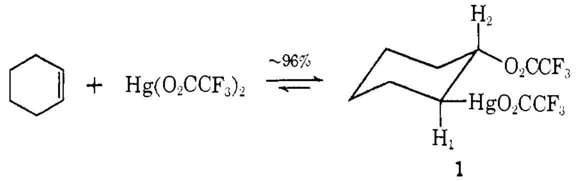
Communications to the Editor

Proton Magnetic Resonance Study of the Fast Reversible Reaction of Mercuric Trifluoroacetate with Cyclohexene, Norbornene, and Apobornylene in Benzene Solution

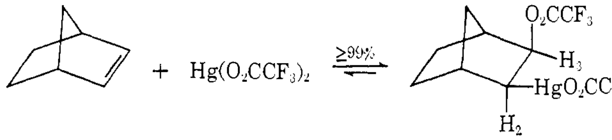
Sir:

Mercuric trifluoroacetate reacts rapidly and reversibly with olefins in aprotic solvents such as tetrahydrofuran to form molecular addition compounds whose stability constants are readily measured.[1] The remarkable ease with which these compounds form and dissociate resembles very closely the behavior of the silver ion complexes and made it desirable to examine more closely the precise nature of the initial products of the reaction. Fortunately, benzene is an excellent solvent for these reactions and its use permits a direct examination of both the equilibration and the nature of the initial adduct by proton magnetic resonance techniques.

We have observed that in benzene at room temperature the reaction of mercuric trifluoroacetate with cyclohexene,[2] norbornene, and apobornylene attains the equilibrium position (approaching 100% reaction) very rapidly, in periods of time of the order of 1 min (eq 1–3). The pmr spectra of the initial reaction products clearly establish that these are of the σ-bonded 1,2-addition type, *trans* for cyclohexene (**1**), and *cis* for norbornene (**2**) and apobornylene (**3**).[3]



1 (1)



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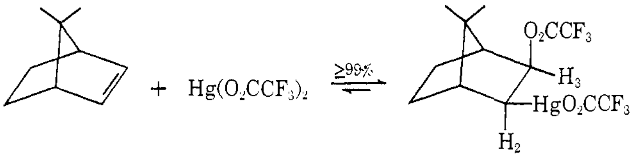

3 (3)

In each case an aliquot of a 2.0 *M* solution of the olefin in benzene was mixed in the pmr tube with an equal volume of a 2.0 *M* solution of mercuric trifluoroacetate in the same solvent and the spectrum was rapidly taken at the probe temperature of 20–27°. The signal of the olefinic protons disappeared or diminished to a small constant value in the very first spectrum taken. No other isomeric material could be detected. The time required for this operation is approximately 1 min after mixing. Therefore, it is clear that the reaction is very fast and proceeds to the equilibrium position in 1 min or less.

Norbornene forms an exceptionally stable adduct.[1] Addition of an equal volume of a 2.0 *M* solution of norbornene in benzene to the reaction mixtures containing **1** and **3** led to the essentially quantitative liberation of cyclohexene and apobornylene in approximately 1 min, as indicated by the pmr spectra.

The equilibrium constants for the olefin–mercuric trifluoroacetate adducts[1] and the olefin–silver nitrate complexes[4] differ considerably in their variation with the structure of the olefin. Consequently, it was concluded that these two types of olefin derivatives must differ markedly in nature. This point is emphasized by the new results with apobornylene, where the mercuric trifluoroacetate derivative is of relatively high stability (exceeded only by norbornene), whereas apobornylene fails to reveal the slightest tendency to coordinate with silver ion[5] (Table I).

Table I. Equilibrium Constants for Olefins and Metal Salts

Olefin	$K[Hg(O_2CCF_3)_2]$[a]	$K[AgNO_3]$[b]
Cyclohexene	38[c]	3.6[e]
Norbornene	500,000[c]	62[e]
Apobornylene	6,800[d]	0[f]

[a] For 0.5 *M* solutions of reactants in THF at 25°. [b] In ethylene glycol at 40°. [c] Reference 1. [d] Present study. [e] Reference 4. [f] Reference 5.

The direct analysis of the 60-MHz pmr spectra associated with decoupling experiments offers an unambiguous answer to the question of the nature of the olefin–mercuric trifluoroacetate adducts in aprotic solvents such as benzene. These products are clearly stereospecific 1,2-addition compounds rather than π complexes, such as those formed by silver ion. In silver ion complexes with symmetrical olefins the methine proton signal appears as a singlet in the vinylic region with only a slight change in chemical shift from that of the parent olefinic protons.[6] On the other hand, in the present system the signal of the olefinic protons rapidly vanishes and the adducts **1–3** exhibit a signal for two methine protons having both chemical shift and spin-splitting patterns compatible with those of protons α to a trifluoroacetoxy group and a trifluoroacetoxymercuri group.[7] The pertinent data are summarized in Table II.

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(1) H. C. Brown and M.-H. Rei, *J. Chem. Soc., D*, 1296 (1969).

(2) The reaction of cyclohexene with mercuric trifluoroacetate in methanol was studied previously: A. Rodgman, D. A. Shearer, and G. F. Wright, *Can. J. Chem.*, **35**, 1377 (1957).

(3) The stereochemistry of the addition of mercuric acetate to norbornene and 1,4,7,7-tetramethylnorbornene in protic solvents was previously established to be *cis-exo:* T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963); T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968).

(4) M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4967 (1962).

(5) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970).

(6) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965).

(7) For example, the chemical shift of the proton α to the trifluoroacetoxy group of *exo*-norbornyl trifluoroacetate in 1 *M* benzene solution is δ 4.50, and the chemical shift of the proton α to the chloromercuri group of 3-*exo*-acetoxyapoisobornylmercuric chloride in 1 *M* pyridine solution is δ 2.75.

Table II. Pertinent Proton Magnetic Resonance Data for the Olefin–Mercuric Trifluoroacetate Adducts

Olefin adduct	K_{obsd} (δ)[a]	H_{irrad}	Pattern[b]	J_{H-H}, Hz	$J_{H-^{199}Hg}$ (*vic*), Hz
Cyclohexene (**1**)	H_1 (2.24)	None	m	$w_{h/2} = 23.5$	
		H_2	m	$w_{h/2} = 15$	
	H_2 (4.80)	None	m	$w_{h/2} = 22.5$	*Ca.* 100
		H_1	m	$w_{h/2} = 14$	
Norbornene (**2**)	H_2 (1.91)	None	dd	7; 2.5	
		H_3	d	2.5	
	H_3 (4.45)	None	d	7	92
Apobornylene (**3**)	H_2 (2.0)	None	d	8	
		H_3	s		
	H_3 (4.55)	None	d	8	110
		H_2	s		

[a] In perdeuteriobenzene solution with TMS as internal reference. [b] m, multiplet; dd, doublet of doublet; s, singlet; d, doublet.

Both α-methine protons in **1** appear as complex multiplets with peak width at half-height ($w_{h/2}$) of about 23 Hz. The one for H_1 is an apparent triplet of doublet, similar to that observed for *trans*-2-methoxycyclohexylmercuric chloride (**4**).[8] Irradiation of the multiplet due to H_1 reduces $w_{h/2}$ for H_2 by about 8.5 Hz, and the same value is also observed for H_1 when H_2 is irradiated. This indicates the two protons have a coupling constant of 8.5 Hz and accordingly are in a *trans*-axial,axial relationship.[9] The vicinal H–^{199}Hg coupling constant for **1**, *ca.* 100 Hz, also agrees with the observed value, 99 Hz, for *trans*-**4**, while the *cis* isomer exhibits a *J* value of 425 Hz.[10]

The distinct doublet for proton H_3 with *J* of 7 Hz in **2** and with *J* of 8 Hz in **3** reveals that it arises from H_{endo}–H_{endo} coupling.[11,12] The presence of a second coupling constant for H_2 in **2** is in line with what has been observed in other stable *cis*-*exo*-norbornyloxymercurials.[5,8,13,14] On the other hand, the adduct **3**, similar to 3-*exo*-acetoxyapoisobornylmercuric chloride[5] (**5**), shows only a doublet for H_3. Moreover, the vicinal H–^{199}Hg coupling constants in Table II correspond to the observed data for 3-*exo*-acetoxy-*exo*-norbornylmercuric chloride (93.2 Hz[10]) and **5** (114 Hz). Consequently, in both **2** and **3** the addition must be *cis*-*exo*, with the minor modification in the spectrum of the H_3 proton apparently arising from some as yet unknown effect of the 7,7-dimethyl substituents.

The lifetime of such 1,2-addition compounds must be longer than the pmr time scale since the resonances of the ^{199}Hg satellites are measurable. Although the reaction reaches its equilibrium position in about 1 min, the system is stable over a period of 24 hr without any significant change in pmr spectrum. Therefore, the observed steric course of the addition is the most favored one. More remarkably, in this typical nonpolar medium the reaction of mercuric trifluoroacetate with the three olefins under discussion exhibits the same stereochemistry as is observed for typical stepwise electrophilic additions.[15]

This facile addition of mercuric trifluoroacetate to olefins and the ready examination of the adducts in solution by pmr appear to provide a powerful new technique for exploring the nature of electrophilic additions to olefins of widely different structures. Further studies are in progress.

Acknowledgment. We are grateful to Professor John B. Grutzner for helpful discussions in the interpretation of the spectra.

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(17) Postdoctorate research associate, 1968–present, on a research grant (GP 6492 X) provided by the National Science Foundation.

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Reaction of Organoboranes with Ethyl 4-Bromocrotonate under the Influence of Potassium 2,6-Di-*t*-butylphenoxide. A Convenient Procedure for a Four-Carbon-Atom Homologation

Sir:

We wish to report that trialkylboranes readily react with ethyl 4-bromocrotonate under the influence of potassium 2,6-di-*t*-butylphenoxide in tetrahydrofuran to give the corresponding unsaturated esters in excellent yields. This provides a new convenient synthetic route to achieve a C-4 homologation.

The reaction of organoboranes with carbon monoxide in the presence of lithium trialkoxyaluminohydride provides a convenient method for a one-carbon-atom homologation[1] (eq 1). Similarly, C-2 homologations can be realized by the reaction of organoboranes with ethyl bromoacetate under the influence of potassium *t*-butoxide[2] (eq 2), by reaction with ethyl diazoacetate,[3] or with other acetic acid derivatives.[4] Moreover, the reaction of organoboranes with acrolein provides a simple C-3 homologation[5] (eq 3). Con-

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(1) H. C. Brown, R. A. Coleman, and M. W. Rathke, *J. Amer. Chem. Soc.*, **90**, 499 (1968); H. C. Brown, E. F. Knights, and R. A. Coleman, *ibid.*, **91**, 2144 (1969); H. C. Brown and R. A. Coleman, *ibid.*, **91**, 4606 (1969).

(2) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968); H. C. Brown and M. M. Rogić, *ibid.*, **91**, 2146 (1969).

(3) J. Hooz and S. Linke, *ibid.*, **80**, 6891 (1968).

(4) J. J. Tufariello, L. T. C. Lee, and P. Wojkowski, *ibid.*, **89**, 6804 (1967).