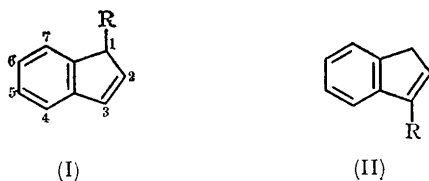


## Tautomerism of 5- and 6-Substituted Indenes

By D. G. LINDSAY, B. J. MCGREEVY, and C. B. REESE

(University Chemical Laboratory, Cambridge)

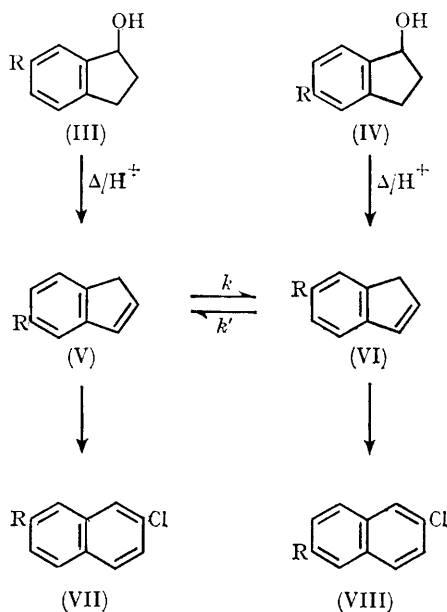
RECENTLY,<sup>1</sup> the problem of the orientation and tautomerism of 1- and 3-substituted indene derivatives (I and II respectively) has been resolved with the aid of n.m.r. spectroscopy. However, as it seemed unlikely that 4-, 5-, 6-, and 7-substituted indenenes could be studied by a similar approach\*, we have developed a method



which, in principle, can be used to investigate the orientation and tautomerism of any indene derivative. Although this procedure, which is based on Parham's naphthalene synthesis,<sup>3</sup> has been applied successfully<sup>4</sup> to 1- and 3-methylindenes (respectively I and II; R=Me), we shall at present consider only its application to 5- and 6-indene derivatives.

The approach followed is outlined in Figure 1. The acid-catalyzed† dehydration of 6- and 5-indan-1-ols (III and IV) respectively) gave isomeric indenenes (V and VI) which, in both the series (a and b) examined, could not be separated by gas-liquid chromatography (g.l.c.). It was not

possible to orientate these indene derivatives on the basis of spectroscopic evidence although both



a, R=OMe  
b, R=Cl

FIGURE 1

\* Elvidge and Foster<sup>2</sup> have suggested that a small long-range coupling occurs between H(3) and H(7) in methylindenes. If general, this would enable a distinction to be made between 4- and 7-substituted indenenes.

† No acid is required in the dehydration of 5-methoxyindan-1-ol (IVa).

<sup>1</sup> A. M. Weidler and G. Bergson, *Acta Chem. Scand.*, 1964, **18**, 1487.

<sup>2</sup> J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1963, 590.

<sup>3</sup> W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Amer. Chem. Soc.*, 1956, **78**, 1437.

<sup>4</sup> B. J. McGreevy and C. B. Reese, unpublished observations.

pairs of isomers had distinguishable infrared, ultraviolet, and n.m.r. spectra. A solution of each indene derivative in anhydrous pentane solution, cooled to 0°, was treated with an excess both of sodium methoxide and ethyl trichloroacetate, and the dichlorocarbene adducts so obtained,<sup>5</sup> decomposed in boiling pyridine solution. In each case, the crude products were shown by g.l.c. to contain one naphthalene derivative, contaminated with at most 1% of its isomer. In this way, the tautomeric purity of the four indene derivatives (Va, Vb, VIa, and VIb) was confirmed.

The orientation of each substituted indene was established by identifying the corresponding naphthalene derivative. 2-Chloro-7-methoxy- (VIIa) and 2-chloro-6-methoxy-naphthalene (VIIIa), both isolated in a pure crystalline state in over 70% yield (m.p. 83–85° and 70–73° respectively) from

treated with 0.3M-triethylamine in 95% ethanol solution, and the equilibration reactions followed spectrophotometrically.† It was found that, as in pyridine solution,<sup>1</sup> indene tautomerism was kinetically a first order equilibration reaction.<sup>6</sup>

From the table, it can be seen that the mean (0.81) of the spectrophotometrically determined values of the equilibrium constant for the methoxy-indenes is in good agreement with that obtained (0.9) by the naphthalene synthesis method. The accuracy of these determinations is probably sufficient to justify the unexpected conclusion that the less conjugated 5-methoxyindene (Va) is marginally *more stable* than the 6-isomer (VIa). It is less certain that 5-chloroindene (Vb) is similarly more stable than its isomer (VIb), as a small error in the initial optical density reading could have led to the low value of  $k/k'$  obtained

TABLE  
Equilibrium<sup>a</sup> and Rate Constants in 0.3 M-Triethylamine-95% Ethanol at 20°

| Indene Derivative     | 10 <sup>4</sup> ×<br>Molarity | $k/k'$                 | 10 <sup>5</sup> ( $k + k'$ ) |
|-----------------------|-------------------------------|------------------------|------------------------------|
| 5-Methoxyindene (Va)  | 4.4                           | 0.75(0.9) <sup>b</sup> | 3.2                          |
| 6-Methoxyindene (VIa) | 3.3                           | 0.87(0.9) <sup>b</sup> | 3.2                          |
| 5-Chloroindene (Vb)   | 9.7                           | 0.95(1.0) <sup>b</sup> | 181                          |
| 6-Chloroindene (VIb)  | 10.4                          | 0.87(1.0) <sup>b</sup> | 187                          |

<sup>a</sup> See Fig. 1: equilibrium constant =  $k/k' = [6\text{-isomer}]/[5\text{-isomer}]$ .

<sup>b</sup> The values of  $k/k'$  in parentheses were obtained from g.l.c. estimations of mixtures of isomeric naphthalenes, prepared from indenenes which had been treated first with 1% NaOMe-MeOH for 2½ hr at 20°. The estimated error in these values is ± 10%.

the reaction mixtures derived from 5- and 6-methoxyindenenes (Va and VIa) respectively, were identical with the diazomethane methylation products of authentic specimens of the corresponding chloronaphthols. In the same way, 2,7- and 2,6-dichloronaphthalenes (VIIb and VIIIb) were both obtained in 68% yield from 5- and 6-chloroindenenes (Vb and VIb) respectively.

When it had been established that the individual methoxy- and chloro-indenes were free from their isomers, it became possible to study the base-catalyzed equilibration of both pairs of tautomers quantitatively. Each indene derivative was

with 6-chloroindene. The observation that the rate of equilibration ( $k + k'$ ) of the chloro-derivatives (Vb and VIb) is about sixtyfold that of the methoxy-derivatives (Va and VIa) is in accord with the similar but smaller effect observed by Shoppee<sup>7</sup> in his studies on the interconversion of 1,3-diarylpropene derivatives.

As well as offering a general approach to the study of indene tautomerism, the present work finally resolves the uncertainty which has surrounded the structures of 5- and 6-methoxyindenenes for over forty years.<sup>8,9</sup>

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† Spectrophotometric measurements were made at 303 m $\mu$  for methoxyindenenes (Va and VIa have  $\epsilon = 2210$  and 712 respectively), and at 296 m $\mu$  for chloroindenenes (Vb and VIb have  $\epsilon = 820$  and 205 respectively).

<sup>5</sup> W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, 1959, **24**, 1733.

<sup>6</sup> A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, 1953, p. 172.

<sup>7</sup> C. W. Shoppee, *J. Chem. Soc.*, 1930, 968.

<sup>8</sup> C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, 1923, 1469.

<sup>9</sup> C. A. Panetta and S. C. Bunce, *J. Org. Chem.*, 1961, **26**, 4859.