tional barrier entropy changes. However, it is more likely that the reversal is caused by electronic effects. The most probable explanation would be the higher polarizability[8] of the larger halo substituents. The atomic polarizabilities α of F, Cl, and Br are 0.53, 2.61, 3.79 Å^3, respectively.[9] The distance r in the acetate ions between one of the O atoms and the halogen substituent may be estimated to be 2.69, 2.85, and 2.89 Å, respectively. Assuming that one-half electronic charge is on the O atom, one calculates, using the electrostatic equation for potential energy $u = \alpha e^2/2r^4$, the negative energies 0.5, 1.6, and 2.2 kcal/mol, respectively. Somewhat larger energies can be obtained with bond polarizabilities.[10] The energy differences in both cases would seem sufficient, to explain the gas-phase results, *only* if the inductive effect, in the absence of polarization, changes (increases) very little from Br to F. There is some independent evidence that this is so. Thus the aqueous acidity of meta-halo-substituted benzoic acids and phenols does not increase from Br to F as might have been expected but increases from F to Cl ≈ Br then decreases slightly for I. Gas-phase acidities of meta-substituted phenols determined recently by McIver[11] also increase in the order F, Cl, Br. Since the stabilizing effect of the substituents in the gas phase increases in the order F, Cl, Br, the higher aqueous acidity of the fluoroacetic acid must be due to solvent effects. Since the halo atom acquires a small negative charge, one water molecule might be hydrogen bonding to it. This bonding interaction will be weaker for the larger Br atom than the smaller F.

The values of Table Ic show that in general the second halogen atom leads to a smaller increase of acidity than the first. This effect is observed also in solution and is generally expected. An exception is the change between difluoro- and trifluoroacetic acid where the gas-phase acidity difference is the same as that between mono- and difluoro-. We are not certain whether this is a true result or an experimental error.

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(8) The effect of polarizability of alkyl groups on gas-phase acidities of alcohols was first suggested by J. I. Brauman and Larry K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).

(9) S. Fraga, K. M. Saxena, and B. W. N. Lo, *Atomic Data*, **3**, 323 (1971).

(10) J. D. Hirshfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1964, p 947.

(11) R. T. McIver, private communication.

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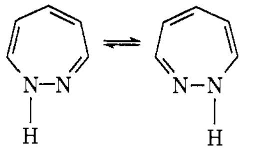
Iron Tricarbonyl Complexes of 1(1*H*),2-Diazepine and Methyl Substituted Derivatives. Novel Fluxional Organometallic Compounds

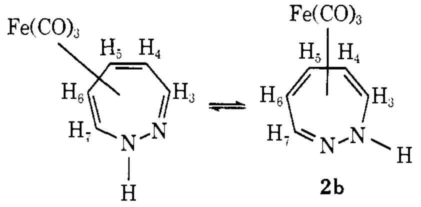
Sir:

The unsubstituted molecule 1(1*H*),2-diazepine has so far escaped synthesis.[1] As a vinylogous analog of pyrazole, 1(1*H*),2-diazepine is a nonaromatic polyene for which N–H tautomerism, represented by structures **1a** → **1b**, is expected.[2]

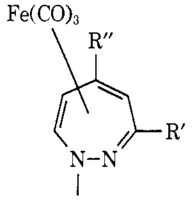
Streith first prepared 1-acylated Fe(CO)$_3$-1(1*H*),2-diazepine complexes.[1b] Our interest in 1,2-diazepines and their complexes[1a, 3–5] led us to investigate the trapping of **1** as an iron tricarbonyl analog of *N*-acetyl-1(1*H*),2-diazepine as a first step in studies on the chemistry of the complexed heterocycle. We describe herein the synthesis of 1(1*H*),2-diazepine iron tricarbonyl (**2**) and the methyl substituted derivatives **3a**,**b**, the conversion of **2** to the *N*-benzyl complex **3c**, and a novel type of fluxional behavior of the N–H complexes **2** and **3b** which is a direct consequence of the tautomeric behavior of the diazepines. Thermodynamic parameters ($\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$) calculated from line-shape analysis of the nmr spectra are of interest in the wider contexts of molecular tautomerism[6] and fluxionality.[7]



1a **1b**



2a **2b**



- **3a**, R = H; R′ = CH$_3$; R″ = H
- **b**, R = H; R′ = H; R″ = CH$_3$
- **c**, R = CH$_2$C$_6$H$_5$; R = R′ = H
- **d**, R = COCH$_3$; R′ = R″ = H
- **e**, R = COOC$_2$H$_5$; R′ = R″ = H
- **f**, R = COCH$_3$; R′ = CH$_3$; R″ = H
- **g**, R = COCH$_3$; R′ = H; R″ = CH$_3$

Treatment of **3e**[1a] with sodium ethoxide in ethanol (0°, 1 hr) gave, after chromatography on alumina, yellow crystals of **2**[8] (60%): mp 121°; ir (C_6H_{14}) 3275 m (N–H), 2052 (s), 1990 (s), 1976 (s) cm^{-1}. The mass spectrum of **2** showed a parent ion at *m/e* 234 together with ions at *m/e* 206, 178, and 150 from successive loss of three CO groups and at *m/e* 94 due to the diazepine $[C_5H_6N_2]^+$ ion. A Mössbauer spectrum of **2** (δ

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(1) For recent summaries of work on 1,2-diazepines see (a) A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, **35**, 433 (1970); (b) J. Streith and J. M. Cassal, *Bull. Soc. Chim. Fr.*, 2175 (1969); (c) G. Taurand and J. Streith, *Tetrahedron Lett.*, 3575 (1972); (d) F. D. Popp and A. C. Noble, *Advan. Heterocycl. Chem.*, **8**, 22 (1967).

(2) L. Hunter, *J. Chem. Soc.*, 806 (1945).

(3) G. Kan, M. T. Thomas, and V. Snieckus, *Chem. Commun.*, 1022 (1971).

(4) A. J. Carty, G. Kan, D. P. Madden, V. Snieckus, and M. Stanton, *J. Organometal. Chem.*, **32**, 241 (1971).

(5) A. J. Carty, D. P. Madden, and T. Birchall, *Inorg. Chem.*, **11**, 1453 (1972).

(6) A. R. Katritzky and J. M. Lagowski, *Advan. Heterocycl. Chem.*, **1**, 312, 341 (1963); **2**, 3, 27 (1963).

(7) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

(8) Satisfactory elemental analyses have been obtained for all compounds described herein.

Table I. Nmr Spectral Parameters for 1(1*H*),2-Diazepine Complexes[a]

	Couplings[b]								
Compd	J_{34}	J_{35}	J_{45}	J_{46}	J_{56}	J_{57}	J_{67}	J_{61}	J_{71}
2	6.4	0.3	6.6	1.8	3.9	1.6	6.1	0.5	4.5
2 (N–D)	6.4	0.3	6.6	1.8	4.0	1.6	6.0		
3a	0.25 (±0.1)	~0.0	7.0 (±0.1)	1.65 (±0.1)	4.5 (±0.1)	1.7 (±0.1)	6.1 (±0.1)	~0.0	~0.0
3b	6.2	~0.0	0.5	2.0 (±0.2)	0.3	0.2	6.3	0.4	4.5

		Positions (ppm)					
Compd	Temp, °C	1	3	4	5	6	7
2	−31.5	7.26	6.89	3.64	4.67	4.05	5.60
2 (N–D)	−39.5		6.89	3.67	4.68	4.09	5.61
3a	+35	6.15	2.16	3.60	4.67	4.0	5.75
3b	−40	6.69	6.78	8.58	1.79	4.0	5.28

[a] In $CDCl_3$ at 100 MHz. [b] All couplings are taken to be positive. The uncertainty in the 3-bond couplings is ±0.2 Hz, while the 4-bond couplings are uncertain to ±0.4 Hz unless otherwise specified. These large error bounds are due to the statistical uncertainty of measurement in very dilute chemically exchanging systems.

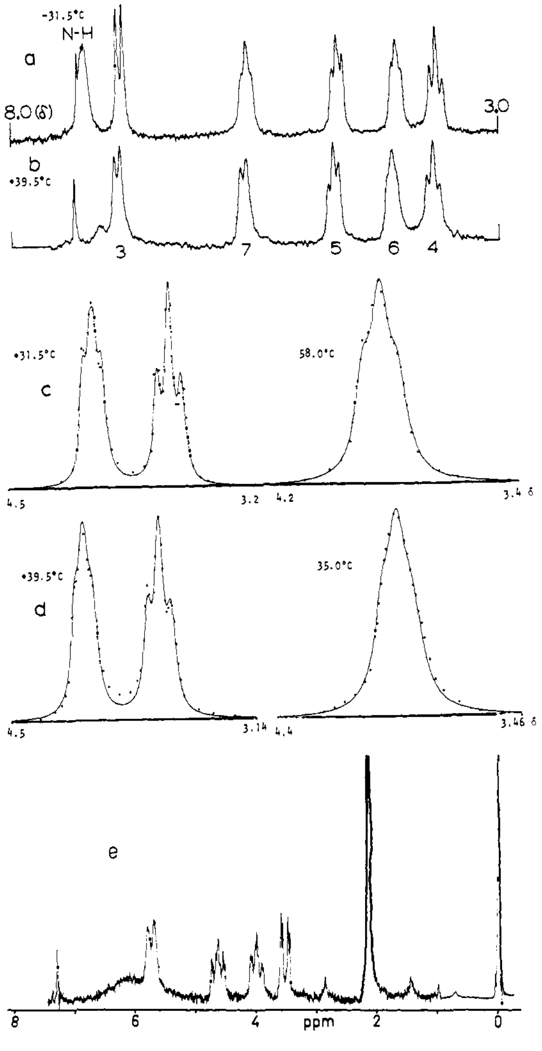

Figure 1. Slow-exchange, 100-MHz nmr spectra ($CDCl_3$) of **2** at −31.5° (a) and N-deuterated **2** at −39.5° (b). Fitted spectra for protons 4 and 6 in **2** (c) and N-deuterated **2** (d) at two different temperatures. Experimental crosses are superimposed on the computer simulated fit. A 60-MHz nmr spectrum ($CDCl_3$) of **3a** at 35° (e).

0.28 mm sec^{-1}, Δ = 1.27 mm sec^{-1})[9] gave parameters characteristic of (diene)Fe(CO)$_3$ complexes.[4] The formulation as the 1(1*H*),2-diazepine complex **2** was confirmed by the ^{1}H nmr spectra of **2** and the deuterated (N–D) derivative at −39.5° (Figure 1). The nmr assignments in Table I were initially deduced from decoupling experiments[10] and established by computer simulated line-shape analysis using a modified version of GPLONK designed for nmr analysis of multisite exchange phenomena.[11] The 3-bond couplings for **2** are closely similar to those of **3d**,[4] with $J_{4,5}$ largest and $J_{5,6}$ smallest in each case. Thus **2** and **3d** have essentially the same geometry. Compound **2** was quantitatively converted into **3d** by sodium hydride and acetyl chloride in THF at room temperature and into **3c** (yellow oil, 40%; ir (C_6H_{14}) ν(CO), 2050 (s), 1987 (s), 1974 (s) cm^{-1}; mass spectrum, M$^+$ 324) *via* reaction with *n*-butyllithium and benzyl bromide in ether. Similar reaction sequences **3d** → **2** → **3e** have been carried out.

The room temperature nmr spectrum of **2** consists of a high field singlet at δ 3.88 due to the coalescence of resonances of H_4 and H_6, which sharpens to a triplet at +70° and a broad H_7 resonance at δ 5.80 which overlaps with a broad peak at δ 6.86 due to the N–H and H_3 protons. The latter resonances coalesce on raising the temperature. The temperature dependence of the nmr spectrum can be ascribed to simultaneous tautomerism and fluxionality **2a** $\rightleftarrows$ **2b**. The process **2a** $\rightleftarrows$ **2b** is a true fluxional process; both **2a** and **2b** have equal energy contents and the Fe(CO)$_3$ moiety moves over a five carbon chain. The hydrogen tautomerism is analogous to that in pyrazole,[12] where, however, the tautomeric interconversion is so rapid that the existence of distinct, equivalent tautomers cannot be demonstrated.[13] Analysis of nmr data for **2** and the N–D derivative yielded free energies and entropies of activation (N–H $\Delta G^{\ddagger}$ (25°) = 13.7 ± 0.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −6.2 ± 4.0 cal deg^{-1} mol^{-1}; N–D $\Delta G^{\ddagger}$ (25°) = 13.4 ± 0.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −6.9 ± 4.0 cal deg^{-1} mol^{-1}) which were the same, within experimental error.

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(9) With respect to sodium nitroprusside standard.

(10) On irradiation of H_3 the resonance due to H_4 collapsed to a doublet and the H_7 resonance decreased to ~25% of its initial intensity. The latter observation is indicative of a process in which sites 3 and 7 are interchanged (*vide infra*). The resonance due to H_6 collapsed to a doublet on irradiation of H_7 while H_3 simultaneously decreased in intensity.

(11) L. W. Reeves and K. N. Shaw, *Can. J. Chem.*, **48**, 3641 (1970).

(12) A. N. Kost and I. I. Grandberg, *Advan. Heterocycl. Chem.*, **6**, 347 (1966).

(13) This type of tautomerism, in which the proton is not localized and the existence of distinct tautomers can only be inferred or rejected, has been described as mesohydric tautomerism,[2] protomerism,[14] or prototropy.[6]

(14) H. Zimmermann, *Angew. Chem. Int. Ed. Engl.*, **3**, 157 (1964).

We interpret this result to mean either that deuterium substitution has little effect on the tautomeric equilibria or that $\Delta G^{\ddagger}$ for the tautomeric hydrogen shift is small compared with the total free energy of activation.[15] It is of interest that $\Delta G^{\ddagger}$ compares favorably with $\Delta G^{\ddagger}$ for fluxional processes in polyolefin–iron complexes.[7] Nevertheless the proton shift is a necessary prerequisite for fluxionality in these 1(1*H*),2-diazepine complexes since **3d–g** are not dynamic at room temperature and attempts to induce fluxionality by raising the temperatures to +100° were unsuccessful. In contrast to azepine complexes,[16,17] dynamic behavior is not expected for iron tricarbonyl complexes of N-substituted 1(1*H*),2-diazepines since the two alternative π sites are nonequivalent.

Further insight was provided by the synthesis of **3a** (yellow crystals, 85%; mp 99°; ir (C_6H_{14}) ν(CO) 2050 (s), 1987 (s), 1974 (s) cm^{-1}; mass spectrum M$^+$ *m/e* 248) from **3f**[4] and **3b** (yellow crystals, 62%, mp 97°; ir (C_6H_{14}) ν(CO) 2049 (s), 1987 (s), 1973 (s) cm^{-1}) from **3g**. Nmr spectral parameters are given in Table I. **3b** exhibited an nmr spectrum characteristic of a dynamic molecule ($\Delta G^{\ddagger} = 15 \pm 0.4$ kcal mol^{-1}) while **3a** gave a well-resolved nonfluxional temperature-invariant spectrum. For **3a** one tautomer, that in which the $Fe(CO)_3$ moiety is bonded to carbon atoms C_4–C_7, is stabilized.

These results suggest that π complexation may be of general utility for modifying tautomeric equilibria. Furthermore dynamic behavior can be expected for π complexes of other heterocycles exhibiting tautomerism.

Acknowledgment. We thank the National Research Council of Canada for financial support.

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(15) The entire process, *viz.*, hydrogen migration, ring double bond shift, and movement of the $Fe(CO)_3$ moiety may be concerted.

(16) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, 34, 2866 (1969).

(17) H. Günther and R. Wenzl, *Tetrahedron Lett.*, 4155 (1967).

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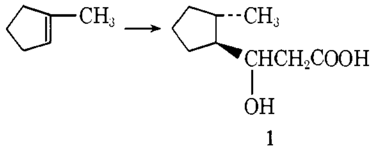
An Intramolecular Michael Reaction Involving Borate Complexes. A Novel Synthesis of β-Hydroxycarboxylic Acids

Sir:

We wish to report an intramolecular version of the Michael reaction involving borate complexes, which provides a novel route to β-hydroxycarboxylic acids from olefins with the possibility of incorporating stereochemically defined groups in the β position (for example eq 1).

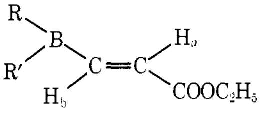


(1)

1

The conjugate addition of organic moieties to α,β-unsaturated carbonyl derivatives, such as the Michael reaction, represents one of the most important classes of carbon–carbon bond-forming reactions.[1] Recently, it has been established that trialkylboranes undergo conjugate addition *via* a free-radical mechanism.[2-4] Although the reaction appears to be of wide applicability, satisfactory reaction conditions have not so far been found to induce successful conjugate addition to α,β-unsaturated carboxylic acids and their derivatives. Furthermore, in accordance with the free-radical mechanism, partial loss of the stereochemistry at the γ carbon of the products has been observed.[2c] These limitations led us to explore the possible use of the borate anions in the conjugate addition reaction. However, when lithium tetraalkylborates, such as lithium tetra-*n*-butylborate, were allowed to react with α,β-unsaturated carbonyl compounds, such as ethyl acrylate, there was little indication for the formation of the desired Michael products.

It then occurred to us that such a reaction might be greatly facilitated by making the process intramolecular.[5] Indeed, we have found that disiamyl(2-ethoxycarbonylethenyl)borane (**2a**) undergoes a facile reaction, on treatment with sodium methoxide, to produce an intermediate which can be oxidized to 3-hydroxy-4,5-dimethylhexanoic acid (47% overall yield). Pmr examination has revealed that the hydroboration product consists of a 67:33 mixture of **2a** and **3a**:[6] pmr (THF, TMS) δ 7.70 (H_a, d, J = 19 Hz), 6.23 (H_b, double d, J = 19 Hz), 6.44 (H_c, d, J = 3 Hz), 5.54 (H_d, d, J = 3 Hz) ppm. The combined yield of **2a** and **3a** by pmr was 98% (benzene as an internal standard). The results of hydroboration are in marked contrast to those reported with β-substituted propiolic acid esters,[8] in-



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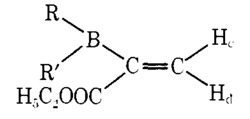

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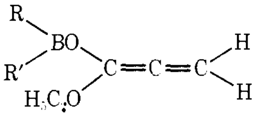

4

a, R = R′ = siamyl; b, R = alkyl; R′ = thexyl

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(1) See, for example, the following: (a) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, 10, 179 (1959); (b) G. H. Posner, *ibid.*, 19, 1 (1972); (c) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972.

(2) (a) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972; (b) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Amer. Chem. Soc.*, 92, 710 (1970); (c) H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, 93, 3777 (1971).

(3) A few methods for the synthesis of β-dimethylamino[3a] and β-hydroxycarbonyl[3b] compounds involving the free-radical conjugate addition of organoboranes have been reported: (a) J. Hooz and J. N. Bridson, *J. Amer. Chem. Soc.*, 95, 602 (1973); (b) T. Mukaiyama, K. Inomata, and M. Muraki, *ibid.*, 95, 967 (1973).

(4) For the related works on organoaluminum compounds, see (a) J. Hooz and R. B. Layton, *J. Amer. Chem. Soc.*, 93, 7320 (1971); (b) R. Pappo and P. W. Collins, *Tetrahedron Lett.*, 2627 (1972); (c) G. W. Kabalka and R. F. Daley, *J. Amer. Chem. Soc.*, 95, 4428 (1973).

(5) The presence of an appropriately located boron atom has made certain otherwise difficult substitution reactions extremely facile. See, for example, (a) ref 2a; and (b) D. S. Matteson, *Progr. Boron Chem.*, 3, 117 (1970).

(6) In contrast to the facile formation of vinyloxyboranes,[7] no indication for the formation of **4** by the tautomerization of **3** was obtained.

(7) D. J. Pasto and P. W. Wojtkowski, *Tetrahedron Lett.*, 215 (1970).

(8) A preferential attack of the α-carbon atom by the boron atom has been reported: J. Plamondon, J. T. Snow, and G. Zweifel, *Organometal. Chem. Syn.*, 1, 249 (1971).