

3. Svennerholm, E. and Svennerholm, L. *Acta Chem. Scand.* **16** (1962) 1282.
4. Svennerholm, E. and Svennerholm, L. *Nature. In press.*
5. Svennerholm, E. and Svennerholm, L. *Biochim. Biophys. Acta. In press.*
6. Klenk, E. and Padberg, G. *Z. physiol. Chem.* **327** (1962) 249.
7. Yamakawa, T. *J. Biochem. (Tokyo)* **43** (1956) 867.
8. Klenk, E. and Uhlenbruck, G. *Z. physiol. Chem.* **311** (1958) 227.
9. Klenk, E. and Heuer, K. *Deut. Z. Verdauungs.-Stoffwechselerkrankh.* **20** (1960) 180.

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Proton-Mobility in the Indene Ring-System

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The proton-mobility in the five-membered ring of indene has been the subject of several investigations. Protium-deuterium or protium-tritium exchange experiments have been made in different ways,¹ and some scattered information is available concerning the isomerization of substituted indenenes². However, only a few quantitative rate studies under unified conditions have been reported.

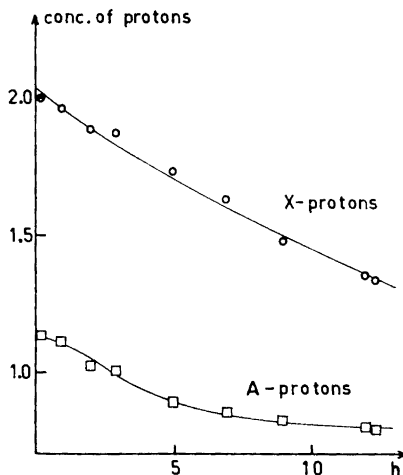
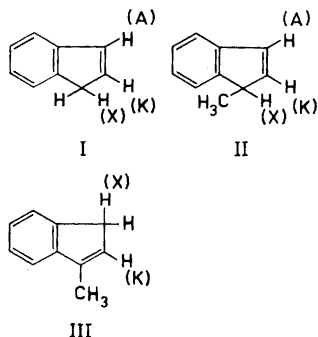


Fig. 1. Hydrogen exchange of indene showing the variation of the proton-concentration (in arbitrary units) with time. Temperature: 25°C.

In this communication we wish to report some preliminary results of an extensive series of investigations now in progress. Protium-deuterium exchange of indene (I) and isomerization of 1- to 3-methylindene (II and III, respectively) under the influence of basic catalysts have been studied with the NMR-technique.

The NMR-spectrum of indene was recently analyzed in detail by Elleman and Manatt,³ and was shown to be of the AKX₂-type. The peaks for the non-equivalent protons in the 5-ring are sufficiently separated to permit a study of the protium-deuterium exchange in each position. A 2 M solution of freshly distilled indene in pyridine together with D₂O (8 moles litre⁻¹) and triethylamine (0.36 moles litre⁻¹) as a catalyst, was studied at various time intervals in a Varian A-60 NMR-spectrometer. The area of the peak due to the K-proton remained constant during the experiment (this was also true for the aromatic proton-peak), whereas the amount of X- and A-protons changed with time as shown in Fig. 1. In the absence of triethylamine there was no measurable hydrogen exchange. Protododeuteration of indene deuterated in the 1- and 3-positions, using H₂O in the above medium has also been carried out with similar results. A mathe-

Table 1. Chemical shifts relative TMS in dioxane and coupling constants for 1- and 3-methylindene.

Compounds	Protons	Shift PPM (δ)	Relative intensity	
1-Methylindene	Methyl	1.19	3	
	X	3.32	1	
	K	6.35	1	
	A	6.71	1	
	$J_{\text{CH}_3\text{-X}} = 7.63 \pm 0.19$		$J_{\text{AX}} = 1.94 \pm 0.02$	
$J_{\text{AK}} = 5.67 \pm 0.07$		$J_{\text{KX}} = 1.95 \pm 0.05$		
3-Methylindene	Methyl	2.06	3	
	X	3.13	2	
	K	6.04	1	
	$J_{\text{CH}_3\text{-X}} = 2.17 \pm 0.05$		$J_{\text{KX}} = 1.77 \pm 0.13$	
	$J_{\text{CH}_3\text{-K}} = 1.66 \pm 0.04$			

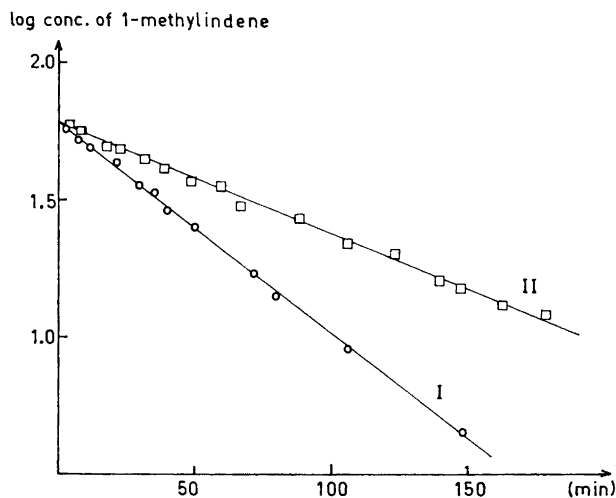


Fig. 2. Rate of isomerization of 1-methylindene to 3-methylindene. I: 2 M solution plus 0.50 ml triethylamine per 10 ml solution. $k_I = 3.0 \times 10^{-4} \text{ sec}^{-1}$. II: 2 M solution plus 0.25 ml triethylamine per 10 ml solution. $k_{II} = 1.5 \times 10^{-4} \text{ sec}^{-1}$. Temperature: 30°C.

matical treatment of the exchange kinetics will be published later.

The NMR-spectrum of III was previously analyzed by us⁴. Quite recently Christol and Plenat⁵ prepared a methylindene which was assigned the structure II. This result is confirmed by the NMR-spectrum recorded in the present investigation (Table 1). When III was dissolved in pyridine + triethylamine no changes were observed. However, II rearranges to III in this solvent system. The isomerization follows first-order kinetics, as shown in Fig. 2, and the rate constant is proportional to the amount of triethylamine added. Isomerization in a medium containing in addition 5.5 moles litre⁻¹ D₂O showed a very small hydrogen exchange rate as compared to the rate of isomerization.

We have also prepared optically active 1-methylindene and studied the rate of racemization in a similar basic medium to the above. The decrease in optical activity is found to be about 1.1 times as fast as the rate of isomerization.

Further experiments and detailed interpretations will be published later.

Investigations of tautomeric benzylindenes and of monodeuterated indene are also in progress.

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1. Cf. the review in Shatenshtein, A. I. *Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds*, New York 1962.
2. Koelsch, C. F. and Scheiderbauer, R. A. *J. Am. Chem. Soc.* **65** (1943) 2311.
3. Elleman, D. D. and Manatt, S. L. *J. Chem. Phys.* **36** (1962) 2346.
4. Weidler, A.-M., Mathiasson, B. and Bergson, G. *Arkiv Kemi. In press.*
5. Christol, H. and Plenat, F. *Bull. Soc. Chim. France* **1962** 1325.

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