Tetrahedron, 1960, Vol. 9, pp. 156 to 162. Pergamon Press Ltd. Printed in Northern Ireland

STERIC HINDRANCE IN THERMAL AND CATALYSED ISOMERIZATIONS OF CHLORINATED $\alpha:\alpha'$-DICHLOROSTILBENES*

M. BALLESTER and J. ROSA
Departamento de Química Orgánica de Barcelona, Instituto de Química "Alonso Barba",
Consejo Superior de Investigaciones Científicas,
Universidad de Barcelona

(*Received* 21 *September* 1959; *in revised form* 18 *January* 1960)

Abstract—Evidence is given for hindrance to thermal stereomutation of *cis*- and *trans*-perchlorostilbenes. Such hindrance is accounted for in terms of steric inhibition of resonance in the transition state of the isomerization due to the *ortho* chlorine atoms.

Also, it is shown that under conditions leading to isomerization in closely related cases, i.e. photochlorination and nuclear perchlorination, the perchlorostilbenes are quite inert. These results are interpreted in terms of steric strain of the reaction intermediates and transition states.

Thermal isomerization of stilbenes

The thermal isomerization of stilbenes is easier than that of non-conjugated ethylenes such as 1,2-dideuteroethylene. This has been accounted for on the basis of single bond character of the ethylene bond in the ground state.[1] The effect is actually due to a lowering of the energy of activation† and therefore a more precise insight can be given when the energies, i.e. the resonance, of both ground and transition states of the molecule are taken into account.‡

It is generally assumed that the transition state in *cis–trans* thermal isomerizations is close to the so-called "perpendicular ethylene", i.e. the spatial molecular arrangement resulting after a 90° rotation around the ethylene bond axis of one ethylene carbon atom with the groups attached to it.[7] In such an arrangement, the ethylene carbon *p*-orbitals, which in the ground state form the π-bond, are perpendicular to each other and therefore the π-bond is practically broken.

In the case of stilbenes, resonance involving the *p*-orbitals of the ethylene carbon atoms and those of the benzene nuclei takes place. Any valence-bond structure participating in the ground state having a single bond between the ethylene carbon atoms participates to a much larger extent in the transition state of the isomerization

---

* Presented in *The XVI International Congress of Pure and Applied Chemistry*. Paris (1957). It contains part of the work done by J. Rosa in fulfilment of D.Sc.

† Reported values: 43 kcal/mol for *cis*-stilbene,[2] 61 kcal/mol for 1,2-dideuteroethylene,[3] and 52 kcal/mol for *cis*-2-butene.[4]

‡ It is generally accepted that the stilbenes isomerize by an "adiabatic" mechanism, i.e. a mechanism involving no singlet-triplet transitions.[5] The mechanism of the thermal isomerization of some strongly resonating substituted stilbenes is however uncertain.[6]

[1] G. W. Wheland, *Resonance in Organic Chemistry* p. 197. John Wiley, New York (1955).

[2] G. B. Kistiakowski and W. R. Smith, *J. Amer. Chem. Soc.* **56**, 638 (1934).

[3] B. S. Rabinovitch, J. E. Douglas and P. S. Looney, *J. Chem. Phys.* **20**, 1807 (1952).

[4] W. F. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *J. Amer. Chem. Soc.* **80**, 2384 (1958).

[5] J. L. Magee, W. Shand and H. Eyring, *J. Amer. Chem. Soc.* **63**, 677 (1941).

[6] M. Calvin and H. W. Alter, *J. Chem. Phys.* **19**, 768 (1951).

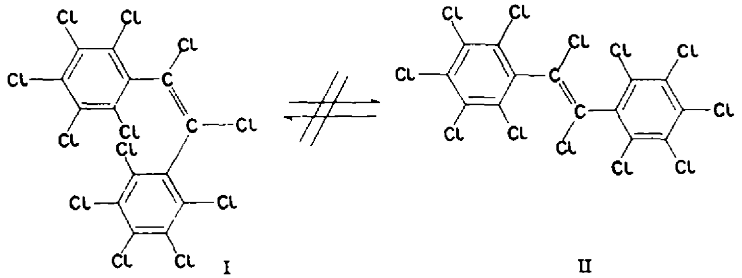
[7] L. Crombie, *Quart. Rev.* **6**, 101 (1952).

since the stability of this state is much more dependent on the contribution of such single-bond structures. In other words, stronger stabilization by resonance in the transition state than in the ground state must be the reason for the lower energy of activation in these isomerizations.

The conjugation between the ethylene bond and the benzene nuclei can be sterically inhibited in both ground and transition states by bulky substituents located in *alpha* and *ortho* positions. Their interactions prevent that degree of approach to coplanarity between the ethylene system and the benzene nuclei which is required to make the overlapping of *p*-orbitals effective.[8] The situation then approaches that of 1,2-dideuteroethylene, and the result should be a much more difficult thermal isomerization.

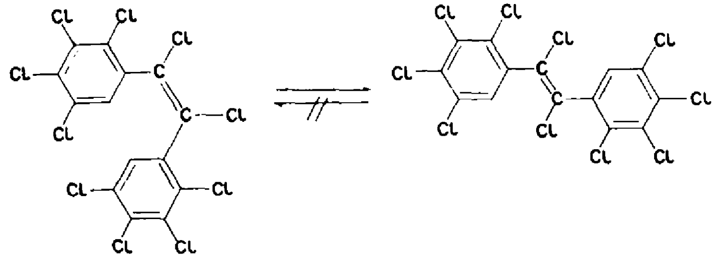
In Fig. 1 the transition state for the perchlorostilbenes is represented. The shaded areas show the steric interaction between chlorine atoms causing the departure from coplanarity in the transition state. Accordingly, while *cis*-α,α′-dichlorostilbene undergoes measurable isomerization in the liquid phase at around 200°[9] here it is reported that extended heating of *cis*-perchlorostilbene (I) at 300°, or *trans*-perchlorostilbene (II) at 400°, fails to give any detectable isomerization.

It can be expected that removal of one *ortho* chlorine in both benzene nuclei of perchlorostilbene would strongly diminish the inhibition of resonance in the transition state. Actually, 1·5 hr heating of *cis*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene (III) at 260° yields an 11 per cent conversion into its *trans*-isomer (IV). This isomer fails to give any *cis*-isomer under the same conditions.



I

II



III

IV

Catalytic isomerizations of stilbenes

Halogen atoms can bring about *cis–trans* isomerizations. The evidence reported in the literature points to a radical chain mechanism occuring essentially in three

---

[8] M. Ballester, C. Molinet and J. Rosa, *Tetrahedron* **6**, 109 (1959).

[9] T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.* 2078 (1938).

steps:[10] (1) Reversible halogen-atom addition to double bond. (2) Rotation isomerization of the resulting radical-adduct to give that of the isomeric ethylene. (3) Reversible dissociation of this second adduct to yield the isomeric ethylene.

The main feature of this mechanism is that with the addition process the high rotational energy barrier of an ethylene bond is replaced by the smaller rotational energy barriers of a single bond between a tetrahedral and a trigonal carbon atom.

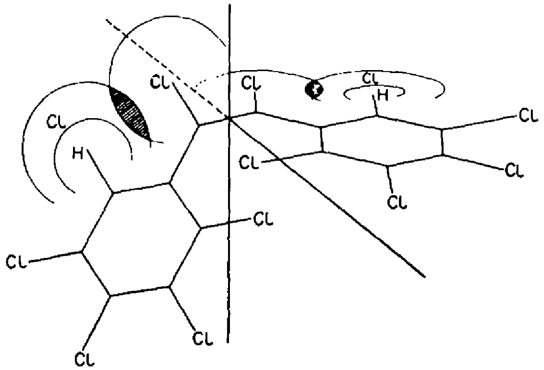


FIG. 1.

If this isomerization mechanism is accepted it can be expected that the introduction in a stilbene of bulky groups in *ortho* and *alpha* positions should prevent its isomerization by halogen either hindering step (1) or (2). This should be the case of perchlorostilbene. Its hypothetical radical adducts with a chlorine atom, IA and IIA, should possess an important steric strain due to overcrowding about the carbon (tetrahedral) atom to which the chlorine atom becomes bonded. This strain would assist the dissociation of the adducts into their original components.

There is a considerable body of evidence showing that compounds of the type $C_6Cl_5CCl_2R$ (R = Cl, CCl_3, $CCl_2C_6Cl_5$, etc.), because of the steric repulsions between the two *ortho* chlorine atoms and the substituents on the *alpha* carbon atom, are energy-rich. In spite of the great number of attempted preparations few of such compounds have been obtained so far.[11] Their ultra-violet absorption spectra reflect strikingly their high strain.[12] Brown *et al.* have estimated on experimental basis the strain of 2,6-dichloro-1-trichloromethylbenzene;[13] their value is 24 kcal/mol. This means that in the case of the perchlorostilbenes there is an additional steric energy barrier to be surmounted in step (1) which obviously is high enough to break up the reaction chain.

It is pointed out that step (1) is an electrophylic attack and therefore it is favoured by electron release to the *alpha* carbon atom. Therefore, it can be expected that steric inhibition of resonance between the benzene nuclei and the double bond due to steric interaction between the two *ortho* chlorine atoms and the substituents attached to the *alpha* carbon atom can hinder that electron accession to the reaction site and consequently also step (1).* However, in view of the magnitude of the energy due to

* The authors are much indebted to the referee of this work for pointing out such possibility and for other valuable suggestions.

[10] H. Steinmetz and R. M. Noyes, *J. Amer. Chem. Soc.* 74, 4141 (1952).

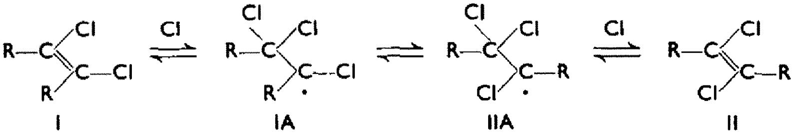
[11] M. Ballester, C. Molinet and J. Castañer, forthcoming publication.

[12] M. Ballester and J. Castañer, forthcoming publication.

[13] H. C. Brown, D. Gintis and L. Domash, *J. Amer. Chem. Soc.* 78, 5387 (1956).

overcrowding and the very small extent of the "styrene" resonance in *both* α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbenes and perchlorostilbenes as ascertained by their ultraviolet spectra[8] and by simple inspection of their Stuart models, the authors do not favour this effect as a major one.

The radical adducts should also have to overcome an important steric energy barrier before reaching the required configuration for step (3) of the isomerization to occur. This would create an additional hindrance and favour further the ineffectual dissociation of the adducts over the stereomutation.



It has been found accordingly that while an attempted photochlorination with chlorine and white light of *cis*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene gives 84·6 per cent yield of its isomer, both *cis*- and *trans*-perchlorostilbene fail to give any detectable isomerization under the same conditions. No isomerization of the *cis*-decachlorostilbene occurs by illumination with white light in the absence of chlorine, the other conditions being equal.

trans-α,2,3,4,5,α′,2′,3′,4′,5′-Decachlorostilbene gives, when treated with sulphuryl chloride containing anhydrous aluminium chloride and sulphur monochloride, an almost quantitative yield of *trans*-perchlorostilbene. However, when *cis*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene is treated with the same reagent and under the same conditions a mixture containing both the *cis*- and *trans*-perchlorostilbene is obtained. Therefore, by the influence of the chlorinating agent stereomutation has occurred.

It has been found that neither *cis*- nor *trans*-perchlorostilbene isomerizes under the reaction conditions. Therefore, the stereomutation has taken place either in the decachlorostilbene or in the undecachlorostilbene stage.

If it is accepted—as in the previously considered case of the radical-catalysed isomerization—that the isomerization here occurs through double-bond addition of an electrophylic particle, it is reasonable to assume that the stereomutation will take place the easier the lesser is the degree of *ortho* substitution by chlorine. In the present case, the hindrance to isomerization in the perchlorostilbenes is interpreted also through consideration of the high steric strain of the intermediate adducts. It can therefore be assumed that stereomutation occurs, at least mostly, prior to any nuclear perchlorination.

The fact that isomerization occurs in a relatively chlorine overcrowded compound such as *cis*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene suggests that the electrophylic particle which adds to the double bond is a small one. One is tempted to assume that Cl^+ is the particle and, consequently, that the isomerization occurs through the intermediate cation $C_6HCl_4CCl_2—\underset{+}{C}Cl—C_6HCl_4$.

EXPERIMENTAL

Some properties of the stilbenes here studied have been given previously.[8] However, it is desirable to emphasize here again that the great differences of solubility between the geometrical isomers permitted treatment with solvent to perform clean and relatively rapid separations.

Some experiments described are intended to show that the isomerization of perchlorostilbenes, if any, is insignificant. It was desirable therefore to perform control experiments concerning the solubilities in the solvents used under the separation conditions to find out whether considerable amounts of the isomers could pass undetected.

Solubility experiments

Finely ground perchlorostilbene was shaken in the solvent during 1½ hr at 16–17°. The undissolved part was filtered off and the residue of a measured part of the solution was weighed.

Ethyl ether *cis*-perchlorostilbene, 0·41 g% ml; *trans*-perchlorostilbene, 0·0040%. *Benzene* *cis*-perchlorostilbene, 5·70%; *trans*-perchlorostilbene, 0·015%.

The solubilities of *trans*-perchlorostilbene in saturated solution of *cis*-perchlorostilbene are: *Ethyl ether* 0·0044%. *Benzene* 0·016%.

Consequently, the differences of solubility and the insolubility of the *trans* isomer are so great as to permit exceptionally clean separations.

Thermal isomerization of cis-*α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene*

In a sealed glass tube 0·106 g *cis*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene, m.p. 141–142°,[8] were heated during 6 hr at 260–265°. The resulting solid mass was treated with boiling pet ether which extracted 0·092 g of the starting material. The residue (0·012 g) was identified as *trans*-decachlorostilbene by m.p., mixed m.p. and ultra-violet spectrum.[8] The yield of the isomerization was therefore 11·3%.

Attempted thermal isomerization of trans-*α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene*

In a sealed glass tube 0·079 g *trans*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene, m.p. 255–257°,[8] were heated during 1·5 hr at 265°. The resulting mass was refluxed with 10 ml pet ether and the residue (0·068 g) was identified by m.p. and mixed m.p. as unchanged *trans*-decachlorostilbene. Concentration of the mother liquor yielded 0·007 g more starting material. No *cis*-decachlorostilbene was detected.

Attempted thermal isomerization of cis-*perchlorostilbene*

In a sealed glass tube 0·211 g *cis*-perchlorostilbene, m.p. 230·5–231·5°,[8] were heated during 4 hr at 300°. The resulting mass (0·210 g) left no insoluble residue by treatment with a few ml cold benzene, and it was identified as starting material by m.p. and mixed m.p.

Attempted thermal isomerization of trans-*perchlorostilbene*

In a sealed glass tube 0·078 g *trans*-perchlorostilbene, m.p. 390°,[8] were heated during ½ hr at 400°. Treatment of the resulting mass with hot carbon tetrachloride gave 0·018 g pure starting material as residue. The carbon tetrachloride solution, after evaporation to dryness and treatment with hot benzene gave 0·053 g more starting material. The part soluble in benzene (0·006 g) gave by concentration 0·003 g more *trans*-perchlorostilbene and 0·003 g of an oil which did not yield crystals, even when seeded with *cis*-perchlorostilbene. The recovered material melted sharply at 390° and it was identified by mixed m.p.

Attempted photochlorination of cis-*α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene*

Through a steam-heated solution of 0·052 g *cis*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene in 3 ml purified carbon tetrachloride placed in a "Pyrex"-brand container a stream of dry chlorine was passed while illuminating with a 500W incandescent lamp located at 20 cm from the container. Partial removal of the solvent yielded 0·023 g *trans*-decachlorostilbene which was identified by m.p., mixed m.p. and ultra-violet spectrum.[8] The residue obtained by total elimination of the solvent was treated with hot pet ether yielding 0·021 g more of the product. Yield of the isomerization, 85%.

Attempted photo-isomerization of cis-*α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene with white light*

A solution of 0·050 g *cis*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene in 3 ml purified carbon tetrachloride was heated during 22 hr in a "Pyrex"-brand flask while illuminating with a 500W incandescent lamp located at 20 cm from the container. Removal of the solvent gave 0·049 g unchanged pure *cis*-decachlorostilbene. It was identified by mixed m.p.

Attempted photochlorination of cis-*perchlorostilbene*

Through a steam-bath heated solution of 0·200 g *cis*-perchlorostilbene in 7·5 ml purified carbon tetrachloride a stream of dry chlorine was passed during 19·5 hr while illuminating with a 500W incandescent lamp situated at 20 cm from the container. By removal of the solvent 0·239 g of a solid residue was obtained which by digestion in ethanol gave 0·189 g starting material. From the ethanol solution 0·05 g perchloroethane was obtained. The recovered *cis*-perchlorostilbene melted at the correct temperature and was completely soluble in cold ethyl ether. This showed the absence of a significant amount of the *trans*-isomer.

Attempted photochlorination of trans-*perchlorostilbene*

Through a steam-bath heated suspension of 0·200 g *trans*-perchlorostilbene in 7·5 ml purified carbon tetrachloride a stream of dry chlorine was passed during 35 hr while illuminating with a 500W incandescent lamp situated at 20 cm from the container. The solid residue obtained by elimination of the solvent was treated with hot pet ether leaving 0·174 g of a residue which was identified as starting material. The soluble part consisted of perchlorobenzene (0·020 g) and perchloroethane the separation of which was performed by treatment with ethanol. The identification was performed by mixed m.p. with authentic samples. The *trans*-perchlorostilbene melted sharply at 390°.

Nuclear chlorination of cis-α,2,3,4,5,α′,2′,3′,4′,5′-*decachlorostilbene*

A solution containing 0·050 g sulphur monochloride in 4 ml of sulphuryl chloride was added gradually to a boiling solution containing 0·100 g *cis*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene, 0·025 g anhydrous aluminium chloride and 3 ml sulphuryl chloride. The resulting solution was then concentrated to 2 ml and the refluxing continued for about 3 hr, keeping constant the volume of the reaction mixture by adding small quantities of sulphuryl chloride. Most of the sulphuryl chloride was distilled off and the residue treated with hot water and powdered sodium bicarbonate. The mass was then acidified with hydrochloric acid to dissolve the aluminium hydroxide formed, treated with ethyl ether and the two layers formed filtered. The insoluble part (0·038 g) was identified as *trans*-perchlorostilbene by m.p., mixed m.p. and ultra-violet spectrum.[8]

By removing the ether from the ethereal layer a solid was obtained which by recrystallization from ethyl acetate gave 0·047 g *cis*-perchlorostilbene, being identified by m.p., mixed m.p. and ultra-violet spectrum.[8] The yields were 33·6% *trans*-isomer and 41·5% *cis*-isomer.

Nuclear chlorination of trans-α,2,3,4,5,α′,2′,3′,4′,5′-*decachlorostilbene*

A solution of 0·100 g sulphur monochloride in 8 ml sulphuryl chloride was added gradually to a refluxing solution containing 0·100 g *trans*-α,2,3,4,5,α′,2′,3′,4′,5′-decachlorostilbene, 0·050 g anhydrous aluminium chloride and 6 ml sulphuryl chloride. The mass was then concentrated to 10 ml and the refluxing continued for about 3 hr as above. The part insoluble in ether (0·118 g) was treated with warm carbon tetrachloride and gave a residue (0·089 g) identified as *trans*-perchlorostilbene by m.p. (390°, sharply), mixed m.p. and ultra-violet spectrum. The part soluble in carbon tetrachloride was washed with pet ether and left 0·023 g more pure *trans*-perchlorostilbene. Yield: 99·1% of the theoretical.

Attempted isomerization of cis-*perchlorostilbene under the nuclear chlorination conditions*

0·300 g *cis*-perchlorostilbene were treated with a mixture containing 0·075 g anhydrous aluminium chloride, 0·150 g sulphur monochloride and 21 ml sulphuryl chloride under the usual conditions, reducing the volume to 2 ml and refluxing during 3 hr. The resulting mass was treated with water solid sodium bicarbonate and acidified with conc hydrochloric acid. The solid residue was filtered off and dried (0·285 g). It melted at 230·0–231·5° and it was identified as pure starting material by mixed m.p. and ultra-violet spectrum. It was soluble in cold ethyl ether leaving no residue.

Trans-*perchlorostilbene under nuclear chlorination conditions*

A solution of 0·050 g sulphur monochloride in 4 ml sulphuryl chloride was added gradually to a gently boiling solution of 0·116 g *trans*-perchlorostilbene, 0·025 g anhydrous aluminium chloride and 3 ml sulphuryl chloride. It was then concentrated to 1–2 ml and the refluxing continued for 2 hr 40 min more. The resulting mass was treated as usual and gave a solid residue (0·114 g) which was treated during ½ hr with boiling ether. The insoluble part (0·105 g) was identified by m.p. and mixed m.p. as starting material. From the ethereal extract by elimination of the solvent a residue (0·009 g) was obtained. This was dissolved in carbon tetrachloride and passed through a very small amount of activated alumina, and the resulting solution evaporated to dryness. The residue was treated with a very small amount of hot pet ether leaving after standing 0·005 g more *trans*-perchlorostilbene melting sharply at 390°. The remaining 0·002 g was a mixture melting poorly containing presumably some *trans*-perchlorostilbene. The ultra-violet spectra confirmed his assumption, giving no indication of the *cis*-isomer being present.