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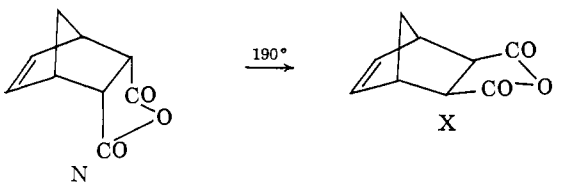
Mechanism of the Diels–Alder Reaction. The Question of the "Internal" Pathway for the Thermal *endo–exo* Isomerizations of the 5-Norbornene-2,3-dicarboxylic Anhydrides[1]

Sir:

Much information bearing on the mechanism of the Diels–Alder reaction has been obtained from studies of isomerizations of various adducts of cyclopentadiene.[2–11] One of the most interesting and important of these isomerizations is the conversion of the *endo*-cyclopentadiene–maleic anhydride adduct [5-norbornene-2,3-*endo*-dicarboxylic anhydride (N)[12]] to the corresponding *exo* isomer (X) at 190°.[13] Berson and coworkers[2,3] have made a detailed study of this process



N X

and have reported that in decalin it takes place *both* by an "external" pathway (a retrogression of the *endo* adduct N to the addends which then recombine to give the *exo* isomer X) and an "internal" pathway (a direct mechanism not involving dissociation into kinetically free fragments).

In connection with a projected study of the stereochemistry of these reactions using the *endo* adduct asymmetrically labeled with ^{14}C, we have re-examined the case for the occurrence of the "internal" pathway.

The following observations prompted our studies. First, under the conditions reported for the N to X conversion [0.102 *M* N and maleic anhydride (M) in boiling decalin, 190°], not all of the maleic anhydride is in solution. In addition, a fairly considerable amount of M sublimes out of the reaction mixture within a few minutes. Obviously, in these circumstances there is no longer an equimolar quantity of M present. As a consequence the results become prejudiced toward the internal pathway.[14]

Table I. Exchange between Radioactive N and X with Inactive M Compared to the Rate of Formation of X

Starting material[a]	Reaction time, min.	Activity recovd., %[b]	X formed, %[c]
N	2	81.06	3.3
N	4	71.11	5.5
N	6	63.26	7.5
N	8	59.55	10.3
N	10	57.58	11.55[d]
N	10	...	13.3 ± 0.15[e]
N	12	...	16.1
X	10	97.9	...
X[f]	10	98.1	...

[a] Starting concentrations: 0.267 *M* radioactive N (436.10 μc./mole) or X (440.84 μc./mole) and 0.267 *M* inactive M. [b] Per cent of original activity in recovered starting material. [c] Determined by n.m.r. integration in $CHCl_3$ from the mixture of N and X by comparison of the ratio of a peak belonging to X only with one common to the sum of N and X. [d] This value is regarded as being somewhat low. [e] Average of three separate runs. [f] Starting concentration: 0.0267 *M* radioactive X (440.84 μc./mole) and 0.267 *M* inactive M.

To get around these difficulties we have studied the N to X isomerization in *t*-pentylbenzene which gives homogeneous solutions and permits use of 0.267 *M* N (labeled with ^{14}C in both carbonyl carbons) and 0.267 *M* nonradioactive M at the boiling point (189–190°).

We have obtained quite conclusive evidence that there is in fact no internal mechanism for the thermal isomerization of the *endo* adduct N to the *exo* isomer X in *t*-pentylbenzene. The rearrangement appears to occur only by dissociation–recombination in exactly the same way as the *endo–exo* isomerization of the cyclopentadiene–acrylic ester[6] and 9-phenylanthracene–maleic anhydride adducts.[5]

Exchange of radioactive N with inactive M was found to occur very rapidly in comparison to the exchange of X with M (Table I).

Clearly, X is only present in small concentrations in the early stages of the exchange between N and M. Therefore it was necessary to determine the activity of X by the isotope-dilution technique.

The activities theoretically to be expected of X arising from N exclusively by an internal mechanism and by an external mechanism were calculated on the basis of the following assumptions: During any small increment of time, the X formed by the internal mechanism has the same activity as the average activity of N during that time, and the X formed by the external mechanism has the same activity as the average activity of M during that time. The data of Table I were plotted to show the decrease in activity of N with time (β_t *vs.* time) and the fraction of N converted to X with time (% X_t *vs.* time). The plots were then subdivided into arbitrarily small time increments (30 sec.). Values for the average activities of N and for the fraction of the total amount of X formed during each of the time increments were determined by graphical interpolation from the plots.

If β_0 is the original activity of N, β_1 the average activity of N during time increment 1, β_2 during time

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(12) For convenience, the same symbols will be used in this paper as by Berson and co-workers.[2,3]
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(14) The evidence previously obtained for the internal pathway by Baldwin and Roberts,[11] based on the N to X interconversion in presence of tetracyanoethylene as a scavenger for cyclopentadiene, has been wholly vitiated by the unanticipated discovery that maleic anhydride reacts with cyclopentadiene at a rate comparable to that of tetracyanoethylene above 150° in decalin (unpublished results of U. Scheidegger) as well as in *t*-pentylbenzene.

increment 2, etc., X_1 the percentage of X formed during time increment 1, X_2 during time increment 2, etc., X_t the total percentage of X formed during reaction time t, then the activity α_A of X theoretically to be expected for the internal mechanism, which is independent of the concentration and activity of M present in the reaction mixture, is approximately

$$\alpha_A = \beta_1 X_1/X_t + \beta_2 X_2/X_t + \ldots\ldots + \beta_i X_i/X_t$$

The activity α_B of X expected for external mechanism is dependent on the concentration of N and M. The decrease of the starting material N is due to formation of X with time and can be extrapolated from the plot $\% X_t$ *vs.* time.

It was noted that some M sublimes out of the reaction mixture. The amount of M actually present during the reaction time was determined by titration.

Considering these two factors, the activity α_B of X theoretically to be expected for the external mechanism is approximately

$$\alpha_B = [(\beta_0 - \beta_1)X_1/X_t]N_1/M_1 + [(\beta_0 - \beta_2)X_2/X_t]N_2/M_2 + \ldots\ldots + [(\beta_0 - \beta_i)X_i/X_t]N_i/M_i,$$

where $\beta_0 - \beta_1$ is the average activity of M during time increment 1, $\beta_0 - \beta_2$ during time increment 2, etc., N_1 the average amount of N present in the reaction mixture during time increment 1, N_2 during time increment 2, etc., M_1 the average amount of M present in the reaction mixture during time increment 1, M_2 during time increment 2, etc.

The theoretical and experimental activities expressed in percentage of the original activity of N obtained are shown for a reaction time of 10 min. (Table II).

Table II. Radioactivity of X[a]

		% of original activity of N
Calculated	internal pathway only	70
	external pathway only	31[b]
Experimental (two runs)[c]		32.4 ± 1.5
		32.3 ± 1.5

[a] For a reaction time of 10 min. [b] A small correction for the rate of exchange of X with outside M (see Table I) is included here. [c] The starting concentrations were 0.267 *M* radioactive N (441.56 μc./mole) and 0.267 *M* inactive M. The activities α_t (143.18 μc./mole, respectively, 142.73 μc./mole) of X formed after time t were calculated from the activities α_r (27.66 μc./mole, respectively, 26.95 μc./mole) of recovered X (determined by isotope-dilution technique), using the formula $\alpha_r = (\alpha_s X_s + \alpha_t X_t)/(X_s + X_t)$, where α_s and X_s are the activity and weight of inactive X added and X_t (13.4%, respectively, 13.15%) the weight of X formed after time t (determined by n.m.r. integration in the same run as α_r).

The results exclude the internal pathway for the thermal interconversion of N to X in *t*-pentylbenzene and for the reasons given above render it highly unlikely in decalin as well.[15] The mechanism appears to be a retrogression of the formation of the *endo* adduct followed by recombination, contrary to the Alder rule,[16] to give the *exo* isomer.

(15) However, Professor J. A. Berson has suggested that it is conceivable that an internal mechanism depending on complex formation between M and diene might not occur in an aromatic solvent such as *t*-pentylbenzene because of competitive solvent–M complexing.

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Acid-Catalyzed 1,5-Hydride Transfer in Acyclic Molecules. Mechanism and Stereochemistry

Sir:

In contrast to the common occurrence of intramolecular 1,2-hydride transfer to carbonium ions (*e.g.*, in many pinacol rearrangements and solvolytic reactions) and of intermolecular analogs,[1] there are relatively few reports of intramolecular transfer of hydride to more remote carbonium ions.[2] Most examples of such reactions are restricted to medium rings[3] or rigid polycyclic compounds in which the reacting sites are in close proximity[4] and have been regarded as due largely to the special geometrical features of these molecules. A single example of an acid-catalyzed 1,5-hydride transfer in a flexible system is the isomerization[5] of steroidal sapogenins at C-25.

Recently the polyphosphoric acid (PPA) catalyzed isomerization of a series of γ-hydroxy olefins to saturated ketones was reported[6] (eq. 1). Several conceivable

$$R_1R_2C{=}CH(CH_2)_2CHOHCH_3 \xrightarrow{PPA} R_1R_2CH(CH_2)_3COCH_3 \quad (1)$$

I, $R_1 = R_2 = CH_3$ III, $R_1 = R_2 = CH_3$
II, $R_1 = CH_3$, $R_2 = C_6H_5$ IV, $R_1 = CH_3$, $R_2 = C_6H_5$

mechanisms for this transformation were listed, including (a) migration of the double bond to an enolic position, (b) internal hydride transfer of the O–H hydrogen, and (c) internal transfer of the carbinol C–H. We wish to report evidence that this latter mechanism is the correct one and that consequently this reaction represents a simple, clear-cut example of intramolecular 1,5-hydride transfer to an acyclic carbonium ion.

Deuterium labeling showed that it is the hydrogen attached to the carbinol carbon which migrates in the isomerization. 2-Deuterio-6-methylhept-5-en-2-ol (I-D), heated with PPA, gave 6-deuterio-6-methylheptanone-2 (III-D) in 47% yield. The position of the label was shown unequivocally by the n.m.r. spectrum of the semicarbazone of III-D, m.p. 154–155°, in which the *gem*-dimethyl group appeared as a sharp

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(2) For examples of 1,3-hydride shifts see (a) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 76, 4501 (1954); (b) N. L. Wendler, R. P. Graber, C. S. Snoddy, Jr., and F. W. Bollinger, *ibid.*, 79, 4476 (1957); (c) J. A. Berson in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 139–155.

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