

Versatile Deuterium Exchange and Isomerization of Hydrocarbons via Phase Transfer Catalysis

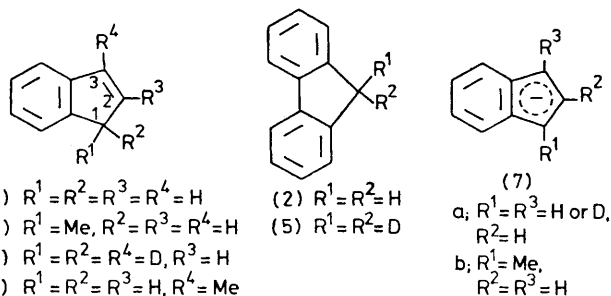
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Summary The complete deuteration of indene (**1**) at C(1) and C(3) and fluorene (**2**) at C(9), and the allylic isomerization of 1-methylindene (**3**) to 3-methylindene (**6**) are reported; phase transfer catalysis is shown to be an easy and efficient method for deuterium exchange and isomerization of acidic hydrocarbons.

PHASE transfer catalysis has proved in recent years to be a versatile, simple, and attractive synthetic tool.¹ Various reactions have been performed by the transfer of the OH⁻ ion into the organic phase,¹ including deuterium exchange at α positions of carbonyl compounds.² Similarly, the theoretical and practical aspects of isomerizations of olefinic compounds have received much attention.³ We report the deuterium exchange of acidic hydrocarbons, *e.g.* indene (**1**) and fluorene (**2**) as well as the isomerization of 1-methylindene (**3**) to 3-methylindene (**6**), by the use of phase transfer catalysis.

Treatment of indene (**1**) in CH₂Cl₂ with NaOD-D₂O in the presence of benzyltriethylammonium chloride afforded 1,1,3-trideuterioindene (**4**) (95%). The ABX₂ ¹H n.m.r. spectrum† observed for the five-membered ring protons in (**1**) changed into a vinylic singlet attributed to C(2)-H of (**4**). Further evidence for the formation of (**4**) comes from



mass spectroscopy. The parent peak of (**1**) appears at m/e 116, while (**4**) shows peaks at m/e 119, 118, and 117 ($M - ^2H$). From the ¹H n.m.r. and mass spectra, > 95% exchange is observed. Treatment of fluorene (**2**) under similar conditions yielded [²H₂]-fluorene (**5**) (98%). The methylene protons disappeared in the n.m.r. spectrum and an increase of two mass units was observed in the mass spectrum. > 99% exchange was observed from the ¹H n.m.r.† and mass spectra.

Treatment of 1-methylindene (**3**) in CH₂Cl₂ and aqueous NaOH in the presence of benzyltriethylammonium chloride afforded complete isomerization to 3-methylindene (**6**):‡

† ¹H n.m.r. spectra were recorded on Varian HA-100D and Bruker WH-270 spectrometers. The assignments were assisted by double resonance experiments. The deuteriated compounds showed satisfactory C, H, and D analyses.

‡ This isomerization was achieved previously by treatment of (**3**) with triethylamine in pyridine (G. Bergson and A. W. Weidler, *Acta Chem. Scand.*, 1963, **17**, 862).

^1H n.m.r.† (CDCl_3) δ 7.28 (m, 4H, ArH), 6.14 [1H, tq, J_1 2.5, J_2 2.0 Hz, C(2)H], 3.25 [2H, d, J 2.5 Hz, $2 \times$ C(1)H], and 2.12 (d, J 2.0 Hz, Me). These observations are interpreted in terms of formation of the intermediate indenyl anion (**7a**) or methyl indenyl anion (**7b**) in equilibrating systems which undergo deuteration at C(1) and C(3) to form (**4**), or protonation of (**7b**) to form the more thermodynamically stable isomer (**6**).

In view of these results, phase transfer catalysis seems to be an efficient tool for deuterium exchange and isomerization of acidic hydrocarbons.

We thank the Weizmann Institute for use of a Bruker WH-270 n.m.r. spectrometer.

(Received, 13th October 1977; Com. 1068.)

¹ R. A. Jones, *Aldrichimica Acta*, 1976, **9**, 35; J. Docky, *Synthesis*, 1973, 441; E. V. Dehmlow, *Angew. Chem. Internat. Edn.*, 1974, **13**, 170; 1977, **16**, 493.

² C. M. Starks, *J. Amer. Chem. Soc.*, 1971, **93**, 195.

³ A. J. Hubert and H. Reimlinger, *Synthesis*, 1969, 97.