Tetrahedron Letters No.43, pp. 3769-3772, 1969. Pergamon Press. Printed in Great Britain.

THE STEREOCHEMISTRY OF METHOXYMERCURATION. I. A FACILE METHOD OF CONFIGURATIONAL ASSIGNMENT BY N.M.R. SPECTROSCOPY.

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(Received in USA 21 March 1969; received in UK for publication 15 August 1969)

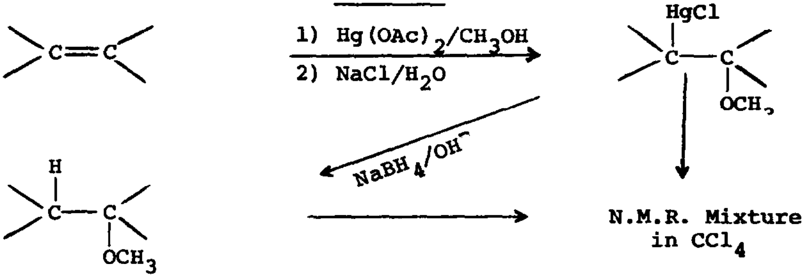
T. G. Traylor (1) has developed a method for the configurational identification of the products from hydroxymercuration of olefins. This method involves measurement of the I.R. OH stretching frequency of the β-hydroxy-α-halomercurialkane products.

Since the *cis/trans* ratio for oxymercuration products often changes according to the particular solvent employed (2), and since the simple hydroxymercuration products of certain olefins have yet to be isolated (3), it was thought that a quick and relatively simple method was needed for configurational identification of methoxymercuration products. The method chosen utilizes a predicted N.M.R. chemical shift change (downfield) for a methoxy group when placed near a mercury function. A greater shift change was predicted for *cis* products since in these the mercury-oxygen distance is less.

The olefins selected to test this deshielding effect were those which gave methoxymercuration products whose configuration had already been proven, or could be easily determined by N.M.R. spin-decoupling experiments.

The experimental procedure is shown in Scheme I. The olefins were oxymercurated in methanol. The products were then converted to the chloromercuri derivatives by shaking with aqueous sodium chloride. Some of the β-methoxy-α-chloromercurialkane was then dissolved in 0.5 M NaOH and reduced with an equivalent amount of $NaBH_4$ in a 0.5 M NaOH solution (4). The resulting ether was then extracted with *ca.* 1 ml CCl_4, washed repeatedly with H_2O until neutral, and dried over $MgSO_4$. To the clear CCl_4 solution of the methyl ether was added a small amount of the chloromercuri ether and an N.M.R. spectrum then taken of the mixture (each compound *ca.* 2%). Finally the frequency difference of the two methoxy lines was measured on an expanded sweep width spectrum.

Scheme I



The results of these reactions are listed in Table I, below:

Table I

Olefin	Product Configuration	$J_{H_a - H_b}$ (5) (±0.2) c.p.s.	$\Delta\nu$-OCH_3 (6) (±0.1) c.p.s.
1. Norbornadiene		---	3.0 (7)
2. Cyclobutene	*trans*	<1.0	7.2
3. Cyclopentene	*trans*	4.1	5.5
4. Cyclohexene	*trans* (8)	9.0	7.8
5. Cycloheptene	*trans*	9.0	7.9
6. *cis*-Cycloöctene	*trans* (9)	8.0	8.5
7. *trans*-Cycloöctene	*trans* (9)	8.0	8.5
8. Dibenzobicyclo-[2.2.2]öctatriene	*trans*	3.2	3.3
9. Bicyclo[2.2.2]-öctene	*trans*	4.1	5.8
10. Norbornene	*cis* (*exo*) (10)	6.9	13.0
11. Benzonorbornadiene	*cis* (*exo*) (10)	6.6	12.4
12. Dibenzobicyclo-[2.2.2]öctatriene	*cis*	7.9	12.5
13. Bicyclo[2.2.2]-öctene	*cis*	8.9	9.3

Table I confirms the predicted enhanced deshielding in the *cis* products. A rough generalization is that methoxymercuration products of cyclic olefins have $\Delta_{\nu\text{-OCH}_3}$ *trans* values of 3-8 c.p.s., and *cis* values of 12-13 c.p.s. (11). These two sets of chemical shift differences complement Traylor's infrared hydroxyl frequency differences of *cis* and *trans* β-hydroxy-α-halomercurialkanes (1).

Of course the success of such an N.M.R. method of isomer identification (as well as the I.R. method for hydroxymercuration products) relies on the rigidness of the mercurial-ether product. As can be noticed in Table I, increasing ring size causes an increase in $\Delta_{\nu\text{-OCH}_3}$ for the *trans* products. The larger saturated rings are more flexible and hence the mercury atom time averages a closer distance to the methoxy function. Although the two sets of values for $\Delta_{\nu\text{-OCH}_3}$ never actually overlap, it can be seen that the $\Delta_{\nu\text{-OCH}_3}$ *cis* values for "flexible" bicyclic methoxymercurials (*e.g.*, from bicyclo[2.2.2]-öctene) approach quite closely the $\Delta_{\nu\text{-OCH}_3}$ *trans* values of the products of the more "flexible" monocyclic olefins (*e.g.*, cycloöctene). Fortunately, such flexible bicyclic olefins always produce both isomers upon methoxymercuration (12), thus making a direct comparison (and hence assignment) of their two $\Delta_{\nu\text{-OCH}_3}$ values possible.

The analytical method described above has proven extremely useful in the study of the methoxymercuration products of cyclic olefins because of its simplicity and general utility (13). Efforts are now being made in this lab to quantitatively relate the $\Delta_{\nu\text{-OCH}_3}$ values with other conformational equilibria data both for the compounds herein and other substituted ring systems.

References

1. T. G. Traylor and A. W. Baker, J. Am. Chem. Soc., **85**, 2746 (1963).
2. T. G. Traylor, *ibid.*, **86**, 244 (1964).
3. T. G. Traylor, private communication.
4. F. G. Bordwell and M. L. Douglass, J. Am. Chem. Soc., **88**, 993 (1966).

5. $J_{H_a-H_b}$, as in $H_a-C(HgCl)-C(OCH_3)-H_b$, was obtained from spin-decoupled spectra and was the basis for preliminary assignment of configuration. See M. M. Anderson and P. M. Henry, Chemistry and Industry, 2053 (1961) for an example of the use of this vicinal coupling constant as configurational proof.
6. This quantity represents the difference in methoxy chemical shift values for the β-methoxy-α-chloromercurialkane and the simple methyl ether.
7. This value might represent a reasonable minimum deshielding effect due to the great $Hg-OCH_3$ distance in this nortricyclic system, thereby serving as a standard for minimum $\Delta_{\nu-OCH_3}$ *trans* values.
8. M. M. Kreevoy and F. R. Kowitt, J. Am. Chem. Soc., 82, 739 (1960).
9. V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, Doklady Adak. Nauk. SSSR, 136 (1966). *trans*-Cycloöctene methoxymercurates by a *cis* mechanism to give the ring-flipped "*trans*" configuration product, *i.e.*, the same as from *cis*-cycloöctene.
10. The *exo* configuration is indicated by other spin-spin coupling constants as shown by Anderson and Henry (ref. 5).
11. The methoxymercuration product of bicyclo[2.2.2]öctene represents a special case in that the entire ring system can undergo twisting to relieve angle strain. The mercury-methoxy distance in the *cis* product is therefore increased considerably and is reflected by an abnormally low $\Delta_{\nu-OCH_3}$ value. Similar twisting cannot occur in the analogous methoxymercuration product of dibenzobicyclo[2.2.2]öctatriene. The latter's $\Delta_{\nu-OCH_3}$ *cis* value of 12.5 c.p.s. reflects this point well.
12. Unpublished results of W.L.W.
13. The method of configurational assignment by vicinal coupling constants (ref. 4) has limited utility. For example, the methoxymercuration products of tri- or tetra-substituted alkenes obviously cannot be assigned a *cis* or *trans* configuration by this technique.