Tetrahedron, 1957, Vol. 1, pp. 158-168. Pergamon Press Ltd., London

STEREOCHEMISTRY OF ELECTROPHILIC AND HOMOLYTIC SUBSTITUTION AT THE OLEFINIC CARBON

A. N. NESMEYANOV and A. E. BORISOV
Academy of Sciences of the U.S.S.R., Moscow

(*Received* 10 *January* 1957)

STEREOCHEMICAL regularities of the exchange reactions at the tetrahedric carbon atom have been under investigation since the time of the classical works of Walden, this type of substitution having been dealt with in numerous investigations. Recently there have also appeared investigations devoted to the electrophilic exchange at the saturated carbon atom, including those by one of us and O. A. Reutov.[1] Until our work dealing with the stereochemistry of the exchange at the olefinic carbon appeared there was almost no information available, neither were there investigations relating to the electrophilic substitution. From the works of Autenrieth[2] one can deduce that in the nucleophilic substitutions *cis* and *trans* configurations of the olefinic carbon are sometimes retained and sometimes inverted. Indeed, the reaction of sodium phenolate with β-chlorocrotonic and β-chloro*iso*crotonic acid gives the same phenoxycrotonic acid. Similar stereochemical changes are observed with sodium ethylate as well as in the Meyer reaction of the above-mentioned acids with sodium arsenite.

Chlorocrotonic and chloro*iso*crotonic acids react with sodium phenyl, ethyl, and benzyl mercaptides, each yielding its isomer of β-aralkylthiocrotonic acid, whether converted or not being unknown. We have similar information concerning the reaction of the chlorocrotonic acids with sodium phenyl-sulphinate.[2]

We have carried out a number of investigations, the first published in 1948,[3] dealing with the stereochemistry of electrophilic and homolytic exchange at the olefinic carbon atom.

The main results of our investigations are shown in Table 1. All exchange reactions of the metallic atom in β-chlorovinyl organo-metallic compounds* in this Table readily take place under mild conditions at room temperature to 80°.

---

* These reactions have been investigated partly by present-day writers, partly by one of the writers of this paper and by R. Kh. Freidlina and A. K. Kochetkov.[3a]

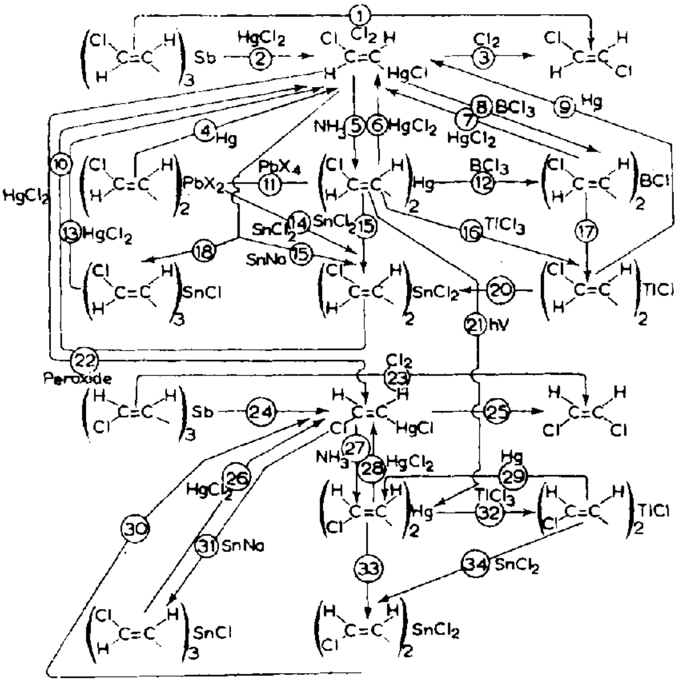
[1] A. N. Nesmeyanov, A. O. Reutov, and S. S. Poddubnaya *Doklady Akad. Nauk SSSR* **88**, 479 (1953); A. N. Nesmeyanov, A. O. Reutov, and S. S. Poddubnaya *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 649 (1953); A. O. Reutov and A. N. Nesmeyanov *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 655 (1953); A. N. Nesmeyanov, A. O. Reutov, and S. S. Poddubnaya *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 850 (1953); A. O. Reutov and M. A. Besprozvanny *Doklady Akad. Nauk SSSR* **80**, 765 (1951).

[2] W. Autenrieth *Lieb. Ann.* **254**, 222 (1889); **259**, 332 (1890); R. Friedrich *Lieb. Ann.* **219**, 322 (1883); H. J. Backer and R. P. van Oosten *Rec. Trav. Chim. Pays Bas* **59**, 41 (1940).

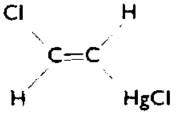
[3] A. N. Nesmeyanov and A. E. Borisov *Doklady Akad. Nauk* **60**, 67 (1948).

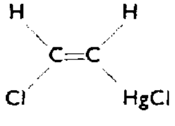
[3a] A. N. Nesmeyanov, R. Kh. Freidlina, and A. K. Kochetkov *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* **127**, 445 (1948).

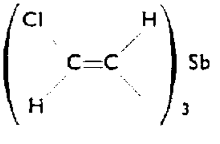
TABLE 1

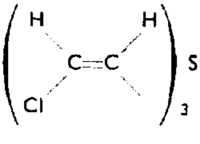


The majority of these reactions are undoubtedly those of electrophilic substitution, the metallic atom shifting and combining without the electron pair. In a number of cases (action of a metal, e.g. mercury, tin-sodium alloy, stannous chloride) it is undoubtedly a homolytic exchange. The starting compounds used in all these conversions were four substances, produced independently of each other from acetylene and mercury chloride[4] and respectively from acetylene and antimony pentachloride.[5]









By the action of ammonia each mercury chlorovinyl was completely converted into its corresponding mercury *bis*-chlorovinyl.

The correct assignment of the configuration of each of the four starting organomercuric chlorovinyl derivatives is of extreme importance in dealing with the problems under consideration. The configurations of β-chlorovinylmercury chlorides

---

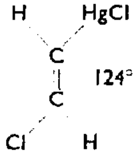
[4] A. N. Nesmeyanov and R. Kh. Freidlina *Doklady Akad. Nauk SSSR* **26**, 59 (1940); A. N. Nesmeyanov and A. E. Borisov *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 289 (1947); R. Kh. Freidlina and O. V. Nogina *Izvest. Akad. Nauk. SSSR, Otdel. khim. Nauk* 105 (1947).

[5] A. N. Nesmeyanov and A. E. Borisov *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 251 (1945); A. N. Nesmeyanov *Izvest. Akad. Nauk SSSR, Otdel khim. Nauk* 239 (1945).

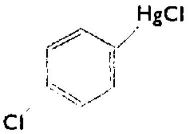
are clear from the comparison of their dipole moments[6] (i.e. the vector sums of two dipole moments of $\overrightarrow{\mathrm{Hg—Cl}}$ and $\overrightarrow{\mathrm{C—Cl}}$ bonds, the larger one being 2·76*D* for the substance to which we assigned the *cis* configuration and the smaller 1·64*D* for the trans compound).

The *trans* configuration of β-chlorovinylmercury chloride, with a high melting-point, as well as that of its corresponding chlorovinylmercury bromide, has also been unambiguously determined by X-ray analysis, carried out at our request by A. I. Kitaigorodsky.[7]

Finally, the assignment of configurations is in agreement with the Werner's rule, as indicated by higher melting-points and lower solubilities of the compounds:

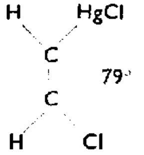


and

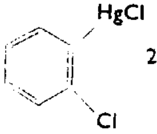


240°

as compared with



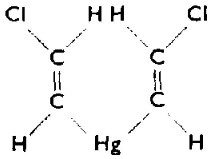
and



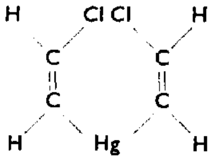
204°

The configurations of the two mercury dichlorovinyl derivatives follow from Werner's rule,

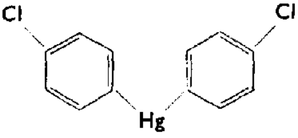
m.p. 70°



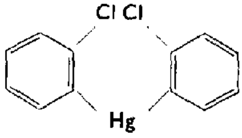
liquid



m.p. 243°



m.p. 145°



as well as from the Raman spectra of the *trans*-isomer. This assignment of the configurations is definitely proved by partial chlorination of both compounds[8] (in CCl_4 solution). Thereby

$$(\mathrm{ClCH{=}CH})_2\mathrm{Hg} + \mathrm{Cl_2} \longrightarrow \mathrm{ClCH{=}CHHgCl} + \mathrm{ClCH{=}CHCl}$$

---

[6] A. N. Nesmeyanov, R. Kh. Freidlina, and A. E. Borisov *Izvest. Akad. Nauk. SSSR, Otdel. khim. Nauk* 137 (1945).

[7] A. I. Kitaigorodsky *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 170 (1945); 259 (1947).

[8] A. N. Nesmeyanov, A. E. Borisov, and A. I. Guskova *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 639 (1945).

In the organo-metallic compound obtained, the ethylenic carbon atoms remain unaffected by the reaction, the chlorovinyl groups thereby retaining their configuration. This reaction is therefore suitable for establishing the stereochemical similarity between dichlorvinyl and monochlorovinyl organo-mercuric compounds. As a result of this reaction, the solid mercury di-β-chlorovinyl forms, pure high-melting *trans*-β-chlorovinylmercury chloride almost quantitatively, and the liquid di-β-chlorovinylmercury yields, also quantitatively, pure *cis*-β-chlorovinylmercury chloride. The pronounced difference in the solubilities of the latter and former chlorides in petroleum ether would have revealed the presence of any isomeric admixture. The assignment of the configurations independently of antimony chlorovinyl compounds obtained from acetylene has been based on the following considerations:

In the readily proceeding exchange-reactions of mercury chloride, the solid (m.p. 48–49°) trichlorovinylstibine immediately forms pure *trans*-(I)-chlorovinylmercury chloride and, correspondingly, the liquid trichlorovinylstibine yields *cis*-(II)-chlorovinylmercury chloride without any stereoisomer admixture.

$$\text{I}\quad (\text{ClCH}{=}\text{CH})_3\text{SbCl}_2\ (\text{m.p. }93\text{–}94^\circ) \longrightarrow (\text{ClCH}{=}\text{CH})_3\text{Sb}\ (\text{m.p. }48\text{–}49^\circ) \xrightarrow{\text{HgCl}_2} \underset{(\text{m.p. }124^\circ)}{\text{ClCH}{=}\text{CHHgCl}}$$

$$\text{II}\quad (\text{ClCH}{=}\text{CH})_3\text{SbCl}_2\ (\text{m.p. }61\text{–}62^\circ) \longrightarrow (\text{ClCH}{=}\text{CH})_3\text{Sb}\ (\text{liquid}) \xrightarrow{\text{HgCl}_2} \underset{(\text{m.p. }79^\circ)}{\text{ClCH}{=}\text{CHHgCl}}$$

It therefore follows that the initial antimony compound could not in the two cases (I, II) have been of a mixed form (*cis-cis-trans* or *cis-trans-trans*).

The configuration of the solid trichlorovinylstibine as *trans-trans-trans* compound follows from the detailed X-ray pattern analysis, made by Kitaigorodsky and Struchkov, on tri-β-chlorovinyldichlorostibine, which, on reduction of an antimony atom, yields solid trichlorvinylstibine. The configuration of chlorovinyl groups does not seem to be thereby affected.

According to Raman spectra analysis carried out by M. I. Batuyev at our request, only the liquid stereoisomer of trichlorovinylstibine displays in the Raman spectra two intensive bands in the 400–600^{-1} cm range, which distinguishes the *cis* compounds of the RCH=CHR′ type from their *trans*-isomers (frequencies, 425 cm^{-1} (intensity, 10) and 581 cm^{-1} (intensity, 7). Analysis of *cis-cis*-dichlorvinylmercury revealed frequencies of 420 cm^{-1} (intensity, 10) and 591 cm^{-1} (intensity, 8). The spectra of trichlorovinylstibine with m.p. 48–49° revealed no bands in this range. These criteria do not hold for *trans*-di-β-chlorovinylmercury, as irradiation converts it into the *cis* form.

As far as the two di-β-chlorovinyldichlorostannanes are concerned, they are pure forms and not *cis-trans* modifications, each of them yielding with mercuric chloride only one stereoisomer of chlorovinylmercury chloride.

The constants of the stereoisomeric dichloroethylenes are well known—(*trans* compound: b.p. 48·3°, $d_{4^\circ}^{15^\circ} = 1{\cdot}2650$, $d_{4^\circ}^{25^\circ} = 1{\cdot}2489$, $n_D^{18} = 1{\cdot}4466$; *cis* isomer: b.p. 59·8°, $d_{4^\circ}^{15^\circ} = 1{\cdot}2896$, $n_D^{17} = 1{\cdot}44992$).

Chlorination of *trans*-chlorovinylmercury chloride immediately led to pure *trans*-dichloroethylene (m.p. 47·5°/741 mm, $d_{4^\circ}^{18^\circ} = 1{\cdot}2574$, $n_D^{18^\circ} = 1{\cdot}4468$).

Chorination of the mercuric *cis*-isomer also gave pure *cis*-dichloroethylene (b.p. 58–59°, $d_{4^\circ}^{20^\circ} = 1{\cdot}2819$, $n_D^{17^\circ} = 1{\cdot}4493$, $n_D^{20} = 1{\cdot}4475$), rectification being carried out on a column with 20 theoretical plate efficiency. Thus, apart from $(ClCH{=}CH)_2PbX_2$(X=Chlorine, CH_3COO), $(ClCH{=}CH)_2TlCl$ compounds and both isomers $(ClCH{=}CH)_2SnCl_2$, configurations of all compounds listed in the table leave no room for doubt.

The following argument proves that of lead, thallium, and crystalline tin chlorovinyl compounds produced from *trans*-dichlorovinylmercury are *trans* forms and that the liquid-tin and thallium chlorovinyl compounds obtained from *cis*-dichlorovinylmercury are *cis* forms. Starting from *trans*-chlorovinylmercury chloride, it is possible to effect cyclic reactions, involving 2, 3, or 4 cycles and always reverting to the same parent *trans*-β-chlorovinylmercury chloride (5, 6), (5,11,4), (5, 16, 9), (5, 15, 10), (5, 11, 14, 10), (5, 16, 20, 10). The di-β-chlorovinyldichlorostannane produced in numerous conversions by different routes with a different number of steps (reactions N 15, 14, 20) is also always the same, melting at 77·5–78·5°. It is inconceivable that in all these different cycles, conversions of the trans configuration of the chlorovinyl radical into *cis* configuration would proceed just the necessary number of times for it to regain its original form. We have named this method as one of odd and even cycles. Starting from *cis*-chlorovinylmercury chloride, the reactions N 27 and N 33 result in liquid di-β-chlorovinyldichlorostannane, which is again converted N 30 into *cis*-chlorovinylmercury chloride, under the action of mercuric chloride.

Thus, the group of compounds obtained by conversions of tri-*trans*-β-chlorovinylstibine and *trans*-β-chlorovinylmercury chloride, on the one hand, and that of compounds obtained from the *cis*-isomers of these compounds on the other, are independent groups interconnected only by means of conversion of di-*trans*-β-chlorovinylmercury into the *cis*-isomer under the effect of irradiation and a similar conversion of *trans*-dichlorovinylstannane into the *cis*-isomer (omitted in the Table).

We have found[9] also that *trans*-chlorovinylmercury chloride is converted into its *cis*-isomer—poorer in energy[10]—when the solution is heated with benzoyl, acetyl, or with sodium peroxides.

Thus, all exchange reactions listed in the table proceed with strict retention of the configuration of the chlorovinyl group when transferred from one atom to another.

It follows therefore, that electrophilic and homolytic substitutions at the olefinic carbon atom take place without any change of configuration.

This assertion, made by the present authors in a paper in 1948,[3] has been further substantiated in our more recent investigations.[11]

In Table 2 are presented three isomeric products of mercury acetate in reaction with dimethylacetylene.

Two of them are stereoisomeric, as shown for instance by ozonolysis (only acetic acid being formed) and regeneration of dimethylacetylene by the action of potassium iodide. One of the isomers (presumably) *trans*-2 acetoxy-3-chloromercury-butene-2, m.p. 140°, is converted by ammonia into a symmetrical compound of the R_2Hg type, m.p. 113–114°, the latter being converted by the action of thallium trichloride into an organic substance of the R_2TlCl type. Each of these conversions can be

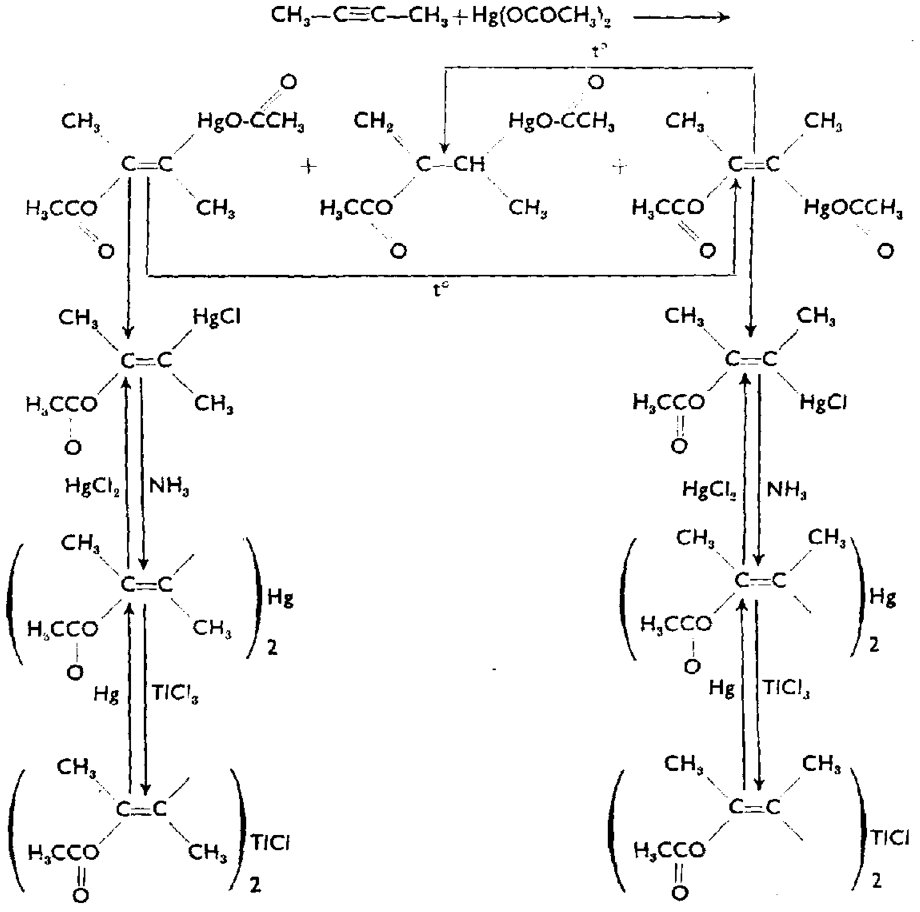
---

[9] A. N. Nesmeyanov, A. E. Borisov, and A. D. Vilchevskaya *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 578 (1949).

[10] E. A. Shilov and I. V. Smirnov-Zamkov, *Dopovidi Akad. Nauk Ukr.SSR* 87-92 (1951).

[11] A. E. Borisov, V. D. Vilchevskaya, and A. N. Nesmeyanov, *Doklady Akad. Nauk SSSR*, **90**, 383 (1953); *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* 1008 (1954).

TABLE 2



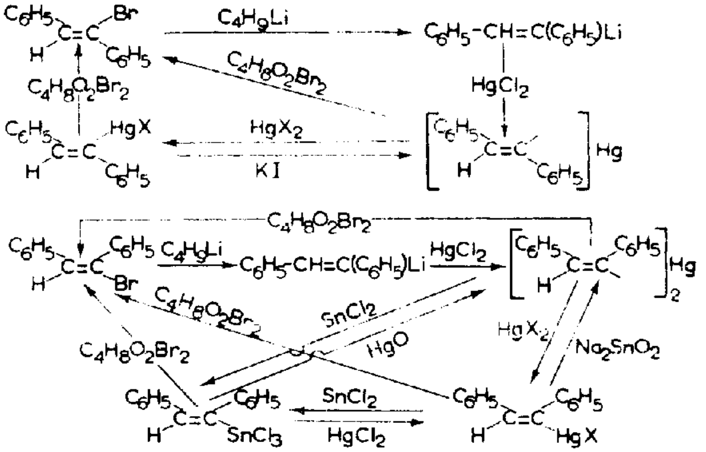
effected in the reverse direction by reacting in the latter case with metallic mercury, and in the former with antimony. All reactions described are of a stereospecific type producing only one stereoisomer. In the same way *cis*-2-acetoxy-3-chloromercury-butene-2, m.p. 95°, appeared to undergo a symmetrical change to give the corresponding compound of the R_2Hg type, m.p. 101–102°, which by the action of thallium trichloride gives the stereoisomeride of the organo-thallium compound mentioned above. These reactions and the reverse ones take place similarly and are of a stereospecific type.

Both series of conversions are separated from each other and do not overlap. To this series of reactions the procedure of odd and even cycles cannot be applied. It is therefore to be assumed that either the configurations in all reactions are retained or that they are inverted in all instances. The latter is extremely unlikely, as the reaction $RHgX \rightarrow R_2Hg$ has in a number of instances been shown to proceed with the retention of the configuration. The possibility of inversion is to be discarded, as the mercury compounds shown in the left-hand column, obtained from *trans*-acetoxy-2-chloromercury-3-butene-2 exhibit a double-bond frequency in the infra-red spectrum invariably higher than that of the corresponding stereoisomer. (*Trans*-acetoxy-2-chloromercury-3-butene-2, m.p. 140°/1667 cm^{-1}; *cis*-acetoxy-2-chloromercury-3-butene-2, m.p. 95°/1655 cm^{-1}; *trans*-di-(1-methyl-2-acetoxy-1-propene-1-il) mercury, m.p. 114°/1621 cm^{-1}; *cis*-isomer, m.p. 101–102°/1616 cm^{-1}).

This fact, as well as that of their higher melting-points, leads us to conclude that each column represents one stereochemical series, the left column undoubtedly indicating the trans configuration.

The following sequence of reactions, shown in Table 3:

TABLE 3



represents exchange reactions of stereoisomeric monobromostilbenes, carried out by us and N. A. Volkenau, using the procedure of odd and even cycles.[12] *Cis*- (m.p. 21°) and *trans*- (m.p. 32°) bromostilbenes were converted into lithium stilbenes under the action of butyllithium at −40°.

Lithiumstilbenes were immediately converted by the action of antimony into di-stilbenylmercury. Then followed the cyclic reactions represented in the scheme.* They were reconverted to their parent bromostilbene. With *cis*-bromostilbene the even and odd cycles are, for example, as follows:

$\text{StBr} \rightarrow \text{StLi} \rightarrow \text{St}_2\text{Hg}$ 3 cycles
Br_2

$\text{StBr} \rightarrow \text{StLi} \rightarrow \text{St}_2\text{Hg} \rightarrow \text{StHgBr}$ 4 cycles
Br_2

$\text{StBr} \rightarrow \text{StLi} \rightarrow \text{St}_2\text{Hg} \rightarrow \text{StHgCl} \rightarrow \text{StSnCl}_3$ 5 cycles
Br_2

Cis-lithiumstilbene is extremely sensitive to heat. Therefore, the reaction of bromostilbene with butyllithium has to be carried out at −40° (in ether-benzene

---

* The melting-points of compounds involved in this cycle of trans conversions are as follows: Bromostilbene 32°, chlorostilbene 53·5°, chloromercurystilbene 142°, bromomercurystilbene 157–158°, mercury-*bis*-stilbene 243–244°. Those of the *cis* series are: bromostilbene 31°, chloromercurystilbene 131°, bromomercurystilbene 118–120°, mercury-*bis*-stilbene 145–147°, stilbenyl-trichlorostannane 109–110°.

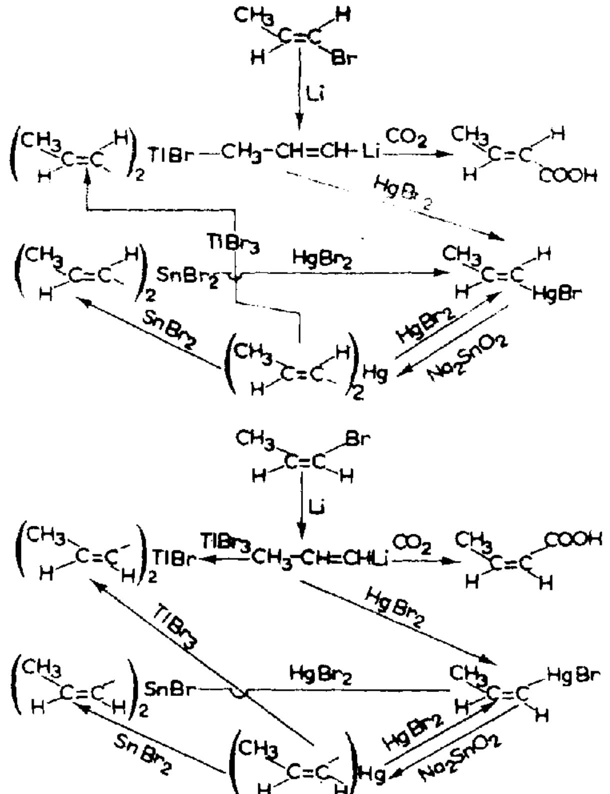
[12] A. N. Nesmeyanov, A. E. Borisov, and N. A. Volkenau *Izvest. Akad. Nauk SSSR*, 992 (1954); 162 (1956).

mixture) and the organo-lithium compound produced must at once be subjected to other reactions: otherwise, *cis*-lithiumstilbene results in compounds of the *trans* series. Experiments have shown that isomerisation does not take place during the reaction of substitution of bromine by lithium, but that it is the organo-lithium compound which is isomerised after formation. *Cis*-mercury-*bis*-stilbene can undergo isomerisation into a *trans* compound after prolonged heating (140°) or being irradiated with ultra-violet rays.

In other respects the compounds obtained from *cis*-stilbene are not similar to those derived from *trans*-bromostilbene. The succession of even and odd cycles proves in this case also the retention of the configuration in each step of the reaction.

Exchange reactions are represented in Table 4, starting from *cis*- and *trans*-1-bromo-propene-1, and were carried out and studied by us and N. V. Novikova.[13]

TABLE 4



In this case one can safely work at temperatures not exceeding room temperature. The formation of propenyllithium took place at 3 6°. Heating propenylmercury halogens dissolved in acetone at the boiling temperature is enough to bring about the interconversion of stereoisomers.

Similarly, prolonged standing (3–5 days) or heating for several hours up to 50° in benzene solution, results in far-reaching interconversion of stereoisomers of dipropenylmercury.

Exchange reactions involve the following cycles:

$$\begin{tikzcd} Pr_2TlBr & PrLi \arrow[l] \arrow[r] & PrHgBr \arrow[r] & Pr_2Hg \arrow[lll, bend left] \end{tikzcd}$$

4 cycles

$$\begin{tikzcd} PrHgBr \arrow[r] & Pr_2Hg \arrow[r] & Pr_2SnCl_2 \arrow[ll, bend left] \end{tikzcd}$$

3 cycles

$Pr_2Hg \rightleftarrows Pr_2SnCl_2$ 2 cycles

$Pr_2Hg \rightleftarrows PrHgBr$ 2 cycles

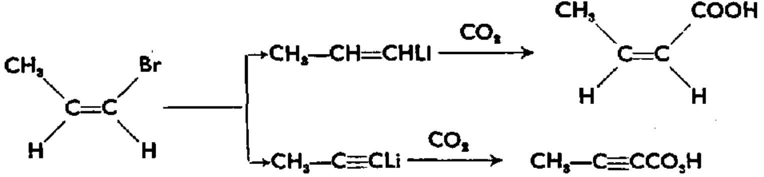
When the exchange reactions are being carried out at low temperature (or lower than room temperature), the fields of the conversions of *trans*-bromopropene and *cis*-bromopropene are isolated from each other.

From the double-bond frequencies in the infra-red spectrum of isomeric bromomercury-propenes it can be deduced that the bromomercury propene produced from trans-bromopropene has a trans configuration, as its frequencies (1625 cm^{-1}) are respectively higher than those of its isomer (1510 cm^{-1} and 1600 cm^{-1}).

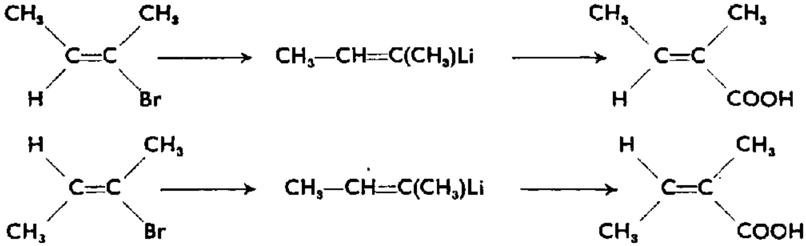
Thus, for the higher-melting (360°) dipropenylthallium bromide obtained from *trans*-bromopropene, the CH-bond frequencies have been found to be higher (1042 cm^{-1}, 960 cm^{-1}) than for its stereoisomer, produced from *cis*-bromopropene (1037 cm^{-1}, 926 cm^{-1}).

The assertion made by us in 1948, that electrophilic and homolytic substitutions at the olefinic carbon take place with retention of the configuration is now shown to be of an entirely general character.

In a paper published by Braude and Coles[14] it was stated that conversion of *cis*-bromopropene through an organo-lithium compound leads to *iso*crotonic acid which is then converted into *cis*-dipropenyl ketone.



In 1954, Dreiding and Pratt[15] effected the carboxylation of organo-lithium compounds, obtained from both stereoisomers of 2-bromobutene-2, to yield acids with a configuration corresponding to that of parent bromides. In both cases the overall retention of the configuration does not prove the stereochemistry of each reaction taken separately, as two successive inversions are possible.



---

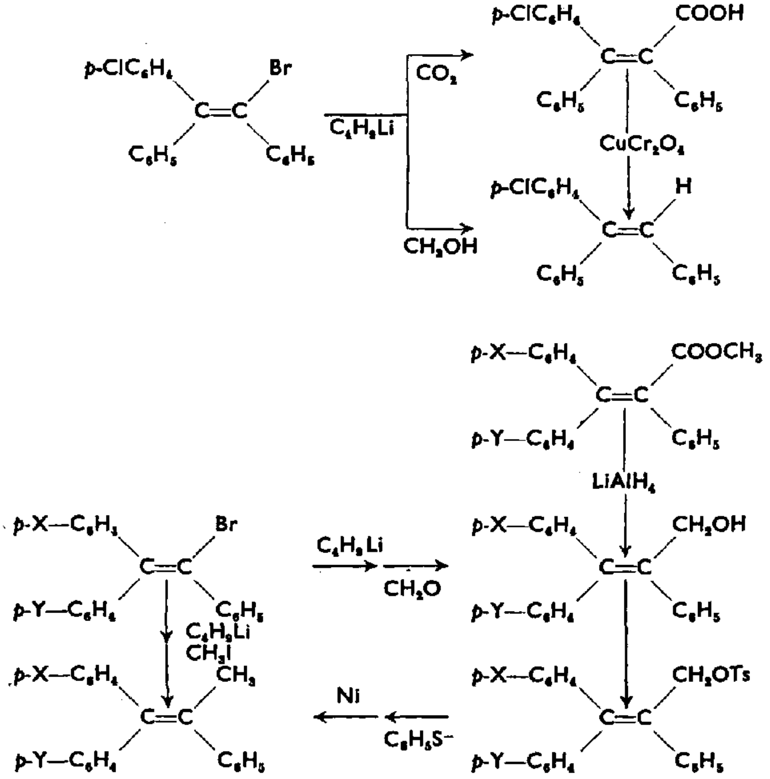
[13] A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk* In press.

[14] E. A. Braude and J. A. Coles *J. Chem. Soc.* 2078 (1951).

[15] A. S. Dreiding and R. J. Pratt *J. Amer. Chem. Soc.* **76**, 1902 (1954).

The investigations of Curtin and Harris[16] and Curtin, Johnson, and Steiner[17] are represented in Table 5.

TABLE 5



Cis-isomer $X = Cl$; $Y = H$; trans-isomer $X = H$; $Y = Cl$

These authors also demonstrate the overall retention of the configuration, but as can easily be seen, this overall retention can be explained in each case as due to two successive inversions.

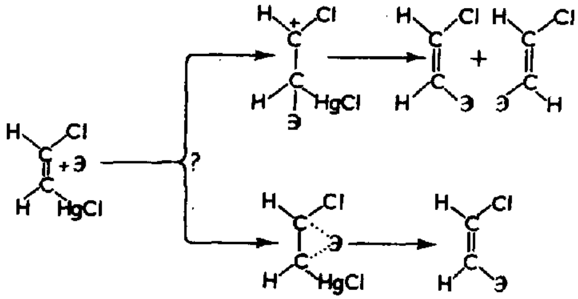
Only in the light of the results of our investigation does it become certain that in the investigations of the above-mentioned authors each reaction proceeds without the inversion of the configuration. The retention of configuration in the reactions of electrophilic (and homolytic) substitution at the trigonal carbon is unexpected not so much in comparison with Walden's inversion as with the electrophilic substitution in the aromatic nucleus. The usual treatment of electrophilic substitution in the benzene nucleus in the case say of ortho chloro-mercury chlorobenzene may be compared with the similar exchange reaction of mercury in *cis*-chlorovinylmercury chloride.

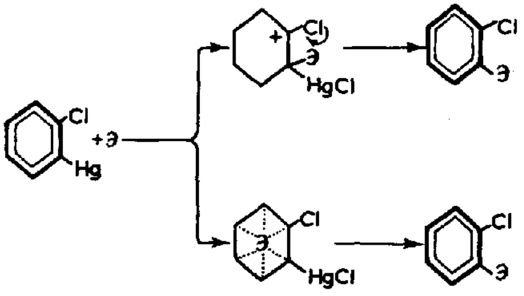
A similar treatment of the substitution reaction of a metallic atom at the olefinic carbon inevitably leads to the inversion of the configuration of the parent olefinic

---

[16] D. J. Curtin and E. E. Harris *J. Amer. Chem. Soc.* 73, 2716 (1951).

[17] D. J. Curtin, H. W. Johnson, and E. G. Steiner *J. Amer. Chem. Soc.* 77, 4566 (1955).





substance. At the same time, it would be impossible to assume that the π bond—in the case of an olefine—should not have participated in the reaction.

The only plausible conclusion would be to assume the formation of a complex in the transition state retaining the configuration. If such be the case, analogous considerations make us think of a similar scheme for the substitution in the aromatic nucleus as the more probable and which is the Dewar scheme for electrophilic aromatic substitution.