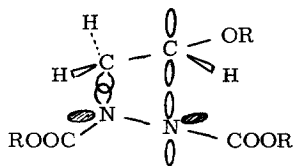
The following conclusions result from these findings:

- 1.) Deuterium substitution at CH<sub>2</sub> = accelerates the formation of II by k<sub>D</sub>/k<sub>H</sub> ≈ 1.21 per deuterium.
- 2.) Deuterium substitution at =CH(OR) decreases the rate of formation of II by

$k_D/k_H \approx 0.89$ , assuming that the effect of D at  $=CH_2$  is the same in I-D<sub>2</sub> as in I-D<sub>1</sub>.

3.) Change of hybridization in the direction  $sp^2$  to  $sp^3$  has occurred in the transition state at  $CH_2 =$  , but, obviously, not at  $=CH(OR)$ .

4.) The following picture can be derived for the transition state of the diazidine formation from azodicarboxylates and vinyl ethers:



According to these results the diazidine formation can be looked upon as a two step reaction. The dipolar character of the intermediate is revealed by trapping it with water in the diazidine formation from indene and 4-phenyl- $\Delta^1$ -1,2,4-triazoline-3,5-dione<sup>10, 15</sup>).

Diazetidines are formed stereospecifically and without appreciable influence of solvent polarity on the rates of reaction. Activation parameters like those observed<sup>10</sup>) ( $\Delta H^*$ : 7 - 11 kcal/mol;  $\Delta S^*$  = -36 to -46 eu) are usually considered as characteristic for concerted reactions. However, these criteria alone do not always allow an unambiguous distinction to be made between one and two step cycloaddition reactions<sup>10, 16</sup>). Therefore, the secondary - deuterium isotope effect appears as a valuable additional probe into the simultaneity of such reactions.

I-D <sub>n</sub>	Run	I-D <sub>o</sub> + I-D <sub>n</sub> moles x 10 <sup>3</sup>	DMAD moles x 10 <sup>3</sup>	$\frac{[I-D_o]}{[I-D_n]}$	$\frac{[I-D_n]}{[II-D_o]}$	$k_D/k_H$
I-D <sub>1</sub>	1	37.3	2.91	2.04	0.58	1.19
	2	30.7	1.74	2.08	0.57	1.19
	3	16.8	0.65	2.14	0.59	1.26
I-D <sub>2</sub>	1	39.8	2.33	2.67	0.41	1.09
	2	32.6	2.05	2.73	0.40	1.09
	3	26.7	1.51	2.66	0.40	1.06
	4	15.8	0.62	2.96	0.36	1.06
I-D <sub>3</sub>	1	70.4	3.22	2.11	0.64	1.35
	2	48.5	2.42	2.00	0.60	1.20
	3	22.9	1.51	2.24	0.58	1.30
	4	10.6	0.55	2.35	0.58	1.36

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D<sub>2</sub>O was used instead of H<sub>2</sub>O in the slightly modified standard procedure.
- 13) According to nmr analysis both I-D<sub>1</sub> and I-D<sub>2</sub> contained minor amounts of the corresponding trans isomers.
- 14) Through the courtesy of Mr. H. Damen on an ATLAS CH-5 from the parent ion intensities.
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