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CONFIGURATIONAL ASSIGNMENT OF OXYMERCURIALS BY NMR

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The oxymercuration of simple unstrained olefins proceeds by a trans addition.[2] However, with highly reactive olefins such as norbornene,[3] bicyclo[2.1.1]hexene[4] and trans-cyclooctene,[5] cis oxymercuration has been observed. With bicyclo[2.2.2]octene[6] both cis and trans oxymercuration has been reported. A method for determining the cis/trans ratio of hydroxymercurials based upon the hydroxyl stretching frequency in the infrared has been reported by Traylor.[7a] More recently, Waters[7b] has reported a convenient nmr method for determining the configuration of methoxymercurials. This method is based upon a deshielding effect of a methoxyl group when it is cis to the HgX moiety resulting in a downfield shift. We now report an nmr method for establishing the cis/trans ratios of acetoxymercurials and an alternate nmr method for determining the configuration of methoxymercurials.

Our experimental procedure involves preparing the oxymercurial in acetic acid or methanol solvent. Saturated aqueous sodium chloride solution is added and the mercurichloride is extracted with CH_2Cl_2. The CH_2Cl_2 is washed with water, sodium bicarbonate solution and saturated sodium chloride. The CH_2Cl_2 is removed under reduced pressure and the nmr spectrum of the oxymercurial is measured in CCl_4 solvent. The CCl_4 is removed and the nmr spectrum of the oxymercurial is then measured in pyridine solvent. The basis of our configurational assignment rests upon the difference in chemical shift of an oxymercurial in CCl_4 solvent versus pyridine solvent ($\Delta\nu$ solvent). Both cis and trans oxymercurials exhibit an aromatic solvent induced upfield chemical shift in pyridine solvent. However, in the examples studied the chemical shift difference for both acetoxymercurials and methoxymercurials is consistently greater for the cis isomer than for the trans isomer. The chemical shifts of the methoxy and acetoxy groups were measured relative to TMS by superposition of the appropriate resonance with the side band of TMS generated using an audiooccilator. The results of our experiments are given in Table I.

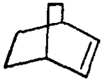
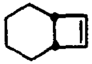
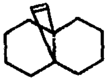
Our data also provide additional examples of configurational assignments based upon the chemical shift difference of the methoxymercurial and its corresponding methyl ether in CCl_4 solvent ($\Delta\nu\ OCH_3$).[8] The results with olefins 2 and 5 are in good accord with Waters data.[7b] However, it should be emphasized that isomeric oxymercurials where the alkoxy group is not in a distinctly different environment have nearly identical chemical shifts. In those cases (e.g., cyclohexene) both of the isomeric oxymercurials should be examined in order to make a definite configurational assignment. We have also included data for an acyclic olefin (1-octene) for comparison with more rigid oxymercurials.

The reasons for the observed chemical shift differences for oxymercurials in pyridine solvent are both complex and intriguing. The difference in chemical shift for the cis- and trans-acetoxymercurials derived from 1 is only 0.4 Hz in CH_2Cl_2 solvent. However, inclusion of one, two, three and four equivalents of pyridine per equivalent of acetoxymercurial in CCl_4 solvent resulted in an upfield shift[9] and a separation of the acetoxy peaks of 1.4, 2.3, 2.8 and 3.1 Hz, respectively. In pyridine solvent, the acetoxy peaks were separated by only 3.6 Hz. In both experiments the ratio of cis and trans isomers can be readily obtained by integration using an expanded sweep width spectrum.

The marked influence of minor amounts of pyridine suggested that the difference in chemical shift of the isomeric acetoxymercurials was due in part to coordination of the pyridine to the mercury. In support of this suggestion, inclusion of one or two equivalents of the relatively hindered 2,6-dimethylpyridine to the acetoxymercurials derived from 1 resulted in an upfield shift[10] but did not cause a measurable separation of the acetoxy resonances in CCl_4 solvent. With four equivalents of 2,6-Lutidine the methyl resonance for the trans isomer appeared as a shoulder on the cis resonance. Further support for the supposition that the separation of the acetoxy resonances derived from 1 is due to a ligand effect on the mercury comes from a similar series of experiments in benzene solvent. An aromatic solvent induced upfield chemical shift of the acetoxy resonances of 9.8 Hz was observed. However, the cis and trans resonances were not resolved. Inclusion of one, two, three and four equivalents of pyridine resulted in a separation of the acetoxy resonances 1.1, 1.6, 1.8 and 2.0 Hz, respectively.[11]

We have also carried out a variable temperature (268-296°K) nmr study in toluene solvent on these acetoxymercurials in the hope of shifting the equilibrium in favor of acetoxy-

TABLE I

									Δν Solvent^g	
Olefin	Product^a	Solvent	Methoxy Mercurial^b	Methyl ether^c	Acetoxy Mercurial	Acetate^d	$\Delta\nu OCH_3^e$	$\Delta\nu \overset{O}{\overset{\|}{C}}-CH_3^f$	OMe	$\overset{O}{\overset{\|}{C}}-CH_3$
 1	cis	CCl_4	201.0	192.7	122.9	117.3	8.3	5.6	12.8	9.5
	trans	CCl_4	198.1	192.7	122.9	117.3	5.4	5.6	5.7	5.4
	cis	C_5H_5N	188.2	192.4	113.4	119.1	-4.2	-5.7		
	trans	C_5H_5N	192.4	192.4	117.5	119.1	0.0	-1.6		
 2	exo-cis	CCl_4	198.8	189.0	120.8	116.7	9.8	4.1	6.0	5.0
	exo-trans	CCl_4	193.2	186.8	120.8	116.7	6.4	4.1	3.5	2.9
	exo-cis	C_5H_5N	192.8	190.7	115.8	117.1	2.1	-1.3		
	exo-trans	C_5H_5N	189.7	186.9	117.9	117.7	2.8	0.2		
 3	cis	CCl_4	201.2	194.0			7.2		8.5	
	trans	CCl_4	201.2	194.0	122.7	117.6	7.2	5.1	7.8	6.6
	cis	C_5H_5N	192.7	194.3			-1.6			
	trans	C_5H_5N	193.4	194.3	116.1	118.0	-0.9	-1.9		
 4	exo-cis	CCl_4	203.1	190.2	121.6	115.3	12.9	6.3	11.7	6.5
	exo-cis	C_5H_5N	191.4	190.3	115.1	116.1	1.1	-1.0		
 5	trans	CCl_4	196.3	189.3			7.0		2.2	
	trans	C_5H_5N	194.1	191.4			2.7			
 6	trans	CCl_4	195.2	187.0	120.9	116.4	8.2	4.5	4.0	4.5
	trans	C_5H_5N	191.2	187.4	116.4	118.0	3.8	-1.6		
1-octene 7		CCl_4	199.7	192.7	121.8	115.9	7.0	5.9	3.7	6.0
		C_5H_5N	196.0	194.6	115.8	117.0	1.4	-1.2		

[a] Exo mercury substitutent. [b] All values are in Hz relative to TMS. [c] Methyl ether obtained by $NaBH_4$ reduction of the oxymercurial. [d] Alkyl acetate obtained by $NaBH_4$ reduction of the oxymercurial. [e] Frequency of the methoxymercurial minus the frequency of the methyl ether. [f] Frequency of the acetoxymercurial minus the frequency of the alkyl acetate. [g] Frequency of the oxymercurial in CCl_4 minus its frequency in pyridine solvent.

mercurial-solvent complex formation to enhance the solvent shifts. We used the method and the assumptions described by Laszlo and Williams[12] that the equilibrium, acetoxymercurial + toluene $\rightleftarrows$ complex, is driven toward complex formation with a decrease in temperature. Using CCl_4 as the "inert" solvent, plots of log K *vs* 1/T gave a heat of formation of the 1:1 complex between *cis*-acetoxymercurial and toluene as -0.94 ± .08 kcal/mole. The ΔH for the trans isomer was measured as -0.87 ± .08 kcal/mole. In pyridine solvent the ΔH of formation of the solvent with 2-acetoxybicyclo[2.2.2]octane was -3.7 ± 0.7 kcal/mole. However, in pyridine solvent the above isomeric acetoxymercurials did not exhibit a linear correlation between temperature and K_{eq}. These data support the above suggestion that the separation of the acetoxy resonances is due to coordination of pyridine with the mercury, as well as, an aromatic solvent induced chemical shift.

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8. The slight differences in $\Delta\nu$ OCH_3 in CCl_4 from those reported by Waters[7b] are most likely due to different experimental procedures. We have observed that the methoxyl resonance of 2-methoxybicyclo[2.2.2]octane was shifted upfield by 0.5 Hz in the presence of one equivalent of a mixture of cis and trans methoxymercurials derived from **1**. The resonances of the methoxymercurials were unchanged.
9. The chemical shift of the cis isomer was 120.6, 118.8, 117.4 and 116.5 Hz, while the chemical shift of the trans isomer was 121.9, 121.1, 120.2 and 119.5 Hz, respectively.
10. The chemical shift of both isomers were 122.0, 121.1 and 120.8 with addition of one, two and four equivalents of 2,6-Lutidine.
11. The chemical shift for the cis and trans isomer is 113.1 Hz in benzene. With four equivalents of pyridine the chemical shift of the cis isomer was 113.5 and the trans isomer 111.6 Hz.
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