A Dynamic Nuclear Magnetic Resonance Study of the Mercury Keto–Enol Tautomerization in Bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedion-5-yl)mercury[1a]

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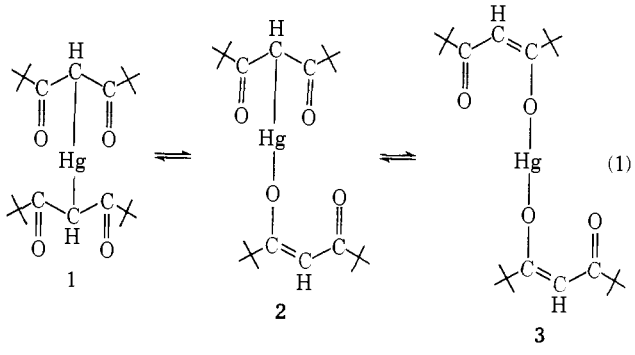
Abstract: The reaction of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (HFOD) with mercuric acetate gave, in quantitative yield, bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedion-5-yl)mercury (**4**). The mercury atom in **4**, which is initially bonded to both central carbon atoms of the two FOD nuclei, undergoes a unique and stereospecific intramolecular keto–enol tautomerization from a central carbon atom to a carbonyl oxygen in one of the FOD nuclei (**4** ⇌ **5**) in acetone-d_6 as studied by dynamic nuclear magnetic resonance spectroscopy (dnmr). The tautomers **4** and **5** were assigned their respective structures on the basis of their $J_{^{199}Hg-H}$ geminal couplings, which was 257 Hz for **4** (C–Hg–C) and 387 Hz for **5** (C–Hg–O) at −75° in acetone-d_6. A total line-shape computer analysis from +40 to −60° gave the following thermodynamic parameters for the process **4** ⇌ **5**. An Arrhenius plot of log k *vs.* $1/T$ gave an activation energy, $E_a^* = 9.90 \pm 0.4$ kcal/mol, and a frequency factor, log $A = 9.82 \pm 1.6$ sec^{-1}, while from an Eyring plot of log k/T *vs.* $1/T$, we obtained $\Delta H^{\pm} = 9.35 \pm 0.4$ kcal/mol and $\Delta S^{\pm} = -3.45 \pm 1.6$ eu. The free energy of activation at 25 and −60° was calculated to be $\Delta G^{\pm} = 10.35 \pm 0.4$ and 10.09 ± 0.4 kcal/mol, respectively. The factors affecting this interesting tautomerization will be discussed.

One of the most interesting findings that Musso and coworkers[2a–c] discovered in their study of the structure of bis(dipivaloylmethyl)mercury (**1**) was that the



mercury atom undergoes a keto–enol tautomerization (eq 1) as studied in chloroform-*d* solution utilizing nuclear magnetic resonance spectroscopy (nmr). However, this keto–enol tautomerization only occurs to a very small extent in **1** and was not unequivocally verified by these workers.[2a–c] Our recent work on the mechanistic aspects of β-diketone–mercury compounds[3a,b] prompted us to reexamine this mercury tautomerization.

In our present dynamic nuclear magnetic resonance spectroscopy (dnmr) study, we found that, indeed, tautomers **1** (>98%) and **3** (<2%) were evident but that tautomer **2** could not be detected. The limited solubility of compound **1** in other organic solvents only allowed us to further study (dnmr) the mercury tautomerization (eq 1) in 95% ethanol-d_6. We found, using 95% ethanol-d_6, nmr signals for **1** (~50%) and **2** (~50%) but could not substantiate their assignments because of experimental problems with this solvent. Unfortunately, 95% ethanol-d_6 masked the ^{199}Hg satellites of **1** and **2** and masked the signal of **3**. Thus, the diagnostic $J_{^{199}Hg-H}$ couplings[3a] which we utilized to identify bonding situations, such as HC–Hg–CH and HC–Hg–O, could not be ascertained in this solvent.

In view of these tenuous results on the mercury tautomerization in compound **1** (eq 1), we wish to present evidence for the first substantiated mercury keto–enol tautomerization occurring in bis(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedion-5-yl)mercury (**4**) as studied by dnmr in acetone-d_6.

Results

Mercury Keto–Enol Tautomerization (4 ⇌ 5). Since our results with compound **1** were tentative with regard to the question of mercury keto–enol tautomerization (see Experimental Section for details), we decided to prepare compound **4** with the hope that it would be a better model system for studying this interesting tautomerization.

We found that compound **4** in the solid state has the mercury atom bonded to the central carbon atoms of both FOD nuclei,[4] while in solution the mercury atom undergoes a facile keto–enol tautomerization. We were able to fully elucidate the process, **4** ⇌ **5** (eq 2), by dnmr.

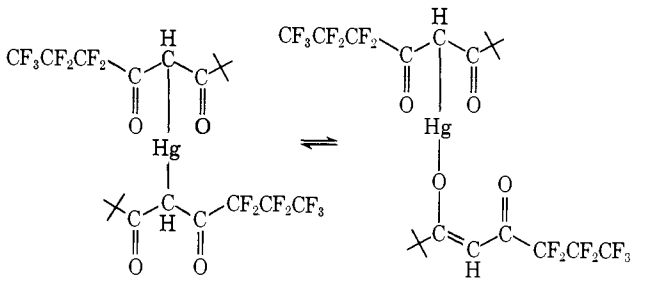
In Figure 1, we present the dnmr spectra of **4** ⇌ **5** in acetone-d_6 from +40 to −60°. This process (**4** ⇌ **5**) is totally reversible, and the key to determining what species are present, at slow-exchange rates, are the HC–Hg–CH and HC–Hg–X $J_{^{199}Hg-H}$ couplings for **4** and **5**. We have found that the bonding systems

(1) (a) Presented in part at the Pacific Conference on Chemistry and Spectroscopy, Oct 16–17, 1972, San Francisco, Calif., and the 6th International Conference on Organometallic Chemistry, Aug 12–17, 1973, University of Massachusetts, Amherst, Mass., Abstract 218; (b) address correspondence to Toxicology Laboratory, College of Natural Resources, 115 Wellman Hall, University of California, Berkeley, Calif. 94720.

(2) (a) H. Musso and K. Flatau, *Angew. Chem., Int. Ed. Engl.*, **9**, 379 (1970); (b) K. Flatau, Thesis, Universitat Bochum, 1970; (c) R. Allmann, K. Flatau, and H. Musso, *Chem. Ber.*, 105, 3067 (1972).

(3) (a) R. H. Fish, R. E. Lundin, and W. F. Haddon, *Tetrahedron Lett.*, 921 (1972); (b) R. H. Fish, R. E. Lundin, and C. Salentine, *J. Organometal. Chem.*, in press.

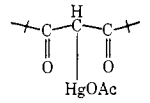
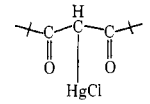
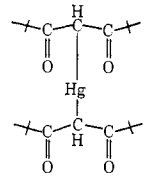
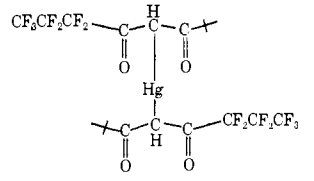
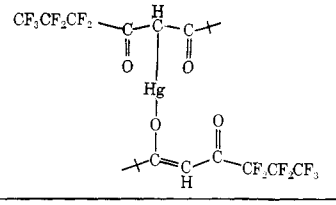
(4) S. Kint, J. R. Scherer, and R. H. Fish, manuscript in preparation.



4 5 (2)

HC–Hg–CH and HC–Hg–X, have diagnostic $J_{^{199}Hg-H}$ couplings, which allow us to unequivocally assign the tautomers (eq 2) to **4** and **5** (Table I). The $J_{^{199}Hg-H}$ in

Table I. $J_{^{199}Hg-H}$ Coupling Constants for Mercury–β–Diketone Compounds

Compd	$J_{^{199}Hg-H}$, Hz	Temp, °C
	314[a]	31
	330[a]	−30
	310[a]	−30
	221[a]	−40
	257[b]	−75
	387[b]	−75

[a] $CDCl_3$. [b] $(CD_3)_2C{=}O$.

the HC–Hg–X system was found to be approximately 1.5 times that in the HC–Hg–CH system. Figure 2 shows an ensemble-averaging experiment that was performed on the process **4** ⇌ **5** at −75° in acetone-d_6. The mercury satellites, each representing 9% of the total area of the main signals which they flank, were enhanced by repetitive scans under conditions where the process **4** ⇌ **5** was slow on the nmr time scale (Figure 1). The signal at 5.29 ppm has a $J_{^{199}Hg-H}$ coupling of 257 Hz at −75° and can readily be assigned to tautomer **4**, while the signal at 5.54 ppm has a $J_{^{199}Hg-H}$ of 387 Hz and can be assigned to the methine proton of tautomer **2**. The signal at 5.92 ppm has no mercury satellites flanking it, and we assumed that mercury does not couple to the enol hydrogen through oxygen.[2a–c] Thus

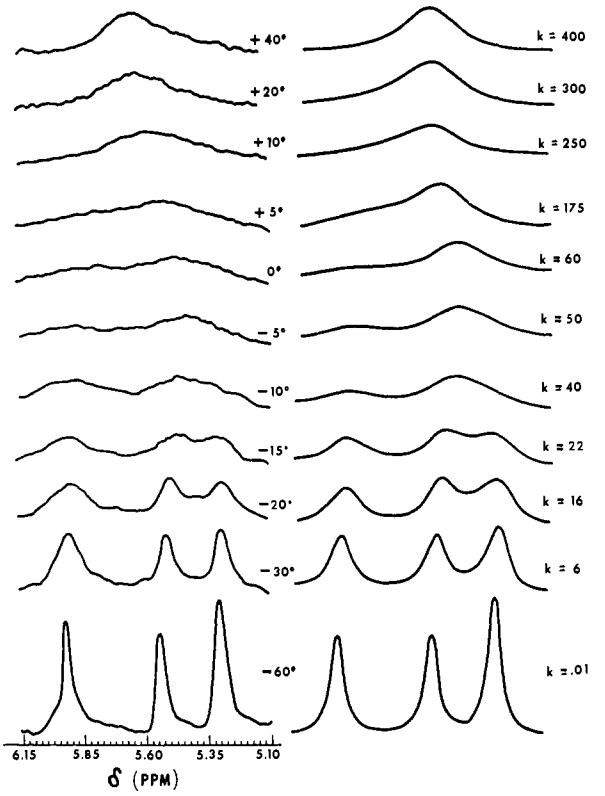


Figure 1. Dnmr spectra of **4** ⇌ **5** from +40 to −60° in acetone-d_6. The experimental spectra are on the left and the computer-simulated are on the right. The rate constants are in sec^{-1}.

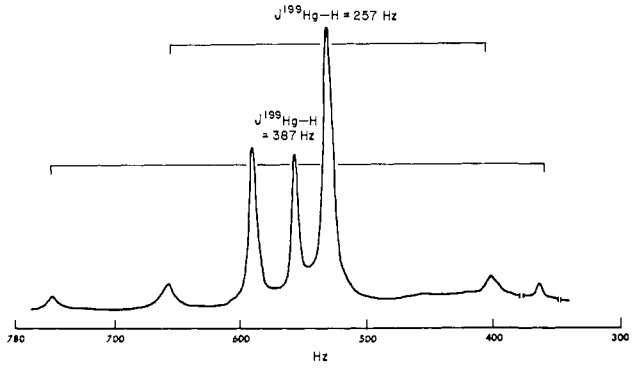
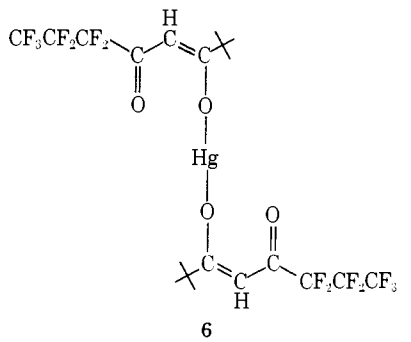


Figure 2. Ensemble averaging (100 scans) of the methine region at −75° in acetone-d_6 in order to determine $J_{^{199}Hg-H}$ couplings for **4** ⇌ **5**.

the signal at 5.92 ppm was assigned to the enol proton of tautomer **2**. Upon measuring the areas of the three signals, we were able to eliminate the tautomer where mercury has migrated to both oxygens (**6**). Thus if **6**



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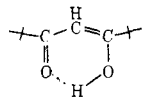
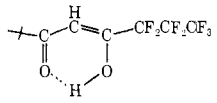
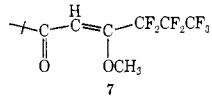
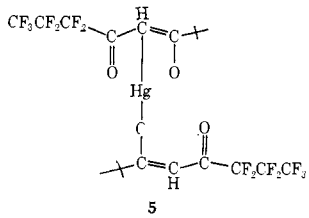
were present, its enol protons would have a signal at a similar chemical shift, if it tautomerizes the second time toward the *tert*-butyl group, and the ratio of area of the signal at 5.92 ppm to that at 5.54 ppm should indicate the presence of **6**. After adding 20% to the area of the signal at 5.54 ppm (^{199}Hg satellites reduce this signal area by 20%) at −60°, its area is indeed equal to that at 5.92 ppm, and this tends to eliminate the presence of tautomer **6**. The ratio of tautomers **4**:**5** at −60° is equal to 1.0, as calculated from the areas of signals at 5.29 ppm to those at 5.54 and 5.92 ppm.

We were also able to ascertain that the mercury atom tautomerizes specifically to the oxygen of the carbonyl bearing the *tert*-butyl group by using model compounds. These model compounds (Table II) were used in order to

Table II. Chemical Shifts of Enol Protons

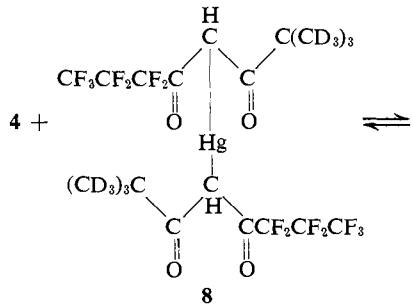
Compd[a]	Enol, O–C=CH– δ, ppm	Temp, °C
 HDPM	5.75 5.95	31 −60
 HFOD	6.32 6.53	31 −60
 7	6.43	31
 5	5.92	−60

[a] Nmr spectra run in acetone-d_6 (TMS).

establish a substituent effect on the chemical shift of the enol protons. It is obvious that the chemical shift for enol protons in HFOD and **7** are at lower field than that of HDPM and **5**. We conclude, therefore, that the mercury atom has tautomerized specifically to the oxygen of the carbonyl bearing the *tert*-butyl group. The intramolecular nature of this tautomerization (**4** ⇌ **5**) was proven by varying the concentration of **4** tenfold and then examining the line shapes of the nmr spectra from +10 to −60°. The line shapes for **4** ⇌ **5** were similar at concentrations of 1, 5, and 10% in acetone-d_6 from +10 to −60°; *i.e., the rates of interconversion were similar and first-order kinetics are upheld since the tautomerization* **4** ⇌ **5** *is concentration invariant and is thus totally intramolecular.*

It was also of interest to define whether intermolecular ligand-exchange reactions were occurring between molecules of compound **4**. We prepared the deuterated analog of **4**, where specifically the *tert*-butyl groups were totally deuterated **8**. Unfortunately, we could not use nmr spectroscopy, since nmr would not differentiate between the partially deuterated compound **9**, and the nondeuterated compound **4** (eq 3). We also could not use the mercury satellites of **4** at high temperature as a criterion for intermolecular ligand exchange; *i.e.*, lack of mercury satellites at the high exchange rates on the nmr time scale would indicate intermolecular exchange reactions taking place,[5a,b] since compound **4** was unstable over 50°. We thus reverted to mass spectrometry for this experiment.[6] Upon mixing compounds **4** and **8** in acetone (1:1) and then recording the mass spectrum, we observed parent ions for compounds **4** and **8** as well as for compound **9** in the ratio of 1:1:2 as expected for complete statistical ligand exchange. We also physically mixed the solids **4** and **8** together and ran the mass spectrum, which showed a similar result as mixing the solution. We therefore are not certain whether compounds **4** and **8** undergo an intermolecular exchange reaction in solution or in the gas phase in the ion source of the mass spectrometer. Interestingly enough, a similar result and conclusion was made by Breuer[7] upon mixing symmetrical mercury compounds and observing unsymmetrical compounds *via* mass spectrometry. Although we cannot, at this time, verify the presence or absence of intermolecular ligand exchange occurring at the fast exchange rates between molecules of compound **4** in solution, we are confident that this process would be negligible at the slow exchange rates on the nmr time scale and would not hinder our conclusions concerning the intramolecular nature of the mercury keto–enol tautomerization.

In order to fully elucidate this tautomerization (**4** ⇌ **5**), we wanted to obtain pertinent thermodynamic data. A total line-shape computer analysis of the experimental spectra (Figure 1) was accomplished using Binsch's DNMR3 line-shape program[8] which gives rate constants directly by visual overlap of the computer-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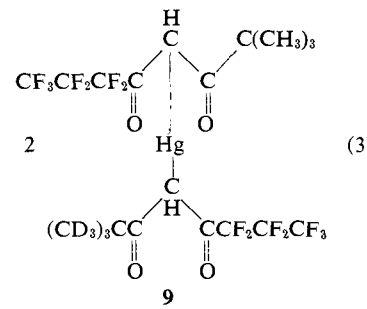
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(3)

(5) (a) A. N. Nesmeyanov, N. S. Kochetkova, L. A. Federov, and R. B. Materikova, *Dokl. Akad. Nauk SSSR*, **199**, 361 (1971); (b) P. West, M. C. Woodville, and M. C. Rausch, *J. Amer. Chem. Soc.*, **91**, 3649 (1969).

(6) R. H. Fish and W. F. Haddon, submitted for publication; a full account of the mass spectra of the mercury–β-diketone compounds will be presented in this paper.

(7) S. W. Breuer, T. E. Fear, P. H. Lindsay, and F. G. Thorpe, *J. Chem. Soc. C*, 3519 (1971).

(8) For an excellent review of this method, see G. Binsch, *Top. Stereochem.*, 3, 97 (1968).

Table III. Thermodynamic Parameters for the Mercury Keto–Enol Tautomerization $4 \rightleftharpoons 5$[a,b]

E_a*, kcal/mol	Log A, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu	$\Delta G^{\pm}$, kcal/mol
9.90 ± 0.4[c]	9.82 ± 1.6	9.35 ± 0.4[d]	-3.45 ± 1.6	10.35 ± 0.4 (25°) 10.09 ± 0.4 (−60°)

[a] The errors represent 95% confidence levels. [b] Solvent acetone-d_6 with TMS as internal standard. [c] Correlation coefficient is 0.965. [d] Correlation coefficient is 0.961.

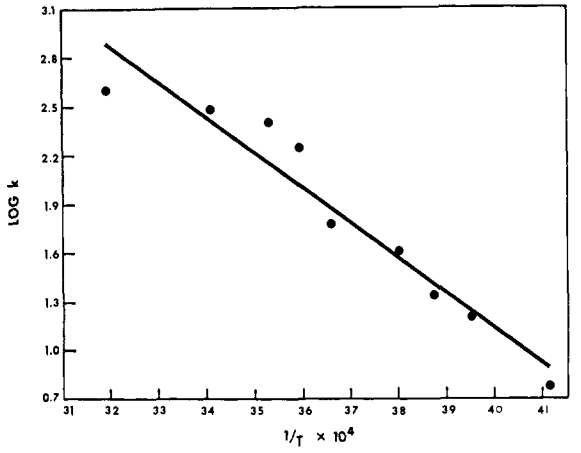


Figure 3. Arrhenius plot of log k *vs.* $1/T$ for $4 \rightleftharpoons 5$.

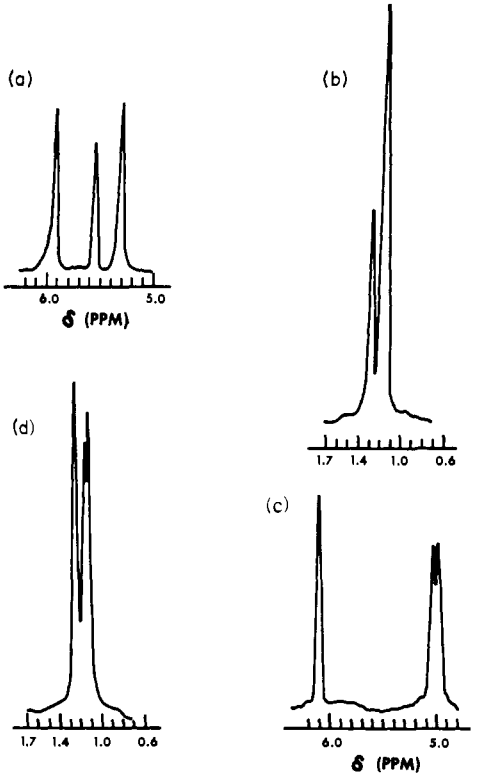


Figure 4. Methine and *tert*-butyl region in the nmr spectra of $4 \rightleftharpoons 5$ at −60° in acetone-d_6 [(a) top left, methine; (b) top right, *tert*-butyl] and chloroform at −30° [(c) bottom right, methine; (d) bottom left, *tert*-butyl].

simulated spectra with that of the experimental spectra. Table III summarizes the thermodynamic data we obtained from an Arrhenius plot of log k *vs.* $1/T$ (Figure 3); E_a* and log A and an Eyring plot of log k/T *vs.* $1/T$ which gave $\Delta H^{\pm}$ and $\Delta S^{\pm}$. The free energy of activation $\Delta G^{\pm}$ was calculated from the equation $\Delta G^{\pm} = \Delta H^{\pm} - T\Delta S^{\pm}$.

The nmr spectra of the *tert*-butyl protons were examined in acetone-d_6 and chloroform (Figure 4) at −60 and −30°, respectively. The nmr spectrum (−60°) in acetone-d_6 shows two *tert*-butyl groups at 1.15 and 1.28 ppm, while that in chloroform (−30°) shows three *tert*-butyl groups at 1.14, 1.17, and 1.26 ppm. We envision that there should be three different *tert*-butyl groups as the nmr shows in chloroform-*d*, with compound **4** having two equivalent *tert*-butyls and compound **5** having two different groups. We assign the signal at 1.14 ppm in chloroform-*d* to the two equivalent *tert*-butyl groups in compound **4** and 1.17 ppm to the *tert*-butyl group on the FOD nucleus in **5**, where the mercury atom is bonded to the central carbon atom, and the signal at 1.28 ppm to that *tert*-butyl group attached to the enol carbon–carbon double bond. This latter assignment is further corroborated by the fact that **7** (Table II) has a *tert*-butyl signal at 1.21 ppm, *i.e.*, upfield from an enol *tert*-butyl group. We also show the methine region in Figure 4 in chloroform-*d* and acetone-d_6 (similar to that in Figure 1). Compound **4** in both solvents showed three signals in the methine region; however, we were not able to perform a dnmr study of $4 \rightleftharpoons 5$ in chloroform-*d* because of a precipitation problem at the lower temperatures (−30 to −40°); this was unfortunate since a comparison of the thermodynamic parameters in two solvents would have been informative.

Discussion

It is interesting to discern the important factors affecting the tautomerization of $4 \rightleftharpoons 5$ and compare this process to compound **1** ($1 \rightleftharpoons 2 \rightleftharpoons 3$) and other metal–β-diketone compounds such as the platinum–trifluoroacetylacetone complex[9a,b] as well as other β-diketone compounds.[10,11a,b]

Since the tautomerization of $4 \rightleftharpoons 5$ is more facile than the corresponding process $1 \rightleftharpoons 2 \rightleftharpoons 3$ in acetone-d_6 or chloroform-*d*, we suggest that the inductive effect of the perfluoropropyl group contributes significantly to the lowering of the activation energy in the mercury tautomerization ($4 \rightleftharpoons 5$). We have attributed the interaction of the carbon–mercury σ electrons with the carbonyl groups of the β-diketone nucleus as being a major factor in the stability of carbon-bonded mercury–β-diketone compounds.[3a,b] Presumably, σ–π conjugation in the mercury–β-diketone systems **1** and **4** would be strongly influenced by inductive effects, and it is highly conceivable that the effect of the perfluoropropyl group would be to increase σ–π conjugation and

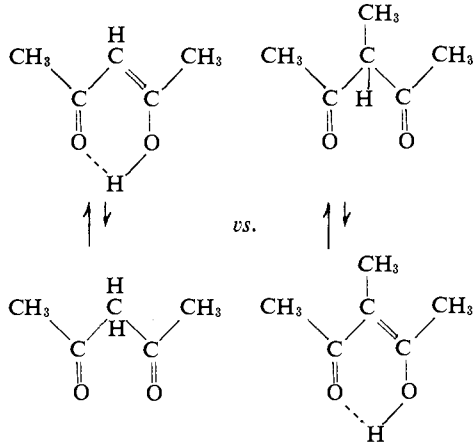
(9) (a) D. Gibson, J. Lewis, and C. Oldham, *J. Chem. Soc. A*, 1453 (1966); (b) J. Lewis and C. Oldham, *ibid.*, 1456 (1966).
(10) A. I. Koltson and G. M. Kheifets, *Russ. Chem. Rev.*, **40**, 773 (1971).
(11) (a) G. Allen and R. A. Dwek, *J. Chem. Soc. B*, 161 (1966); (b) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

thus increase mercury's ability to tautomerize in **4**.[12a-f] It is also reasonable that the inductive effect of the perfluoropropyl group contributes to the stereospecificity of the mercury migration. The oxygen of the carbonyl bearing the *tert*-butyl group is probably more nucleophilic, as compared with the oxygen of the carbonyl bearing the perfluoropropyl group; hence mercury migrates to the carbonyl oxygen with the higher electron density. Although steric factors may be important, their role in mercury tautomerizations is more difficult to ascertain. It is possible that the *tert*-butyl groups in **1** cause 1,3 nonbonding interactions upon tautomerization of mercury from carbon to oxygen. Thus by replacing a *tert*-butyl group with a perfluoropropyl group, this effect is alleviated to some extent.

Several papers have discussed substituent as well as solvent effects on the position of the keto–enol equilibrium in β-diketones.[11a,b]

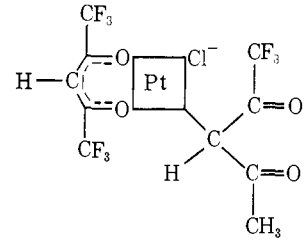
We compared the position of the keto–enol tautomerization in proton tautomerizations (β-diketones) with that of mercury tautomerizations (**1** ⇌ **2** ⇌ **3** and **4** ⇌ **5**), as the substituents were varied on the 1, 2, and 3 positions of the β-diketone nucleus.

The equilibrium constant (K = enol/keto) for acetylacetone is 3.65 (CCl_4, nmr),[11a] while that for a 2-methylacetylacetone goes to 0.39 (CCl_4, nmr).[11a] Thus, by placing an electron-donating group on the central carbon atom (2 position) of the acetylacetone nucleus, one can shift the equilibrium from the enol to the keto form.



This means that electron-donating groups stabilize the keto form (as in **1** ⇌ **2** ⇌ **3**) and destabilize the enol form.[11a] By substituting a trifluomethyl group for a methyl on the 1 position of the acetylacetone nucleus, the enol : keto ratio is raised to 32 from 3.65. Thus, electron-withdrawing groups on the 1 position of the β-diketone nucleus stabilize the enol tautomer, as we see also for **4** ⇌ **5**. In the two cases studied, the mercury is attached to the central carbon atom of the β-diketone nucleus and acts as an electron-donating substituent (σ–π conjugation),[3b] and this should stabilize the keto form (**4**), while electron-withdrawing groups attached to a carbonyl group, *i.e.*, perfluoropropyl, stabilize the enol form **5**. The result in our case reflects this difference at −60° with **4** and **5** being both present in a 1 : 1 (K = 1.0) tautomeric equilibrium mixture. Solvent effects[11a,b] can also influence proton tautomeric equilibrium. It has been shown that polar solvents (*e.g.*, DMSO) increase the keto tautomer, while nonpolar solvents (CCl_4, $CHCl_3$) increase the concentration of the enol tautomer.[11a,b] In the tautomeric equilibrium **4** ⇌ **5** we only see a qualitative change in the rate of interconversion but no change in the position of equilibrium since K = ~1.0. Thus, the dielectric effect which occurs in β-diketone proton tautomerization does not seem to be important in mercury tautomerization in both acetone and chloroform.

We wish to now compare **4** ⇌ **5** with other known carbon-bonded metal–β-diketone compounds. We preface these examples with the fact that none of the systems studied by other workers were dynamic processes observed *via* nmr. They were only concerned with metal bonding to carbon or oxygen, and since no mention of line widths were given, we presume that these processes are slow-exchange processes on the nmr time scale. The platinum complex of trifluoroacetylacetone was found[9a] to bond both to the carbon atom of one trifluoroacetylacetone nucleus and the oxygens of the other, **10**.

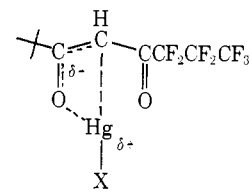


10

Variable-temperature nmr was not reported for **10**; however, signals of the methine proton at 5.65 ppm ($J_{^{195}Pt-H}$ = 120 Hz) and for the enol proton at 5.80 ppm were present at 37°. We can only assume that slow exchange at room temperature is taking place. In another example, a gold atom was also shown to be attached to the central carbon atom of the acetylacetone nucleus.[13] It is evident that mercury is more labile in metal keto–enol tautomerization as compared to platinum or gold. The reasons for this are influenced to a great extent by electronic and steric effects.

Solvent effects are more difficult to understand since most of the metal complexes will not dissolve in a wide range of organic solvents of varying dielectric constants.

Finally, we wish to dramatize the intramolecular nature of the mercury keto–enol tautomerization (**4** ⇌ **5**) by the fact that the carbon–mercury bond length is ~2.16 Å,[2c] and close proximity to the carbonyl oxygen should greatly facilitate tautomerization from carbon to oxygen **13**.



13, X = FOD

(12) (a) A. N. Nesmeyanov and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, **59**, 707 (1948); (b) A. N. Nesmeyanov, K. A. Perchskaya, A. N. Akramovich, and L. M. Miakova, *ibid.*, **121**, 660 (1958); (c) A. N. Nesmeyanov and I. I. Kritshaya, *ibid.*, **121**, 477 (1958); (d) T. G. Traylor, H. J. Berwin, L. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, 30, 599 (1972), and references therein; (e) R. D. Bach and P. A. Scherr, *J. Amer. Chem. Soc.*, **94**, 220 (1972); (f) R. D. Bach and P. A. Scherr, *Tetrahedron Lett.*, 1099 (1973).

(13) D. Gibson, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 367 (1970).

The facility of this tautomerization is also consistent with the low activation energy we found; however, the only comparison we can make of our thermodynamic data is to those of β-diketone compounds themselves.[11a] The enthalpy of conversion in keto–enol tautomerization of β-diketones was found to be in the order of $-\Delta H = 2$ to 10 kcal/mol. The lower enthalpy values for β-diketone keto–enol tautomerization are probably related to the stabilization of the enol form *via* intramolecular hydrogen bonding. However, it was interesting that the bulky *tert*-butyl group raised the enthalpy of conversion to 4.9 kcal/mol over the methyl-substituted derivative which had a value of 2.8 kcal/mol. The substitution of an electron-donating group, *i.e.*, methyl, on the central carbon atom of the β-diketone nucleus lowered the enthalpy of conversion to 1.3 kcal/mol, while an electron-withdrawing group, *i.e.*, chloro, raised ΔH to 5.9 kcal/mol. It is apparent that metal–β-diketone, *i.e.*, mercury, derivatives have higher enthalpy values and that comparisons to β-diketone systems are complicated by steric and electronic factors. Hopefully, other workers will gather thermodynamic data on other metal–β-diketone tautomerizations that will allow a more relevant evaluation of the role of the metal in these keto–enol tautomerizations.

Experimental Section

Materials and Spectroscopic Equipment. The dynamic nuclear magnetic resonance spectra were recorded on a Varian HR 100 with internal field frequency lock and equipped with a variable-temperature probe and a 1024 channel signal averager.

The Raman spectral data reported in the Experimental Section, but to be discussed elsewhere,[4] were recorded on a Spex 1401 with a Coherent Radiation argon-ion laser operating at 5148 Å. Similarly, the infrared (mid and far) were recorded on a Cary-White 90 (KBr) and a Perkin-Elmer IR II (Nujol with polyethylene plates), respectively. The uv spectral data were recorded on a Cary 15 with a variable-temperature cell. The mass spectral experiments were obtained on a CEC 21-110A (Du Pont) instrument. The HFOD was obtained from Pierce Chemical Co. and used without further purification, while trimethyloxonium hexafluorophosphate was obtained from Cationics, Inc.

Preparation of 4. In a flask was placed 3.19 g (0.01 mol) of mercuric acetate in 200 ml of 95% ethanol. To this was added dropwise with stirring 6.0 g (0.02 mol) 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione in 50 ml of 95% ethanol. After addition, a clear solution was present, and to this was added 200 ml of distilled deionized water. A precipitate formed immediately, and this was collected, washed with ~50% ethanol, and dried to give 7.8 g (100%) of product. The analytical sample was prepared by dissolving the material in a minimum of 95% ethanol and refrigerating. This gave pure compound, mp 117–119°.

See nmr data in text (Figures 1 and 3); Raman (solid) 1726 (s) and 1656 (s) (C=O), 538 (m), 465 (w), 420 (m) cm^{-1} (C–Hg); far-ir (Nujol) 633 (m), 578 (m), 534 (s), 490 (m), 293 (s), and 275 (s) cm^{-1}; mid-ir (KBr) 1726 (m), 1719 (m), 1650 (sh), and 1630 (m) cm^{-1} (C=O); uv $\lambda_{max}^{CHCl_3}$ 292 nm (ε 11,200) at room temperature, while lowering the temperature to −33° showed two absorptions at 292 and 250 nm; HFOD had $\lambda_{max}^{CHCl_3}$ 292 nm (ε 9200).

Anal. Calcd for $C_{20}H_{20}F_{14}O_4Hg$: C, 30.37; H, 2.55; Hg, 25.36. Found: C, 30.4; H, 2.65; Hg, 25.3.

Dnmr Study of 4. The sample of **4** for nmr analysis was also recrystallized before use because of the instability, which caused the compound to yellow slightly. The solutions at concentrations of 1, 3, 5, or 10% by weight were prepared by accurately weighing **4** into a clean and dry nmr sample tube. Then 0.5 ml of acetone-d_6 (TMS) was added in a drybox. The dnmr spectra were recorded twice from +40 to −75° at 5° intervals. Care should be taken to maximize signal to noise but not to saturate spectrum signals which can cause erroneous line shapes to occur. The temperature (±2°) was standardized using a methanol thermometer. The dnmr spectra were simulated using Binsch's DNMR3 program utilizing a CDC 6600 computer with a Calcomp plotter located at the Lawrence Berkeley Radiation Laboratory, Berkeley, Calif. At static conditions (−60° and lower), we assumed that the signals at 5.54 and 5.92 ppm were equal in population since the ^{199}Hg satellites would have complicated the analysis. We then varied T_2 and the populations at all temperatures in order to fit the correct chemical shifts and line shapes for the simulated spectra to those of the experimental spectra. The least-squares regression analysis on the log k *vs.* $1/T$ and log k/T *vs.* $1/T$ plots were performed on an IBM 1800 by Dr. Bruce Mackey.

Dnmr Study of 1 ⇌ 2 ⇌ 3. We carefully repeated Musso's experiment[2a,b] on compound **1** in chloroform-*d* from 37 to −40° and found only two signals. The signal (−30°) at 4.89 ppm (~98%) did indeed possess two ^{199}Hg satellites with $J_{^{199}Hg-H}$ being 221 Hz; however, the signal at 5.75 ppm (−30°) had no ^{199}Hg satellites flanking it. This corrects Musso's statement[2a,b] that both tautomers **2** and **3** had similar chemical shifts. Tautomer **2**, which should have a signal between 5.16 and 5.30 ppm, was not evident.

The solubility of **1** limited the dnmr work to 95% ethanol-d_6. A dnmr study in this solvent from 31 to −90° was performed. The rates of interconversion were faster in 95% ethanol-d_6 than in chloroform-*d* since the sharp singlet at 5.05 ppm did not broaden until −60°. At −90°, this broad signal splits into two signals at 4.89 and 5.35 ppm. Unfortunately, HDO had a chemical shift at 5.75 ppm at −90°, which is exactly where tautomer **3** should have its signal. We then enhanced the signal at 4.89 ppm (**1**, ~50%) by ensemble averaging, but interfering solvent signals prevented us from being able to unequivocally identify (^{199}Hg satellites) tautomers **1** and **2**.

Preparation of 7.[14] In a one-necked, 100-ml, round-bottom flask were placed 1.68 g (5.7 mmol) of HFOD and 1.3 g (6.3 mmol) trimethyloxonium hexafluorophosphate in 75 ml of methylene chloride. To this stirring mixture was added 1.0 ml (5.7 mmol) of diisopropylethylamine, and the reaction mixture was stirred at room temperature for 24 hr. The methylene chloride solution was then extracted with three 50-ml portions of 1 *N* hydrochloric acid, three 50-ml portions of 1 *N* potassium bicarbonate, and a single 50-ml portion of a saturated sodium chloride solution. The methylene chloride layer was then dried over anhydrous magnesium sulfate, and then the methylene chloride distilled at atmospheric pressure. The resulting yellow liquid was gas chromatographed on a 6 ft × 1/8 in. SE 30 column (tc detector) to show two peaks in the ratio of 40:60. The first peak was starting HFOD and the second peak desired **7**. This was confirmed by a nmr spectrum of the mixture. The product was collected *via* preparative gas chromatography using a 20 ft × 3/8 in. SE 30 column on Chromosorb P at 110° (flow rate 120 ml/min). Samples of 200 μl were easily separated. The pure **7** had a nmr spectrum which was consistent with its assigned structure (see text): *tert*-butyl, 1.21 (singlet 9 H); OCH_3, 3.85 ppm (singlet 3 H); enol, OC=CH, 6.43 ppm (singlet 1 H) in acetone-d_6 with TMS as the internal standard. Infrared (neat): 1695 (s, C=O) and 1630 (w, C=C) cm^{-1}. Raman (liquid): (w, C=O) and (s, C=C) cm^{-1}. Mass spectrum $M\cdot^+$, *m/e* 310 (0.08%); $M\cdot^+ - 57$, *m/e* 253 (24.62%). *Anal.* Calcd for $C_{11}H_{13}F_7O_2$: C, 42.6; H, 4.10. Found: C, 42.6; H, 4.50.

Mass Spectrometry Exchange Experiments. Compound **8**[6] was prepared similarly to compound **4**. Thus, 3 mg each of **8** and **4** were dissolved in 1 ml of acetone. A 10-μl aliquot of the above solution was placed in a capillary and then introduced into the mass spectrometer (direct probe). The source temperature was 180° and the parent ion region was scanned. We found parent ions ($M\cdot^+$) for $(FOD)_2Hg$-d_0 *m/e* 792 (^{202}Hg), $(FOD)_2Hg$-d_9 *m/e* 801, and $(FOD)_2$-Hg-d_{18} *m/e* 810 in the ratio of 1:2:1 as expected for complete statistical mixing of ligands. Upon physically mixing equal quantities of **8** and **4** in the solid state and then using the direct probe technique, we also observed similar results as the above described solution experiment.

Acknowledgments. The author wishes to express his deep appreciation to Ms. Rosalind Wong for her patience in converting DNMR3 for use on the CDC 6600 computer system and to Dr. R. Lundin and C. Salentine for help in the time-averaging experiment and several of the dnmr runs. I also wish to express my thanks to Ms. Saima Kint for running all the infrared and Raman spectra and to Dr. J. Scherer for help in interpretation of these spectra, as well as to Dr. W. Haddon for performing the mass spectral experiments.

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