

Cope Rearrangement of 3,3-Dicyanohexa-1,5-diene

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AM1 Calculations indicate that the Cope rearrangement of 3,3-dicyanohexa-1,5-diene takes place by a synchronous pericyclic mechanism involving an aromatic transition state rather than by the biradicaloid path usual in chair Cope rearrangements.

Some years ago experimental¹ and theoretical² work indicated that the chair³ Cope rearrangements of hexa-1,5-diene (**1**) and its derivatives take place by the nonsynchronous mechanism suggested by Doering *et al.*,⁴ involving a biradicaloid transition state (TS) (**2**), rather than by the synchronous pericyclic mechanism, involving an aromatic TS (**3**), that had been previously assumed. Recent AM1⁵ studies⁶ have fully confirmed this conclusion. One problem, however, remained, *i.e.* the anomalous entropy of activation for the boat Cope rearrangement of (**1**) itself. If the chair and boat rearrangements of (**1**) take place by the same mechanism, they would be expected to have similar entropies of activation, and the calculations^{2,6} indeed predicted this to be the case. The experimental value reported⁷ for the boat rearrangement is, however, much less negative (-13 ± 14 vs. -54 ± 4 J/K). Similar small values (-15 ± 13 ; -29 ± 8 J/K) have been

reported by Doering and Troise⁸ for the boat rearrangements of derivatives of (**1**) bridged across the 2,5-positions. Since entropies of activation calculated by our procedures usually agree with experiment to within 10 J/K, there was a strong implication that the boat and chair Cope rearrangements of (**1**) do *not* involve the same mechanism.

Further theoretical studies⁹ of the boat and chair rearrangements of (**1**) led to the remarkable conclusion that each of these reactions can take place by either of two distinct reaction paths, one corresponding to the Doering biradicaloid (BR) mechanism and the other to the conventional aromatic (ARO) pericyclic one. While the ARO chair TS was higher in energy than the BR chair TS by 27 kJ/mol, the difference for the boat was only 11 kJ/mol. The entropy of activation calculated for the latter (-26 J/K) was consistent with experiment^{7,8} and the calculated activation parameters indicated that the aromatic

path should be faster at the temperatures used in the kinetic measurements. These conclusions have been further supported by recent *ab initio* calculations.¹⁰

Gajewski and Conrad¹¹ have measured secondary deuterium kinetic isotope effects (SDKIE) for the chair Cope rearrangements of (1) and a number of its derivatives. In all cases but one, the $k_{\text{H}}/k_{\text{D}}$ rate ratios for deuterium at C(3) or C(4) were much closer to unity than the $k_{\text{D}}/k_{\text{H}}$ rate ratios for deuterium at C(1) or C(6). These results indicate that the C(1)–C(6) bond has been largely formed in the TS while the C(3)–C(4) bond is still largely intact, as would be expected if the reactions are of BR type. The isotopic rate ratios reported¹¹ for three key compounds [(1), 2-phenylhexa-1,5-diene (4), and 2,5-diphenylhexa-1,5-diene (5)] also agreed well with our calculations⁶ (Table 1), which predicted all three reactions to take place by the BR mechanism.

1,2-Diethyl-3,3-dicyanohexa-1,5-diene (6) was the one exception. Here the observed $k_{\text{H}}/k_{\text{D}}$ rate ratio for deuterium at C(4) was *greater* than the $k_{\text{D}}/k_{\text{H}}$ rate ratio for deuterium at C(6). In view of the results indicated above, this seems to suggest that here the ARO mechanism is preferred, a conclusion which is not in fact surprising. The effect of a substituent (X) at C(3) or C(4) is due primarily to the change in hybridization of these atoms on forming the TS, due in turn to the weakening of the bond between them. This leads to an increase in the s character of the carbon atomic orbital used to form the C–X bond and hence to a corresponding increase in its bond strength. Since the C(3)–C(4) bond is longer and weaker in an ARO TS than in a BR TS, substituents at C(3) or

C(4) should accelerate the ARO mechanism more than they do the BR one. The *two* substituents at C(3) in (6) could therefore well lead to a change of mechanism.

We decided to test this conclusion by carrying out AM1 calculations for the boat and chair Cope rearrangements of 3,3-dicyanohexa-1,5-diene (7) to 1,1-dicyanohexa-1,5-diene (8), the ethyl groups in (6) being omitted for computational convenience since it seemed very unlikely that they could have any large effect. The calculations were carried out using the normal (RHF) version of AM1 because previous studies^{6,9} had shown this to be effective for the biradicaloid TSs in BR Cope reactions, these being effectively closed shell species with relatively little biradical character.

Two distinct TSs (9) and (10) were again located. The calculated heats of formation (ΔH_{f} , kJ/mol) and relevant bond lengths (Å; 1 Å = 100 pm) are shown in (7)–(10) while Table 2 shows the corresponding activation parameters and calculated isotopic rate ratios for the 4,4- and 6,6-dideuterio derivatives of (7), together with the values reported by Gajewski and Conrad for the rearrangement of (6).

The geometries of (9) and (10) are not reported in detail since they were similar to those^{6,9} of the corresponding TSs (4) and (5) from (1). The calculated bond lengths (Å) are indicated in the formulae. As in the case of (4) and (5), (9) and

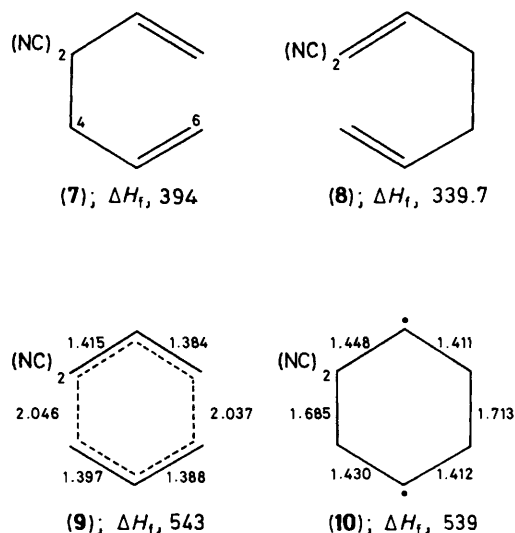
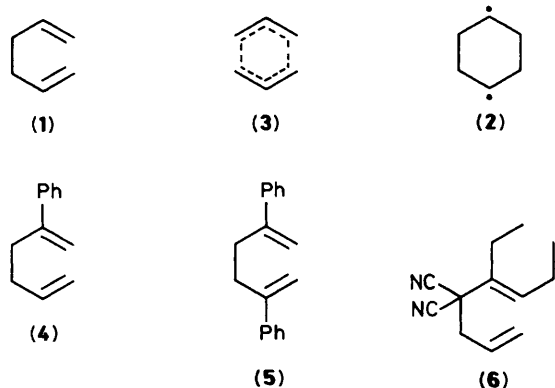


Table 1. Kinetic isotope effects for Cope rearrangements.

Compound	Temp. /K	$k_{\text{H}}/k_{\text{D}}$ (3,3,4,4-[² H ₆]) ^a		$k_{\text{D}}/k_{\text{H}}$ (1,1,6,6-[² H ₆]) ^a	
		calcd.	obsd. ^b	calcd.	obsd. ^b
(1)	512	1.00	1.07 ± 0.025	1.15	1.129 ± 0.019
(4)	448	1.01	1.09 ± 0.02	1.28	1.295 ± 0.003
(5)	328	1.07	1.07 ± 0.024	1.51	1.57 ± 0.035

^a Rate ratios for specified deuteration. ^b Ref. 10.

Table 2. Cope rearrangements of 3,3-dicyanohexa-1,5-diene.

TS	$\Delta H^{\ddagger ab}$	$\Delta S^{\ddagger bc}$	$k_{\text{H}}/k_{\text{D}}$ (4,4-[² H ₂]) ^b		$k_{\text{D}}/k_{\text{H}}$ (6,6-[² H ₂]) ^b	
			calc.	obs. ^d	calc.	obs. ^d
(9)	149	-25	1.073	1.119 ± 0.02	1.118	1.06 ± 0.02
(10)	146	-41	1.001		1.181	

^a Enthalpy of activation (kJ/mol). ^b At 90 °C. ^c Entropy of activation (J/K). ^d Ref. 10.

(10) had similar geometries, the only large differences referring to the lengths of the forming [C(1)–C(6)] and breaking [C(3)–C(4)] bonds. Their values in (9) (2.037, 2.046 Å) corresponded⁹ to an ARO TS while those in (10) (1.685, 1.713 Å) corresponded⁹ to a BR one. Here, however, the energies of the two TSs are almost the same. Thus (7) is predicted to rearrange preferentially by the ARO mechanism, its entropy of activation being less negative.

The k_H/k_D ratios calculated for the BR rearrangement of (7) are similar to those calculated and observed for (1), (4), and (5) but quite different from those observed¹⁰ for (6). The latter, however, agree reasonably well with the values calculated for the ARO rearrangement of (7), implying greater weakening of the C(3)–C(4) bond, and less formation of the C(1)–C(6) bond, in the TS. While the numerical agreement between the calculated and observed rate ratios may seem at first sight inferior to that for (1), (4), and (5), the average unsigned differences between the calculated and observed values are in fact similar (0.05 vs. 0.04). The alkyl substituents in (6) may also have some influence on the structure of the TS.

A further check could be provided by measurement of the entropy of activation for the rearrangement of (4). Our calculations indicate that this should be similar to that for the boat rearrangement of (1).

These results further support our earlier conclusion,⁹ that Cope rearrangements normally take place by one or other of two distinct alternative mechanisms, one a typical pericyclic one involving an aromatic TS while the other involves biradical-like intermediates, rather than by a continuous spectrum of mechanisms of intermediate type. A similar dichotomy of ARO and BR mechanisms has been suggested¹²

for the Diels–Alder reaction and supported by recent high level *ab initio* calculations by Bernardi *et al.*¹³ Appropriate studies of a number of other pericyclic reactions are in progress.

This work was supported by the Air Force Office of Scientific Research and the Robert A. Welch Foundation.

Received, 29th June 1988; Com. 8/02592D

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