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ON THE MECHANISM OF THE INDENE-MALEIC ANHYDRIDE REACTION[1a]

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Abstract—The benzonorbornenedicarboxylic anhydride formed in the reaction of the title results from hydrogen rearrangement in the indene and not from carbon rearrangement in a hypothetical intermediate cycloadduct.

The formation of the 1:1 adduct (II) when indene (I) and maleic anhydride are heated in benzene[2] has been interpreted as involving the unknown hydrocarbon isoindene III.[2,3] Although the mechanism of the assumed indene → isoindene transformation is not explicitly stated, a 1,2-hydrogen shift and double bond migration (mechanism 1) seem to be implied.[3] As has been pointed out elsewhere,[4] a conceivable alternative[5] (mechanism 2) involves preliminary formation of a cyclo adduct (IV) followed by a two-step cyclopentene → vinylcyclopropane → cyclopentene conversion, without hydrogen rearrangement. We now report experiments designed to test mechanism 2.

Indene (I) is converted by sodium methoxide in methanol-O-*d* at room temperature to a mixture of deuterated indenes. The NMR spectrum[7] (at 60 Mc with tetramethylsilane as internal standard) of the deuterated sample shows no change from that of undeuterated material in the ratio (4:1) of aromatic ($\delta \sim 7{\cdot}3$ ppm) to C.2 ($\delta \sim 6{\cdot}5$ ppm) protons and an increase from 4:3 to 4:0·6 in the ratio of aromatic to the sum of C.1 ($\delta \sim 3{\cdot}3$ ppm) and C.3 ($\delta \sim 6{\cdot}9$ ppm) protons. This shows that no appreciable hydrogen-deuterium exchange occurs at C.2 under these conditions and that about 81% of the C.1 and C.3 protons have been replaced by deuterium. The total deuterium content on this basis is thus about 2·4 atoms D/molecule, in rough agreement with the more accurate value 2·33 atoms D/molecule obtained by mass spectrometric analysis,[8] which shows the following percentage distribution of deuterated species: d_0, 1·2; d_1, 11·2; d_2, 41·2; d_3, 45·7; d_4, 0·7.

In the mechanism 2, C.1 of indene becomes the bridge carbon of the adduct II;

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[2] K. Alder, F. Pascher and H. Vagt, *Chem. Ber.* **75**, 1501 (1942).

[3] K. Alder and M. Fremery, *Tetrahedron* **14**, 190 (1961).

[4] J. A. Berson and J. W. Patton, *J. Amer. Chem. Soc.* **84**, 3406 (1962).

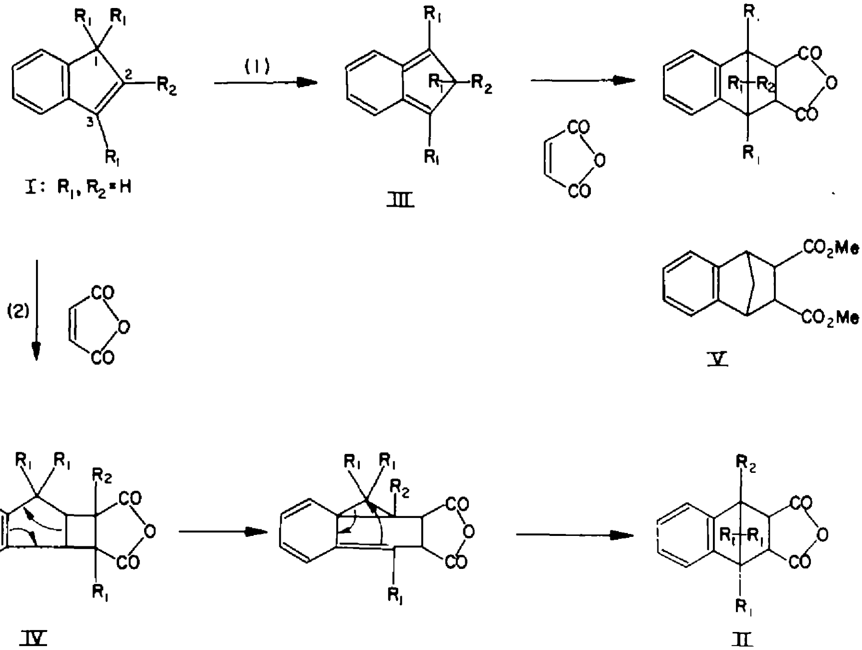
[5] It is unfortunate that our indication[4] of the *possibility* of this alternative seems to have been interpreted by some[6] as a proposal that it be adopted in favour of the isoindene mechanism.

[6] K. Sisido, R. Noyori, N. Kozaki and H. Nozaki, *Tetrahedron* **19**, 1185 (1963).

[7] For assignments of the NMR absorptions of indene, see [a] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.* **36**, 2346 (1962); [b] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.* 590 (1963).

[8] By Mr. Edward B. Miller, Instrumentation Laboratory, Department of Chemical Engineering, New York University.

the extent of deuteration at this site remains unchanged from start to finish of the process. If it is assumed that the deuteration in the d_1 and d_2 indene species is statistical (i.e., in the d_1 and d_2 species, half and three-fourths, respectively, of the deuteriums are at C.1) and that any secondary kinetic isotope effect is negligibly small, the total number of protons on the bridge methylene group of the adduct II formed by mechanism 2 would be 0·40. The NMR spectrum of the derived methyl ester V, m.p. 76·5–77·5°, reported[2] 77°, shows a ratio of aromatic ($\delta \sim 7{\cdot}1$ ppm) to bridge ($\delta \sim 1{\cdot}7$ ppm) protons of 2·0 when prepared from undeuterated indene *via* II according to Alder's procedure[2,3] and 3·17 when prepared under the same conditions from the above deuterated sample. The number of protons on the bridge in the labeled material is thus 1·26, and mechanism 2 cannot be a major path for the formation of II.[9]

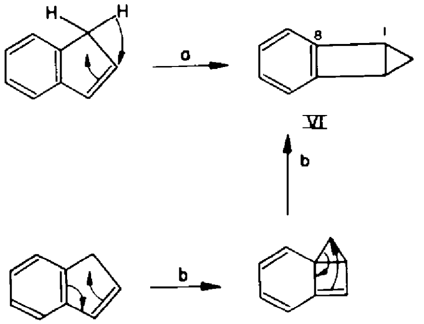


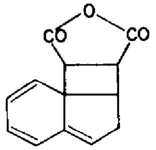
The results are consistent with the formation of isoindene III by hydrogen shift, followed by rapid capture by maleic anhydride before retrogression of III to I can cause much scrambling of the label. The I → III reaction in this mechanism involves a potentially non-negligible *primary* deuterium isotope effect, and a precise value for the expected deuterium burden of the bridge carbon therefore cannot be calculated. Nevertheless, a range of permissible values can be calculated by again assuming statistical distributions of deuterium in the d_1 and d_2 indenes, deuterium isotope effects in the I → III reaction (k_H/k_D) between[10a] 0·1 and 10, and irreversible formation of III from I. This gives the values 1·06 to 1·30 protons on the bridge, a range that includes the experimental value.[10b]

[9] The labelled ester V had 2·17 atoms D/molecule, as shown by a falling drop analysis, performed by Mr. Josef Nemeth, Department of Chemistry, University of Illinois. Thus, little if any loss of deuterium to the surroundings accompanies adduct formation.

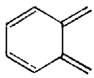
[10a] Values outside this range seem highly unlikely. Cf. F. H. Westheimer, *Chem. Revs.* 61, 265 (1961). [b] In formula II of mechanism 1, no stereochemical implication is intended for R_1 and R_2 on the bridge.

The possibility that the hypothetical molecule *pseudoindene* (VI) may be involved cannot yet be excluded rigorously. If VI is formed, it comes from C.1–C.2 hydrogen shift (*a*) (the reverse of a cyclopropane → propylene rearrangement), and not from carbon skeletal rearrangement (*b*), since the latter process would produce V with the same deuterium distribution as mechanism 2. Pseudoindene (VI) might serve as a source of adduct II either by conversion to isoindene III or by direct reaction with maleic anhydride across C.1–C.8[11] followed by rearrangement of the resulting adduct VII.[12]





VII



VIII

It seems likely that the intermediate in the formation of II is the same that Roth[13] recently showed to be involved in the thermal intramolecular hydrogen rearrangement of indene. Roth's data demonstrate that the concentration of the reactive entity in hydrogen rearrangement must be much less than that of indene at 220°. If adduct formation involves the same intermediate, our results show that this small concentration still permits the species to be trapped bimolecularly by maleic anhydride at a rate substantially faster than unimolecular reversion to indene occurs. This behavior is consistent with the exceptionally high Diels–Alder reactivity that would be expected of isoindene III, a molecule which, like *o*-xylylene VIII, has an unusually high free valence index at the termini of the conjugated system and a Hückel delocalization energy (D.E.) of $1{\cdot}95\beta$.[14] In terms of π-electron energetics, isoindene III and *o*-xylylene VIII should be among the most reactive Diels-Alder dienes known. Whereas an ordinary diene must sacrifice $0{\cdot}47\beta$ of Hückel D.E. in forming a Diels–Alder adduct, isoindene (or *o*-xylylene) actually gains $0{\cdot}05\beta$. These systems are thus uniquely

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[11] Analogous to the α-cyclopropylstyrene–maleic anhydride addition reported by S. Sarel and E. Breuer, *J. Amer. Chem. Soc.* **81**, 6522 (1959).

[12] Analogous to one of the possible mechanisms for the bicyclo[3.2.0]heptene → bicyclo[2.2.1]heptene rearrangement.[4]

[13] W. R. Roth, *Tetrahedron Letters* No. 17, 1009 (1964).

[14] J. D. Roberts, A. Streitwieser and C. M. Regan, *J. Amer. Chem. Soc.* **74**, 4579 (1952).

capable of making available the full electronic driving force associated with the Diels–Alder reaction, i.e., twice the difference in strength between a π-bond and a sigma bond, without having to pay any partial compensation in loss of D.E. in the diene.[15]

EXPERIMENTAL

1,1,3-*Trideuterioindene.* A solution of 0·37 g sodium methoxide and 0·60 g freshly distilled indene in 10·2 g methanol-O-*d*-was stirred in a N_2 atm. for 21 hr at room temp, whereupon most of the methanol was distilled off through a Vigreux column while the bath temp was kept below 75°. The residue was treated with 2 ml D_2O and extracted with pentane. The extract was washed with water, filtered through activated charcoal, and dried (Na_2SO_4). Several batches of indene were processed in this way and combined. The pentane was removed by distillation and the product was distilled through a short fractionating column to give material, b.p. 76° (20 mm). The mass spectrum was run[8] at 10 v with a Consolidated Electrodynamics Model 21-103C instrument. The isotopic composition given in the text was calculated from the appropriate peak heights and is corrected for natural isotopic abundances. The NMR spectrum of this sample was taken on a CCl_4 solution and is described in the text.

Under more vigorous conditions (potassium t-butoxide in boiling t-butyl alcohol), some exchange of hydrogen at C.2 for deuterium was observed to occur.

Reaction of 1,1,3-*trideuterioindene with maleic anhydride.* A mixture of 1·25 g of the above deuterated sample, 0·73 g freshly sublimed maleic anhydride, 1·22 g benzene, and a pinch of hydroquinone was sealed *in vacuo* in a heavy-walled Pyrex Carius tube of 65 ml capacity. The tube and 20 ml benzene were sealed in a steel pressure vessel and heated at 180° for 5·5 hr. The tube was opened, benzene was added, and the benzene layer was decanted off from some insoluble material. Evaporation of the benzene solution gave a residue which was washed with hexane and then recrystallized from ethyl acetate to give 0·30 g of white crystals of the adduct II, m.p. 185·5–187°, reported[2] m.p. 187–188°.

This material was converted to the dimethyl ester (V) according to Alder's procedure.[2] This substance had m.p. 76·5–77·5°, reported[2] m.p. 77°. Its NMR spectrum in CCl_4 solution showed a ratio of 3·17 in the intensities of aromatic to bridge protons, as described in the text. This ratio is the average of several repeated integrations. During the same period of operation of the spectrometer (Varian AR-60), an undeuterated sample of V showed a value of 2·0 for this ratio.

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[15] For some quantitative correlations of lack of Diels–Alder dienic reactivity and loss of D.E., see R. D. Brown, *J. Chem. Soc.* 691, 2730 (1950); 1612 (1951).