ON THE STEREOCHEMISTRY OF EXCHANGE AT OLEFINIC CARBON

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(Received June 15th, 1968)

SUMMARY

The compounds *cis*-chlorovinylmercuric chloride of m.p.78–79° and bis(*cis*-chlorovinyl)mercury with n_D^{20} 1.6308, which had been described by the authors in 1945, were examined by ^{1}H NMR spectroscopy and it was found that they contained a constant amount of the *trans*-isomers. Pure *cis*-chlorovinylmercuric chloride (I) was prepared and the m.p. was found to be 59–61°; from this compound pure bis(*cis*-chlorovinyl)mercury (II) with n_D^{20} 1.6047 was prepared.

Starting with these compounds, metal exchange cycles were carried out each time returning to the original compound (I). The corrected constants of the *cis*-chlorovinylmetal derivatives are given. By ^{1}H NMR and IR spectroscopy the retention of the *cis*-configuration during these exchanges was confirmed. So the "system of even and odd cycles" in the configuration in exchange reactions was confirmed by independent means.

In a previous paper[1], we reported on an investigation into the stereochemistry of electrophilic and homolytic exchange reactions at the olefinic carbon atom. We confirmed that the configuration in such exchanges is rigorously retained for *trans*- and *cis*-chlorovinylmetals (Hg, Tl, Sn, Pb, Sb). Since then we have verified our rule in many cases, *e.g.*, the reactions of *cis*- and *trans*-propenyl[2,3], and 1,2-diphenylvinyl derivatives of metals, including lithium[5,6]. More complex regularities for nucleophilic substitution at the olefinic carbon atom are generalised in ref. 7.

Two factors have caused us to return to our previous work[1,8]. The first is the availability of the rapid and convenient method of proton magnetic resonance (PMR) for establishing configuration (*cis* and *trans*). Using this method we have recently established that whereas our initial *trans-β*-chlorovinylmercury chloride was free from its stereoisomer, its *cis*-isomer contained a significant amount of the *trans*-compound which was difficult to remove.

It was necessary to undertake a lengthy crystallisation of *cis-β*-chlorovinylmercury chloride (obtained by heating the *trans*-isomer with a small amount of benzoyl peroxide)[9] before it was sufficiently pure by PMR standards (Fig. 1). It was also obtained by treating ether and benzene solutions with pyridine[10,11] and by the reaction of di-*cis-β*-chlorovinylmercury with mercuric chloride in ether solution. The melting point of pure *cis-β*-chlorovinylmercury chloride is 59–61° and the physical constants of di-*cis-β*-chlorovinylmercury obtained from it by ammonia symmetrisa-

tion are: 35–36° (8.5·10⁻³ mm) 76–78° (0.5 mm); n_D^{20} 1.6047; d_4^{20} 2.7810*. These values should replace those published[9] previously. It then became necessary to repeat the series of transformations that were earlier carried out with impure sub-stances, using these pure cis-compounds.
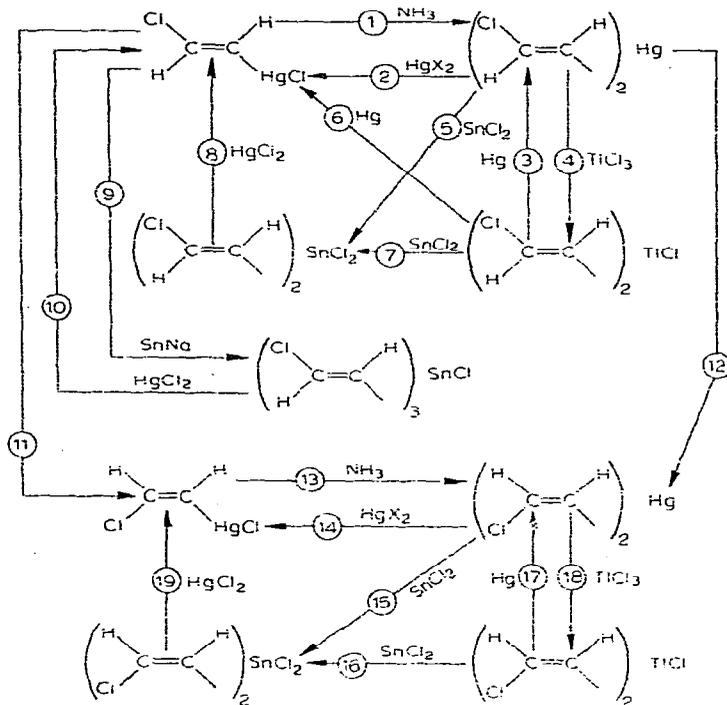
SCHEME 1

X=Cl, Br

The cycle of these transformations is shown in Scheme 1, and the constants of the cis-chlorovinyl derivatives of metals obtained by exchange reactions and purified until shown by PMR to be completely free of the trans-isomers are shown in Table 1.

The second factor in deciding us to undertake this work, was the remark made in the paper of Curtin and Crump, doubting the applicability of our method in establishing the retention of configuration by the method of "even" and "odd" cycles. Regarding the work in which we confirmed the retention of configuration of trans–cis propenyl radicals in the transformation cycles with metal (and halogen) exchange, they stated:

'Although their work certainly provides additional** weight of evidence in

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* Di-cis-β-chlorovinylmercury (PMR spectra δ_α=6.28 ppm; δ_β=6.95 ppm; $J_{\alpha\beta}$=7 cps) contains less than 3% of the cis–trans-isomer.

** It should be noted that the work of Curtin and Crump cited appeared 10 years later than that in which we established the retention of configuration rule. Our work was the first on this theme so that it is not clear in what way the authors consider our arguments to be additional.
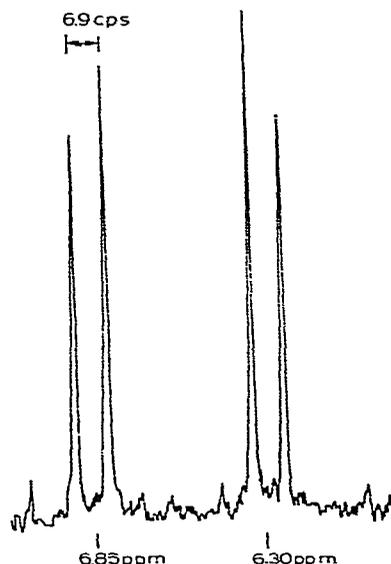
Fig. 1. PMR-spectrum of pure cis-β-chlorovinylmercury chloride.

favor of the assumption of reaction with retention, "the Method of Odd and Even Cycles" does not appear to have the absolute authority attributed to it. For example the three cycles at the bottom of p. 164 in ref. 8 are explained satisfactorily if the conversion of bromide to lithium reagent and the reaction of all organometallics with bromine to give back the bromide proceed with inversion while all other reactions in cycles proceed with retention'.

From the beginning it was clear to us that such an objection was incorrect since it isolates a single cycle from the general system of even and odd cycles of the exchange reactions of one of the stereoisomers, which constitute in the ensemble the area of reactions which are isolated from the exchange reactions of the second stereoisomer.

A check of the "retention of configuration rule" made on a series of cis-β-chlorovinylmetals using PMR criteria showed definitely that the method of even and odd cycles cannot be faulted since it gave independent criteria in assessing the configuration of each compound.There was no difficulty in carrying out an analogous investigation for a series of transformations of trans-β-chlorovinylmercury in order to verify the applicability of the method of odd and even cycles for a wider range of data (see Scheme 1 and Tables 1 and 2). Additional independent proof of the configuration of each substance in the transformation cycles is given by the infrared spectra shown in Table 2. The method of even and odd cycles, used by us to prove the retention of configuration of the propenyl órganometallic compounds[13] was independently confirmed by an investigation of the PMR spectra of these compounds[14].

PMR enables the trans- and cis-β-chlorovinyl groups to be easily distinguished. The PMR spectrum of the trans-compound is a quadruplet of the AB system with a small internal chemical shift, $\Delta\delta_{AB}$ and a large $J_{AB}/\Delta\delta_{AB}$ ratio (where J_{AB} is the spin–spin coupling constant). For β-chlorovinylmercury chloride, this spectrum is seen practically as a doublet with a small splitting since the outer peaks of the

TABLE 1

PMR-SPECTRA OF THE *cis*- AND *trans*-ISOMERS OF THE β-CHLOROVINYL COMPOUNDS OF MERCURY, THALLIUM AND TIN

No.	Compounds	Cis-isomers			Solution	Trans-isomers			Solution
		δ_α (ppm)	δ_β (ppm)	$J_{\alpha\beta}$ (cps)		δ_α (ppm)	δ_β (ppm)	$J_{\alpha\beta}$ (cps)	
1	ClCH=CHHgCl	6.30	6.85	7	30% in acetone	6.22	6.28	15	30% in acetone
2	ClCH=CHHgBr[a]	6.36	6.95	7	30% in acetone	6.37	6.39	15	30% in acetone
3	(ClCH=CH)$_2$Hg	6.28	6.95	7	without	6.13	6.45	15.5	30% in acetone
4	(ClCH=CH)$_2$SnCl$_2$	7.00	7.55	6.8	without	6.52	6.79	15.4	40% in acetone
5	(ClCH=CH)$_3$SnCl	—	—	—		6.36	6.65	15.4	30% in acetone
6	(ClCH=CH)$_2$TlCl	6.85	7.20	7	40% in THF	[b]	—	15	15% in THF

[a] An estimation of the relative chemical shift between vinyl protons of the *trans*-isomer was made by ^{119}Sn–H–

[b] Identification was made on the left half of spectrum; the right half of the doublet induced by Tl–H coupling, is obscured by solvent absorption.

TABLE 2

IR-SPECTRA OF THE *cis*- AND *trans*-ISOMERS OF THE β-CHLOROVINYL COMPOUNDS OF MERCURY, TIN AND THALLIUM

No.	Compound	M.p. (°C)	Con-figurn.	Frequencies (cm^{-1})
1	ClCH=CHHgCl	61	*cis*	693 s, 772 s, 918 s, 1135 w, 1275 s, 1520 w, 1580 s
		124	*trans*	663 s, 773 s, 783 s, 940 s, 1154 s, 1280 w, 1580 s, 1680 w
2	ClCH=CHHgBr	77	*cis*	690 s, 760–770 s, 915 m, 1130 w, 1275 m, 1580 s
		122	*trans*	663 m, 768 s, 940 s, 1150 s, 1570 s, 1672 w
3	(ClCH=CH)$_2$Hg	liquid	*cis*	692 s, 765 s, 920 m, 1125 w, 1273 s, 1565 s
		71	*trans*	760 s, 950 s, 1157 m, 1270 w, 1570 s, 1675 w
4	(ClCH=CH)$_2$SnCl$_2$	liquid	*cis*	680 s, 770 s, 920 w, 943 m, 1270 m, 1517 w, 1575 s
		78	*trans*	740 m, 785 s, 936 s, 1145 m, 1295 w, 1535 s, 1578 s
5	(ClCH=CH)$_2$TlCl	151	*cis*	690 s, 710 m, 770 s, 915 w, 1125 w, 1260 m, 1510 w, 1580 s
		169	*trans*	670 m, 750 m, 805 s, 935 s, 1140 s, 1285 w, 1545 m, 1590 s
6	(ClCH=CH)$_3$SnCl	121	*trans*	745 m, 760 s, 942 s, 1142 m, 1278 w, 1500 m, 1565 s

The IR-bands of the out-of-plane vibrations =C–H (v=915–920 cm^{-1}) and of the in-plane vibrations =C–H (v=1260–1275 cm^{-1}) characterise the *cis*-isomers. The out-of-plane frequencies 935–950 cm^{-1} and in-plane frequencies 1140–1157 cm^{-1} characterise the *trans*-isomers of the compounds listed[15–16] in the Table.

quadruplet have a low intensity (Fig. 2). For di-β-chlorovinylmercury, the chemical shift, $\Delta\delta_{AB}$, is somewhat larger, and all four lines of the AB system are observed. The chemical shift in the *cis*-compound is about ten times larger and J_{AB} about half so that the peak intensities of the corresponding spectrum are nearly equal (Fig. 3).

Integral intensity measurements enabled the concentration of the *trans*- and *cis*-isomer to be established. Our data show that *cis*-β-chlorovinylmercury chloride with a melting point of 59–61° contains 2–5% of the *trans*-isomer. The product of m.p. 61° is purest, the concentration of the *trans*-isomer being outside the limits of the sensitivity of the spectrometer. This corresponds to a 3% impurity for the 30% acetone solutions used.

In the symmetrical compounds (one of low melting point, and the other a liquid) the impurity of the *cis–trans*-isomer and the opposite isomer can be determined within 0.5%.
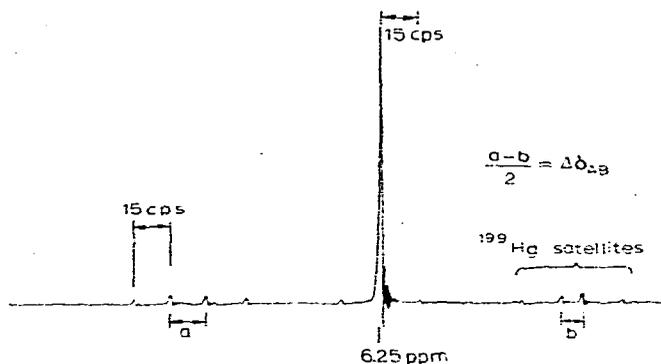
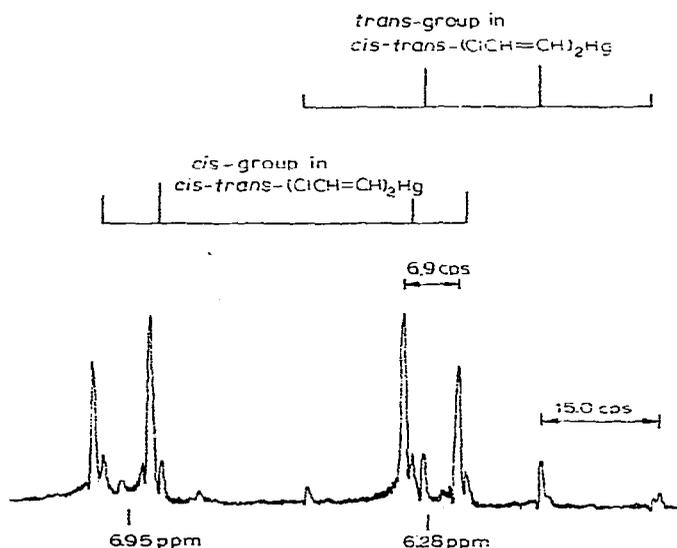Fig. 2. PMR-spectrum of *trans*-β-chlorovinylmercury chloride (recorded on Perkin–Elmer R-12 spectrometer).

Fig. 3. PMR-spectrum of 80% *cis–cis*-(ClCH=CH)$_2$Hg and 20% *cis–trans*-(ClCH=CH)$_2$Hg mixture.

The chemical shifts, δ_α and δ_β, of the protons in the β-chlorovinyl groups are strongly dependent on the concentration of the compound in solution.

The data shown in Table 1 correspond to the concentrations given. The concentration-dependence of the chemical shifts will be described separately.

The PMR spectra were taken on the Hitachi H-60 spectrometer. The accuracy of the chemical shifts measured is ±0.02 ppm and of the spin–spin coupling constants, ±0.5 cps.

EXPERIMENTAL

The purification of *cis*-β-chlorovinylmercury chloride is described above. Symmetrisation of this compound by ammonia into *cis*-β-dichlorovinylmercury, and all exchange reactions, were carried out as in the previous work[1], the only difference

being that the crude reaction product is immediately controlled by PMR either as it is (for liquid and low-melting products) or as a concentrated acetone solution. The other constants are determined after the usual crystallisation or distillation.

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