

slowly. Crystallization from cyclohexane afforded III, 0.15 g of light yellow needles, m.p. 107–109°.

*Alkaline degradation, IV.* III (0.65 g) was dissolved in ethanolic potassium hydroxide solution (100 mg KOH in 2 ml ethanol). A yellow precipitate was formed after a couple of hours. Recrystallization from methanol gave IV, 20 mg, m.p. 180–181° (decomp.). (Found: C 34.92; H 4.32. Calc. for  $C_7H_{11}N_2O_4K$  (242.3): C 34.71; H 4.57).

The radical V was prepared as previously described.<sup>6</sup>

VI. Bromotrinitromethane (6 g) and cyclohexene (6 g) in chloroform (15 ml) were left standing for two days at room temperature. The solution was washed with sodium bicarbonate, dried over sodium sulphate and the solvent evaporated *in vacuo*. A yellow oil remained which was extracted once with hexane (25 ml) and chromatographed on silica. After the first eluate (benzene) a second fraction was collected (chloroform), which contained VI, 1.0 g, m.p. 74–75° from methanol. (Found: C 45.03; H 5.74; Calc. for  $C_7H_{10}N_2O_4$  (186.2): C 45.14; H 5.41). The gas chromatogram of the hexane solution showed at least 5 components in substantial amounts.

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## On the Rotation of Ammonium Ions within Ammonium-Carbanide Ion Pairs\*

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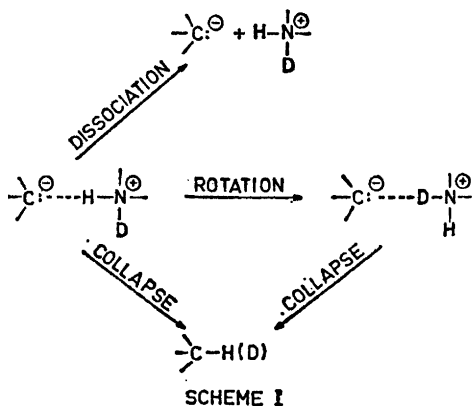
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It has been proposed that ion pairs containing a carbanion and an ammonium or substituted ammonium ion are involved in hydrogen exchange<sup>1,2</sup> and tautomeric rearrangements<sup>3,4</sup> of carbon acids. Some years ago, we showed that the triethylamine catalyzed rearrangement of 1-methylindene to 3-methylindene in pyridine-deuterium oxide occurs without hydrogen exchange.<sup>5</sup> This intramolecular course of the rearrangement can be interpreted in such a way that the collapse of the ion pair with the formation of 3-methylindene is more rapid than ion pair dissociation. Evidence of the internal rotation of ammonium ions in ammonium-carbanide ion pairs have been found by Cram.<sup>1,2</sup> An elegant demonstration of this phenomenon is provided by the comparison of the ammonia catalyzed racemization and exchange for a deuterated fluorene derivative in tert-butanol or tetrahydrofuran.<sup>6</sup> This experiment shows that rotation of the ammonium ion within the ion pair (and collapse of the ion pair) is faster than ion pair dissociation. Thus, comparisons have been made between dissociation and collapse and between dissociation and rotation. From these experiments no comparisons can be made, however, between collapse and rotation rates. This communication will describe some experiments in which internal rotation competes with collapse.

The hexylamine ( $R-ND_2$ ) catalyzed rearrangement of 1-methylindene in pyridine-deuterium oxide was studied by the NMR-technique, and the results of the experiment are given in Fig. 1. The deuterium oxide served as a deuterium pool.

Careful analysis of the NMR-spectrum showed that no deuterium was incorporated into the 1-methylindene, whereas

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the product, 3-methylindene, contains a considerable proportion of deuterium. A control experiment showed that hydrogen exchange between 3-methylindene and the reaction medium is very slow compared with the exchange observed in the rearrangement experiment. These facts suggest that the steps involved in the rearrangement may, to a good approximation, be formulated in terms of the irreversible scheme II. This means that ion pair collapse with the formation of 1-methylindene is, as expected, much slower than collapse to 3-methylindene. Furthermore, the formation of deuterated 3-methylindene shows that the hexylammonium ion can rotate within the ion pair. The deuterium incorporation cannot be due to ion pair dissociation, since experiments using tertiary amines have shown that ion pair collapse is faster than dissociation.<sup>7</sup>

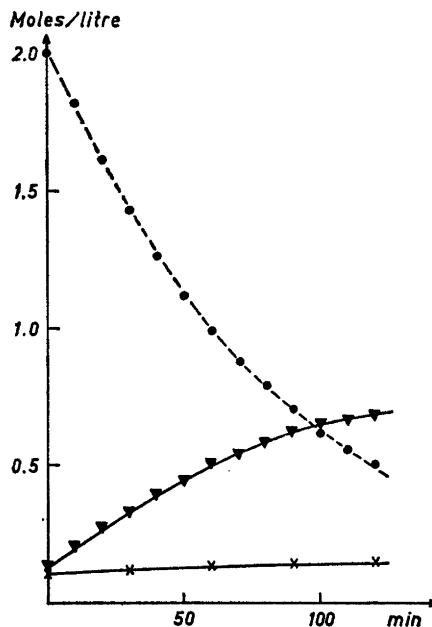
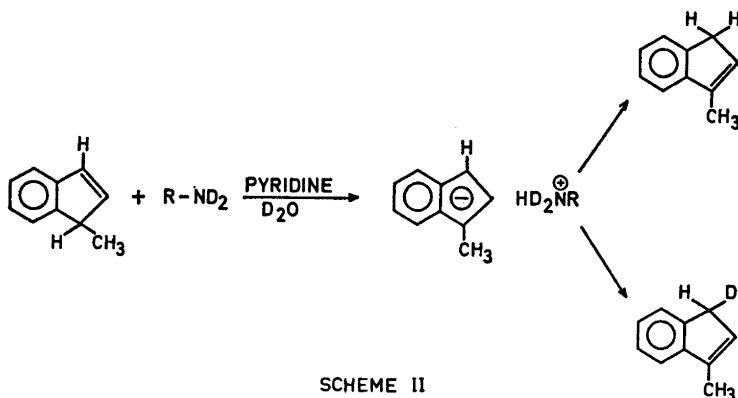


Fig. 1. Rearrangement of 1-methylindene in pyridine in the presence of deuterium oxide (5.20 M) and hexylamine- $d_2$  (0.074 M) at 40.8°C. 1-Methylindene concentration (●) and concentration of protons in the reaction medium (▼) are given as a function of time. The curve (×) represents the concentration of protons in the medium in a control experiment using the same reaction conditions as above but with 3-methylindene instead of 1-methylindene.

A detailed analysis of the data given in Fig. 1 shows that there is, after correction for the statistical factor, a virtual isotope effect of about 3 in the ion pair collapse, which means that the carbanion captures the proton more easily than the deuteron. This can be interpreted either as a real isotope effect in combination with free rotation of the ammonium ion or by the assumption that some fraction of the ion pairs collapse before rotation has occurred. Thus, our conclusion is that the rate of rotation is faster or about equal to the collapse rate. The latter interpretation is in agreement with preliminary experiments using 1,3-dimethylindene where an isotope effect near to unity was found for the ion pair collapse. In view of the fact mentioned above that protonation giving 3-methylindene is much more rapid than protonation to 1-methylindene it is not unreasonable to assume that the hexylammonium-1,3-dimethylindenyl ion pair is long-lived enough to permit equilibration of the rotamers.

The observations described in the present paper may, of course, be explained in a more complicated way by assuming that an internal concerted mechanism competes with the ion pair mechanism. At present this seems, however, to be an unnecessary sophistication in view of the quantity of strong evidence for ammonium-carbanide ion pairs put forward, especially by Cram.<sup>3</sup> Further studies of the phenomena reported in this paper with respect to the indene system are in progress.

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## Sulphated Polysaccharides in Brown Algae.

### II. Isolation of 3-O- $\beta$ -D-Xylopyranosyl-L-fucose from *Ascophyllan*

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Aqueous extracts of the brown seaweed *Ascophyllum nodosum* (L.) Le Jol. contain, in addition to alginate, three sulphated glucuronoxylifucans which differ sharply with respect to electrophoretic mobility and quantitative composition.<sup>1</sup> The major component of this group, named "ascophyllan", has been shown<sup>1</sup> to consist of a polyuronide backbone composed of D-glucuronic acid residues, to which are attached side-chains, composed of residues of D-xylose, L-fucose, and half-ester sulphate. In connection with this work, it was important to establish whether the xylose and fucose residues are present in separate side-chains, or are directly linked together in heteropolymeric side-chains. The isolation and identification of a new disaccharide is now reported, which helps to answer this question.

Ascophyllan (1 g), prepared as described earlier,<sup>1</sup> was heated at 100°C for 30 min in 0.5 N oxalic acid (200 ml). The mixture was then cooled, neutralised with sodium carbonate, and dialysed three times against water (500 ml). The non-dialysable residue was subjected to further hydrolysis in the same way, and the combined dialysates were de-ionised by passage through a column of Dowex 50 W (H<sup>+</sup> form) resin, followed by neutralisation of the effluent with calcium carbonate, and filtration. Concentration of the solution afforded 504 mg of a mixture of mono- and oligo-saccharides, which was examined by ascending paper chromatography in benzene-butanol-pyridine-water (1:5:3:3 v/v), with aniline trichloroacetate as the location reagent.<sup>1</sup> Fucose and xylose were detected, together with a series of oligosaccharides among which a component having  $R_{gal} = 1.24$  was predominant. This component was isolated on large sheets of Whatman No. 17 paper, irrigated in the descending direction with ethyl acetate-pyridine-water