reverse procedure (OH^- into Hg^{++}), α was the same. When Ag^+ was added to excess OH^-, α was 1.016. For the reverse addition, α was significantly smaller; all values were less than 1.013. Thus, for a given sample to Ag_2O, it appears possible to deduce the order in which the reactants were originally mixed by measurement of the O^{18}/O^{16} ratio.

These results are suggestive of a kinetic isotope effect. For the Hg^{++} aquo-ion, the preferential rupture of O^{16}-H relative to O^{18}-H would concentate O^{16} in the HgO. For Ag^+, the situation is more complex. An alternative mechanism for the fractionation involves the equilibrium isotopic exchange between OH^- and H_2O, favoring the concentration of O^{16} in the OH^-.[3]

Further work is in progress to extend the data and examine other cations. We appreciate the discussions with R. W. Parry, the assistance of W. E. Barrett with the mass spectrometer, and the financial support of the A.E.C. and the Michigan Memorial-Phoenix Project.

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[3] The ionic hydration fractionation effect of Feder and Taube (*J. Chem. Phys.*, **20**, 1335 (1952)) wherein O^{18} concentrates in the aquo-ion relative to the solvent water would probably be of negligible importance since most of the experiments were carried out at low concentrations.

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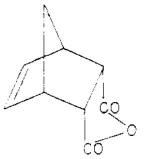
RECEIVED JUNE 14, 1955

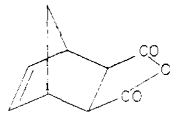
ON THE STEREOCHEMISTRY AND MECHANISM OF THE DIELS-ALDER REACTION[1]

Sir:

We wish to report the first conclusive evidence that isomerization of a bicyclic Diels–Alder adduct of *endo*-stereochemistry to the *exo*-isomer can occur without dissociation into kinetically free addends.[2] When the *endo* cyclopentadiene–maleic anhydride adduct (N), radioactively labeled with C^{14} in the carbonyl carbons, was heated with an equimolar quantity of non-radioactive maleic anhydride (MA) in boiling decalin (190°), rapid exchange of N with MA occurred simultaneously with slower conversion of N to the *exo*-isomer (X). (Exchange of X with MA was small at short reaction times.)



N



X

The variation of *endo*-activity with time was determined by re-isolating N from quenched reaction mixtures. Since isolation of X directly from reaction mixtures at small concentrations of X was not feasible, the activity and concentration of X were determined by an isotope dilution technique.

The activities theoretically to be expected of X arising exclusively by an "internal" path from N (path A) and by an "external" path (path B) were calculated by a graphical integration method.

$$\begin{tikzcd}
 & X \arrow[dl, "k_5"'] \arrow[dr, "k_3"] & \\
N \arrow[ur, bend left, "A\ k_6"] \arrow[rr, shift left, "k_1"] & & MA + C_5H_6 \arrow[ul, bend right, "B\ k_4"'] \arrow[ll, shift left, "k_2"]
\end{tikzcd}$$

The data for activity of N *vs.* time and for moles of X formed *vs.* time were plotted. A reaction period of t minutes was subdivided into arbitrarily small time increments. If X_1 is the number of moles of X formed during time increment 1, X_2 during time increment 2, etc., and X_t during time t, α_0 the original activity of N, α_1 the average activity of N during time increment 1, etc., then the activity of X to be expected by the "internal" path (A) is $\alpha_1X_1/X_t + \alpha_2X_2/X_t + \cdots \alpha_iX_i/X_t$. Since the only source of activity in the system is N,[3] the activity of MA at any time is $\alpha_0 - \alpha_j$ where α_j is the average activity of N during any given time increment. The activity of X to be expected by the "external" path (B) is therefore $(\alpha_0 - \alpha_1)X_1/X_t + (\alpha_0 - \alpha_2)X_2/X_t + \cdots (\alpha_0 - \alpha_i)X_i/X_t$. Application of these calculations to the data show that after three minutes and ten minutes 31.4% and 45.4% respectively of the X present has been formed by path A.[4]

Although epimerization of N to X *via* enolic species formally satisfies the requirement that part of the isomerization occur by path A, we consider this an unlikely mechanism, since the isomerization does not appear to be catalyzed by bases and does not occur with the dihydro derivative of N.[2c] The results also do not formally exclude a mechanism involving intermediate formation of a diradical followed by hydrogen transfer, as proposed by Craig,[2c] or a diffusion-controlled secondary recombination of original partners.[5] However, we consider the most probable detailed description of path A to be conversion of N to a complex in which MA and cyclopentadiene are relatively free to rotate with respect to each other, followed by recombination of the fragments in either stereochemically possible sense. On the basis of the present evidence, this is indistinguishable from primary recombination in a Franck–Rabinowitch solvent cage.

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[1] Sponsored by the Office of Ordnance Research, U. S. Army.

[2] For previous discussion of the mechanism of such isomerizations see (a) R. B. Woodward and H. Baer, THIS JOURNAL, **66**, 645 (1944); (b) K. Alder and W. Trimborn, *Ann.*, **566**, 58 (1950); (c) D. Craig, THIS JOURNAL, **73**, 4889 (1951); (d) D. Craig, J. J. Shipman, J. Kiehl, F. Widmer, R. Fowler and A. Hawthorne, *ibid.*, **76**, 4573 (1954); (e) J. A. Berson and R. Swidler, *ibid.*, **75**, 1721 (1953).

[3] This is true if the exchange of X with MA is neglected. The correction for this is small. Its omission leads to a slightly more conservative estimate of the importance of the "internal" path (A).

[4] The ratio of the amounts of X formed by the two paths is $(k_6N - k_5X)/(k_4M \cdot C_5H_6 - k_3X)$. This need not be time invariant if $k_5 \neq k_3$ or if C_5H_6 is being irreversibly removed from the system, *e.g.*, by polymerization.

[5] *Cf. inter alia*, R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).