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Hydrogen displacements, IV *)

Kinetic isotope effect of the 1.5-hydrogen displacement in *cis*-pentadiene-(1.3)

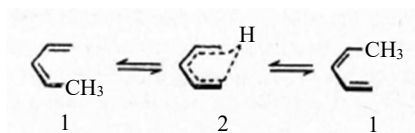
by Wolfgang R. Roth and Joachim König

From the Institute of Organic Chemistry at the University of Cologne

Received on April 29, 1966

The thermal 1.5-hydrogen displacement of *cis*-1.1-dideutero-pentadiene-(1.3) (3) was followed kinetically at 185–205° and an intramolecular, non-catalyzed, first-order reaction with activation parameters of $\Delta H^\ddagger = 35.4$ kcal/mol and $\Delta S^\ddagger = -7.1$ cal/degree-mol was ensured. Comparison with the kinetic data of the analogous 1.5-deuterium displacement results in a kinetic isotope effect of $k_H/k_D = 1.15 \cdot \exp[1400/RT]$, which is consistent with a symmetric transition state of the reaction.

In recent years, relatively easy 1.5-hydrogen displacements have been observed for a large number of cyclic¹⁻³ and acyclic^{2c, 4, 5} polyenes, relatively easy 1.5-hydrogen displacements have been observed. The required cisoid geometry⁴, the intramolecular nature^{1a, 3b, 3c}, the first order kinetics^{1-3, 5}, and the independence of the reaction rate from the polarity of the solvent¹⁻³ led to the formulation of a synchronous reaction¹⁻⁵ in accordance with theoretical considerations⁶).



A critical test of such a model of the transition state should be the kinetic hydrogen-deuterium isotope effect of the reaction. Its extent is largely determined by

*) III. Notification: W. R. Roth and J. König, Liebigs Ann. Chem. **688**, 28 (1965).

¹⁾ 1a) A. P. ter Borg, H. Kloosterziel and N. van Meurs, Recueil Trav. chim. Pays-Bas **82**, 717 (1963). – ib) A. P. ter Borg and H. Kloosterziel, ibid **82**, 741, 1189 (1963); **84**, 245 (1965).

²⁾ 2a) D. S. Glass, J. Zirner and S. Winstein, Proc. chem. Soc. [London] **1963**, 276. – 2b) J. W. H. Watthey and S. Winstein, J. Amer. chem. Soc. **85**, 3715 (1963). – 2c) D. S. Glass, R. S. Boikess and S. Winstein, Tetrahedron Letters [London] **1966**, 999.

³⁾ 3a) R. Roth, Liebigs Ann. Chem. **671**, 10 (1964). – 3b) **671**, 25 (1964). – 3c) Tetrahedron Letters [London] **1964**, 1009.

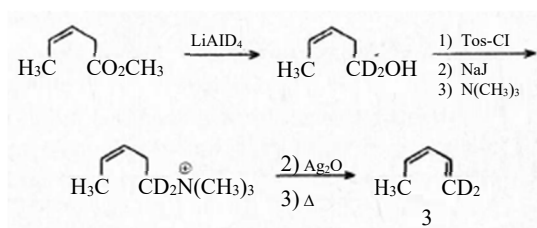
⁴⁾ J. Wolinsky, B. Chollar and M. D. Baird, J. Amer. chem. Soc. **84**, 2775 (1962).

⁵⁾ H. M. Frey and R. J. Ellis, J. chem. Soc. [London] **1965**, 4770.

⁶⁾ R. B. Woodward and R. Hoffmann, J. Amer. chem. Soc. **87**, 2511 (1965).

the symmetry of the transition state and reaches a maximum value with a linear, symmetrical arrangement of the activated complex⁷⁸). *cis*-pentadiene-(1.3) (**1**) therefore seemed particularly suitable for investigating the isotope effect of the 1.5-hydrogen displacement. A synchronous reaction process here requires an ideally symmetrical transition state (**2**), with the migrating hydrogen arranged halfway between the carbon atoms C-1 and C-5, and should lead to a large isotope effect. The detection of only a small effect would be a reliable criterion for a non-symmetrical transition state, for a dent in the energy profile of the reaction⁹).

We determined the rate of the hydrogen displacement by isomerization of *cis*-1.1.1-dideutero-pentadiene-(1.3) (**3**). The structure of **3** clearly results from the synthesis pathway and the spectral properties. In the NMR spectrum, the hydrogen vinyl signals H-1 of *cis*-pentadiene-(1.3) (**1**) are missing at $\tau = 4.93$ and 4.98, respectively, and the fine structure of H-2 ($\tau = 4.42$) has simplified to a doublet that undergoes strong line broadening due to coupling with the deuterium atoms (Fig. 1). The characteristic kink vibration of the terminal vinyl hydrogens of *cis*-pentadiene-(1.3) is also missing in the IR spectrum at 902 cm^{-1} .



If **3** is heated in the gaseous phase to temperatures around 200° , a redistribution of the deuterium is observed in the NMR spectrum of the otherwise unchanged substance. The relative intensity of the methyl hydrogen signals ($\tau = 8.24$) decreases, and the signals of the previously missing, terminal vinyl hydrogens H-1 appear (Fig. 1). In the equilibrium state, the area ratio of the signals H-2 : H-3 : H-4 : H-1 : H-5 equals 1 : 1 : 1 : 1.2 : 1.8, corresponding to a statistical distribution of the marking between positions 1 and 5. We observe the result of consecutive 1.5-hydrogen or deuterium displacements.

⁷⁾ Even if the theoretical models⁸⁾ are based on a linear arrangement of the three atoms mainly involved in the transition state, this geometry does not appear to be a necessary prerequisite for the occurrence of a large isotope effect; cf. E. L. Mackor and C. MacLean, *Pure appl. Chem.* **8**, 393 (1964).

⁸⁾ F. H. Westheimer, *Chem. Reviews* **61**, 265 (1961); H. S. Johnston, *Advances chem. Physics* **3**, 131 (1961); J. Bigeleisen, *Pure appl. Chem.* **8**, 217 (1964).

⁹⁾ If the initial product and the rearrangement product are identical, this necessarily follows from the principle of microscopic reversibility.

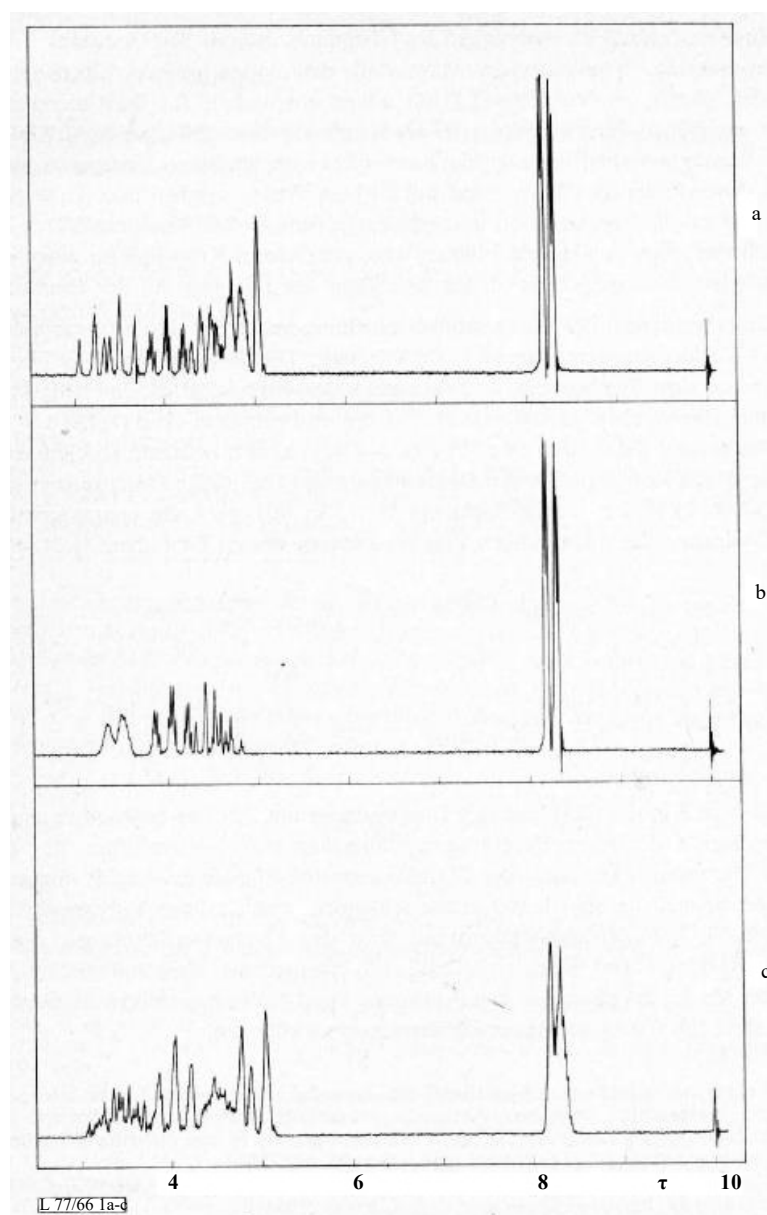
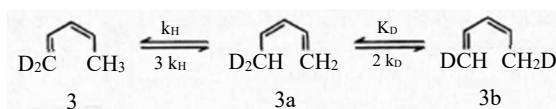


Figure 1. NMR spectrum of *cis*-pentadiene-(1.3) (**1**) (a), *cis*-1.1-dideutero-pentadiene-(1.3) (**3**) (b) and of **3** after 15 hours of heating to 250° (c)

Mass spectroscopic analyses of the starting product **3** ($d_1 = 4.3\%$; $d_2 = 95.7\%$) and the equilibrium mixture ($d_1 = 4.4\%$; $d_2 = 95.6\%$) ensure a strictly intramolecular course of isomerization¹⁰⁾.

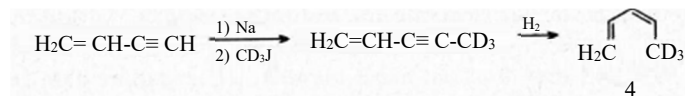


We determined the kinetics of the rearrangement in the temperature range 185–205° from the change in the intensity ratio of the vinyl to methyl signals occurring in the NMR spectrum. The hydrogen displacement is a non-catalyzed, homogeneous first-order gaseous phase reaction. The temperature dependence of the rate constants¹¹⁾ can be described by the Arrhenius equation

$$k_H = 2.8 \cdot 10^{11} \exp[-(36.3 \pm 0.5)\text{kcal/RT}] \text{ sec.}^{-1}$$

A comparison with the activation parameters of the 1,5-hydrogen displacement in 2-methyl-pentadiene-(1,3)^{2c,5)} reveals a small activating influence of the methyl group on the rate of the hydrogen displacement, the extent of which is comparable to the substituent effect in the hydrogen displacement in cycloheptatriene¹²⁾.

We determined the rate of deuterium migration analogous to hydrogen migration **3** → **3a** by isomerization of *cis*-5,5,5-trideutero-pentadiene-(1,3) (**4**), which was prepared by reacting vinyl acetylene sodium with trideuteromethyl iodide in liquid ammonia followed by partial hydrogenation. The structure of **4** is clear from its NMR spectrum (Fig. 2). The signals of the methyl hydrogens of the *cis*-pentadiene (1,3) (**1**) at $\tau = 8.24$ are missing, and the vinyl hydrogen H-4 ($\tau = 4.57$), which appears as a double quartet in **1**, becomes a doublet broadened by deuterium coupling in **4**. The triplet of the hydrogen vinyl H-3 ($\tau = 4.07$) in **4** also no longer shows a fine structure caused by the coupling with the methyl group.



If **4** is heated in the gaseous phase to temperatures around 200°, a redistribution of the deuterium is also observed in the NMR spectrum (Fig. 2). The following appear

¹⁰⁾ We also observed the same isomerization during irradiation (Hg high-pressure burner, quartz apparatus) of **3** in the gaseous phase. The intramolecular course was also determined here by mass spectroscopic analysis of the starting product and equilibrium product.

¹¹⁾ k_H is defined as the rate constant for a single hydrogen displacement, taking into account the statistical conditions.

¹²⁾ A. P. ter Borg, E. Rozenberg and H. Kloosterziel, Recueil Trav. chim. Pays-Bas 84, 1230 (1965).

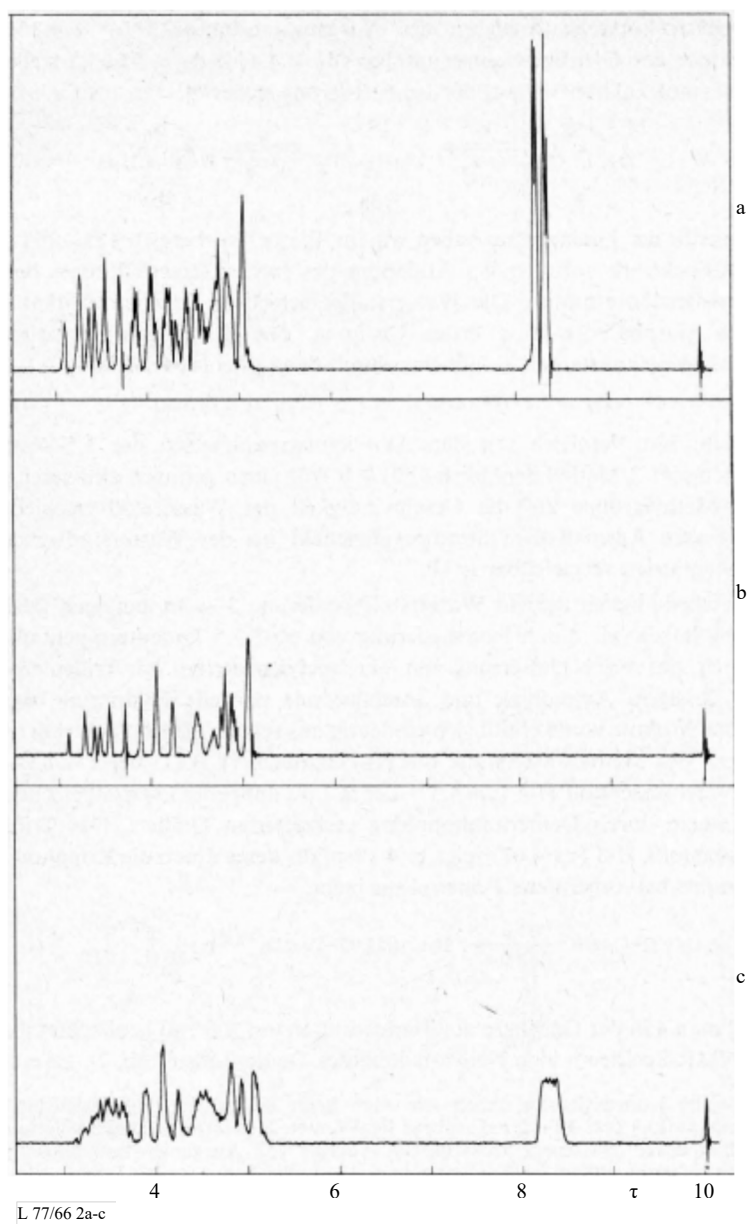


Figure 2. NMR spectrum of *cis*-pentadiene-(1.3) (**1**) (a), *cis*-5.5.5-trideutero-pentadiene-(1.3) (**4**) (b) and of **4** after 15 hours of heating to 250° (c)

pentadiene isomerization and indicates the general symmetric transition state of 1,5-hydrogen displacements.

We would like to thank Professor Dr. E. Vogel for funding this work. We would also like to thank the *German Research Foundation* for material resources and a grant to J. König.

Description of the experiments

The *gas chromatographic analyses* were carried out using Perkin-Elmer 116 E and F 6 instruments. The columns used were: Silicone column, 0.2–0.3 mm diatomaceous earth with 20% silicone oil 100 (Farbenfabriken Bayer, Leverkusen); polyethylene glycol column, 0.2 to 0.3 mm diatomaceous earth with 20% polyethylene glycol 4000 (Chemische Werke Hüls, Marl). – The *NMR spectra* were recorded with a Varian, model A-60; the signals are given in the τ scale (TMS = 10). – A CH-4 device (MAT, Bremen) was available for the *mass spectroscopic analyses*.

cis-1,1-dideutero-pentadiene-(1.3) (3). – *butyne-(1)-carboxylic acid-(1)*¹⁶⁾ was converted to the isomeric *butyne-(2)-carboxylic acid-(1)* according to Whiting and coworkers^{*17)} and from this *cis-butene-(2)-carboxylic acid-(1)* was obtained by partial catalytic hydrogenation in acetic ester with *Pd/carbon*¹⁸⁾. After esterification with *diazomethane*, 13.5 g of the *cis-butene-(2)-carboxylic acid (1)-methyl ester* was added to the boiling solution of 2.5 g of *LiAlD₄* in 100 cc of ether, heated under reflux for 10 min, and then hydrolyzed with diluted sulfuric acid. After workup, 8.4 g of *cis-1,1-dideutero-pentene-(3)-ol-(1)* were isolated¹⁹⁾ from Sdp.35 64 – 65°, which were slowly added to a solution of 19 g of tosyl chloride in 50 cc of pyridine cooled to about -10° with stirring. Stirring was then continued for approx. 3 hours, poured onto ice and absorbed into ether. Evaporation yielded 11.9 g of oily *tosylate*, which was dissolved in 50 cc of acetone and boiled with 10 g of *NaI* in 50 cc of acetone for 3 hours. After cooling, the precipitated sodium tosylate was filtered off, washed several times with warm acetone, evaporated and the residue taken up in ether. After washing with water and aqueous thiosulfate solution, the ether was removed and the residue distilled at 21 Torr. The 4.9 g of *iodide* passing at 55–56° were converted to a methanol solution of 7.5 g of *trimethylamine* and heated for 2 hours under reflux (dry ice cooler). The excess trimethylamine was then evaporated off and the *ammonium salt* was separated at -70° by adding 20 cc of acetic ester. After washing with petroleum ether, 5.5 g of a salt melting at 201° was isolated, which was dried, dissolved in 100 cc of water, and then reacted with *silver oxide* (from 7.3 g of silver nitrate and 1.7 g of NaOH) for 3 hours with frequent shaking. The filtered solution was evaporated in vacuo and the residue was heated to 100–120° under argon at 70 Torr. The product was distilled off via a column and collected in a trap cooled to -70°.

¹⁶⁾ A. O. Zoss and G. F. Hennion, J. Amer. chem. Soc. **63**, 1151 (1941).

¹⁷⁾ E. R. H. Jones, G. H. Whitham and M. C. Whiting, J. chem. Soc. [London] **1954**, 3201.

¹⁸⁾ E. Schjänberg, Svensk Kern. Midcutr. **50**, 98 (1938) [C. **1939** 1, 4759],

¹⁹⁾ cf. L. Crombie and St. H. Harper, J. chem. Soc. [London] **1950**, 873.

The distillate was taken up in 8 cc of cyclohexane, the organic phase was separated and 0.8 g of spectroscopically pure **3** was isolated by gas chromatography (2 m silicone column, 50°, 1.8 at He, retention time 4.0 min).

cis-5.5.5-trideutero-pentadiene-(1.3) (**4**). - To 5.4 g of sodium in 200 cc of liquid ammonia, 14.8 g of vinyl acetylene²⁰⁾ was added with stirring at -70° until the solution decolorized. Then 29 g of trideuteromethyl iodide were added, stirred for 2 hours, mixed with 80 cc of cyclohexane and, after evaporation of the ammonia, the residue was hydrolyzed. When fractionated on a rotating belt column between 57–78°, the organic phase yielded 25 g of a product which, after gas chromatographic analysis (2 m silicone column, 50°, 1.6 at He), consisted of 33% 5.5.5-trideutero-pentene-(1)-in-(3) (retention time 6.9 min) and 67% cyclohexane. This fraction was hydrogenated in 25 cc of cyclohexane with 200 mg of Lindlar catalyst²¹⁾ at 0° until 0.7 mol of hydrogen was taken up. After filtration, fractionation was carried out on a rotating belt column. From the distillate, which was converted at 37–58°, 1.2 g of spectroscopically pure **4** was isolated by gas chromatography (2 m polyethylene glycol column, 43°, 1.7 at He, retention time 2.1 min).

Kinetics: 30 mm³ of samples were melted in vacuo (0.1 Torr) in 30 cc of Pyrex ampoules and heated in a high temperature thermostat (Colora-Meßtechnik GmbH, Lorch) with a temperature constancy of $\pm 0.1^\circ$. The reaction was stopped by quenching the ampoules and the area ratio of the vinyl to the methyl signals (V/M or V/M*²²⁾) was determined from the carefully integrated NMR spectrum of the reaction product. This ratio is a function of the concentrations of **3**, **3a** and **3b** or **4**, **4a** and **4b**, which in turn are functions of time. V/M or V/M* can only be expressed as functions of the reaction rate k_H or k_D and the time t if k_H/k_D is known. We determined the rate constants k_H and k_D using an iteration procedure. With an estimated k_H/k_D ratio, we have expressed V/M or V/M* as an approximate function of k and t . It gives practically correct k values for the initial stage of the reaction, as the reactions **3a** $\rightarrow$ **3b** and **4a** $\rightarrow$ **4b** can still be neglected here. From the time-dependent change of the V/M value between the limits of V/M = 1 to 1.4 or V/M* = ∞ to 20 (corresponding to a maximum concentration of **3b** of 0.5% and **4b** of 1.5%), approximate values for k_H and k_D were determined, which provided a corrected k_H/k_D ratio with which V/M could be expressed as a corrected function of k and t . Repeated correction led to practically no further change in the k values. For the temperature of 195.1°, the best functions for V/M and V/M* were obtained:

$$\begin{aligned} V/M &= \frac{4.2 - 1.493 \exp[-4.114 k_H t] + 0.293 \exp[-0.486 k_H t]}{1.8 + 1.493 \exp[-4.114 k_H t] - 0.293 \exp[-0.486 k_H t]} \\ V/M^* &= \frac{3.8 + 0.174 \exp[-15.85 k_D t] + 1.026 \exp[-3.160 k_D t]}{1.2 - 0.174 \exp[-15.85 k_D t] - 1.026 \exp[-3.160 k_D t]} \end{aligned}$$

²⁰⁾ We are indebted to Dr. K. Kaiser, Knapsack AG, for providing us with vinyl acetylene.

²¹⁾ H. Lindlar, Helv. chim. Acta 35, 446 (1952).

²²⁾ V/M refers to the transfer from **3**, V/M* to the one from **4**.

The slight changes in this function in the investigated temperature interval (185–210°) caused by the temperature dependence of the isotope effect only influence the k values within the error limit.

For the isomerization of **3** and **4**, rate constants were determined for 5 temperatures between 185–210° using the above functions, which were based on 6 values of V/M and V/M^* , respectively (see Table 1). Increasing the wall area by plugging the ampoules with glass wool only caused a change in the rate constants within the error limit ($\pm 1\%$).

Table 1. Velocity constants of the rearrangements of **3** and **4**

Temperature	185.0°	190.1°	190.2°	195.1°	200.0°	205.3°	210.6°
$k_H \cdot 10^6$ [Sec. ⁻¹] (3 → 3a)	1.38	–	1.80	3.13	4.47	7.10	–
$k_O \cdot 10^6$ [Sec. ⁻¹] (4 → 4a)	–	0.394	–	0.600	0.900	1.39	2.26

[77/66]