requirements of the alkali ions. This seems to apply also to the mesophase with a reversed two-dimensional tetragonal structure observed in the potassium caprate-octanol-water system (type K), where the parallel water rods with their surrounding amphiphile molecules are tetragonally arranged,[7] (Table 1, Fig. 2).

The experimental material as a whole thus provides convincing evidence that it is the alkali ion-carboxylate group that determines the minimum water content in the phases of the soap-alcohol-water systems with reversed micellar and meso-morphous structures and indicates that these structures can form only when the water content covers the hydration requirements of the alkali ions.

It is thus possible to displace the regions of existence of the reversed micellar and mesomorphous structures in alkali soap-alcohol-water systems towards a lower water content by replacing in turn the lithium ions with sodium and potassium ions. This fact and the knowledge of the minimum water content that can be achieved in the various cases, might well be of interest in technical contexts where structures of this type are concerned. The fact that the stability of the reversed micellar and mesomorphous structures of amphiphilic systems of the type in question changes when one alkali ion is replaced by another — for instance potassium by sodium ion — would suggest a mechanism that may be of significance in biologic lipid systems.

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Some Remarks on a Recent Paper by J. Almy, R. T. Uyeda and D. J. Cram on the 1,3-Proton Transfer in an Indene System

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In a recent paper,[1] Almy, Uyeda and Cram report some elegant studies which make considerable contributions to our knowledge of the 1,3-asymmetric induction in the proton transfer in the indene system, a phenomenon discovered by Bergson and Weidler.[2] In their discussion of our work,[3] however, Cram et al. make some serious mistakes which are of such a kind that they ought to be clarified.

The studies by Cram et al. of the isomerization of 1-methyl-3-*tert*-butylindene confirm our conclusions that the proton transfer in 1,3-dialkylsubstituted indenes is highly stereospecific in certain cases. Regarding our deduction,[3] however, Cram and his co-workers make the following statement: "Their earlier conclusion of *high* 1,3-asymmetric induction rested on unsupported assumptions".[4]

Let us consider the isomerization of 1-methyl-3-isopropylindene (I) to 1-isopropyl-3-methylindene (II), which was the first reaction of this kind studied.[2,3] In this system we found an equilibrium constant $K = [II]/[I]$ of about 4 from direct NMR observations. Even if Cram et al., using quite different methods,[1] have found an equilibrium constant different from ours in the system 1-methyl-3-*tert*-butylindene $\rightleftharpoons$ 1-*tert*-butyl-3-methylindene, there is no doubt about the fact that a considerable amount of (I) is present at equilibrium in the system I $\rightleftharpoons$ II. The rate constants, as specified in our papers, for the isomerization were also determined from direct NMR studies. Furthermore, we studied the optical rotation of the reaction mixture as a function of time and found a change, for example[2] from −1.60° to + 1.35°, at a rate comparable with the isomerization rate.

The crucial point is, however, what happens to the optical rotation when the state of isomerization equilibrium has been reached (practically). If the rotation then is independent of time, or more exactly, if

I   II
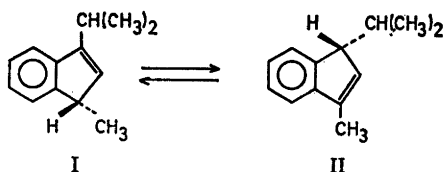
it asymptotically approaches a value different from zero, this fact implies that the rearrangement is 100 % stereospecific.*

In fact we found [2,3] that this criterion is almost, although not exactly, fulfilled in our experiments. The optical rotation slowly changed from its maximum value (e.g. + 1.35° in one reported experiment) towards 0°, but this change occurred at a much slower rate (specified in Ref. 3) than the mutarotation during the period when the relative concentrations of I and II were changing appreciably. These facts, clearly stated in our papers, led to our conclusion of *high* 1,3-asymmetric induction.

The only assumption inherent in this discussion is that in our system, where appreciable amounts of both I and II are present at equilibrium, the isomerization reaction (in both directions) is going on even when equilibrium has been reached. It seems very strange indeed that conclusions based on such a fundamental physico-chemical law should be quoted as "unsupported assumptions".[1]

It is true that very important advances have been made by Cram et al.[1] by their use of reaction media containing

* Provided, of course, that optical rotation does not come from irrelevant compounds which may be present (from side reactions, impurities or the use of optically active catalysts or solvents). In such cases, due corrections have to be made. This remark has always been considered in our work.

isotopic reservoirs of the same pK_a as the conjugate acid of the catalyzing base. This fact has, however, nothing to do with our discussion,[2,3] since we have never made any statement about the degree of asymmetric induction in systems different from those experimentally investigated by us.

With regard to the steric direction of the rearrangement, *i.e.* the configurational relationship between reactants and products, we have always clearly pointed out that we had a lack of knowledge in our earlier work,[3] although this has been successively removed by later work,[5] as correctly quoted by Cram et al.[1] This has, of course, nothing to do with the question of the degree of asymmetric induction. It is quite explicitly stated [4] that it is our conclusions of high 1,3-asymmetric induction which are critizised by Cram and his co-workers. As explained in the present paper, our remarks in this respect, regarding the reaction I⇌II, have never "rested on unsupported assumptions".

In addition we may finally point out that the new value of the equilibrium constant for the methyl-*tert*-butyl system reported by Cram et al.[1] further strengthens our conclusion about the stereospecificity of this particular system.[3]

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