The unique success of LiICA may be due in part to its high solubility. A majority of the bases studied appear to be only slightly soluble in tetrahydrofuran at low temperatures, while LiICA readily forms 1 *M* solutions in this solvent at −78°.

LiICA is equally successful in converting other esters to the corresponding enolates as shown by the data in Table I. In each case, quenching experiments indicate formation of the enolate is complete in less than 15 min at −78°. Attempts to generate several of the enolates at 0° resulted in appreciable condensation of the esters (see Table I). However, solutions of the enolates, prepared at −78°, remain stable at room temperature.

Tetrahydrofuran solutions of lithio ethyl acetate prepared according to eq 1 are inert to *n*-butyl iodide at a temperature of −78°. At higher temperatures, only modest yields (20–30%) of the alkylation product, ethyl hexanoate, are obtained. Apparently, condensation of the very reactive ester enolate with the product occurs at a rate which is comparable to that of the alkylation step. Use of the less reactive lithio *tert*-butyl acetate produces a 60% yield of the corresponding alkylation product, *tert*-butylhexanoate. Finally, this yield can be increased to 85% by adding the ester enolate to a solution of *n*-butyl iodide (50% excess) in dimethyl sulfoxide at room temperature. Examination of the crude reaction mixture by glpc demonstrated the complete absence of dialkylated product. Consequently, for the present we are assuming that ester condensation is the major factor limiting the yields.

Enolates derived from esters of substituted acetic acids appear to be less susceptible to condensation and here even the ethyl esters function satisfactorily as shown by the results presented in Table II.

Enolate anions derived from aldehydes or ketones are extremely useful reagents, undergoing a wide variety of synthetically useful reactions. It is possible that the present results will allow a similar versatility for the enolate anions derived from esters. We are actively investigating this possibility.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

acid prepared from lithium diisopropylamide.[13] Recovered *o*-toluic acid showed no detectable deuterium incorporation.

(13) P. L. Creger, *J. Amer. Chem. Soc.*, **92**, 1396 (1970).

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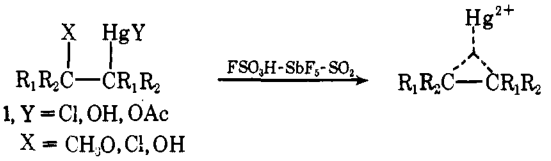
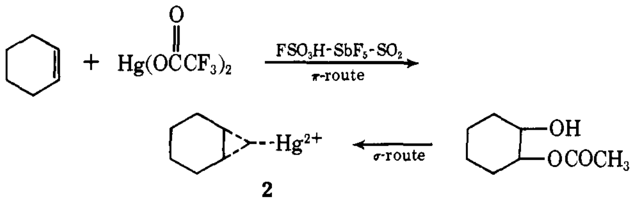
Organometallic Chemistry. II.[1] Direct Mercuration of Olefins to Stable Mercurinium Ions

Sir:

Mercurinium ions have been postulated as intermediates in the mercuration of olefins for many years.[2] Although considerable effort was directed toward direct observation of these ions, it was only recently that we were able to report formation of the first stable, long-lived mercurinium ions.[1] The ions were produced by treating organomercurials of the type **1** with $FSO_3H-SbF_5-SO_2$ solution. We now wish to report the first direct observation of mercurinium ions formed by the mercuration of olefins.



Mercuric trifluoroacetate is soluble in $FSO_3H-SbF_5-SO_2$ solution. When a cyclohexene–sulfur dioxide solution is added to a solution of mercuric trifluoroacetate in a slight excess of $FSO_3H-SbF_5-SO_2$, the cyclohexylenemercurinium ion **2** is formed. The pmr spectrum of this ion at −60° consists of a singlet at δ 8.35 (2 H), an unresolved multiplet at 3.10 (4 H), and a broad, unresolved multiplet at 2.12. The cmr chemical shift of C_1 and C_2 is +35.1 ppm (relative to CS_2). These spectral data are quite analogous to the data previously reported for the ethylene- and norbornylenemercurinium ions. Ion **2** may also be generated directly by addition of cyclohexene in SO_2 to either a solution of mercuric acetate in a slight excess of $FSO_3H-SbF_5-SO_2$ or a mixture of mercuric acetate and FSO_3H-SO_2. Alternatively, ion **2** may be formed by ionization of 2-acetoxymercuricyclohexan-1-ol in $FSO_3H-SbF_5-SO_2$ solution (eq 1). On warming to −30°, ion **2** decomposes.



(1)

The *cis*- (**3**) and *trans*-1,2-dimethylethylenemercurinium ions (**4**) may also be produced by either direct olefin mercuration or by ionization of the appropriately substituted organomercurial. Ion **3** has a pmr spectrum consisting of two broad singlets at δ 7.89 and 2.83 (with J_{CH_3-H} too small to be observed) while ion **4** shows a quartet at 8.23 and a doublet at 2.87 (J_{CH_3-H} = 4 Hz). Somewhat surprisingly, it is *erythro*-3-acetoxymercuributan-2-ol which ionizes to ion **3** in $FSO_3H-SbF_5-SO_2$ while *threo*-3-acetoxymercuributan-2-ol ionizes to **4**. These are the ions obtained by a cis elimination process. Furthermore, it is interesting to note that on warming to +25° for several minutes, ion **3** is converted to ion **4**. Spectral assignments are based on the results of the direct mercuration of *cis*- and *trans*-2-butene as well as comparison with the pmr spectra of the silver complexes of *cis*- and *trans*-2-butene.

Direct mercuration of norbornylene to give the norbornylenemercurinium ion **5** has also been achieved. The pmr spectrum of ion **5** produced in this manner is identical with the previously reported[1] pmr spectrum obtained on treatment of *exo-cis*-3-hydroxy-2-norbornylmercuric acetate with $FSO_3H-SbF_5-SO_2$.

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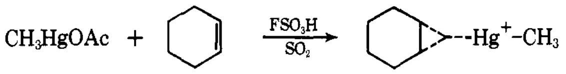
(1) Part I: G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **93**, 1261 (1971).

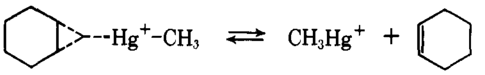
(2) For a recent review of the role of mercurinium ions in the mercuration of olefins see W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

It has also been possible to obtain the cyclohexylenemethylmercurinium ion **6** by the direct mercuration of cyclohexene. Methylmercuric acetate dissolves in FSO_3H–SO_2 to give CH_3Hg^+ (**7**) ($\delta_{CH_3} = 1.58$, $J_{^{199}Hg-CH_3} = 246$ Hz)[3,4] and protonated acetic acid. If equimolar mixtures of CH_3HgOAc in FSO_3H–SO_2 and cyclohexene in SO_2 are mixed, ion **6** is formed. The pmr spectrum of ion **6** at −90° is quite analogous to that of ion **2** consisting of a singlet at δ 7.27 (2 H, $J_{^{199}Hg-H} = 54$ Hz), a multiplet at 2.65 (4 H), a multiplet at 1.86 (4 H), and a singlet at 1.46 (3 H). In addition, singlets at 2.86 (due to protonated acetic acid) and 1.54 (due to excess CH_3Hg^+) may be observed.[5]



6

When a solution of ion **6** prepared in this manner is progressively warmed to −60°, the singlets at δ 1.54 and 1.46 merge into a single line while the peaks due to the ring protons of ion **6** broaden slightly. These observations are consistent with the equilibrium process shown below. If such a process were occurring, one would expect to see a considerable broadening of the mercury–proton satellites due to the exchange of cyclohexene between $CH_3{}^{199}Hg^+$ [6] and $CH_3{}^{200}Hg^+$ or $CH_3{}^{201}Hg^+$. In fact, at −60° the mercury–proton satellites have broadened to the point of virtual disappearance.



The same equilibrium process may be observed for ion **6** at other concentrations of cyclohexene and methylmercuric acetate. However, there are no spectral indications for the occurrence of such a process for either ion **2** or for any of the other ions studied.

Acknowledgment. Partial support of our work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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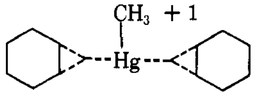
(3) CH_3HgClO_4 in water is thought to be $CH_3HgOH_2{}^+$ and has $J_{^{199}HCH} = 259$ Hz.[4] Thus, CH_3HgOAc in FSO_3H may well be CH_3HgOSO_2F. However, for simplicity the designation CH_3Hg^+ will be used. CH_3Hg^+ may well be generated from CH_3HgCl and SbF_5 in SO_2 or SO_2ClF. In these solvents, the coupling constants are $J_{^{199}HgCH} = 312$ Hz and $J_{^{199}HgCH} = 328$ Hz, respectively.

(4) J. V. Hatton and W. O. Schneider, *J. Chem. Phys.*, **39**, 1330 (1963).

(5) We have attempted to determine if **6** is actually the 1:1 complex indicated or is better represented as the 2:1 complex **6′** by a study of the stoichiometry of ion formation. In the solvent system used such determinations are extremely difficult and no conclusive results were so far obtained.



6′

(6) The natural abundance of ^{199}Hg is 16.86%.

(7) National Institutes of Health Postdoctoral Research Fellow, 1969–1970.

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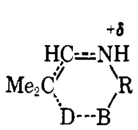
Bifunctional Catalysis of the Dedeuteration of Acetone-d_6 by 3-Dimethylaminopropylamine and 2-(Dimethylaminomethyl)cyclopentylamines[1]

Sir:

Species of the type B–R–NH_2 may catalyze the dedeuteration of isobutyraldehyde-*2-d* bifunctionally; the amino group may transform the aldehyde to an imine, which is in equilibrium with the corresponding iminium ion, and the basic group B may then remove the deuterium internally *via* a transition state such as **1**.



1

No evidence for bifunctional catalysis was found with amino acids of the type $^+H_3N(CH_2)_nCO_2{}^-$, where *n* was 1–5, as catalysts,[1c] but bifunctional catalysis was found with polyethylenimines.[2] This difference in behavior was attributed to the largely trans stereochemistry of the intermediate iminium ion. The amino acids used are not long enough for the basic carboxylate anion group to reach the deuterium atom when the iminium ion is trans, but the much higher molecular weight polyethylenimines are.

We have now studied diamines of the type $Me_2N(CH_2)_nNH_2$, where *n* is 2–5, as catalysts for the dedeuteration of isobutyraldehyde-*2-d* and of acetone-d_6 (which undergoes enzymatic dedeuteration *via* an iminium ion[3]), in which the problem of cis–trans isomerism of the iminium ion is avoided. The results of runs made at pH's where the concentration of the monoprotonated form of the diamine is a maximum (so that the rate of the bifunctionally catalyzed reaction will be a maximum if deuterium removal is rate controlling) are summarized in Figure 1. The first-order rate constants for the dedeuteration of ∼0.1 *M* isobutyraldehyde-*2-d* were obtained as described previously[4] in the presence of ∼0.13 *M* total diamine, and those for the transformation of 0.5 *M* acetone-d_6 to less deuterated species were obtained by a mass spectral method[5] in the presence of ∼0.05 *M* total diamine. Corrected apparent second-order rate constants, obtained by subtracting that part of the reaction due to hydroxide ions (less than 3%) and then dividing the first-order rate constants by the total diamine concentrations, are plotted logarithmically against the acidity constants of the diprotonated diamines. If the monoprotonated diamines are acting as simple basic catalysts such a Brønsted plot should approximate a straight line, but if bifunctional catalysis is occurring, a maximum might appear where the cyclic transition state has the optimum ring size. The ability of the monoprotonated diamines to catalyze the dedeuteration of isobutyraldehyde-*2-d* is seen to increase mono-

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(1) (a) This investigation was supported in part by Public Health Service Research Grants AM 06829-MCB and AM 10378; (b) Catalysis of α-Hydrogen Exchange. X. For Part IX see: (c) J. Hine, B. C. Menon, J. Mulders, and R. L. Flachskam, Jr., *J. Org. Chem.*, **34**, 4083 (1969).

(2) J. Hine, F. E. Rogers, and R. E. Notari, *J. Amer. Chem. Soc.*, **90**, 3279 (1968).

(3) W. Tagaki and F. H. Westheimer, *Biochemistry*, **7**, 901 (1968).

(4) *Cf.* J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Amer. Chem. Soc.*, **87**, 5050 (1965).

(5) J. C. Kaufmann, M.S. Thesis, The Ohio State University, 1969.