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THE STEREOCHEMISTRY OF OXYMERCURATION OF 5-NORBORNENE-2-*endo*-CARBOXYLIC ACID

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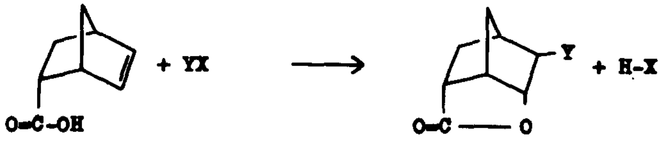
Addition of the common electrophiles to 5-norbornene-2-*endo*-carboxylic acid (I) generally results in lactonization as shown by eq. 1 (1). This type of reaction has proven useful as a means of separating the acid I from its *exo*-counterpart (1c,2) and also as a probe for the intervention of a positively charged intermediate in addition reactions (3).

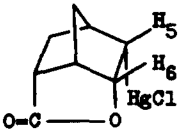


(1)

I

II a, Y=H d, Y=HgCl
b, Y=I e, Y=ArS
c, Y=Br

By analogy with additions to norbornene (4), it has usually been assumed that the electrophile Y reacts from the *exo*-side of the double bond of I as implied by eq. 1 (1b-1d). In recent studies in this system, however, two groups (5,6) have independently assigned a *cis*-*endo* configuration (III) to the lactone which results from the addition of mercuric acetate to I. (The product was isolated as the alkyl mercuric chloride.) Wright and Maliyandi based their structural assignments on a comparison of the measured and the calculated dipole moments for the



III

oxymercuration product (α-isomer) and its epimer (β-isomer), assuming for the calculations a C-Hg-Cl bond angle of 96° (5). Traylor and Factor made the assignment by NMR analysis based on the spectrum of the α-isomer which reportedly shows the proton alpha to the oxygen (H_6) as a simple doublet with J = 6-7 cps. This splitting was considered to be due to coupling with H_5, which cannot be identified in the spectrum, and as a result, H_5 was assigned an exo-configuration on the basis of the magnitude of the coupling (6).

In the present paper, NMR data for the α- and β-oxymercurials derived from I are given which provide compelling evidence for trans-stereochemistry in the reaction product (α-isomer) and a cis-configuration in the epimer (β-isomer).

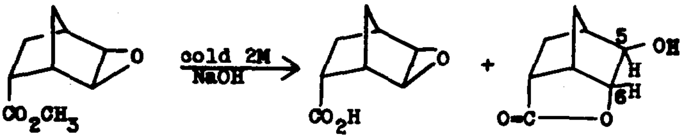
The α-5-chloromercurilactone was obtained in 94% yield by treatment of I with mercuric acetate in methanol followed by the addition of aqueous sodium chloride: m.p. 224.5-225.0° from acetone-water [lit. (5) m.p. 222.5-224°]. The β-isomer was prepared by first isomerizing the H-C-Hg center of the α-isomer with benzoyl peroxide in pyridine (7), and then selectively destroying the α-isomer by treating the mixture of organomercurials with hydrochloric acid. The β-isomer exhibits m.p. 187.5-188.0° as compared to the lit. (5) value of 186.5-187°. That these isomers differ only in configuration at C-5 is established by 1) the method of preparation, 2) deoxymercuration of each isomer with hydrochloric acid in methanol to acid I, and 3) reduction of each isomer with sodium trimethoxyborohydride to lactone IIa, which is identical in all respects to the known compound prepared by acid-catalyzed isomerization of I (1b).

NMR spectra were recorded at 100 and at 60 Mc on the Varian HA-100 and A-60 spectrometers. The 100 Mc spectrum of the _α_-isomer in pyridine displays a doublet (J = 5.0 cps) at τ 4.67 (H_6), a broadened triplet with spacings of about 4-5 cps at τ 6.92 (H_2), complex absorption from τ 7.29 - τ 7.64 (H_1, H_4, H_5), and complex absorption between τ 7.70 and τ 8.75 (4 protons). The spectrum of the _β_-isomer under the same conditions is similar to that of the _α_-isomer excepting that H_6 appears as a triplet (overlapping doublet of doublets) at τ 5.17 with the sum of the two coupling constants equal to 12.4 cps. The spacings in this multiplet are identical at 60 and 100 Mc. H_6 of the lactone IIa absorbs at τ 5.23 and appears as a broadened triplet with $(J_{1,6} + J_{5,6}) = 11.0$ cps.

These three spectra demonstrate that H_6 of the lactone IIa, IId and III is strongly coupled to a proton other than those at C-5, beyond doubt to H_1, and further that $J_{5,6} = 6\text{-}7$ cps for one configuration of H_5 and $J \sim 0$ cps for the other configuration. Additional evidence that $J_{5,6} \sim 0$ cps for one configuration of H_5 in this class of compounds is available from the spectra of IIc and IIe. In these, both H_5 and H_6 are well-separated from absorptions by the remaining protons and in both compounds H_6

appears as a clean doublet with J = 5.0 cps and H_5 as a sharp doublet with J = 2.1-2.2 cps. Clearly any coupling between H_5 and H_6 in the latter two compounds is less than 1 cps. The coupling of H_5 in these is most likely with the anti-7-proton (3b). The pertinent aspects of the spectra of the five compounds are gathered into Table I.

The Karplus equations (8) indicate that the isomer of IId with the smaller coupling between H_5 and H_6 is that with Y in an *exo*-configuration. The validity of the Karplus relationship has been abundantly demonstrated for 2,3-disubstituted norbornyl compounds (9) as well as for the lactone II (10). From models, Crundwell and Templeton (10) have estimated dihedral angles in II and calculated coupling constants of 5.4, 7.9 and 0.8 cps for $J_{1,6}$, $J_{(\underline{exo}\text{-}5),6}$ and $J_{(\underline{endo}\text{-}5),6}$ respectively, in good agreement with their findings and the results reported here. Of the compounds investigated by Crundwell and Templeton to test the predicted coupling constants, the one with the most definitely established stereochemistry was prepared as shown by eq. 2. H_6 of the lactone IV appears as a doublet of doublets with coupling constants of 5 and 1 cps, and H_5 appears as a doublet with J = 1-2 cps.



(2)

IV

It is therefore concluded that the original (5,6,11) stereochemical assignments of the oxymercurials are incorrect and that the primary product (*α*-isomer) of the oxymercuration of I has a

TABLE I

Coupling Constants and Chemical Shifts in the NMR Spectra of II in Pyridine.

Y	H	τ	Multiplicity[a]	J(cps)	$(J_{1,6}+J_{5,6})$ (cps)	Coupled with Proton(s)
α-HgCl	H_6	4.67	d	5.0		1
β-HgCl	H_6	5.17	t		12.4	1,5x
H	H_6	5.23	t		11.0	1,5x
Br[b]	H_5	6.23	d	2.2		anti-7
Br[b]	H_6	5.21	d	5.0		1
RS[c]	H_5	6.68	d	2.1		anti-7
RS[c]	H_6	5.43	d	5.0		1

[a] d = doublet, t = triplet or doublet of doublets.

[b] Prepared according to procedure given in (1c). Spectrum recorded in carbon disulfide.

[c] R = *p*-tolyl (3c).

trans-stereochemistry (IId) and its epimer (*β*-isomer) has the *cis*-*endo*-configuration (III).

The results reported here cast doubt on the assertion (6) that the observed *cis*-oxymercuration of norbornene results because a *trans*-transition state for compounds of this type would be twisted and very highly strained, and suggest that the *cis*-*exo*-addition to norbornene is due to steric inhibition to *endo*-approach of the nucleophile.

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11. After submission of this paper we were informed by Prof. Traylor that he had revised his structural assignment into agreement with the results reported herein soon after the appearance of ref. 6.