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Tautomerism in Isotopically Substituted Indenes*

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Some time ago, the author showed[1] that intramolecular proton-transfer takes place in indene under certain conditions, and preliminary results were reported of a study of this tautomeric rearrangement using 1-D-indene in pyridine solution with triethylamine as a catalyst at 30°C. We have also shown in a study of dialkyl-indenes that the reaction is completely stereospecific under the above mentioned conditions.[2]

Quite recently, Roth[3] reported evidence for intramolecular proton-migration in 1-deutero-indene and 1,1,3-trideutero-indene in the gas phase at about 200°C, and McLean and Haynes[4] found similar rearrangements in substituted cyclopentadienes. Roth's results indicate the intermediate formation of isoindene, implying a deuterium shift to the 2-position. Under the conditions used by the present author, however, only shifts between positions 1 and 3 have been observed. Since reaction conditions as well as the results are quite different in our investigations, it is evident that different mechanisms for the rearrangements are operative.

In this paper, the results of kinetic measurements of the rates of the tautomeric rearrangements I ⇌ II and III ⇌ IV are
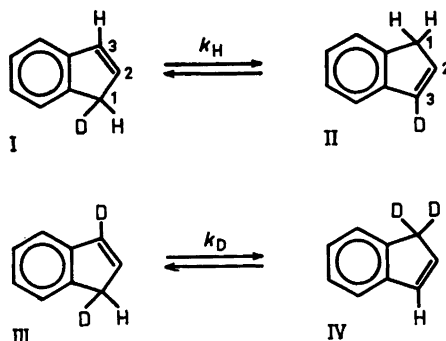
reported. The former reaction involves protium-migration (deuterium-migration is non-observable) and the latter, deuterium-migration. Thus, the kinetic isotope effect can be studied if I and III (or II and IV) are prepared and subjected to tautomerizing conditions.

I was prepared by deuteration of indenyl sodium and III by protonation of 1,3-dideuteroindenyl sodium. The latter was made from trideuteroindene which was obtained from hydrogen exchange between indene and D_2O. The structures of I and III were confirmed by their NMR-spectra. Thus, I shows signals at 6.76 and 6.27 ppm (δ, relative to TMS, neat) due to the protons at the 3- and 2-position, respectively. Each of these signals is split into two doublets with the coupling constants $J_{23} = 5.5 \pm 0.1$, $J_{12} = 1.9 \pm 0.1$ and $J_{13} = 1.8 \pm 0.1$ cps which are in good agreement with those found for indene.[5] The signal at 3.02 ppm, due to the proton in position 1, is split into seven peaks in accordance with the coupling scheme shown in Fig. 1. The geminal $H-D$ coupling constant, J_{HD}, is 3.2 ± 0.2 cps, corresponding to $J_{HH} = 20.8$ cps since $\gamma_D/\gamma_H = 0.1535$.[6]
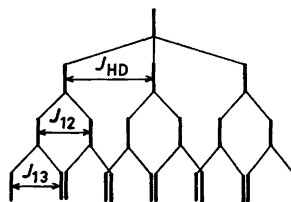

Fig. 1. Spin-spin coupling scheme for the proton in position 1 of compound I.

According to the Karplus and Gutowsky relation,[7] $J_{HH} = 20.8$ cps should correspond to a H—C—H angle of $104-105°$, but it is known that hyperconjugated CH_2 groups show larger coupling constants than those predicted theoretically.[8] The valence angle is therefore certainly larger than $105°$.

The kinetic investigation of the tautomeric rearrangements was made by determination of the area of the 1-proton signal as a function of time at $30°C$. Pyridine was used as a solvent and triethylamine as a catalyst. The indene concentration was 2 M and various triethylamine concentrations (B) were used. With $B = 5.4 \times 10^{-3}$ M, the half-life of the reaction $I \rightleftharpoons II$ was about 200 min. If the concentration of the indene species are denoted by C_i, we get the rate equations (1) and (2) for the protium and deuterium migration reactions respectively. Furthermore, if X is the signal intensity of the proton in position 1, we obtain the subsidiary conditions (1a) and (2a), respectively (omitting an unimportant proportionality factor). Therefore, we get the simple rate-law (3), with X as a reaction variable common to both reactions $I \rightleftharpoons II$ and $III \rightleftharpoons IV$ with the only distinction that $k = k_H$ for the former and $k = k_D$ for the latter. In these derivations we have assumed that secondary isotope effects can be neglected.

$$dC_1/dt = -k_H B(C_1 - 2C_2) \qquad (1)$$

$$dC_3/dt = -k_D B(C_3 - 2C_4) \qquad (2)$$

$$C_1 + C_2 = X_0; \quad C_1 + 2C_2 = X; \quad X_\infty = \tfrac{4}{3}X_0 \qquad (1a)$$

$$C_3 + C_4 = X_0; \quad C_3 = X; \quad X_\infty = \tfrac{2}{3}X_0 \qquad (2a)$$

$$dX/dt = -3kB(X - X_\infty) \qquad (3)$$

$$\frac{1}{B}\log|X - X_\infty| = -\frac{3k}{2.303}t + \text{const.} \qquad (4)$$

The results of the application of the integrated rate-law (4) are presented in Fig. 2. We found $k_H = 0.22$ and $k_D = 0.038$ lit. mole^{-1} min^{-1}. The primary isotope effect, k_H/k_D is therefore 5.8 in good agreement with the value, 5.5, found in methylindene.[9] Further studies of deuterated indenes, their intramolecular tautomerism and their isotope effect are in progress.

Experimental. The indene used was fractionated by vacuum distillation (N_2-atm.) shortly before use (b.p. $59°/10$ mm Hg).

Trideuterated indene. 23.2 g (0.2 mole) of indene and 18.0 g (0.9 mole) of D_2O (99.8
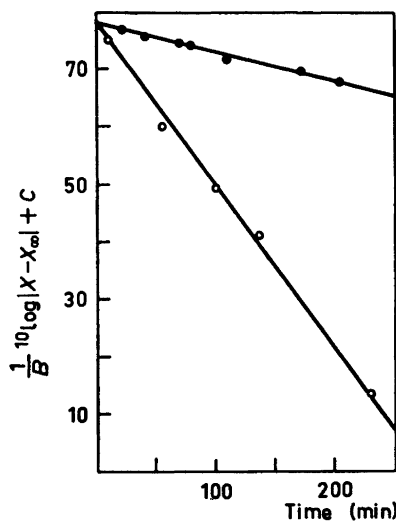

Fig. 2. Logarithmic plot of protium migration (O) and deuterium migration (●).

g/100 g, from Norsk Hydro) was dissolved in 60 ml of pyridine (Mallincrodt, anal., dried over CaH_2). In a nitrogen atmosphere, 2 ml of a 40 % Triton B (benzyltrimethylammonium hydroxide) solution in pyridine was added. After 20 min the reaction mixture was rapidly neutralized with acetic acid (ice cooling) and poured into 150 ml of water. The indene was extracted with ether. After evaporation of the ether in vacuum, the entire process was repeated twice more. The product was fractionated in vacuum (10 mm Hg, N_2-atm.) yielding 15 g of 95 % trideuterated indene. The protium content was determined by NMR-spectroscopy. No difference in boiling point from ordinary indene could be detected.

Indenylsodium. A sodium dispersion was prepared from 5.5 g (0.24 mole) of sodium in 75 ml of dry toluene by means of a "Polytron" dispersion stirrer. The dispersion was cooled to room temperature and then 5 ml of a solution of 13.5 g (0.12 mole) of freshly distilled chlorobenzene in 30 ml of toluene was added under nitrogen. When the reaction had started, the rest of the chlorobenzene solution was added dropwise (30 min) with occasional cooling in a dry ice-acetone bath, to keep the temperature between 20 and 40°. After complete addition, the reaction mixture was kept at room temperature for 15 min and then 11.6 g (0.1 mole) of indene or 11.9 g (0.1 mole) of trideuterated indene in 30 ml toluene was added dropwise

(30 min). The mixture was heated at 75° for 2 h to complete the reaction. The toluene was then filtered off (N_2-atm.) and 150 ml of tetrahydrofuran (dried and distilled over $LiAlH_4$) was added. The resulting solution (partly suspension) of indenylsodium was used in the preparation of deuterated indenes.

1,3-Dideutero-indene (III). The solution of indenylsodium prepared from trideuterated indene (11.9 g), was poured in a thin stream into excess water (ice-cooling, stirring). The reaction mixture was acidified with acetic acid a few seconds after the addition of indenylsodium. (Alternatively, the indenylsodium solution may be added to dilute acetic acid). The product was extracted with ether, the ether dried with $MgSO_4$ and evaporated in vacuum. Fractionation of the residue in vacuum (10 mm Hg, N_2-atm.) gave 6.5 g of the dideuterated indene (III).

1-Deutero-indene (I). This substance was prepared in the same way as (III) by adding the solution of indenylsodium (from ordinary indene) to excess D_2O.

The NMR-spectra were recorded with a Varian A-60 high resolution spectrometer. The kinetic runs were made at 30°C with 2 M indene concentration. Pyridine was used as a solvent and triethylamine as a catalyst.

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Algal Carotenoids

IV. On the Structure of Fucoxanthin

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Evidence for the chemical constitution of fucoxanthin has been presented [1-6] which allows a formula (I) to be proposed as a reasonable working hypothesis.

This structure is based on the assumption that fucoxanthin is closely related to the other carotenoids of brown algae, especially to violaxanthin (3,3'-dihydroxy-5,6,5',6'-diepoxy-β-carotene), all of which are bicyclic. Considered together, the results of oxidative degradation,[3,7] the presence of two tertiary hydroxy groups and the NMR-evidence (methyl peaks at τ-values: 9.03 (3H), 8.98 (3H), 8.94 (3H), 8.78 (3H), 8.66 (3H), 8.62 (3H), 8.19 (3H), 8.08 (3H), 8.02 (6H) and 7.97 (3H); no isopropylene methyls) revealed the presence of at least one cyclic end-group, and are best accounted for by a bicyclic structure of the pigment. The chromophore of fucoxanthin (λ_{max} 449 mμ) requires the equivalent of 8 C=C and 1 C=O, all of which must be conjugated in an aliphatic system.[5] The moderate fine-structure of the spectrum together with the normal shift (25 mμ) in absorption maximum upon reduction of the conjugated keto group indicates that the chromophore is not cross-conjugated.

If the allene grouping [2,3] of fucoxanthin is to be accommodated in a bicyclic carotenoid structure, it has to be placed at one end of the active chromophore, and in ω-position to the conjugated carbonyl group. The relatively high stability of the allene group is best accounted for if it is placed in an exocyclic position as shown in structure I.

The structural formula suggested requires an uptake of 9 moles of hydrogen upon catalytic hydrogenation. Karrer, Helfenstein, Wehrli, Pieper and Morf [7] reported the absorption of 10 moles when acetic acid was used as solvent. Heilbron and Phipers [8] managed to remove four of the six oxygen atoms of fucoxanthin by hydrogenation in moderately forcing conditions. Thus hydrogenolysis may easily take place.