QUARTERLY REVIEWS

GEOMETRICAL ISOMERISM ABOUT CARBON-CARBON DOUBLE BONDS

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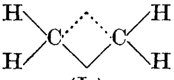
This review of geometrical isomerism, which is written primarily from the point of view of an organic chemist, deals only with the $>C=C<$ system. It is divided into three sections, these being examinations of (i) some general properties of the $>C=C<$ system, (ii) methods for the determination of geometrical configuration, and (iii) methods for the preparation of geometrical isomers. Attention is drawn to the existing reviews ; [1-3] those of more specialised aspects will be mentioned later.

Some General Properties of $>C=C<$ Systems

As a corollary to the theory that the valencies of carbon are disposed tetrahedrally, van't Hoff suggested a model (I) for ethylene.[4] The imaginary tetrahedra encompassing the directed valencies of the two carbon atoms are placed edge to edge and inspection shows that the six atoms involved are then coplanar, that $\angle$HCH is 109° 28′, that $\angle$CCH is 125° 16′, and that the $>C=C<$ bond distance is $0{\cdot}577 \times$ the C–C distance, i.e. 0·89 Å.



(I.)

Physical measurement has since shown that the $>C=C<$ distance in ethylene and substituted ethylenes is actually 1·33 Å (a little longer when in conjugation). But as the van't Hoff model indicates, ethylenes are planar except when bulky substituents interfere and cannot be accommodated without some twisting of the double bond. Modern theory shows that the two members of the double bond are not equal, as in the original model. One is cylindrically symmetrical about the bond direction (a σ bond), the other consists of two inseparable streamers of electron density above

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[1] A. Werner, " Lehrbuch der Stereochemie ", G. Fischer, Jena, 1904 ; M. Ramart Lucas and J. Hoch, *Ann. Chim.*, 1930, [x], **13,** 385 ; K. Freudenberg, " Stereochemie ", F. Deuticke, Leipzig, 1933, Vol. II ; H. Gilman, " Organic Chemistry ", Vol. I, J. Wiley, New York, 1943 (Contributor, C. S. Marvel) ; G. W. Wheland, " Advanced Organic Chemistry ", J. Wiley, New York, 1949.

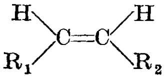
[2] A. Michael, *J. Amer. Chem. Soc.*, 1918, **40,** 704, 1674.

[3] V. Grignard, " Traité de Chimie Organique ", Masson et Cie., Paris, 1935, Vol. I (Contributor, C. Dufraisse).

[4] J. H. van't Hoff, *Bull. Soc. chim.*, 1875, [ii], **23,** 295 ; " The Arrangement of Atoms in Space ", Longmans, Green, London, 2nd Edn., 1898.

and below the plane of the ethylene :[5] the latter (a π bond) is therefore not cylindrically symmetrical. Because of this lack of symmetry, it is only when the molecule is planar that there is maximum overlap of the two atomic p orbitals which together constitute the π bond. The hybridisation of the carbon atoms involved is trigonal and the angle between the lobes of maximum electron density 120°. Measurement[6] shows that the bond angles in ethylenes in fact vary a little from this ($\angle$HCH in ethylene $110° \pm 5°$, $\angle$HCCl in dichloroethylene $116° \pm 2°$).

As a consequence of the geometry of the system certain substituted ethylenes must exist in two isomeric but non-enantiomorphic forms,[4] *e.g.*, types *Aa* (*cis*) and *Ab* (*trans*). The substituents R_1 and R_2 need not be different. Types *B* and *C* are often encountered, but *D* (*e.g.*, fulvenes) and *E* (*e.g.*, indigo) are less common. The criterion for the existence of geometrical isomers is that a rotation of one carbon atom through 180° gives a new planar arrangement of the substituents. It may be noted that certain *trans*-isomers, *i.e.*, *Ab*$(R_1 = R_2)$, *C*$(R_1 = R_3, R_2 = R_4)$ or *E*$(R_1 = R_2)$, have centres of symmetry. This has useful consequences (see below).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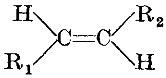
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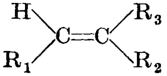
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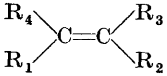
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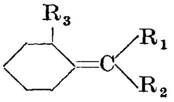
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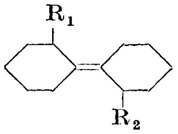
Type *E* *

* The ring size is immaterial but the system must be unsymmetrical about the C=C axis.

The double bond in an approximately planar ring system must be constrained in the *cis*-configuration (*e.g.*, *cyclo*hexene) but when the ring is multiplanar, *cis*- and *trans*-isomers exist (e.g., civetone[7]). Geometrical isomers about a single bond forming part of a ring system (*e.g.*, *cis*- and *trans*-*cyclo*hexane-1 : 2-diol) are very common, and theoretically *cis*- and *trans*-isomers about ordinary single bonds (*e.g.*, 1 : 2-dichloroethylene or buta-1 : 3-diene) can exist, though because of the low energy barrier separating the two forms they have not been isolated. Steric hindrance may raise the energy barrier and the two forms of (II) have been isolated and

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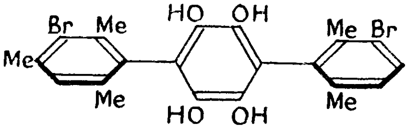
[5] C. A. Coulson, *Quart. Reiews*, 1947, **1**, 144.

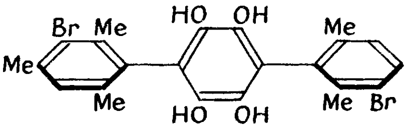
[6] Landolt–Börnstein, " Atom und Molekularphysik ", 2te Teil, Molekulen, I, Springer-Verlag, Berlin, 1951.

[7] M. Stoll, J. Hulstkamp, and A. Rouvé, *Helv. Chim. Acta*, 1948, **31**, 543.

are quite stable.[8] Configurations about single bonds will not be discussed further except when they are directly relevant to the $>C{=}C<$ system.



cis-(II)



trans-(II)

When two double bonds are present as in $CR_1H{=}CH{\cdot}CH{=}CHR_2$, four isomers exist if $R_1 \neq R_2$ (*trans-trans*, *cis-trans*, *trans-cis*, and *cis-cis*) and three if $R_1 = R_2$. The number of isomers possible increases rapidly as the number of double bonds increases. For a symmetrical conjugated compound with n double bonds the number of isomers possible (N) can be obtained from the expression :[9] $N = 2^{n-1} + 2^{p-1}$ (when n is even, $n = 2p$: when n is odd, $n = 2p - 1$).

A long-chain *trans*-compound (III) is essentially linear and simulates the corresponding saturated one (IV), whereas the corresponding *cis*-isomer has a bent structure (V).* This bending is most marked when the double

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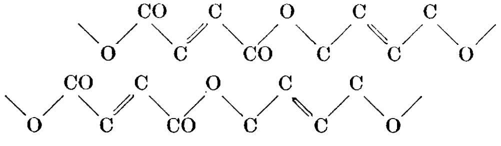
[8] P. R. Shildneck and R. Adams, *J. Amer. Chem. Soc.*, 1931, **53,** 2203.

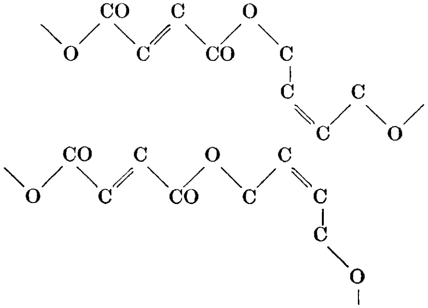
[9] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, 1928, **11,** 87.

[10] W. M. Smith and K. C. Eberly, 117th Meeting, Amer. Chem. Soc., Detroit, April, 1950 ; H. Mark, *Research*, 1951, **4,** 167.

* The bending caused by a *cis*-double bond is illustrated by the two polymers formed by esterifying fumaric acid with *cis*- and *trans*-butenediol.[10]. One polymer (the *cis*) is rubbery and of low softening point but the other (*trans*) is a high-melting crystalline solid.



trans-trans,† fits easily into the crystal lattice in long chains; crystalline.

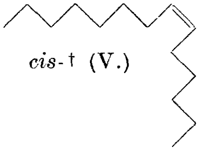


trans-cis,† alignment of chains difficult ; rubbery.

† Angles are somewhat distorted by limitations of printers' type.

bond is at the centre of the chain. In a polyene chain where there are many possible permutations and combinations of *cis*- and *trans*-arrangements about the double bonds, a great diversity of molecular shape is possible.

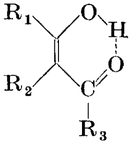
Saturated (IV.)



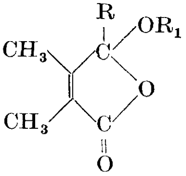
cis-† (V.)

trans- (III.)

Some Factors affecting the Stability of Geometrical Isomers.—The repulsion of like dipoles oriented *cis* to each other (*e.g.*, the two C=O groups in *cis*-dibenzoylethylene) contributes to the instability of this form whereas interaction between unlike dipoles may be expected to increase stability. In specific cases internal hydrogen bonding can be envisaged as a stabilising factor as in the *cis*-enol (VI).[11] An extreme case of *cis*-stabilisation is *pseudo*-acid formation (VII).[12] Two bulky *cis*-substituents, preventing planarity in one form, increase its energy. Moreover, when the double bond is in conjugation, the departure from planarity prevents maximum delocalisation of the π orbitals and the resonance energy is decreased.



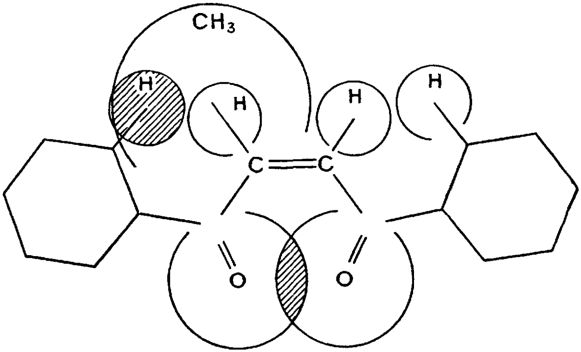
(VI.)



(VII.)

Scale drawings of planar projections of *cis*- and *trans*-dibenzoylethylene would illustrate the operation of steric hindrance in the *cis*-form [cf. (VIII)].

[The following values are used for the bond lengths : C–C, 1·54 ; C=C,



(VIII)

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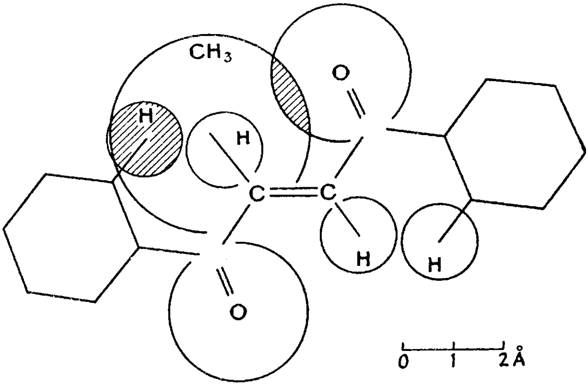
[11] B. F. Eistert, F. Weygand, and E. Csendes, *Chem. Ber.*, 1951, **84**, 745. Cf., however, H. Henecka, *Chem. Ber.*, 1948, **81**, 189.

[12] R. E. Lutz and M. Couper, *J. Org. Chem.*, 1941, **6**, 77.

1·33 ; C–H, 1·09 ; C═O, 1·20 ; C–C (benzene), 1·40 Å. The bond angles C═C—R and O═C—C are taken as 123° and the atoms and groups are drawn by using van der Waals radii for oxygen 1·40, hydrogen 0·75, and methyl 2·00 Å. Van der Waals radii are too large a measure of steric hindrance, and covalent radii too small : here a compromise is effected by the use of a low value for the van der Waals radius of hydrogen.]



(IX)

A rather more complicated case is that of the *cis*- and *trans*-methyldibenzoylethylenes [13] (see VIII and IX). It is known experimentally that the *cis*- is more stable than the *trans*-isomer. From an electrostatic point of view the *cis*-isomer would be expected to be the less stable. But there is steric hindrance in both forms. In the *trans*-isomer this can only be relieved by rotating both phenyl nuclei about the Ph•CO–C bonds. In the *cis*-isomer rotation of one Ph•CO–C system is enough to relieve the hindrance and this leaves the Ph•CO•CH═C(CH_3)— system planar and in conjugation. The resonance energy contribution from this more than offsets any energy increase due to electrostatic repulsions.

If the sterically hindered double bond lies between two long conjugated systems, a considerable loss of resonance energy may be caused by the fact that it breaks or decreases conjugation between them. L. Pauling has discussed the carotenoids.[14] In this case the system —C(CH_3)CH═CH—CH═ (X) is highly hindered in the *cis*- but not in the *trans*-form. It is clear from other examples that, although it may result in an isomer being unstable, hindrance—even considerable hindrance—does not in itself preclude the existence of a *cis*-isomer.* However, in the carotenoids and vitamin A the loss of resonance energy is large and investigators in the field have felt justified in discounting the existence of *cis*-isomers of system (X)—the so-called " sterically ineffective double bond ".

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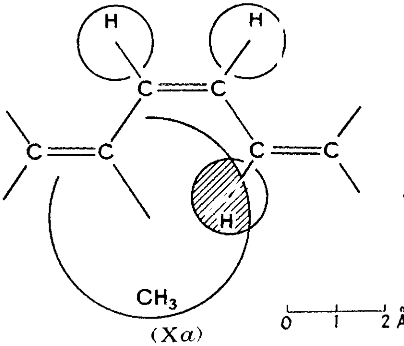
[13] L. P. Kuhn, R. E. Lutz, and C. R. Bauer, *J. Amer. Chem. Soc.*, 1950, **72**, 5058 ; R. E. Lutz and C. R. Bauer, *ibid.*, 1951, **73**, 3457.

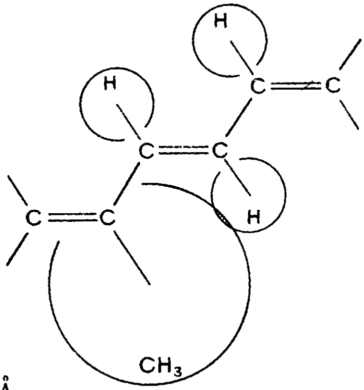
[14] L. Pauling, *Fortschr. Chem. Org. Naturstoffe*, 1939, **3**, 203.

* Recent careful work [16] has not, however, enabled the isolation of *cis-cis-β*-methylmuconic acid to be achieved, all attempts giving a *trans-cis*-isomer.

Caution is desirable in eliminating isomers in this way. The length of the resonating system and the position of the double bond are determining factors, as the loss of resonance energy is much less when the double bond is situated at the end of the chain than when it is near the centre. The calculations of L. Pauling illustrate this.[15]



(*Xa*)



(*Xb*)

Stereomutation of Geometrical Isomers.—A pure geometrical isomer may be converted into an equilibrium mixture with its stereoisomer by thermal isomerisation. The proportions of each in this mixture depend on the relative thermodynamic stabilities under the conditions employed, the more stable predominating. Strong illumination markedly affects the composition of the equilibrium mixture and the thermodynamically less stable isomer is often favoured. This is because the photochemically excited molecules spend the greater part of their time in phases of high potential and when such a molecule goes back into its normal state, that isomer predominates whose configuration corresponds to these phases of higher potential.[17]

The ease of stereomutation is governed by the activation energy E_2 for the particular mechanism (Fig. 1). This must be influenced by the electron density at the double bond and, consistently with this, conjugated stereomutate more easily than do unconjugated compounds.

The energy difference (E_1) between *cis*- and *trans*-isomers about a double and a single bond may not be very different, but in the former case the activation energy (E_2) is much higher and the two forms exist separately.

G. B. Kistiakowsky has discerned experimentally at least two mechanisms for thermal stereomutations.[18 cf. 19] Both are kinetically of the first

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[15] L. Pauling, *Helv. Chem. Acta*, 1949, **32**, 2241.

[16] J. A. Elvidge, R. P. Linstead, and P. Sims, *J.*, 1951, 3398.

[17] A. R. Olsen and F. L. Hudson, *J. Amer. Chem. Soc.*, 1933, **55**, 1410 ; A. R. Olsen and W. Maroney, *ibid.*, 1934, **56**, 1320 ; G. N. Lewis, T. T. Magel, and D. Lipkin, *ibid.*, 1940, **62**, 2973.

[18] G. B. Kistiakowsky and W. R. Smith, *ibid.*, 1935, **57**, 269.

[19] J. L. Magee, W. Shand, and H. Eyring, *ibid.*, 1941, **63**, 677.

order and their rate constants are *ca.* 10^{11} exp. $-$ 40,000/kT and *ca.* 10^4 exp. $-$ 25,000/kT respectively. In order to effect geometrical interconversion the double bond must be " dissociated " in some way, so that rotation can occur and one of the carbon atoms be twisted through 180° relatively to the other. When the carbon atom has been twisted through 90°, rotation may proceed onwards to give the stereoisomer or may become reversed to yield the original isomer again. This " perpendicular ethylene " is the transition state in simple cases. By linear combination of the two atomic p orbitals of the carbon atoms, besides the low energy π orbital in planar ethylene, a second high-energy anti-bonding orbital (π^*) can be formed. In " perpendicular ethylene " the order of stabilities is reversed. Throughout the actual twisting operation the electrons occupy the lowest energy orbital, formed by hybridisation of the two.[22] The electrons in the " perpendicular ethylene " formed by the continuous adiabatic rotation are anti-parallel (*i.e.*, transition is from the singlet ground state to an upper singlet state).[20–22] H. Eyring associates this with stereomutations having a frequency factor of 10^{11} and an energy of activation of *ca.* 40 kcals. Since in excited ethylene the two electrons occupy separate orbitals, their spins can also be parallel (triplet state). But the probability of this reversal of spin occurring is low, although the low activation energy favours this, the second isomerisation mechanism (frequency factor 10^4, energy of activation 25 kcals.). The triplet mechanism is of nearly the same height in the various molecules considered but the singlet level differs greatly from one molecule to another depending on the ability of the two electrons from the double bond to enter into some other kind of binding. When a phenyl

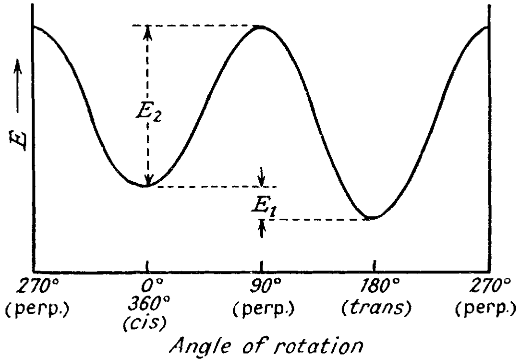

FIG. 1*

* If steric hindrance or other causes inhibit rotation in one direction, one of the energy barriers will be higher than the other. Steric hindrance may also cause a displacement of the energy minima from the 0° and the 180° position.

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[20] R. A. Harmann and H. Eyring, *J. Chem. Phys.*, 1942, **10,** 557.

[21] H. M. Hulbert, R. H. Harman, A. V. Tobolsky, and H. Eyring, *Ann. N.Y. Acad. Sci.*, 1943, **44,** 371.

[22] M. J. S. Dewar, " Electronic Theory of Organic Chemistry ", Oxford Univ. Press, 1949.

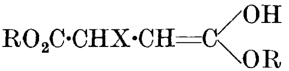
group is available there is resonance, and stilbenes isomerise by the adiabatic singlet mechanism. Resonance stabilisation is smaller in the case of but-2-ene or maleic ester and these use the triplet mechanism.

Besides the purely thermal and the purely photochemical *cis-trans*-equilibrations there are many examples which are catalysed. The rôle of catalysts is still not clear and a number of different mechanisms are probably involved. The suggestions in the literature are largely concerned with schemes which allow the catalyst to add in some way—thus reducing the π electron density and permitting rotation—and then to disengage.

Evidence indicates that the halogens cause stereomutation by a free-radical mechanism.[23] Thus the bromine-catalysed conversion of *cis*-stilbene into an essentially *trans*-product occurs only in the presence of light and is sensitive to the effects of peroxides and antioxidants. The following scheme involving bromine atoms [24] has been suggested :

$$\begin{array}{ll} cis\text{-PhCH=CHPh} + \mathrm{Br}^{\bullet} \longrightarrow & \mathrm{PhCHBr{—}\overset{\bullet}{C}HPh} \\ & \quad \upharpoonleft\!\downharpoonright \ cis\text{-PhCH=CHPh} \\ & trans\text{-PhCH=CHPh} + \mathrm{PhCHBr{\cdot}\overset{\bullet}{C}HPh}, \text{ etc.} \end{array}$$

The PhCH in the intermediate is considered to be planar and the PhCHBr-pyramidal, free rotation being possible. Both the *cis*- and the *trans*-isomer can pass through the intermediate and equilibrium is attained. It is likely that stereomutations catalysed by other atoms, free radicals, and paramagnetic substances proceed by similar mechanisms. The thermal and photochemical iodine-catalysed stereomutation of di-iodoethylene is viewed [25] as passing through the intermediate $\mathrm{IH\overset{\bullet}{C}{—}CHI_2}$ rather than proceeding by a type of mechanism which A. R. Olson proposed (see later).[26]

A number of acid-catalysed stereomutations are known and an intermediate of the type $\mathrm{RO_2C{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}CO_2R}$ has been invoked in the case of the maleic–fumaric system : there is evidence against this.[27] An alternative mechanism has been suggested by K. Nozaki and R. Ogg.[28] HX is considered to give an intermediate  $\mathrm{RO_2C{\cdot}CHX{\cdot}CH{=}C}\!\!\begin{smallmatrix}\diagup \mathrm{OH}\\ \diagdown \mathrm{OR}\end{smallmatrix}$; on subsequent elimination of HX the isomerised or the original compound may be formed. A similar view (Wheland [1]) postulates a resonating system :

$$\mathrm{RO_2C{\cdot}CH{=}CH{—}\underset{\displaystyle |\atop \displaystyle O{\cdot}CH_3}{\overset{+}{C}}{\cdot}OH} \qquad \mathrm{RO_2C{\cdot}\overset{+}{C}H{\cdot}CH{=}\underset{\displaystyle |\atop \displaystyle O{\cdot}CH_3}{C}{—}OH}$$

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[23] M. S. Kharasch, J. V. Mansfield, and F. R. Mayo, *J. Amer. Chem. Soc.*, 1937, **59,** 1155 ; Y. Urushibara and O. Shimamura, *Bull. Chem. Soc., Japan*, 1937, **12,** 507 (*Chem. Abs.*, 1938, **32,** 1682).

[24] A. Berthoud and C. Urech, *J. Chim. phys.*, 1930, **27,** 291.

[25] R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Amer. Chem. Soc.*, 1945, **67,** 1319.

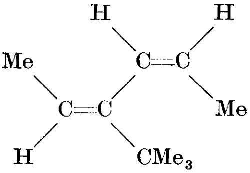
[26] A R. Olsen, *J. Chem. Phys.*, 1933, **1,** 418.

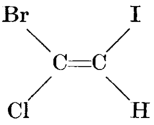
[27] C. Horrex, *Trans. Faraday Soc.*, 1937, **33,** 571.

[28] K. Nozaki and R. Ogg, *J. Amer. Chem. Soc.*, 1941, **63,** 2583.

Aluminium trichloride and boron trifluoride,[29] acids in the wider sense, also catalyse stereo-equilibrations but their action is not general. Catalysis by paramagnetic substances has been discussed by Eyring.[20, 21] The numerous catalysts available for the process are listed on p. 139.

Nomenclature.—Compounds of type *A* present no difficulty in nomenclature, but for types *B* and *C* the groups to which the prefix *cis* or *trans* applies must be specified in some way. Rules [30] for the systematic naming of long-chain olefinic geometrical isomers were adopted by I.U.P.A.C. Commission of Nomenclature of Organic Chemistry in New York, Sept. 1951. The compounds are regarded as derivatives of the longest chain which contains the maximum number of double bonds, the *cis*- or *trans*-prefix describing the juxtaposition of the carbons of the main chain, being placed immediately before the numbering of the double bond, *e.g.*, 3-*tert.*-butyl-*cis*-2 : *cis*-4-hexadiene (XI).


(XI.)


(XII.)

Some of the better known pairs of isomers have trivial names, *e.g.*, angelic and tiglic acids, citraconic and mesaconic acids, and compounds may be named as derivatives of these. Sometimes the less stable isomer has been designated by the addition of the prefix *iso* to the name of the stable compound (*iso*crotonic acid, *iso*stilbene) ; *allo* may also be used (*allo*cinnamic acid). The use of *iso* is particularly undesirable.

In order to name certain simple stereoisomers, such as those of 1-bromo-1-chloro-2-iodoethylene, it is suggested that the groups to which the prefix applies be italicised in cursive text, *e.g.*, (XII) is *cis*-1-*bromo*-1-chloro-2-*iodo*-ethylene or *trans*-1-bromo-1-*chloro*-2-*iodo*ethylene, but there are manifest difficulties in indexing on this convention and it has no value in speech.

Methods for the Determination of Geometrical Configuration

As a result of the difference in shape and symmetry between corresponding *cis* and *trans*-isomers there are differences in a large number of physical and chemical properties.* The process of determining configura-

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[29] C. C. Price and M. Meister, *J. Amer. Chem. Soc.*, 1939, **61**, 1595.

[30] M. B. Epstein and F. D. Rossini, *Chem. Eng. News*, 1948, **26**, 2959 ; cf. *ibid.*, 1949, **27**, 1303.

[31] L. Crombie and S. H. Harper, *J.*, 1950, 873.

[32] W. Sanderman, *Seifensieder Ztg.*, 1941, **68**, 41.

* There are also marked differences in physiological properties. Thus *cis*-hex-3-en-1-ol has the odour of fresh grass, but the *trans*-isomer smells of chrysanthemums.[31] Taste,[32] vitamin A activity,[33] serum reactions,[34] enzyme reactions,[35] reproduction of algæ,[36] and many more such properties are markedly dependent on geometrical configuration. Normally, *cis*- or *trans*-isomers are synthesised stereospecifically in Nature : *cis*-type-*A* forms are very common.

tion is therefore one of detecting the differences and relating them to the configurations of the isomers. It is the latter step which presents the difficulty as the relation between molecular shape and symmetry and physical or chemical properties may be indirect, and the results require very critical evaluation. Indiscriminate use of rules or regularities without reference to their basis has sometimes led to erroneous conclusions.

The solution of a more difficult configurational problem may come from the convergence of a number of lines of evidence, the single lines each carrying in themselves insufficient weight. Some of the methods described below have been tested only on limited ranges of stereoisomers, and these readily available rather than representative. Furthermore, the possibility of stereomutation under experimental conditions must always be kept in mind. Many of the methods have limited scope : those which give promise of determination of configuration when only one isomer is available are very valuable. In all cases however it is desirable to examine both isomers, if possible, before making an assignment.

Melting and Boiling Points and Related Phenomena.—It has been found empirically that usually (but not always) *cis*-compounds of type *A* have lower melting points than their *trans*-isomers and this is generally related to the higher symmetry of the *trans*-type which results in better packing and greater forces in the crystal lattice. Melting-point regularities within a series of the more complex types (*B* and *C*) may also give indications of configuration. Since the formation of an anisotropic liquid phase (" liquid crystal " or smectic state) demands, among other factors, a linear molecule in this type of case, its formation has been cited to support *trans*-configurations : [37] the compound melts sharply to a turbid liquid which melts equally sharply to a clear liquid, *e.g.*, *trans*- but not *cis*-*p*-methoxycinnamic acid.[38] It has been cited in support of the *trans*-configurations of one 1 : 4-di-*p*-methoxyphenylbutadiene [39a] and an anil of *trans*-*p*-aminostilbene.[37]

Because of the similarity in shape, *trans*-isomers frequently form solid solutions (" mixed crystals ") with the corresponding saturated compounds whereas the *cis*-isomers do not, *e.g.*, *trans*-crotonic acid (but not the *cis*-acid) with butyric acid, *trans*-cinnamic acid (but not the *cis*-acid) with phenylpropionic acid.[39b] Substituted *trans*-stilbenes form mixed crystals

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[33] L. Zechmeister in " Vitamins and Hormones ", Vol. VII, Acad. Press Inc., New York, 1949.

[34] K. Landsteiner and J. van der Schier, *J. Exp. Med.*, 1934, **59**, 751.

[35] A. Jung and H. Müller, *Helv. Chim. Acta*, 1922, **5**, 239 ; W. Fabisch, *Biochem. Z.*, 1931, **234**, 84 ; G. B. Crippa and S. Maffei, *Gazzetta*, 1940, **70**, 212 ; D. Pressmann, J. H. Bryden, and L. Pauling, *J. Amer. Chem. Soc.* 1948, **70**, 1352.

[36] I. M. Heilbron, *J.*, 1942, 79.

[37] C. Weygand and R. Gabler, *Ber.*, 1938, **71**, 2474.

[38] R. Stoermer, *Ber.*, 1911, **44**, 637.

[39a] Y. Hirshberg, E. Bergmann, and F. Bergmann, *J. Amer. Chem. Soc.*, 1950, **72**, 5120.

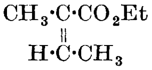
[39b] G. Bruni and F. Gorni, *Atti R. Accad. Lincei*, 1899, **8**, I, 454 ; G. Bruni, *ibid.*, 1904, **12**, I, 626 ; C. Dufraisse, *Ann. Chim.*, 1922, [ix], **17**, 133 ; G. B. Semeria, *Atti Accad. Sci. Torino*, 1924, **59**, 700 ; *Gazzetta*, 1925, **55**, 79 ; J. Timmermans, *Bull. Soc.*

with the *meso*-forms of the corresponding saturated compounds but eutectics with the racemic.[39c]

Boiling-point and solubility regularities between the *cis*- and the *trans*-series have been claimed (*i.e.*, that the *cis*-isomer has the higher b.p. and greater solubility). A number of factors is involved in the manifestation of these and similar properties and there are numerous exceptions.

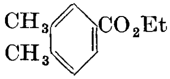
A. Langseth [40] and K. von Auwers and L. Harres [41] have compared the physical properties of a series of geometrical isomers with those of a series of comparably substituted aromatic compounds and, on the assumption that similar alterations in the positioning of groupings cause similar changes in physical properties, have assigned configurations by comparison. A favourable example [41] illustrates the principle :

(XIII.)

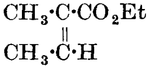


$\begin{array}{c} CH_3\cdot C\cdot CO_2Et \\ \| \\ H\cdot C\cdot CH_3 \end{array}$

(XIV.)



(XV.)



$\begin{array}{c} CH_3\cdot C\cdot CO_2Et \\ \| \\ CH_3\cdot C\cdot H \end{array}$

(XVI.)

	(XIII.)	(XIV.)	(XV.)	(XVI.)
B.p./mm..	118·5°/12	49°/11	134°/15	55·5°/11
d_4^{20} . .	1·017	0·917	1·025	0·924
n_{He}^{20} . .	1·5086	1·4308	1·5149	1·4353

Compounds (XIII) and (XIV) have lower boiling points, densities, and refractive indices than their isomers (XV) and (XVI) and, if the structures of the aromatic compounds are accepted as known, then (XIV) and (XVI) are given the configurations shown. Unfortunately there are numerous exceptions.[41]

Surface-film Properties.—Because of their shape, molecules of long-chain *trans*-acids and -alcohols can form close-packed surface films : this is not possible with the bent *cis*-forms. Also, whereas the *trans*-forms can pack closely with the corresponding saturated ones, the *cis*-compounds cause expansion when introduced into a film of saturated acid or alcohol. On collapse, the *cis*-films usually give oil lenses, but the *trans*-films tend to give solids or smectic liquids by chain adlineation.[42]

Energy Contents.—By measurement of heats of combustion or hydrogenation an estimate of the difference between the energies of two geometrical isomers may be made. If this energy difference can be related to the juxtaposition of groupings, then configurations may be assigned : usually in type-*A* isomers the *cis* is the less stable but in other cases decision *a priori* on relative stabilities may not be possible.

Theoretically the measurements of heat of combustion should be made on the vapour because of lattice effects. However the *cis*- normally packs less well than the *trans*-isomer and for this reason the solid *cis*-compound

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chim. Belg., 1927, **36,** 179 ; H. Keller, R. Pasternak, and H. von Halban, *Helv. Chim. Acta*, 1946, **29,** 512.

[39c] F. von Wessely and H. Welleba, *Ber.*, 1941, **74,** 785.

[40] A. Langseth, *Z. physikal. Chem.*, 1925, **118,** 49.

[41] K. von Auwers and L. Harres, *ibid.*, 1929, **143,** 1.

[42] J. Marsden and E. K. Rideal, *J.*, 1938, 1163 ; A. E. Alexander, *J.*, 1939, 777.

has an even higher heat of combustion than expected. Thus the heat of isomerisation ($-\Delta H$)—the difference between the two heats of combustion—of maleic to fumaric acid is 4·4 kcal. in the gas phase but 6·9 in the crystalline state. A few examples are collected in Table 1: the different heats of combustion for the three polymorphic *cis*-cinnamic acids are noteworthy. An inherent difficulty in the method is that the energy difference is a small quantity derived by difference of two large ones and is therefore subject to considerable error.

TABLE 1

	Heat of combustion, kcal./mole	Heat of isomerisation ($-\Delta H$), kcal./mole
Dimethyl maleate solid (– 19°) [43]	667·2	3·1
,, fumarate ,, (– 19°) [43]	664·1	
cis-Cinnamic acid solid (m.p. 42°) [44]	1043·8	2·9
,, ,, ,, ,, (m.p. 58°) [44]	1045·2	4·3
,, ,, ,, ,, (m.p. 68°) [44]	1047·6	6·7
trans- ,, ,, ,, (m.p. 133°) [45]	1040·9	
cis-4-Nitrostilbene solid (m.p. 61°) [46]	1723·2	7·0
trans- ,, ,, (m.p. 157·5°) [46]	1716·2	

TABLE 2

	Heat of hydrogenation, kcal./mole	Heat of isomerisation, kcal./mole
trans-But-2-ene (gas) [47]	27·62	0·95
cis- ,, ,, ,, (gas) [47]	28·57	
Methyl *cis*-cinnamate (liq.) [48]	28·19	4·01
,, *trans*- ,, (liq.) [48]	24·18	
Diethyl maleate (liq.) [48]	33·52	4·22
Diethyl fumarate (liq.) [48]	29·30	

From this point of view, measurement of heat of hydrogenation gives a more reliable energy difference. Measurements are available for *cis*- and *trans*-butenes in the gas phase [47] and certain stereoisomers in the liquid state [48] (Table 2). It must be noted that the two isomers must give the *same* compound on hydrogenation—not an *erythro*- and *threo*-pair as these have different energies themselves.

X-Ray Crystallographic Measurements.—A complete *X*-ray structural analysis can give an unequivocal decision on the *cis*- or *trans*-configuration

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[43] A. Wassermann, *Z. physikal. Chem.*, 1930, **146,** 418.

[44] F. Eisenlohr and A. Metzner, *ibid.*, 1937, **178,** 339.

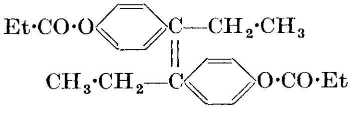
[45] P. Landrieu, F. Baylcoq, and J. R. Johnson, *Bull. Soc. chim.*, 1929, [iv], **45,** 44.

[46] C. M. Anderson, L. G. Cole, and E. C. Gilbert, *J. Amer. Chem. Soc.*, 1950, **72,** 1263.

[47] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughn, *ibid.*, 1935, **57,** 876.

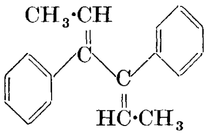
[48] R. B. Williams, *ibid.*, 1942, **64,** 1395.

of a compound. Thus stilbene [49] (m.p. 124°) and the side-chain double bond ($C_{22:23}$) of calciferol [50] are *trans*, and sorbic acid [51] (m.p. 134·5°) has the *trans-trans*-structure. But the less arduous earlier stages of *X*-ray crystallographic analysis may be used to determine molecular symmetry which, in suitable cases, enables an allocation of configuration to be made. Thus one of the isomers of diethylstilbœstrol dipropionate (XVII) has a centre of symmetry and must therefore be *trans*.[52] The centre of symmetry in dimethyl *trans-trans*-muconate and dimethyl *trans*-fumarate shows that the accepted configurations are correct.[53]

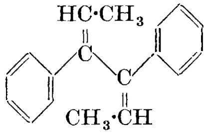


(XVII.)

In the case of αβ-diethylidenedibenzyl (3 : 4-diphenylhexa-2 : 4-diene) (m.p. 101°) the molecule has again been shown to have a centre of symmetry, but two structures (XVIII) and (XIX) are possible and a decision between them must be made on other evidence ; (XVIII) is favoured.[54]



(XVIII.)



(XIX.)

Amongst long-chain aliphatic compounds the structures of the synthetic polyenes prepared by R. Kuhn's procedure have been shown to be all-*trans* (as are many natural carotenoids). The distinctive *X*-ray diffraction " side spacings " of glycerides of *trans*-acids resemble those of the corresponding saturated acids, but those of the *cis*-forms are different—another consequence of the bent chain.[55] For the field of high polymers mention must be made that a *cis*-structure for the isoprene units of natural rubber and a *trans*-structure for those of gutta percha, which has totally different properties, have been confirmed by *X*-ray measurements : this has also revealed other interesting details.[56]

The structures of *cis*- and *trans*-but-2-enes [57] and dichloroethylenes [58] have been determined in the gas phase by electron-diffraction measurement.

Ultra-violet and Visible-light Absorption.—It has long been realised that

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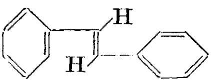
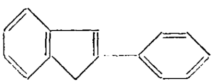
[49] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568.
[50] D. Crowfoot and J. P. Dunitz, *Nature*, 1948, **162**, 609.
[51] K. Lonsdale, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.*, 1941, *A*, **178**, 43.
[52] C. H. Carlisle and D. Crowfoot, *J.*, 1941, 6.
[53] I. E. Knaggs and K. Lonsdale, *J.*, 1942, 417.
[54] G. A. Jeffrey, H. P. Koch, and S. C. Nyburg, *J.*, 1948, 1118.
[55] M. G. R. Carter and T. Malkin, *J.*, 1947, 554.
[56] C. W. Bunn, *Proc. Roy. Soc.*, 1942, *A*, **180**, 40.
[57] L. O. Brockway and P. C. Cross, *J. Amer. Chem. Soc.*, 1936, **58**, 2407.
[58] L. O. Brockway, J. Y. Beach, and L. Pauling, *ibid.*, 1935, **57**, 2693.

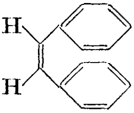
differences exist between the ultra-violet light absorptions of *cis*- and *trans*-isomers.[3, 59] An empirical approach compares the absorption of a cyclic model having the chromophoric system in question held rigidly in one configuration, with that of the unknown isomer. Thus the absorption spectrum of *trans*-stilbene (XX) resembles that of 2-phenylindene (XXI) whilst that of *cis*-stilbene (XXII) differs markedly.[60] However, less empirical methods are now available.



(XX.)



(XXI.)



(XXII.)

The light absorption of polyenes has been extensively studied.[61] If in a planar " all-*trans* "-carotenoid, one of the double bonds is inverted to give a planar non-sterically-hindered *cis*-isomer, three effects are observed. The long-wave-length *K* band is shifted to a slightly shorter wave-length (by *ca.* 5 mμ), its extinction coefficient is lowered, and a new band called a " *cis*-peak " appears at considerably shorter wave-length. The *K* band arises (on classical views) from the absorption of light by a system of electrons oscillating from one end of the conjugated chain to the other (transition from the ground state to the first excited state). The intensity of the band, a factor dependent on the dipole moment, is proportional to the square of the distance between the ends of the conjugated system.[62] As the *trans*-isomer is the most extended form, a fall in intensity is therefore to be expected on conversion into *cis*-forms. The magnitude of the change is naturally dependent on the position of the *cis*-double bond. The alteration of the *K* band to shorter wave-lengths by the *trans*-*cis*-change is ascribed to an alteration in the energy difference between the ground and the first excited state.

A " *cis*-peak " arises from a transition from the ground to the second excited state : this involves the oscillation of the electrons from the ends of the conjugated system towards the middle and from the middle towards the ends. In the case of an all-*trans*-polyene (which possesses a centre of symmetry) this oscillation causes no dipole change and no band appears in the *cis*-peak region. But *cis*-isomers have a dipole moment for this transition perpendicular to a line drawn between the ends of the conjugated system : hence *cis*-peaks arise. When the *cis*-double bond is situated at the centre of the polyene chain the dipole change, and therefore the *cis*-peak, reaches

[59] V. Henri and J. Errera, *Compt. rend.*, 1925, **180**, 2049 ; 1925, **181**, 548 ; J. Errera, *J. Phys. Radium,* 1926, [vi], **7**, 215.

[60] C. Wiegand and E. Merkel, *Med u. Chem. Abhandl. med. chem. Fortschungstätten, I.G. Farbenind.*, 1936, **3**, 320 (*Chem. Abs.*, 1937, **31**, 5797) ; U. V. Solmssen, *J. Amer. Chem. Soc.*, 1943, **65**, 2370.

[61] L. Zechmeister, *Chem. Reviews*, 1944, **34**, 267 ; *Ann. N.Y. Acad. Sci.*, 1947, **49**, 220, and references cited therein.

[62] L. Zechmeister, A. L. Le Rosen, W. A. Schroeder, A. Polgár, and L. Pauling, *J. Amer. Chem. Soc.*, 1943, **65**, 1940.

maximum intensity.[61, 62] The difference between the light absorption of a *trans*- and a *cis*-carotenoid (not homogeneous) is shown in Fig. 2. L. Zechmeister has made subtle use of the three effects mentioned in assigning probable stereochemical configurations to carotenoids.[61]

Similar considerations apply to the light absorptions of shorter conjugated systems of double bonds. In certain cases (*e.g.*, dienes or $\alpha\beta$-unsaturated acids) the length of the chromophore is identical in both the *cis*- and the *trans*-form, but even here progress may be made as another factor—partial or complete steric inhibition of resonance—may supervene. Often the spectral differences arise from the superimposition of effects due to both chromophore length and resonance inhibition.

If, in one form of the geometrical isomers, the *cis*-arrangement of bulky substituents prevents the achievement of coplanarity, and thus full conjugation of the chromophore system, a marked fall in extinction coefficient (compared with that expected for an unhindered case) occurs. In more extreme cases the wave-length is shifted to shorter regions as well. E. A. Braude [63] has discussed the effects as follows : when the steric inhibition of planarity is small, the electronic transitions may be restricted to vibrational states in which, as a result of the various stretching and bending vibrations of a polyatomic molecule, a sufficient degree of coplanarity is attained. In such a case, although the intensity falls, the wave-length is not appreciably shifted. When the degree of steric hindrance is large, though not large enough to prevent resonance altogether, the energy level of the excited state (which is more influenced by ionic resonance contributions than is the ground state) will be raised relative to the latter. The effect of this is to displace the *K* band to a shorter wavelength : in addition the fall in intensity is pronounced. In both cases bands characteristic of the partial chromophores may also obtrude.

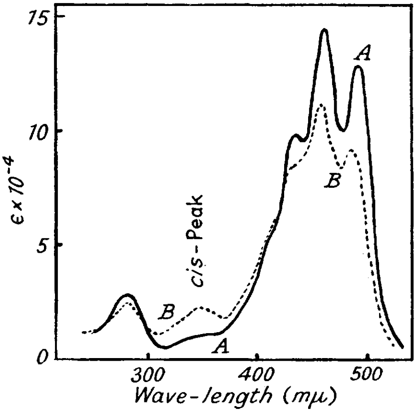


FIG. 2

A, *All*-trans-*γ-carotene in hexane.*
B, *Mixture of stereoisomers of γ-carotene formed by iodine- and light-catalysed stereomutation.*

Some typical examples of the light absorption of *cis*- and *trans*-isomers are given in Table 3 (cf. also refs. 64, 65) and these can be interpreted on the

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[63] E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer, and J. B. Toogood, *J.*, 1949, 1890.

[64] H. P. Koch, *Chem. and Ind.*, 1942, 273 ; A. G. Caldwell and E. R. H. Jones, *J.*, 1946, 599 ; A. W. Nineham and R. A. Raphael, *J.*, 1949, 118 ; M. E. Herr and F. W Heyl, *J. Amer. Chem. Soc.*, 1950, **72,** 1753 ; R. Kuhn and M. Hoffer, *Ber.*, 1932, **65,** 651.

[65] B. Arends, *Ber.*, 1931, **64,** 1936.

lines indicated above. In type-*A* compounds steric hindrance is possible only in the *cis*-forms and as the latter, from chromophore-length considerations, have lower extinction coefficients and sometimes main absorption at slightly shorter wave-lengths than the *trans*-isomers, the two effects reinforce each other. Other types must be considered individually in conjunction with models: classes may be envisaged in which steric hindrance and chromophore-length effects work in opposition.

The use of vacuum ultra-violet spectra in stereochemical diagnosis has been mentioned by certain authors but is as yet of little importance.[66]

TABLE 3

	cis		*trans*	
	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
CHPh:CHPh [65, 67] . . .	278	9 350	294	23 400
CPhMe:CHMe* [68] . . .	235	8 200	243	12 100
CHPh:CH·CHMe·OH [69] .	240	12 000	246 252	19 500
Ph·CO·CH:CH·COPh [13] .	253	17 800	265	21 400
Ph·CO·CH:CHPh [13] . .	247 289	14 000 8 900	225 298	12 200 23 700
CHPh:CH·CH:CH$_2$ [70] . .	268	14 300	280	23 000
CHPh:CH·CO$_2$H [71] . . .	261	10 500	272	19 500

* *cis* and *trans* refer to Ph and Me (*not* to the two Me).

The light absorption within pairs of geometrical isomers in the solid state differs, as might be expected. Thus *trans*-dibenzoylethylenes are yellow but the *cis*-forms are colourless.[3,72]

Infra-red and Raman Spectra.—In favourable examples, infra-red and Raman spectroscopy can distinguish between *cis*- and *trans*-isomers because of symmetry differences. *trans*-Dichloroethylene has a centre of symmetry (C_{2h}) whereas the *cis*-compound has not (C_{2v}). Because of this, the rule of "mutual exclusion" holds for the former but not for the latter.[73] This means that for *trans*-dichloroethylene all frequencies present in the infra-red spectrum are absent in the Raman spectrum and *vice versa*. As a corollary the C═C stretching frequency present in the infra-red spectrum of the *cis*- is absent in that of the *trans*-form. These features are illustrated in the following extract from the spectra of the two dichloroethylenes: [73]

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[66] E. P. Carr and H. Stückeln, *J. Amer. Chem. Soc.*, 1937, **59**, 2138; I. I. Rusoff, J. R. Platt, H. B. Klevens, and G. O. Burr, *ibid.*, 1945, **67**, 673.

[67] A. Smakula and A. Wassermann, *Z. physikal. Chem.*, 1931, *A*, **155**, 353.

[68] D. J. Cramm, *J. Amer. Chem. Soc.*, 1949, **71**, 3883.

[69] E. A. Braude and J. A. Coles, *J.*, 1951, 2078 2085.

[70] O. Grummitt and F. J. Christoph, *J. Amer. Chem. Soc.*, 1951, **73**, 3479.

[71] E. Havinga and R. J. F. Nivard, *Rec. Trav. chim.*, 1948, **67**, 846.

[72] J. B. Conant and R. E. Lutz, *J. Amer. Chem. Soc.*, 1923, **45**, 1303.

[73] G. Herzberg, "Infra-Red and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Inc., New York, 1945, pp. 330, 256, and refs. cited therein.

cis		*trans*	
Infra-red (cm.$^{-1}$)	Raman (cm.$^{-1}$)	Infra-red (cm.$^{-1}$)	Raman (cm.$^{-1}$)
	1179	1200	
1303			1270
1591*	1587*		1576*
	1689		1626
3086	3077		1692
	3160		3071
		3089	
			3142

* Denotes the C═C stretching frequency.

The spectra of *cis*- and *trans*-butene show similar features (here the C═C stretching is at 1663 cm.$^{-1}$ in the infra-red).[74] In the case of *cis*- and *trans*-1 : 2-dichloroprop-1-ene an argument on these lines has been employed to support assignment of structure.[75] The C–H of dichloroethylene is here replaced by $C{-}CH_3$ which has a similar electric moment. The C═C frequency does not disappear in the infra-red spectrum of the *trans*- but it is much weaker than in that of the *cis*-form. There are also more lines in the *cis*-spectrum.

The method is limited, though the extent of the limitations has not been fully explored. Support for the assignment of configuration to *cis*- and *trans*-selachyl alcohols has been claimed because of the intensity differences of the C═C stretching frequency (1652 cm.$^{-1}$) in the infra-red.[76]

M. Bourguel, B. Grédy, and L. Piaux[77] have established empirically that the strong frequency associated with the C═C stretching mode in the Raman spectrum is lower in the *cis*- (by *ca.* 15 cm.$^{-1}$) than in the *trans*-form, *e.g.*, *cis*-hept-2-ene 1658 cm.$^{-1}$, *trans*-, 1674 cm.$^{-1}$. Though both frequencies vary with substitution, the difference is upheld over a considerable variety of compounds.[78] Much use has been made of the effect for assignment of structure and quantitative estimation.[79] As the frequency difference is small, examination of both members of the *cis*–*trans*-pair is needed for decisions to be made with confidence. The shift has also been noted in the infra-red.[80]

The Raman spectra of *cis*- and *trans*-isomers are normally rather similar, though the *cis*-forms are said to contain more lines at shorter wave-lengths.[81] Displacement of a strong frequency from *ca.* 1300 cm.$^{-1}$ for the

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[74] H. Gershinowitz and E. B. Wilson, *J. Chem. Phys.*, 1938, **6**, 247.

[75] H. J. Bernstein and J. Powling, *J. Amer. Chem. Soc.*, 1951, **73**, 1843.

[76] E. Baer, H. O. L. Fischer, and L. J. Rubin, *J. Biol. Chem.*, 1947, **170**, 337; cf. J. W. McCutcheon, M. F. Crawford, and H. L. Welsh, *Oil and Soap*, 1941, **18**, 9.

[77] M. Bourguel, B. Grédy and L. Piaux, *Compt. rend.*, 1932, **195**, 129.

[78] B. Grédy, *Bull. Soc. chim.*, 1935, [v], **2**, 1029 ; 1936, [v], **3**, 1093, 1101 ; 1937, [v], **4**, 415 ; *Compt. rend.*, 1936, **202**, 322.

[79] B. Grédy and L. Piaux, *ibid.*, 1934, **198**, 1235 ; G. Goethals, *Bull. Soc. chim. Belg.*, 1937, **46**, 409.

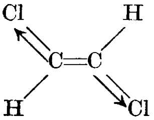
[80] P. Couvreuier and A. Bruylants, *ibid.*, 1950, **59**, 436 ; L. Crombie, *J.*, 1952, in the press.

[81] A. Dadieu, A. Pongratz, and K. W. F. Kohlrausch, *Sitzungsber. Akad. Wiss. Wien, Math. Naturw. Klasse*, Abt. IIa, 1931, **140**, 353 (*Chem. Abs.*, 1932, **26**, 1515).

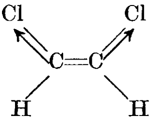
trans- to *ca.* 1270 cm.$^{-1}$ for the *cis*-form has been noted on a number of occasions.[78, 82, 83]

A medium-strong band at *ca.* 970 cm.$^{-1}$ (10·35 μ) occurs in the infra-red spectra of *trans*-compounds of type $R\cdot CH_2\cdot CH{=}CH\cdot CH_2R'$ but is weak or absent in the *cis*-forms. It is ascribed to the out-of-plane deformation of the two hydrogen atoms attached to the *trans*-double bond.[84, 85] The correlation has been proved valid for hydrocarbons,[84] acids,[86, 87] esters,[86, 87] alcohols,[31, 88] halides,[89] ketones,[90] and steroids [91] and is proving of great value in both diagnostic and quantitative work.[83, 87] Only very small samples are needed. An increase in the intensity of infra-red absorption at 675—715 cm.$^{-1}$ (14—15 μ) has been recorded on passing from the *trans*- to the *cis*-isomer. Although stereoisomers with greater substitution at the double bond can be distinguished by their infra-red spectra, correlations with their stereochemistry have not been obtained.[92]

Dipole Moments.—Interpretation is simplest when the ethylenic compound possesses one polar substituent on each ethylenic carbon atom and when the substituents have their axes of symmetry in the direction of bonding, *e.g.*, dichloroethylene.[93] In such cases the results are decisive, for in the *cis*-compounds the two C–Cl moments add vectorially whereas in the *trans*-compounds they cancel out:



μ = 0·00 D



μ = 1·74 D

Similarly one $\alpha\beta$-dichlorostilbene (m.p. 144°) has zero moment whilst the isomer (m.p. 60°) has a moment of 2·69 D and is therefore *cis*.[94] When the two polar substituents are not the same, the moments of the two stereoisomers must be calculated by vector addition so that comparison with the experimental values may be made. Complexities, however, arise.

[82] L. Ruzicka, H. Schinz, and B. P. Susz, *Helv. Chim. Acta,* 1944, **27,** 1561.

[83] L. Crombie and S. H. Harper, unpublished.

[84] R. S. Rasmussen, R. R. Brattain, and P. S. Zucco, *J. Chem. Phys.*, 1947, **15,** 135.

[85] N. Sheppard and G. B. B. M. Sutherland, *Proc. Roy. Soc.*, 1949, *A*, **196,** 195.

[86] P. C. Rao and B. F. Daubert, *J. Amer. Chem. Soc.*, 1948, **70,** 1102.

[87] O. D. Shreve, M. R. Heather, H. B. Knight, and D. Swern, 116th Meeting, Amer. Chem Soc., Atlantic City, N.J., 1949; *Analyt. Chem.*, 1950, **22,** 1261.

[88] L. Crombie and S. H. Harper, *J.*, 1950, 1707, 1714.

[89] L. F. Hatch and S. S. Nesbitt, *J. Amer. Chem. Soc.*, 1950, **72,** 727.

[90] L. Crombie and S. H. Harper, *J.*, 1952, 869; L. Crombie, S. H. Harper, R. Stedman, and D. Thompson, *J.*, 1951, 2445.

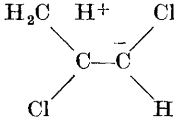
[91] J. H. Turnbull, D. H. Whiffen, and W. Wilson, *Chem. and Ind.*, 1950, 626; R. N. Jones, *J. Amer. Chem. Soc.*, 1950, **72,** 5322.

[92] D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard, and G. B. B. M. Sutherland, *J.*, 1950, 915.

[93] G. P. Mikhailov and D. V. Tischenko, *J. Gen. Chem. U.S.S.R.*, 1939, **9,** 782.

[94] E. Bergmann, *J.*, 1936, 402.

Thus *trans*-dichloropropylene has a higher moment (0·84 D) than would be expected and this is attributed to contributions by resonance structures of the type (XXIII).[95] *trans*-1-Chloropropylene actually has a higher moment (1·97 D) than the *cis*-isomer (1·718 D), and this also has been explained by recourse to resonance.[96]



(XXIII.)

When the substituents no longer have axial symmetry, free rotation complicates the system. In calculations of the dipole moment, two extreme values must be obtained corresponding to the limits of rotation, the experimental value lying somewhere between them. A recent case is *cis*- and *trans*-2-chlorovinyldichloroarsine : [97]

	cis		*trans*
$\mu_{calc.}$	$\left\{\begin{matrix}2·14\\3·20\end{matrix}\right\}$	limits of rotation	2·03
Found	2·61 D		2·21

In the *trans*-compound free rotation does not affect the calculated value as the As–C and the C–Cl bond are parallel.

E. Bergmann has employed the method for assigning geometrical structures to compounds such as the $\alpha\beta$-dibromocinnamic acids, the methyl β-bromocinnamates, 4-bromo- and 3 : 4-dibromo-1 : 4-diphenylbut-3-en-2-one, etc.[94, 98, 99] Sometimes assignment has been made on only one isomer, *e.g.*, the foregoing 3 : 4-dibromo-compound (μ = 3·17 D). The argument is that the dipole moment is close enough to that of benzylideneacetophenone (μ = 2·93 D) to justify the conclusion that the two bromine atoms cancel each other. E. Bergmann also found that *cis*-*p*-chlorodiphenylvinyl bromide and certain other compounds have moments about double those of the *trans*-isomers.[99, 100] He suggests that the latter are molecular compounds of *cis*- and *trans*-forms in 1 : 1 proportions though a different opinion has recently been expressed.[101] Among long-chain compounds oleyl and elaidyl alcohols have been examined but show little difference (1·72 and 1·70 D respectively).[102]

The dipole moments of more than twenty pairs of geometrical isomers have now been measured.[103] In some cases results give clear-cut decisions but in many others the complexities cause the results to be equivocal.

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[95] H. A. Smith and W. H. King, *J. Amer. Chem. Soc.*, 1948, **70**, 3528.

[96] N. B. Hanny and C. P. Smyth, *ibid.*,, 1946, **68**, 1005.

[97] C. A. McDowell, H. G. Emblem, and E. A. Moelwyn-Hughes, *J.*, 1948, 1206.

[98] E. Bergmann and A. Weizmann, *Chem. Reviews*, 1941, **29**, 529 ; E. Bergmann, *J.*, 1935, 987.

[99] E. D. Bergmann, " Isomerism and Isomerisation ", Interscience Publ., New York, 1948.

[100] E. Bergmann, L. Engel, and H. Meyer, *Ber.*, 1932, **65**, 446.

[101] D. Y. Curtin and E. E. Harris, *J. Amer. Chem. Soc.*, 1951, **73**, 2716, 4519.

[102] A. I. Wildschut, *Physica*, 1932, **12**, 194.

[103] A number of values are collected in " Dipole Moments ", by L. G. Wesson [The Technology Press (M.I.T.), Mass., 1948].

Kinetic Methods.—(i) C. Paal [104] found that *cis*-ethylenes of type *A* are hydrogenated faster than the corresponding *trans*-forms when a supported palladium catalyst is used and this " rule " has sometimes been used in deciding geometrical structures ; [105] recently Z. Csüros has demonstrated its restricted validity.[106] The rate of hydrogenation of both *cis*- and *trans*-isomers, in the presence of supported palladium and platinum catalysts, does not vary in a linear manner with the amount of catalyst. This is shown for palladium in Fig. 3. Only when (under the experimental conditions) the amount of catalyst is in the region *A* does Paal's rule hold. Z. Csüros suggests that the rule should be modified to the form : in the presence of palladium catalysts the maximum rate of hydrogenation is always attained by the *trans*-compound when smaller concentrations of catalyst are used. For platinum catalysts this statement is true for *cis*- rather than for *trans*-isomers.

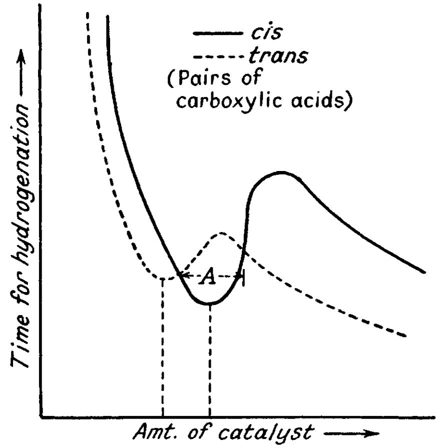
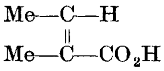


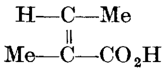
FIG. 3

(ii) Differences in the speeds of esterification, ascribed to steric effects, were used to support the formulations of tiglic (XXIV) and angelic (XXV) acids.[107] Tiglic acid with no methyl *cis* to the carboxyl group is esterified the faster.



$$\begin{array}{c} \text{Me—C—H} \\ \| \\ \text{Me—C—CO}_2\text{H} \end{array}$$

(XXIV.)



$$\begin{array}{c} \text{H—C—Me} \\ \| \\ \text{Me—C—CO}_2\text{H} \end{array}$$

(XXV.)

(iii) Dehydrohalogenation occurs more rapidly when the hydrogen and the halogen atom are juxtaposed *trans* about the double bond than when they are *cis*.[108] Thus chlorofumaric acid, *trans*-2-bromobut-2-ene, *trans*-3-

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[104] C. Paal and H. Schiedewitz, *Ber.*, 1927, **60,** 1221 ; 1930, **63,** 766 ; C. Paal, H. Schiedewitz, and K. Rauscher, *Ber.*, 1931, **64,** 1521 ; M. S. Platonov, *J. Russ. Phys. Chem. Soc.*, 1929, **61,** 1055 (*Chem. Abs.*, 1933, **27,** 539) ; M. S. Platonov, Yu. A. Borgman, and G. Ya. Salaman, *ibid.*, 1930, **62,** 1975 (*Chem. Abs.*, 1932, **26,** 16).

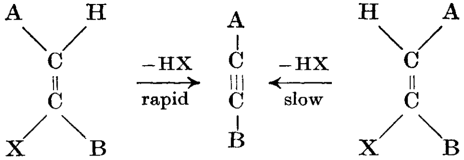
[105] I. E. Muskat and B. Knapp, *Ber.*, 1931, **64,** 779 ; A. K. Plisov and V. P. Golendeev, *Rep. U.S.S.R. Fat and Margarine Inst.*, 1935, No. 2, 12 (*Chem. Abs.*, 1936, **30,** 4465) ; contrast, however, C. Weygand, A. Werner, and W. Lanzendorf, *J. pr. Chem.*, 1938, **151,** 231.

[106] Z. Csüros, K. Zech, and I. Géczy, *Hung. Chim. Acta*, 1941, **1,** 1 (*Chem. Abs.*, 1947, **41,** 109) ; Z. Csüros, *Muegyetemi Közlemények*, 1947, 110 (*Chem. Abs.*, 1948, **42,** 3726) ; *idem, Research*, 1951, **4,** 52.

[107] J. J. Sudborough and M. J. P. Davies, *J.*, 1909, **95,** 975.

[108] S. J. Cristol, N. L. Hause, and J. S. Meek, *J. Amer. Chem. Soc.*, 1951, **73,** 674 ; S. J. Miller and R. M. Noyes, *ibid.*, 1952, **74,** 629.

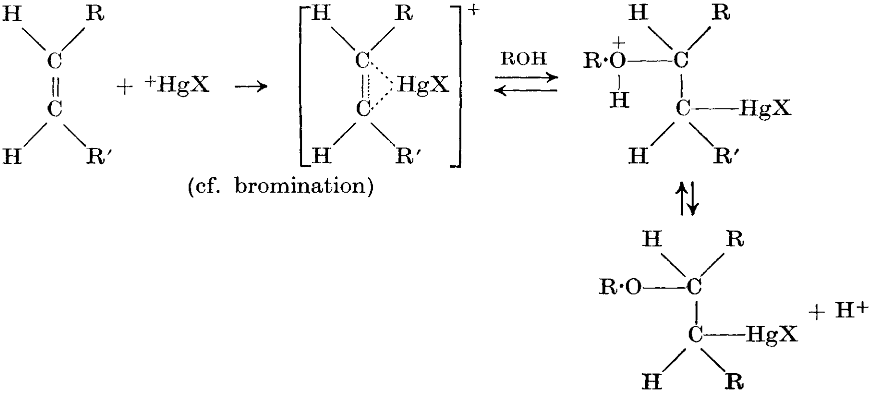
chloroprop-2-en-1-ol, and *cis*-dichloroethylene are dehydrohalogenated faster than their stereoisomers : [2, 109]



An example in which the differences are small and complicated by interconversion during reaction has been noted.[110] In other cases the expected acetylenic compound can only be obtained from the form allowing *trans*-eliminations, and different products are obtained by treatment of its stereoisomer with alkali (cf. p. 130).[111]

(iv) Attempts have been made to decide the configuration of allylic halides by studying the reactivity of the halogen atom.[112, 113] L. F. Hatch *et al.* examined the rates of hydrolysis of *cis*- and *trans*-1 : 3-dichloropropene and the rates of the replacement reaction with potassium iodide, and concluded that the low-boiling isomer is the *trans*-form.[112] Their interpretations are in error, as later work has shown that the latter is *cis*.[114, 115] Differences in the reaction rates of *cis*- and *trans*-1 : 3-dichlorobut-2-ene with OEt$^-$ and OH$^-$ are too small to be of value.[115]

(v) G. F. Wright[116] has found that *cis*-ethylenes are mercurated by alcoholic mercuric acetate faster than are the *trans*-isomers : the reaction may be used diagnostically or for quantitative estimation.[117] If the rate of addition is slow it may be catalysed by nitric acid or boron trifluoride. The excess of mercuric acetate is determined by thiosulphate or dithizone titration. J. Chatt[118] has suggested a mechanism for the stereospecific *trans*-addition of the reagent :



(cf. bromination)

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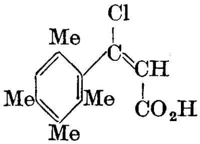
[109] A. Michael, *J. pr. Chem.*, 1895, [ii], **52,** 289 ; J. Wislicenus and P. Schmidt, *Annalen*, 1900, **313,** 210 ; G. Chavanne, *Compt. rend.*, 1912, **154,** 776 ; L. F. Hatch and A. C. Moore, *J. Amer. Chem. Soc.*, 1944, **66,** 285 ; R. E. Lutz, D. F. Hinkley, and

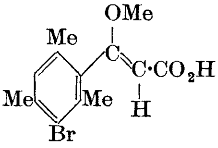
(vi) Another method of diagnosis and estimation consists of bromination of the ethylene, addition of potassium iodide, and titration with thiosulphate.[119, 120, 121] Iodine is liberated faster from the *erythro*-dibromide derived from the *trans*-ethylene than from the *threo*-dibromide derived from the *cis*-ethylene :

$$\mathrm{R{\cdot}CHBr{\cdot}CHR'Br} + 3\mathrm{I}^- \longrightarrow \mathrm{R{\cdot}CH{=}CH{\cdot}R'} + \mathrm{I_3}^- + 2\mathrm{Br}^-$$

Resolvability into Enantiomorphs.—In some cases, because of restricted rotation caused by steric hindrance, one of the geometrical isomers is resolvable and the other not. Thus the compound assigned structure (XXVI) should be dissymmetric as coplanarity of the ring and carboxyl is prevented : it is in fact resolvable and the structure is thus supported.[122]



(XXVI.)



(XXVII.)

Compound (XXVII) is so formulated because it is not resolvable : models show that its geometrical isomer, like (XXVI), would be dissymetric. A negative result from a resolution is always rather uncertain, however, and the enantiomorphs might be very easily racemised.

Intramolecular Cyclisation.—This method—one of the earliest to be used—applies in its simplest form to pairs of geometrical isomers only one of which can be cyclised under mild conditions which do not cause stereomutation. Thus only one (and hence the *cis*-) *o*-aminostilbene (XXVIII) undergoes the Pschorr reaction to yield phenanthrene (XXIX).[123, 124] Similar reactions which have been applied to decide configuration are lactone

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R. H. Jordan, *J. Amer. Chem. Soc.*, 1951, **73,** 4647 ; L. J. Andrews and R. E. Kepner, *ibid.*, 1947, **69,** 2230.

[110] L. F. Hatch and P. S. Hudson, *ibid.*, 1950, **72,** 2505.

[111] M. Fitzgibbon, *J.*, 1938, 1218.

[112] L. F. Hatch, L. B. Gordon, and J. J. Russ, *J. Amer. Chem. Soc.*, 1948, **70,** 1093.

[113] L. F. Hatch and G. B. Roberts, *ibid.*, 1946, **68,** 1196.

[114] L. F. Hatch and R. H. Perry, *ibid.*, 1949, **71,** 3262.

[115] L. J. Andrews and R. E. Kepner, *ibid.*, 1948, **70,** 3456 ; 1947, **69,** 2230.

[116] G. F. Wright, *ibid.*, 1935, **57,** 1993.

[117] W. H. Brown and G. F. Wright, *ibid.*, 1940, **62,** 1991 ; M. H. Thomas and F. E. W. Wetmore, *ibid.*, 1941, **63,** 136 ; T. Connor and G. F. Wright, *ibid.*, 1946, **68,** 256.

[118] J. Chatt, *Chem. Reviews*, 1951, **48,** 7.

[119] R. T. Dillon, W. G. Young, and H. J. Lucas, *J. Amer. Chem. Soc.*, 1930, **52,** 1953 ; W. G. Young, D. Pressmann, and C. D. Coryell, *ibid.*, 1939, **61,** 1640.

[120] C. E. Wilson and H. J. Lucas, *ibid.*, 1936, **58,** 2396.

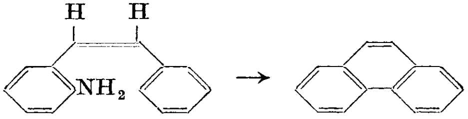
[121] W. G. Young, S. J. Cristol, and T. Skei, *ibid.*, 1943, **65,** 2099.

[122] R. Adams and C. W. Theobald, *ibid.*, p. 2383.

[123] R. Stoermer, *Annalen*, 1915, **409,** 13.

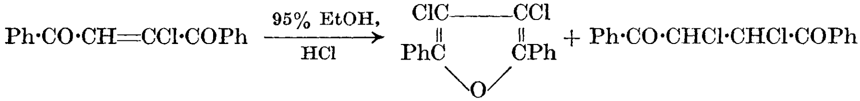
[124] J. M. Gulland and C. J. Vernon, *J.*, 1928, 1478 ; P. Ruggli *et al.*, *Helv. Chim. Acta*, 1936, **19,** 1288 ; 1937, **20,** 37 ; 1941, **24,** 173.

formation from suitable *cis*-hydroxy-acids,[125] formation of anhydrides from *cis*-dibasic acids,[4] furans from *cis*-dibenzoylethylenes,[126] dihydrofurans from *cis*-diols,[127, 128] carbostyrils from *cis*-aminocinnamic acids,[123] indenones from *cis*-cinnamic acids,[129] and coumarins from coumarinic acids. If the sequence *cis* ⟶ cyclic ⟶ *cis*-compound can be carried out under mild conditions the case is further strengthened.



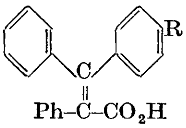
(XXVIII.) (XXIX.)

Sometimes cyclisation occurs very readily, as for carbostyril, coumarin, and some cases of lactol formation, so it may not even be possible to isolate the *cis*-acid. As rather drastic methods are needed on other occasions, stereomutation may complicate the issue, though by adjustment of conditions a decisive result can often be obtained. For instance, A. Valette finds that whereas one butenediol (*trans*) gives a mixture of 2 : 5-dihydrofuran and crotonaldehyde, the other (*cis*) gives only the dihydrofuran.[128] The cyclisation of both *cis*- and *trans*-compounds (XXX), as shown, gives the same mixture of products, but other cyclisation conditions can be found which differentiate between them.[130, 131]

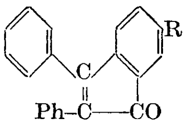


(XXX.) (XXXI.) (XXXII.)

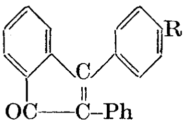
The method of intermolecular cyclisation may also be applied to stereoisomeric pairs which are cyclised under the same conditions but give different products. C. F. Koelsch [132] assigned the structures of some substituted triphenylacrylic acids by indenone formation : one geometrical isomer (XXXIII) gave (XXXIV), and the other gave (XXXV) (structures demonstrated by synthesis).



(XXXIII.)



(XXXIV.)



(XXXV.)

(R = Cl or OMe)

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[125] L. J. Haynes and E. R. H. Jones, *J.*, 1946, 954 ; J. English and J. D. Gregory, *J. Amer. Chem. Soc.*, 1947, **69**, 2123.

[126] R. E. Lutz, W. G. Revely, and V. R. Mattox, *ibid.*, 1941, **63**, 3171 ; R. E. Lutz and C. E. McGinn, *ibid.*, 1942, **64**, 2583.

[127] R. Lespieau, *Compt. rend.*, 1907, **144**, 144 ; J. Salkind, *Ber.*, 1923, **56**, 187.

[128] A. Valette, *Ann. Chim.*, 1948, [xii], **3**, 644.

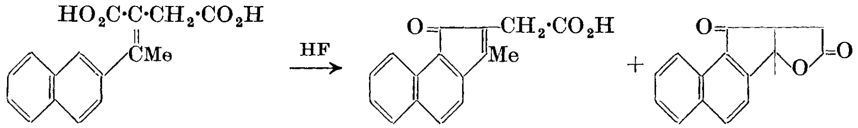
[129] R. Stoermer and E. Laage, *Ber.*, 1917, **50**, 981.

[130] R. E. Lutz and F. N. Wilder, *J. Amer. Chem. Soc.*, 1934, **56**, 1193.

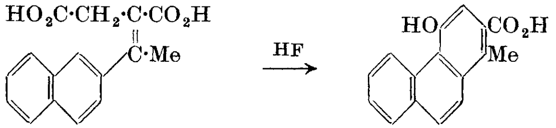
[131] R. E. Lutz, A. H. Stuart, F. N. Wilder, and W. C. Connor, *ibid.*, 1937, **59**, 2314.

[132] C. F. Koelsch, *ibid.*, 1932, **54**, 2487.

Another interesting example is the cyclisation of the substituted *iso*-itaconic (XXXVI) and itaconic (XXXVII) acids.[133] Further examples are known.[134]



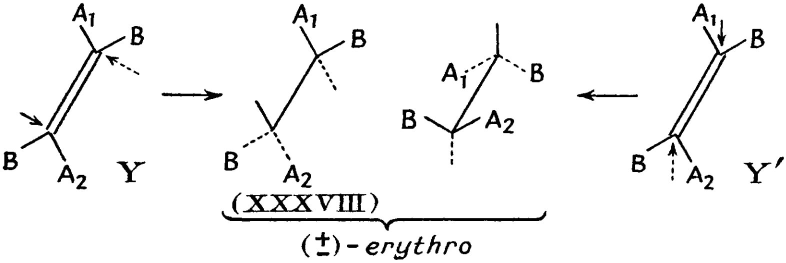
(XXXVI.)



(XXXVII.)

Stereospecific Additions.—Certain reagents add stereospecifically in a "*trans*-" fashion and produce from a *cis*-ethylene a *threo*- and from a *trans*-

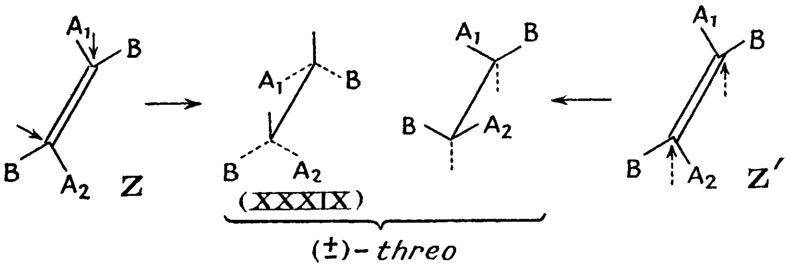
trans-*Addition to a* trans-*double bond.*



(XXXVIII)

(±)-*erythro*

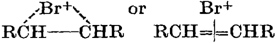
cis-*Addition to a* trans-*double bond.*



(XXXIX)

(±)-*threo*

* The diagrams do not necessarily imply synchronous addition although this will explain retentions of configuration. Bromine addition is considered to proceed through an intermediate $\overset{Br^+}{RCH—CHR}$ or $RCH{=}\overset{Br^+}{|}{=}CHR$, the process being completed by attack by Br^- from the other side.



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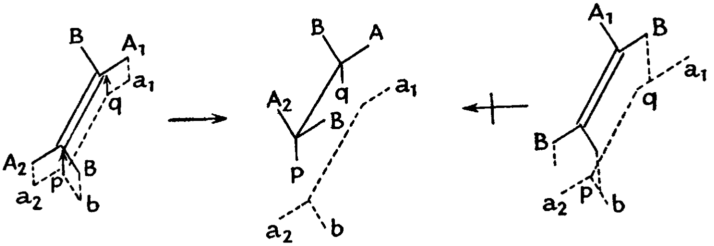
[133] W. S. Johnson and A. Goldman, *J. Amer. Chem. Soc.*, 1944, **66**, 1030; 1945, **67**, 430.

[134] H. Stobbe, *Ber.*, 1904, **37**, 1619; M. Ramart-Lucas and J. Hoch, *Ann. Chim.*, 1930, [x], **13** 385.

ethylene an *erythro*-configuration. Conversely other reagents add "*cis*" and produce from a *cis*-ethylene an *erythro*- and from a *trans*-ethylene a *threo*-form. To illustrate this, the process is shown diagramatically in two cases for a symmetrical addendum. If $A_1 = A_2$ then the (±)-*erythro*-becomes a *meso*-compound. When the addendum is unsymmetrical, two (±)-pairs can, if there is no orienting influence, be produced in each case.

If stereospecific addition occurs in one sense only, an optically active product can result, *e.g.*, Y → (XXXVIII) or Z → (XXXIX). Conditions giving rise to this may be envisaged. Thus, if the geometrical isomer must be adsorbed with at least three of its atoms uniquely attached to certain corresponding atoms of a surface before reaction can occur, attack may be directed in one sense only. The appropriate oriented adsorption and *cis*-attack is not possible in the sense required to produce the diastereoisomer :



As a minimum requirement adsorption on one centre other than the two reaction centres, making three in all, is sufficient.

If an olefinic compound can be converted by known stereospecific reactions into a saturated compound of known configuration, then its own stereochemistry can be deduced. This is the basis of the method on p. 121. Reagents[135, 136] which on present evidence add largely or entirely *trans* are the halogens,* hypohalous acids, performic acid, the iodine–silver benzoate complex, hydrogen peroxide in the presence of pervanadic or pertungstic acid, and 2 : 4-dinitrobenzenesulphenyl chloride. Alkaline permanganate and osmium tetroxide–hydrogen peroxide cause *cis*-additions. The finding that pent-2-en-4-yn-1-ol gives (±)-*erythro*pent-4-yne-1 : 2 : 3-triol (configuration demonstrated by degradation to known reference substance) with performic acid, shows that the double bond is *trans*.[135]

The addition of a dienophile to a diene in the Diels–Alder reaction is stereospecific, *cis*-addition being the rule. Consequently, the diene can be converted into a cyclic compound the configuration of which may be

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[135] R. A. Raphael, *J.*, 1949, S.44.

[136] D. Swern, *J. Amer. Chem. Soc.*, 1948, **70**, 1235 ; M. Mugdan and D. P. Young, *J.*, 1949, 2988.

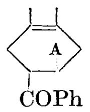
[137] R. E. Buckles, W. E. Steinmetz, and N. G. Wheeler, *J. Amer. Chem. Soc.*, 1950, **72**, 2496.

* It has been shown that bromine will convert a (±)-dibromide into a *meso*-compound in certain cases.[137] Further there are certain other irregularities in bromine addition, although explanations have been given.

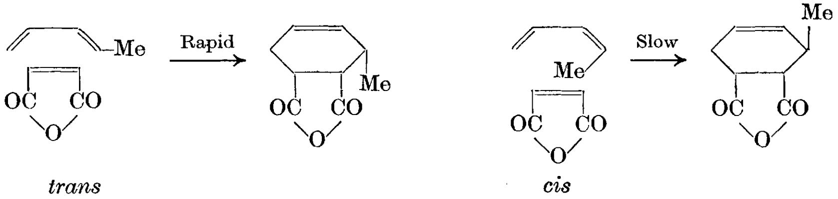
known or easily determined. Moreover, the reactivity of a dienophile towards geometrical isomers provides evidence of their configuration.

Butadiene reacts with *cis*- and *trans*-isomers (*e.g.*, the cinnamic acids [138]) as follows :

Similarly, *cyclo*pentadiene gives stereoisomeric adducts with *cis*- and *trans*-dibenzoylethylenes,[139] and a series of *trans*-acids when allowed to react with anthracene give products stereochemically different from those derived from the *cis*-anhydrides.[140] H. L. Holmes *et al.*[141] support a *trans*-configuration for the yellow form of β-benzoylacrylic acid because it gives a *trans*-adduct (XL) with 2 : 3-dimethylbutadiene. *trans*-Dienes of the type $R\cdot CH{=}CH\cdot CH{=}CH_2$ react readily with dieneophiles but *cis*-forms react much more sluggishly (often with resinification) or not at all. This is exemplified by the reactivity of *trans*-piperylene [142] and *trans*-1-cyanobuta-1 : 3-diene [143] towards maleic anhydride or acrylic acid under conditions such that the *cis*-isomers are unaffected. Separations of *cis*- and *trans*-isomers may thus be effected. The differences are attributed to hindrance in the *cis*-form to the approach of the dienophile to the ends of the conjugated system. The failure of natural pyrethrolone to give adducts with dienophiles supports the *trans*-structure indicated by other evidence.[144] The stereochemistry of the addition of maleic anhydride to *cis*- and *trans*-piperylenes is shown below.[145]



(XL ; A = CO_2H)



In the series $CHR{=}CH\cdot CH{=}CHR'$ similar differences in reactivity are shown. *trans-trans*-1 : 4-Diphenylbutadiene reacts with maleic anhydride to

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[138] K. Alder, H. Vagt, and W. Vogt, *Annalen*, 1949, **565,** 135.

[139] R. Adams and M. H. Gold, *J. Amer. Chem Soc.*, 1940, **62**, 56.

[140] W. E. Bachman and L. B. Scott, *ibid.*, 1948, **70,** 1458.

[141] H. L. Holmes, R. M. Husband, C. C. Lee and P. Kawulka, *ibid.*, p. 141.

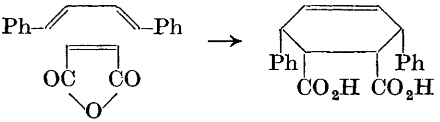
[142] R. F. Robey, C. E. Morrell and H. K. Wiese, *ibid.*, 1941, **63**, 627 ; R. F. Robey, *Science*, 1942, **96,** 47 ; D. Craig, *J. Amer. Chem. Soc.*, 1943, **65,** 1006.

[143] H. R. Snyder, J. M. Stewart, and R. L. Meyers, *ibid.*, 1949, **71,** 1055 ; H. R. Snyder and G. I. Poos, *ibid.*, 1950, **72,** 4104.

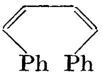
[144] L. Crombie, S. H. Harper, and D. Thompson, *J.*, 1951, 2906.

[145] D. Craig, *J. Amer. Chem. Soc.*, 1950, **72,** 1678.

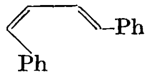
yield (on hydrolysis) (XLI). The *trans-cis-* (XLII) and the *cis-cis*-isomer (XLIII) do not react under conditions which avoid inversion to the *trans-trans*-compound.[146]



(XLI.)

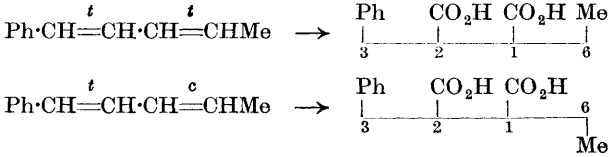


(XLII.)



(XLIII.)

As expected *trans-trans*-1-methyl-4-phenylbutadiene and 1 : 4-dimethylbutadiene are more reactive than their *cis-trans*-isomers, though adducts can be obtained from both : [146, 147]



$$\mathrm{Ph{\cdot}CH\overset{t}{=}CH{\cdot}CH\overset{t}{=}CHMe} \longrightarrow$$

$$\mathrm{Ph{\cdot}CH\overset{t}{=}CH{\cdot}CH\overset{c}{=}CHMe} \longrightarrow$$

Conversion into Compounds of Known Configuration.—If suitable geometrical isomers of well-established configuration are available for reference, this method is highly attractive though it depends on use of reactions which do not cause stereomutation. Samples of crotyl alcohol,[89] penta-2 : 4-dien-1-ol,[144] and hex-3-en-1-ol [31] have been shown to be *cis*, *trans*, and *trans*, respectively, because they can be derived from the appropriate known acids by reduction with lithium aluminium hydride. Similarly the lower-boiling isomer of 1 : 3-dichloroprop-2-ene is *cis* as it gives the known *cis*-1-chloroprop-1-ene on reduction with this reagent.[115]

The configuration of the ketone $\mathrm{Pr^nCH{=}CH{\cdot}COMe}$ as *trans* was demonstrated by deriving it from *trans*-hex-2-enoic acid *via* the acid chloride and methylzinc iodide.[148] A well-known example is the conversion of one form of 3 : 3 : 3-trichlorocrotonic acid on the one hand into (*trans*)-fumaric acid and on the other into one of the crotonic acids which is therefore *trans*.[149] There are other examples scattered in the literature though the method has not been much used.

Certain reactions described in the next section are known to give almost exclusively *cis-* or *trans*-isomers, and the configuration then needs only confirmation.

Methods for the Preparation of Geometrical Isomers

The required stereoisomer may be synthesised by a stereospecific process or separated from the mixture of *cis-* and *trans*-isomers made either by a non-stereospecific synthesis or by stereomutation of the other isomer. In

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[146] K. A. Alder and M. Schumacher, *Annalen*, 1951, **571**, 87, 122.

[147] K. Alder and W. Vogt, *ibid.*, p. 137.

[148] E. N. Eccott and R. P. Linstead, *J.*, 1930, 905.

[149] K. von Auwers and H. Wissebach, *Ber.*, 1923, **56**, 715.

the following section some generalisations have been attempted : in certain cases these must be accepted with reserve because of the fragmentary nature of the evidence.

Results obtained must be evaluated with the following points in mind : (i) that stereomutation may have occurred under the conditions of reaction or isolation, (ii) that one of the stereoisomers may have been eliminated during the purification or not specifically looked for, (iii) that one of the isomers may have reacted further, *e.g.*, a *cis*-unsaturated hydroxy-acid may have lactonised, and (iv) that the reaction conditions may be critical and the observations not general. Only detailed and extensive investigations can settle these points.

Addition of Reagents to Acetylenes.—The hydrogenation of acetylenes with a palladium catalyst gives good yields of olefins if continued until one mol. of gas is absorbed.[150, 151] Sometimes hydrogenation stops spontaneously here if the catalyst is weak but usually the ethylene absorbs hydrogen as fast as does the acetylene. Ordinary platinum catalysts are said to give mixtures containing acetylenic, ethylenic, and saturated compounds, though there have been favourable reports of their specificity.[69]

C. Paal [152] and other early investigators found that the ethylenes produced were essentially *cis* though some succeeding workers reported stereoisomeric mixtures. M. Bourguel attributed some of the confusion to the instability of the *cis*-products and impurities in the protecting agents for the catalysts.[153] To combat this he introduced a colloidal palladium–starch catalyst though nowadays palladium on such supports as calcium, strontium, or barium carbonate, barium sulphate, charcoal, or polyvinyl alcohol is used. All these give essentially *cis*-ethylenes, as do Raney nickel,[154–156] iron powder, and platinum poisoned with carbon monoxide.[156] Careful examination by physical methods (Raman [157] and infra-red spectra,[158] freezing-point methods [159]) has shown that in many hydrogenations carried out in the usual way the *cis*-isomer is contaminated with some of the *trans*-compound.[159a] Generally this is not serious in preparative work, except when high purity is essential. There are indications that temperature [160] and speed of hydrogenation [161] may influence the configuration of the product.

It has been suggested that catalytic hydrogenations involve simultaneous

[150] K. N. Campbell and B. K. Campbell, *Chem. Reviews*, 1942, **31,** 77.

[151] A. W. Johnson, " Acetylenic Compounds ", Vols. I & II, Arnold, London, 1946, p. 1950.

[152] C. Paal, *Ber.*, 1909, **42,** 3930.

[153] M. Bourguel, *Bull. Soc. chim.*, 1929, [iv], **45,** 1067.

[154] G. Dupont, *ibid.*, 1936, [v], **3,** 1030.

[155] K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.*, 1941, **63,** 216, 2683.

[156] K. Ahmad, F. H. Bumpus, and F. M. Strong, *ibid.*, 1948, **70,** 3391.

[157] G. Smets, *Acad. roy. Belg., Classe Sci.*, 1947, **21,** 3.

[158] F. Sondheimer, *J.*, 1950, 877.

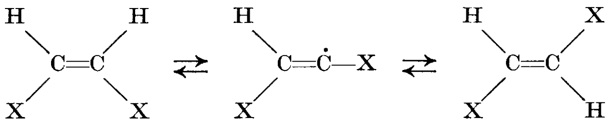
[159] A. L. Henne and K. W. Greenlee, *J. Amer. Chem. Soc.*, 1943, **65,** 2020.

[159a] D. E. Ames and R. E. Bowman, *J.*, 1952, 677.

[160] S. Takei, *Ber.*, 1940, **73,** 950.

[161] E. Ott and F. Schürmann, *Ber.*, 1928, **61,** 2119.

cis-addition of hydrogen from the catalyst to the acetylene.[162, 163] On such a theory no *trans*-isomer is to be expected and its occurrence is ascribed to secondary isomerisation. During the catalytic hydrogenation a concomitant rupture of the C–H bond of the olefin occurs and the radical subsequently reunites with another hydrogen atom formed by dissociation of a hydrogen molecule, to give either the original olefin or its stereoisomer :[162]



The preferential reduction of the acetylene is ascribed to its preferential adsorption on the catalyst to the exclusion of the ethylene.

This method is the most valuable general one available for the synthesis of *cis*-type-*A* ethylenes of many kinds.

In contrast with catalytic hydrogenation, " chemical " methods often yield mainly *trans*-isomers.[150, 151] A liquid-ammonia solution of sodium reduces acetylenic hydrocarbons and alcohols (and sometimes the sodium salt of an acetylenic acid[164]) to stereochemically pure *trans*-ethylenes.[155] A mechanism has been suggested.[165] Zinc and acetic acid have been used to reduce acetylenic acids to *trans*-ethylenic acids[166] though oleic acid (*cis*) from stearolic acid has been claimed to result from its use in the presence of titanous chloride.[167] Zinc and ammonia react with phenylpropiolic acid to yield *trans*-cinnamic acid[168] but when ammonium chloride is present some *cis*-isomer is obtained (10%). E. Ott *et al.*[169] have studied this reaction, using various metals in the presence of ammonia and ammonium chloride. Manganese gives mainly *cis*-cinnamic acid (14% *trans*). Metals more noble than zinc, used as couples, yield predominantly *trans* (Zn/Ag 24% *cis*, Zn/Cu 37% *cis*). Metals more electropositive than zinc, *e.g.*, magnesium, barium, or sodium, give mixtures of saturated and unchanged materials. Hexa-amminocalcium, $Ca(NH_3)_6$,[170] and lithium aluminium hydride[171] reduce disubstituted acetylenes to *trans*-olefins.

Electrolytic reduction of acetylenes at spongy nickel cathodes gives *cis*-ethylenes in good yields, but lead, lead amalgam, and platinum cathodes are not effective.[172a]

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[162] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1937, **33**, 837.

[163] R. P. Linstead, W. E. Doering, S. B. Davies, P. Levine, and R. R. Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.

[164] D. R. Howton and R. H. Davis, *J. Org. Chem.*, 1951, **16**, 1405.

[165] K. W. Greenlee and W. C. Fernelius, *J. Amer. Chem. Soc.*, 1942, **64**, 2505.

[166] L. Aronstein and A. F. Holleman, *Ber.*, 1889, **22**, 1181 ; A. Holt, *Ber.*, 1892, **25**, 961 ; A. Gonzalez, *Anal. Fís. Quím.*, 1926, **24**, 156 (*Chem. Abs.*, 1926, **20**, 2310).

[167] G. M. Robinson and R. Robinson, *J.*, 1925, **127**, 175.

[168] E. Fischer, *Annalen*, 1912, **394**, 361.

[169] E. Ott, V. Barth, and O. Glemser, *Ber.*, 1934, **67**, 1669.

[170] K. N. Campbell and J. P. Mc.Dermott, *J. Amer. Chem. Soc.*, 1945, **67**, 282.

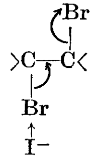
[171] V. M. Mitchovitch and M. L. Mihailovic, *Compt. rend.*, 1950, **251**, 1238.

[172a] K. N. Campbell and E. E. Young, *J. Amer. Chem. Soc.*, 1943, **65**, 965.

Early investigators considered that halogens or halogen acids added *cis* to a triple bond but later it was suggested that *trans*-addition was normal.[2] Considerations of space prevent adequate discussion but it seems that the experimental facts do not warrant a generalised statement, and a thorough investigation is needed. Often mixtures of stereoisomers are obtained, but sometimes only one isomer has been isolated. It is unfortunate that many of the examples chosen give rather easily stereomutable products. An excellent summary of the information available on the addition of halogens and halogen acids to acetylenic acids and alcohols is available.[151]

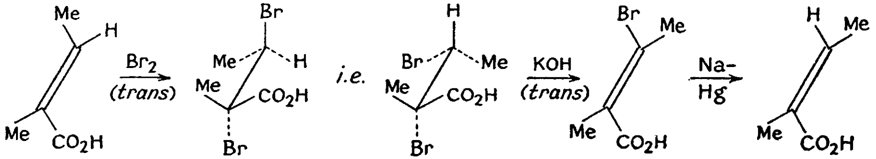
Addition of hydrogen bromide or hydrogen iodide to long-chain acetylenic acids, followed by reductive elimination of the halogen with zinc and acid or sodium and alcohols, is said to yield *trans*-isomers. This indicates that the halogen acid has added *trans*.[172b]

Elimination Reactions.—The elimination of bromine from a diastereoisomeric dibromide with metallic zinc or iodide ions proceeds by *trans*-stereospecific reaction. An *E*2-type elimination mechanism has been suggested with the transition state as shown in (XLIV).[173] The literature contains a number of other elimination reactions which yield geometrical isomers stereospecifically when one diastereoisomer is used.



(XLIV.)

Tiglic acid (XLV) can be converted into its pure stereoisomer, angelic acid (XLVI), by (*trans*-)addition of bromine, elimination of hydrogen bromide with methanolic potassium hydroxide, and removal of the vinyl halogen with sodium amalgam.[174] If *trans*-elimination and replacement at the trigonal carbon atom without inversion, as seems reasonable, are allowed, then the reaction is explained thus :



(XLV) (XLVI)

Sodium in liquid ammonia may also be used to replace such vinyl halogen atoms.[175]

The α- and β-stilbene dichlorides give *cis*- and *trans*-monochlorostilbene respectively on treatment with alcoholic potassium hydroxide,[176] and *meso*-

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[172b] F. Krafft and R. Seldes, *Ber.*, 1900, **33**, 3571 ; A. Arnaud and S. Posternack, *Compt. rend.*, 1910, **150**, 1130 ; 1916, **162**, 944 ; C. Collaud, *Helv. Chim. Acta*, 1943, **26**, 1064.

[173] S. Winstein, D. Pressman, and W. G. Young, *J. Amer. Chem. Soc.*, 1939, **61**, 1645.

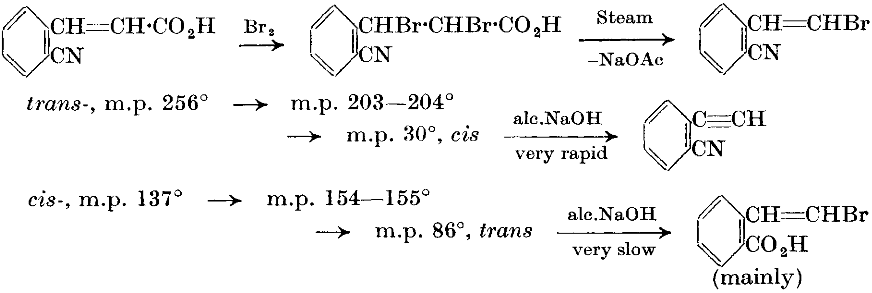
[174] H. P. Kaufmann and K. Kuchler, *Ber.*, 1937, **70**, 915 ; R. E. Buckles and G. V. Mack, *J. Org. Chem.*, 1950, **15**, 680.

[175] M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Amer. Chem. Soc.*, 1951, **73**, 3329.

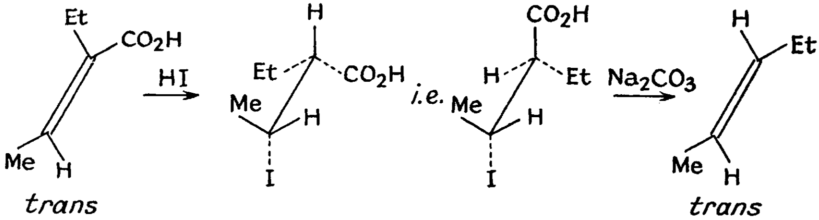
[176] T. W. J. Taylor and A. R. Murray, *J.*, 1938, 2078.

$\alpha : \alpha' : 4 : 4'$-tetrachlorostilbene with the same reagent gives only one of the trichlorostilbenes (probably *cis*).[177]

The elimination of the elements of hydrogen bromide and carbon dioxide from $\alpha\beta$-dibromo-acids occurs stereospecifically and the evidence supports *trans*-elimination. An illuminating series is : [178]



Similarly addition of hydrogen iodide to *trans*-α-ethylcrotonic acid yields α-ethyl-β-iodobutyric acid which on treatment with sodium carbonate gives the *trans*-isomer as expected : [179, 180]



The *cis*-acid gives the *cis*-hydrocarbon. Another case is the bromination of *trans*-crotonic acid followed by treatment with sodium carbonate which yields the expected *cis*-propenyl bromide.[69, 181a] In certain cases different dehydrohalogenating agents give ethylenes of different stereochemistry from one diastereoisomer.[181b] This may be due to stereomutation or change of reaction mechanism.

The stereochemistry of the Boord olefin synthesis is not certain as there seems to be no information on pure diastereoisomers. As would be expected there are reports of the isolation of *cis-trans*-mixtures of olefins,[180, 182] *e.g.* :

$$\underset{\textit{threo} + \textit{erythro}}{\mathrm{Me_2CH{\cdot}CH(OEt){\cdot}CHMeBr}} \xrightarrow{\mathrm{Zn}} \underset{\textit{cis} + \textit{trans}}{\mathrm{Me_2CH{\cdot}CH{=}CHMe}}$$

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[177] E. E. Fleck, *J. Org. Chem.*, 1947, **12,** 708.

[178] W. Davies, B. M. Holmes, and J. F. Kefford, *J.*, 1939, 357.

[179] H. J. Lucas and A. N. Prater, *J. Amer. Chem. Soc.*, 1937, **59,** 1682.

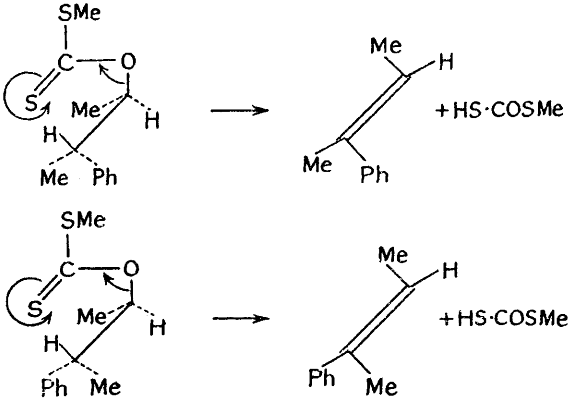
[180] M. L. Sherrill and E. S. Matlock, *ibid.*, p. 2135.

[181a] J. Wislicenus and H. Langbein, *Annalen*, 1888, **248,** 318 ; G. Chavanne, *Compt. rend.*, 1914, **158,** 1698.

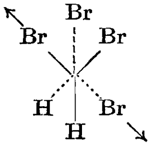
[181b] L. N. Owen and M. U. S. Sultanbawa, *J.*, 1949, 3105.

[182] C. G. Schmidt and C. E. Boord, *J. Amer. Chem. Soc.*, 1932, **54,** 751 ; C. R. Noller and R. A. Bannerdot, *ibid.*, 1934, **56,** 1563.

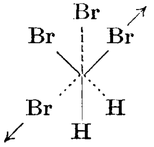
The thermal elimination involved in the Tschugaev reaction is considered to be a *cis*-elimination. Thus the *erythro*-racemate yields largely *cis*-, and the *threo*-racemate largely *trans*-olefin.[68]



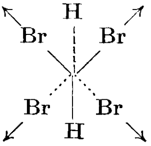
When elimination occurs at a pair of adjacent carbon atoms which are not involved in diastereoisomer formation, the product, if capable of geometrical isomerism, should be a mixture of *cis*- and *trans*-isomers. Thus when tetrabromoethane is treated with zinc in ethanol a mixture of *cis*- and *trans*-dibromoethylene is obtained.[183]



(XLVII.)



(XLVIII.)



(XLIX.)

Three conformations are possible by rotating the rear (dotted bonds) carbon atom. *trans*-Dehalogenation being assumed, two conformations (XLVII) and (XLVIII) will give the *cis*- and (XLIX) the *trans*-form, though in the latter case two eliminations are possible. A well-known case of this type of elimination is the preparation of *cis*-crotonic acid in which a mixture of the two stereoisomeric chloro-esters is obtained and separated :

$$\mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et} \longrightarrow \mathrm{Me{\cdot}CCl_2{\cdot}CH_2{\cdot}CO_2Et} \longrightarrow$$

$$\underset{\beta(+\alpha)}{\mathrm{Me{\cdot}CCl{=}CH{\cdot}CO_2Et}} \xrightarrow[\mathrm{Hg}]{\mathrm{Na-}} \underset{cis}{\mathrm{Me{\cdot}CH{=}CH{\cdot}CO_2H}}$$

the β-chloro-*cis*-crotonic ester is formed in only poor yield.[89, 187]

In some of the eliminations of this type conformational specificity has been inferred. Thus, only *trans*-$\mathrm{CMe_3{\cdot}CH{=}CHCl}$ is obtained when 1 : 2-dichloro-3 : 3-dimethylbutane is treated with alkali.[184] Also, alkaline

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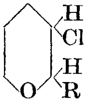
[183] A. Pongratz, *Ber.*, 1936, **69**, 1267.

[184] G. G. Eke, N. C. Cooke, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1950, **72**, 1511.

dehydrochlorination of Me·CCl$_2$·CH$_2$Cl will give *trans*-Me·CCl=CHCl[185] whereas when Me·CCl$_2$·CHCl·CO$_2$H is treated with a base *cis*-Me·CCl=CHCl is obtained.[186] The evidence here is unsatisfactory, but if such cases can be substantiated, then the indication is that certain conformations are more favourable to elimination reactions than others : the effect should be reflected in the relative proportions of *cis*- and *trans*-isomers in other reactions.

With a wide variety of reagents *cis-trans*-mixtures have been isolated when hydroxy-compounds are dehydrated ;[180, 188, 189] occasionally only a *trans*-isomer has been isolated[70, 190] but this may be due to stereomutation or to experimental difficulties. Many of the hydroxy-compounds have been derived from the Reformatski reaction or the reaction of aldehydes or ketones with Grignard reagents. They are of two types, racemic non-diastereoisomers and mixtures of racemic diastereoisomers. The isolation of mixtures of geometrical isomers from both classes is to be expected, even if the dehydration is stereospecific. The latter point does not seem to have been tested—pure diastereoisomers would be needed for this : in any case dehydration at high temperature over a contact catalyst would be expected to proceed by a different mechanism from the lower-temperature chemical elimination. It is clear from the literature that mixtures of stereoisomers are frequently obtained and that the type of dehydration catalyst and the conditions influence the relative proportions of each.[189, 191] This may be due to stereomutation or elimination from different preferred orientations in different cases.



(L.)

$\longrightarrow$ R·CH=CH·[CH$_2$]$_3$·OH

The ring scission of 2-alkyl-3-chlorotetrahydropyrans (L) may be classed here as an elimination reaction. The cyclic compound exists in *cis*- and

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[185] E. Huntress and F. Sanchez-Nieva, *ibid.*, 1948, **70,** 2813 ; cf. 1950, **72,** 3459; 1951, **73,** 1843.

[186] W. Szenic and R. Taggesell, *Ber.*, 1895, **28,** 2665.

[187] K. von Auwers, *Annalen*, 1923, **432,** 46.

[188] R. Stoermer, F. Grimm, and E. Laage, *Ber.*, 1917, **50,** 959 ; W. Chalmers, *Trans. Roy. Soc. Canada*, 1928, **22,** III, 69 ; G. A. R. Kon, R. P. Linstead, and J. M. Wright, *J.*, 1934, 599 ; H. Burton and C. W. Shoppee, *J.*, 1935, 1156 ; H. van Risseghem, *Bull. Soc. chim. Belg.*, 1938, **47,** 47 ; H. Okazaki, *J. Chem. Soc. Japan*, 1942, **63,** 368 ; R. C. Fuson and P. L. Southwick, *J. Amer. Chem. Soc.*, 1944, **66,** 679 ; M. Rubin, A. Kozlowski, and M. R. Salmon, *ibid.*, 1945, **67,** 192 ; D. T. Mowry and A. G. Rossow, *ibid.*, 1945, **67,** 926 ; R. Neher and K. Miescher, *Helv. Chim. Acta*, 1946, **29,** 449 ; S. Miron and G. H. Richter, *J. Amer. Chem. Soc.*, 1949, **71,** 453 ; R. E. Buckles and G. V. Mock, *J. Org. Chem.*, 1950, **15,** 680.

[189] S. H. Harper and J. F. Oughton, *Chem. and Ind.*, 1950, 575.

[190] L. F. Fieser and M. Fieser, *Experientia*, 1948, **4,** 285 ; R. E. Lutz and R. S. Murphey, *J. Amer. Chem. Soc.*, 1949, **71,** 479.

[191] R. Kuhn and M. Hoffer, *Ber.*, 1932, **65,** 651 ; C. F. F. Bergmann, M. Weizmann, E. Dimant, J. Patai, and J. Szmuskowicz, *J. Amer. Chem. Soc.*, 1948, **70,** 1612 ; C. Cauquil, M. H. Barrera, and G. Turpin, *Compt. rend.*, 1950, **231,** 779.

trans-forms and on treatment with sodium each gives the same *trans*-ethylenic alcohol. But in the case of 2-alkyl-3-chlorotetrahydrofurans (alkyl = Me and Et), the *trans*-isomer gives a largely *trans*-alk-3-en-1-ol and the *cis*-isomer a mixture of *cis*- and *trans*-alcohols (R = Et ; 55% *cis*). A mechanism for this has been suggested.[88]

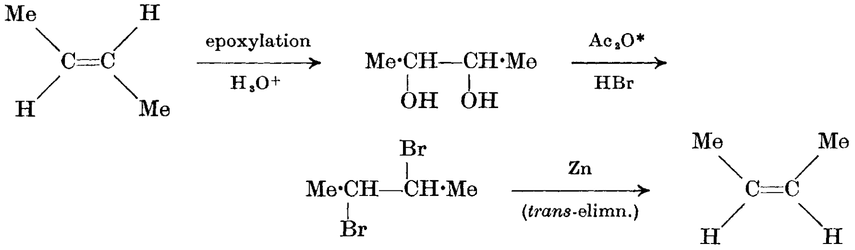
A method has been developed for the synthesis of geometrical isomers as follows :

$$R{\cdot}CO_2Me + R'{\cdot}CO_2Me \xrightarrow{Na} R{\cdot}CO{\cdot}CHR'{\cdot}OH + R'{\cdot}CO{\cdot}CHR{\cdot}OH \xrightarrow[\text{or Raney Ni} + H_2]{\text{Pondorff}}$$

$$HO{\cdot}CHR{\cdot}CHR'{\cdot}OH \xrightarrow[H_2SO_4,\ HOAc]{HBr,} CHRBr{\cdot}CHR'Br \xrightarrow{Zn} CHR{=}CHR'$$

$$\begin{array}{l}\text{sepd.}\\ \text{by crystn.}\end{array}\left\{\begin{array}{l}\textit{erythro}\\ \\ \textit{threo}\end{array}\right.\begin{array}{c}\xrightarrow{\hspace{4em}}\\ \text{one inversion}\\ \xrightarrow{\hspace{4em}}\end{array}\begin{array}{c}\textit{threo}\\ \\ \textit{erythro}\end{array}\begin{array}{c}\xrightarrow{\hspace{4em}}\\ \textit{trans}\text{-elimn.}\\ \xrightarrow{\hspace{4em}}\end{array}\begin{array}{c}\textit{cis}\\ \\ \textit{trans}\end{array}$$

This acyloin method has been applied to the synthesis of long-chain acids of the type $R{\cdot}[CH_2]_n{\cdot}CH{=}CH{\cdot}[CH_2]_n{\cdot}CO_2H$ (where R = alkyl or $[CH_2]_n{\cdot}CO_2H$) in both the *cis*- and the *trans*-forms, the *erythro*- and the *threo*-glycols being separated by crystallisation.[192] One step involves a single inversion : this can also be made use of in passing from a *cis*- to a *trans*-olefin as follows :[120,193]



* One inversion.

It has been mentioned above that zinc debromination gives essentially *trans*-elimination. It has been pointed out however that, if a pure dibromide is treated with zinc and the resulting hydrocarbon is then brominated, a proportion (3—20%) of the unexpected diastereoisomer is formed.[121, 194] The amount increases with chain length. There is some evidence that the partial inversion occurs at the zinc debromination stage but it is probably a secondary effect due to the zinc halide formed.[121] Careful scrutiny of the products of the acyloin method by physical examination is therefore desirable since limitations reminiscent of the route concerning semi-hydrogenation of acetylenes may be involved.

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[192] L. Ruzicka, Pl. A. Plattner, and W. Widmer, *Helv. Chim. Acta*, 1942, **25**, 604, 1086 ; P. Baudart, *Bull. Soc. chim.*, 1946, **13**, 87 ; D. E. Ames and R. E. Bowman, *J.*, 1951, 1079, 1087 ; B. W. Boughton, D. E. Ames, and R. E. Bowman, *J.*, 1952, 671.

[193] W. G. Young, Z. Jasaitas, and L. Levanas, *J. Amer. Chem. Soc.*, 1937, **59**, 403 ; S. Winstein and H. J. Lucas, *ibid.*, 1939, **61**, 1576, 1581.

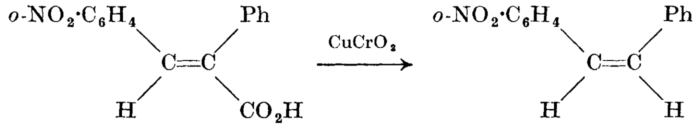
[194] H. van Risseghem, *Bull. Soc. chim. Belg.*, 1938, **47**, 194.

Condensation Reactions.—The $\alpha\beta$-unsaturated acid isolated in the Doebner reaction is generally considered to be *trans*.[195] The same assignment has been made for the $\beta\gamma$-acid derived from the similar triethanolamine-catalysed condensation.[31] However, the oily and neutral materials are normally discarded in these reactions and the presence of *cis*-acid or a product of subsequent reaction is possible. It has been found that, dependent on conditions, 6—17% of hexenolactone—which might have been derived from a *cis*-precursor—can be isolated from preparations of sorbic acid by the Doebner method.[196]

The condensation of benzaldehyde and ketones is recorded as yielding a *trans*-$\alpha\beta$-unsaturated ketone.[197] E. N. Eccott and R. P. Linstead [148] have described an unusual case. When *n*-butaldehyde and acetone are condensed without check to the exothermic reaction a *cis*-ketone $Pr^nCH{=}CH{\cdot}COMe$ is obtained. But, if the reaction is controlled, a hydroxy-acid is isolated which on dehydration with various reagents gives the *trans*-isomer. The two ketones are resistant to configurational change but on Ponndorf–Meerwein reduction yield the same alcohol.[198]

The Perkin reaction,[124, 199, 200] as applied to the synthesis of substituted stilbenes, gives a product with the aryl groups *cis* to each other, *e.g.* :

$NO_2{\cdot}C_6H_4{\cdot}CHO + Ph{\cdot}CH_2{\cdot}CO_2H \rightarrow$



By use of *trans*-*o*-nitrocinnamaldehyde, a *trans*-*cis*-diene has been obtained.[200]* The configuration of the products from the Kuhn–Winterstein modification of the reaction is less certain though *trans*-ethylenes have been isolated.[200]

Scission of Ring Systems containing Double Bonds.—Under suitable conditions ring systems containing olefinic linkages, which must be constrained in the *cis*-configuration in an approximately planar ring, can be opened with retention of configuration. Maleic anhydride or α-methylaconitic anhydride may be hydrated to the *cis*-acids, and unsaturated

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[195] W. H. Lauer and W. J. Gensler, *J. Amer. Chem. Soc.*, 1945, **57**, 1171.

[196] R. Joly and G. Amiard, *Bull. Soc. chim.*, 1947, 139.

[197] M. T. Bogert and D. Davidson, *J. Amer. Chem. Soc.*, 1932, **32**, 334 ; but cf. B. Koechlin and T. Reichstein, *Helv. Chim. Acta*, 1944, **27**, 549.

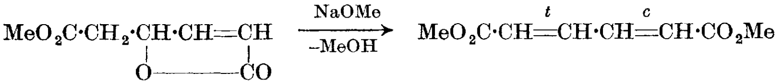
[198] C. L. Arcus and J. Kenyon, *J.*, 1938, 698.

[199] T. W. J. Taylor and C. E. J. Crawford, *J.*, 1934, 1130 ; E. D. Amstutz and E. R. Spitzmiller, *J. Amer. Chem. Soc.*, 1943, **65**, 367 ; E. F. M. Stephenson, *J.*, 1949, 655.

[200] G. B. Bachman and H. I. Hoaglin, *J. Org. Chem.*, 1943, **8**, 300.

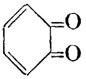
* Recent work (S. Ishraelashvili, Y. Gottlieb, M. Imber, and A. Habas, *J. Org. Chem.*, 1951, **16**, 1519) indicates that, contrary to expectation, a number of dienes with unsubstituted aryl groups which have been thus prepared have entirely *trans*-*trans* configurations. A methoxynaphthylacraldehyde, however, gave a mixture of *trans*-*trans*- and *trans*-*cis*-isomers.

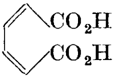
lactones can also yield the *cis*-acids : in this way, *trans-cis*-muconic half ester has been prepared.[201]



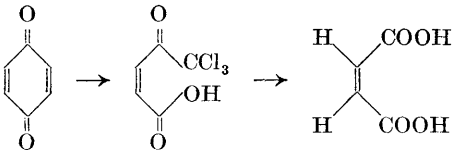
$$MeO_2C{\cdot}CH_2{\cdot}CH{\cdot}CH{=}CH{\cdot}CO(O) \xrightarrow[-MeOH]{NaOMe} MeO_2C{\cdot}\overset{t}{CH{=}CH}{\cdot}\overset{c}{CH{=}CH}{\cdot}CO_2Me$$

Peracetic acid oxidation of an *o*-quinone,[202] phenol,[203, 204] or catechol [204] yields *cis-cis*-muconic acid :

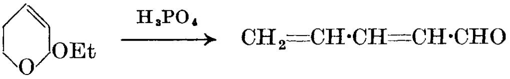




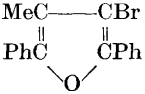
p-Benzoquinone is oxidised by chloric acid to maleic acid : [205]

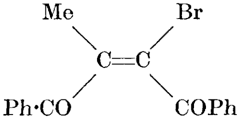


The ring scission of 2-ethoxy-5 : 6-dihydro-2-pyran, however, seems to give *trans*-penta-2 : 4-dienal [144] (probably because of subsequent stereomutation by H^+).



Nitric acid oxidation of substituted furans has been used repeatedly to prepare *cis*-aroylethylenes,[206] e.g. :





Thiophen derivatives may also be oxidised to similar compounds.[207]

Rearrangement Reactions.—The conversion of secondary allylic alcohols into bromides, by phosphorus tribromide, gives under the ordinary preparative conditions, an equilibrium mixture containing mainly the primary bromide :

$$HO{\cdot}CHR{\cdot}CH{=}CH_2 \rightarrow Br{\cdot}CHR{\cdot}CH{=}CH_2 \rightarrow CHR{=}CH_2{\cdot}CH_2Br$$

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[201] J. A. Elvidge, R. P. Linstead, P. Sims and B. A. Orkin, *J.*, 1950, 2235.

[202] J. Böeseken and G. Sloof, *Proc. Acad. Sci., Amsterdam*, 1929, **32**, 1043.

[203] J. Böeseken and R. Engelberts, *ibid.*, 1931, **34**, 1292.

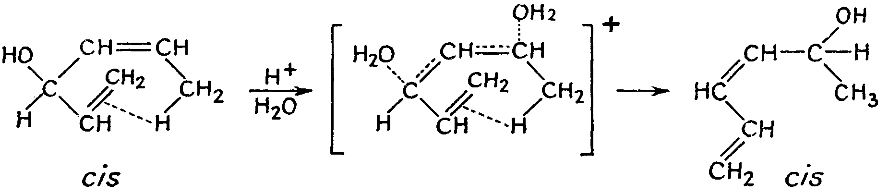
[204] J. Böeseken, *ibid.*, 1932, **35**, 750.

[205] A. Kekulé and O. Strecker, *Annalen*, 1884, **223**, 170.

[206] R. E. Lutz and C. E. McGwin, *J. Amer. Chem. Soc.*, 1942, **64**, 2583.

[207] A. Angeli and G. Ciamician, *Ber.*, 1891, **24**, 74, 1347.

the latter has the *trans*-configuration.[208] Acid-catalysed anionotropic rearrangement of *cis*-phenylpropenylcarbinol (like that of the *trans*-isomer) gives largely or exclusively *trans*-methylstyrylcarbinol. But *cis*-propenylvinylcarbinol, unlike its *trans*-isomer, rearranges with retention of configuration to *cis*-butadienylmethylcarbinol.[69] An explanation involving a *pseudo*-cyclic intermediate (LI), annelised because of "π hydrogen bonding", has been suggested : [69]



(LI.)

The conditions and mechanisms by which a compound such as *cis*-crotyl chloride (which rearranges less readily than does the corresponding bromide) retains and loses configuration when it reacts raises interesting possibilities but the subject has not yet been investigated.

The rearrangement of (LII) with sodium methoxide in ether yields a *trans*-$\beta\gamma$-ester with a smaller amount of ketone,[209] but the similar rearrangement of (LIII) gives a mixture of *cis*- and *trans*-esters.[210]

$$\underset{\text{(LII.)}}{\text{Me·CHBr·CMeBr·COMe}} \xrightarrow{\text{NaOMe}} \underset{\textit{trans}}{\text{Me·CH=CMe·CH}_2\text{·CO}_2\text{Me}}$$

$$\underset{\text{(LIII.)}}{\text{C}_2\text{H}_5\text{·CMeBr·CO·CH}_2\text{Br}} \longrightarrow \underset{\textit{cis} + \textit{trans}}{\text{C}_2\text{H}_5\text{·CMe=CH·CO}_2\text{Me}}$$

The carbinol (LIV) rearranges to yield a mixture of *cis*- and *trans*-isomers (LV).[212]

$$\underset{\text{(LIV.)}}{p\text{-Me·C}_6\text{H}_4\text{·CPh(OH)·C}\equiv\text{CPh}} \qquad \underset{\text{(LV.)}}{p\text{-Me·C}_6\text{H}_4\text{·CPh:CH·COPh}}$$

Replacement Reactions at a Trigonal Carbon Atom.—A. R. Olson [26] suggested that the replacement reaction, *e.g.*, between iodide ion and iodine bonded to a trigonal carbon atom, proceeds with inversion at each replacement. This view does not accord with later evidence : it has been demonstrated that some one hundred exchanges occur for each inversion of con-

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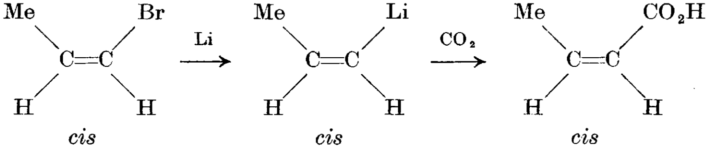
[208] M. Bouis, *Ann. Chim.*, 1928, [x], **9**, 403 ; S. Winstein and W. G. Young, *J. Amer. Chem. Soc.*, 1936, **58**, 104.

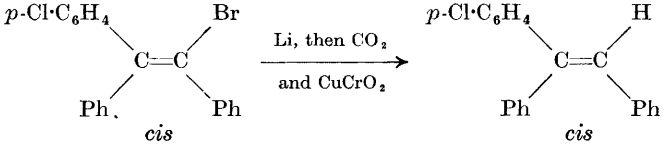
[209] R. B. Wagner, *ibid.*, 1949, **71**, 3214.

[210] R. B. Wagner and J. A. Moore, *ibid.*, 1950, **72**, 974.

[212] M. Badosche, *Bull. Soc. chim.*, 1928, **43**, 337.

figuration.[25] It is also considered that metalation and carboxylation or replacement of the metal by hydrogen does not involve inversion : [69, 101]





(LVI.) (LVII.)

Carboxylation of the Li derivative of *cis*-(LVI) gives the expected acid with the carboxyl and the *p*-chlorophenacyl group in *cis*-relation : decarboxylation with copper chromite yields *cis*-(LVII), again indicating absence of inversion.[101] A number of other examples of decarboxylation at a trigonal carbon atom are known to proceed with retention of configuration.[124, 176, 180] Reductive elimination of a vinyl halogen atom by sodium amalgam or sodium in liquid ammonia is also best interpreted in these terms.[174, 175, 187, 213]

A. N. Nesmeyanov *et al.* record that reactions of the type :

$$\begin{tikzcd} (Cl\cdot CH{=}CH)_3Sb + HgCl_2 \arrow[r] & Cl\cdot CH{=}CH\cdot HgCl \arrow[d, shift right, "NH_3"'] \\ (Cl\cdot CH{=}CH)_2SnCl_2 & (Cl\cdot CH{=}CH)_2Hg \arrow[l, "SnCl_2"'] \arrow[u, shift right, "Cl_2"'] \end{tikzcd}$$

proceed with retention of configuration at all stages when either stereoisomer is used.[214]

The Meerwein [215] reaction yields, in most recorded examples, *trans*-stilbenes though this may be due to the fact that the starting materials are *trans* :

$$Ph\cdot CH{=}CH\cdot CO_2H + Ph\cdot N_2Cl \longrightarrow Ph\cdot CH{=}CHPh + CO_2 + N_2 + HCl$$

It has been found that the two isomers of p-$Br\cdot C_6H_4\cdot CPh{=}CH\cdot CO_2H$ react with diazotised aniline to give the same isomer. More information on the mechanism is needed.

Miscellaneous Reactions.—The reaction of unsymmetrical diarylethylenes with oxalyl chloride, which is, formally at least, a substitution reaction,

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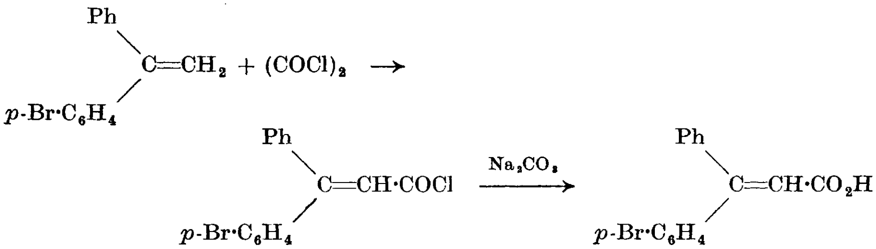
[213] A. Michael and O. Schulthess, *J. pr. Chem.*, 1892, [ii], **46**, 236.

[214] A. N. Nesmeyanov, A. E. Borisov, and A. N. Abramova, *Izvest. Akad. Nauk. S.S.S.R. Otdel. Khim. Nauk.*, 1947, 647 (*Chem. Abs.*, 1948, **42**, 6316) ; A. N. Nesmeyanov and A. E. Borisov, *Doklady Akad. Nauk. S.S.S.R.*, 1948, **60**, 67 (*Chem. Abs.*, 1949, **43**, 560) ; A. N. Nesmeyanov, A. E. Borisov, and A. N. Gus'kova, *Bull. Acad. Sci. U.R.S.S., Classe Sci. chim.*, 1945, 639 (*Chem. Abs.*, 1946, **40**, 4659).

[215] F. Bergmann, J. Weizman, and D. Schapiro, *J. Org. Chem.*, 1944, **9**, 408.

generally gives mixtures of *cis*- and *trans*-$\beta\beta$-diarylacrylic acids, though certain examples have only yielded one isomer.[216]



A well-known preparative method for *trans*-diaroylethylenes is the Friedel–Crafts reaction between fumaroyl chloride and a hydrocarbon : [217] a similar reaction between aromatic hydrocarbons and maleic anhydride yields *trans*-aroylacrylic acids.

Catalytic hydrogenation of aromatic $\alpha\beta$-diketones over a platinum catalyst in methanol gives mainly a *cis*-stilbenediol but if the hydrogenation is continued the conditions cause stereomutation to the *trans*-diol.[218] In another example, if the hydrogenation is conducted in methanol the *cis*-form is obtained, but if in light petroleum the product is the *trans*-isomer.[219]

Stereomutation (cf. p. 106).—A wide variety of catalysts for thermal equilibration of geometrical isomers has been used and a selection is as follows : nitrous acid (or Poutet's reagent, mercury and nitric acid),[220] sulphur,[221] selenium black,[222] platinum black, alkali metals, halogen acids,[223] sulphuric acid,[224] phosphoric acid,[225] red phosphorus and water,[225] ammonia, primary and secondary amines,[226] and tetranitromethane.[227] Recent patents [228] recommend, *inter alia*, alkanethiols, thiuram disulphides, salts of dithio-acids, thiazoles, thiazolines, and thioamides. For photochemical equilibrations halogens—usually iodine—are commonly used as catalysts. The choice of solvent influences the equilibrium in some cases.

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[216] F. Bergmann, M. Weizmann, E. Dimant, J. Patai, and J. Szmuskowicz, *J. Amer. Chem. Soc.*, 1948, **70,** 1612.

[217] J. B. Conant and R. E. Lutz, *ibid.*, 1923, **45,** 1303.

[218] R. C. Fuson, S. L. Scott, E. C. Horning, and C. H. McKeever, *ibid.*, 1940, **62,** 209.

[219] R. C. Fuson, C. H. McKeever, and L. C. Behr, *ibid.*, 1941, **63,** 2648.

[220] H. N. Griffiths and T. P. Hilditch, *J.*, 1932, 2315 ; J. C. Smith, *J.*, 1939, 974.

[221] G. Rankoff, *Ber.*, 1931, **64,** 619 ; E. Rosemann, *Chem. Umschau Fette, Öle, Waschse, Harz*, 1932, **39,** 220 (*Chem. Abs.*, 1933, **27,** 702).

[222] G. Rankov, *Annuaire univ. Sofia Faculté phys. math.*, 1941, **38,** Livre 2, 133 (*Chem. Abs.*, 1948, **42,** 2453) ; J. P. Kass and G. O. Burr, *J. Amer. Chem. Soc.*, 1939, **61,** 1062 ; D. Swern, E. F. Jordan, and H. B. Knight, *ibid.*, 1946, **68,** 1673.

[223] F. H. Malpress, *Nature*, 1946, **158,** 790 ; R. E. Lutz and R. H. Jordan, *J. Amer. Chem. Soc.*, 1950, **72,** 4090.

[224] P. Ruggli and H. Zaeslin, *Helv. Chim. Acta*, 1935, **18,** 853.

[225] G. Rankov, *Ber.*, 1936, **69,** 1231.

[226] G. R. Clemo and S. B. Graham, *J.*, 1930, 213.

[227] H. P. Kaufmann, *Ber.*, 1942, **75,** 1201.

[228] U.S.P. 2,404,103/1946 ; 2,414,066/1947 ; 2,454,385/194 (*Chem. Abs.*, 1946, **40,** 6500 ; 1947, **41,** 2437 ; 1949, **43,** 1798).

The value of the method turns on the availability of satisfactory procedures for isolation. A solvent may be chosen from which one isomer continually crystallises on irradiation, thus effecting complete conversion. Sometimes a trace of catalyst is added to the distillation-vessel and the lower-boiling isomer removed continuously by distillation. Fractional crystallisation and distillation have often been used and great success has attended chromatographic separations, particularly in the polyene series where stereomutation is often the only way in which many geometrical isomers may be obtained.

The Reviewer is indebted to Professor R. P. Linstead, C.B.E., F.R.S., and Dr. E. A. Braude for criticism of the manuscript.