The method selected for these determinations was that used by Albert for the determination of the second dissociation constant of 3-aminopyridine[7-9] and which we previously used.[6]

It can be seen that the second pK_a' value of 1-aminoisoquinoline is in the same general area of those of 2-aminopyridine ($pK_a' = -8.1$) and 2-aminoquinoline ($pK_a' = -9.08$).[6] This is probably due to the close proximity of the two positive charges on the molecule and some interaction with the peri hydrogen atom. In the case of 3-aminoisoquinoline where there exists two adjacent positive charges, however, the second pK_a' is considerably less than would be expected for an amino substituent α to the ring nitrogen. At first glance, the value obtained for the second pK_a' of 4-aminoisoquinoline is larger than that for a β-amino group, *e.g.*, 3-aminoquinoline ($pK_a' = -0.40$),[6] but it may be pointed out that this value is in the general area of 3-aminopyridine ($pK_a' = -1.5$).[6]

In the cases of the 6- and 8-aminoisoquinoline and 5- and 7-aminoquinoline, the pK_a' value should be less than those found for 5- and 7-aminoisoquinoline and 6-aminoquinoline owing to the second protonation of the additional ionic resonance forms described by Albert.[5]

The ultraviolet spectra of the 1-, 4-, and 5-aminoisoquinolines in 0.10 *N* hydrochloric acid have been recorded by Ewing and Steck.[3] It seems that they were not concerned with pure electronic species, for they have a mixture of mono- and dications in the 5 isomer. The ultraviolet spectra of all the pure mono- and dicationic species of the aminoisoquinolines were determined in sulfuric acid of accurately known pH and H_0 values. The results, as well as those of other workers, are recorded in Table II.

The effect on the ultraviolet spectra of monoprotonation of the isomeric aminoisoquinolines has been described previously.[10] Upon diprotonation, 1-, 6-, and 8-aminoisoquinoline undergo small changes in all the absorption bands. Large hypsochromic shifts occur of the long wavelength band for 3-, 4-, and 5-aminoisoquinolines. 7-Aminoisoquinoline is partly anomalous in that it exhibits large shifts in all the ultraviolet absorption bands. The data in Table II for all of the isomers of the aminoisoquinolines show that the spectra of all their dications resemble those of the isoquinolinium ion, which is to be expected since the same phenomena occur with the aminoquinolines.[6]

Experimental Section

The experimental procedure used was that of Brown and Plasz[6] except for 1-aminoisoquinoline. A stock solution of this amine was prepared by weighing out 0.0721 g (0.0005 mol) of the solid and dissolving it in 500 ml of Baker Analyzed sulfuric acid. It was then diluted to the proper H_0 by the addition of water and/or sulfuric acid and the pK_a' value was determined as above.

The preparation and purification of the aminoisoquinolines is described below.

1-Aminoisoquinoline.—This compound was purified by vacuum sublimation at 85°, mp 120–121° (lit.[11] 122–123°).

3-Aminoisoquinoline.—This compound was purified by vacuum sublimation at 140°, mp 175–176° (lit.[12] 178°).

4-Aminoisoquinoline.—This compound was recrystallized twice from benzene, mp 107–108° (lit.[13] 108.5°).

5-Aminoisoquinoline.—This amine was recrystallized from benzene–hexane, vacuum sublimed at 105–110°, and recrystallized again from benzene–hexane, mp 129° (lit.[13] 128–129°).

6-Aminoisoquinoline.—6-Acetamidoisoquinoline (0.1 g) was refluxed with 10 ml of 20% sodium hydroxide in water for 1 hr. After cooling, the amine was crystallized, removed by filtration, and sublimed under vacuum at 190°, mp 217–217.5° (lit.[14] 217–218°).

7-Aminoisoquinoline.—This compound was prepared by the method of Osborn and Schofield.[10] Purification was accomplished by recrystallization from benzene and sublimation under vacuum at 160°, mp 203–204° (lit.[10] 204°).

8-Aminosoquinoline.—This compound was purified by vacuum sublimation at 100° followed by recrystallization from heptane, mp 173–174° (lit.[15] 173–174°).

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The Effect of Solvent and Cation on the Isomer Ratio of the Enolates of 3-Methylcyclohexanone[1a]

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If the enolization of an unsymmetrical ketone is carried out in the presence of excess ketone, the enolate mixture is thermodynamically controlled, whereas, if it is carried out with excess base, the mixture is kinetically controlled. The difference between kinetic and thermodynamic control has been demonstrated with a number of different ketones.[2-5] House and Kramer[6] have shown that the enolate mixture can be quenched with acetic anhydride to produce a mixture of enol acetates in the same isomer ratio as that of the original enolates.

This paper reports studies of the equilibrium and kinetic control of the enolization of 3-methylcyclohexanone and of the effect of changing the solvent or cation on the equilibrium mixture.

The preparation of the mixture of lithium enolates followed the procedure described by Huff[7] and was essentially similar to that previously described by other authors.[6] In a flame-dried apparatus, under nitrogen pressure, triphenyl methane was dissolved in the appropriate solvent, and to this a solution of phenyllithium in diethyl ether was added. 3-Methylcyclohexanone was then added with a syringe, and, after an appropriate length of time, the enolate mixture was quenched with excess acetic anhydride. In the case of equilibrium control, the ketone was in excess and the enolate mixture was stirred for over 18 hr before being

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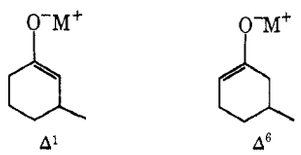
quenched. In the case of kinetic control, the tritylithium was about 20% in excess. The excess acetic anhydride was removed, the enol acetates were extracted with pentane, and the solution was distilled under vacuum. All the material which boiled below 150° at about 40 mm was collected and subjected to vapor phase chromatography. A 10 ft × 3/4 in. copper tube packed with Carbowax on firebrick (9% Carbowax) was used. The column was operated at 150°. The two peaks due to the enol acetate of 3-methylcyclohexanone were collected and identified on the basis of their nmr spectra. In particular, the vinyl proton peak for the Δ^1 isomer was a doublet, and for the Δ^6 isomer it was a triplet.



The two vpc peaks are clearly separated, but are right next to each other. Retention times were not determined; however, a peak due to 3-methylcyclohexanone was identified from the vpc of the pure ketone, and the Δ^1 peak always appeared at 1.52 and the Δ^6 peak at 1.64, the time that the 3-methylcyclohexanone peak appeared. The areas under the two peaks were assumed to be proportional to the amounts of Δ^1 and Δ^6 isomers.

Tritylsodium and tritylpotassium were prepared directly from the metal and triphenylmethane, in the appropriate solvent, according to the method of House and Kramer.[8] Otherwise, the procedure was the same as that with tritylllithium. Each experiment was performed in duplicate, and in no case was disagreement greater than 2%.

The solvents which were used were monoglyme (1,2-dimethoxyethane), diglyme [1,2-bis (2-methoxyethoxy)-ethane], triglyme [bis-2-(2-methoxyethoxy)ethyl ether], and tetrahydrofuran. Attempts to carry out the experiment in diethyl ether were unsuccessful. The enolization of 3-methylcyclohexanone in monoglyme, with tritylllithium as the attacking agent, led to 18% Δ^1 isomer and 82% Δ^6 isomer under kinetic control, which is probably indicative of partial blockage by the methyl group of the approaching base. Equilibrium control was studied under a variety of conditions and the results are summarized in Table I.

TABLE I

Solvent	Cation	Δ^1, %	Δ^6, %
Monoglyme	Li^+	46	54
Monoglyme	Na^+	43	57
Monoglyme	K^+	48	52
Diglyme	Li^+	47	53
Diglyme	Na^+	26	74
Triglyme	Li^+	47	53
Tetrahydrofuran	Li^+	42	58

Under equilibrium conditions, the enolization of 3-methylcyclohexanone leads to a nearly 50:50 mixture of Δ^1 and Δ^6 isomers in all cases but one. In every case, the Δ^6 isomer is favored over the Δ^1 isomer.

As far as the lithium enolates are concerned, it apparently makes little or no difference whether the solvent is monoglyme, diglyme, or triglyme. On the other hand, there appears to be a significant difference for the sodium enolates. This may be a reflection of variations in cation–solvent interactions. The small lithium cation is perhaps equally as well solvated by any of the glymes. With tetrahydrofuran, for which the carbon chain is pulled out of the way of the oxygen, the equilibrium is shifted towards the Δ^6 isomer to a greater extent than with the glyme solvents. Indeed, in a situation in which the coordinating ability of the glyme molecule is eliminated, Agami and Prevost[9] have found that monoglyme is actually a better base than diglyme toward forming a hydrogen bond with chloroform. Zakharkin[10] and coworkers reported that Mg^{2+} is more strongly solvated by monoglyme than by diglyme. It should be pointed out, however, that other authors[11] have interpreted their results in terms of increased Li–glyme interaction in going up the glyme series. The nature of the anion may be significant. The studies reported in this paper involved an enolate anion which should bond to lithium *via* an oxygen, whereas the studies by Chan and Smid[11] involved the fluorenyl anion separated from the cation by a glyme molecule. With the larger sodium ion, it may be possible for the glyme molecule to wrap itself around the cation, and hence diglyme may interact to a considerably greater extent than monoglyme with Na^+. That is, the Na^+–diglyme system may involve solvent-separated ion pairs, whereas the other systems reported here may involve contact ion pairs. Perhaps, since the oxygen–sodium bond is weaker than the oxygen–lithium bond, the diglyme molecule is able to insert itself between cation and anion in the former case, but not in the latter. There is agreement among authors[11-13] that glyme–Na^+ interaction increases as the glyme series is ascended.

Registry No.—3-Methylcyclohexanone Δ^1-enol, 33521-81-2; 3-methylcyclohexanone Δ^6-enol, 33521-82-3.

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Mechanism of the Formation of 1,8,*exo*-9,11,11-Pentachloropentacyclo-[6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$]dodecan-5-one in the Photolysis of Endrin

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Endrin (1) reportedly photolyzes to 2[1,2] and two isomers, 3 and 4.[3] Although proposed previously,[1] 2

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