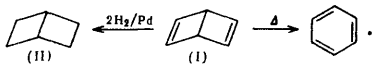
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REVERSIBLE VALENCE ISOMERISATION

T. V. Domareva-Mandel'shtam
and I. A. D'yakonov

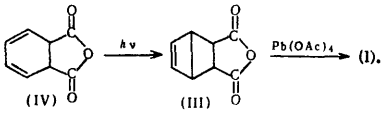
In recent years many examples of isomeric conversions have become known that differ phenomenologically from most ordinary isomerisations. A characteristic of the new type of isomerisation is that it occurs without displacement of atoms or atomic groups within the molecule. The isomerisations are accompanied by corresponding changes in the relative arrangement of σ- and π-bonds and only by small changes in interatomic distances and valence angles. In the literature, this kind of isomeric conversion has been given the name valence isomerisation [1]†.

A striking example of a valence-isomeric conversion is the recently described thermal isomerisation of "Dewar benzene", or bicyclo[2,2,0]hexa-2,5-diene (I) to ordinary benzene [5]:



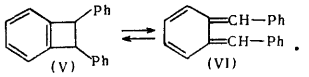
At room temperature "Dewar benzene" is fairly stable, having a half-life of 2 days, but at 90° it is converted into benzene in 30 min.

The structure of "Dewar benzene" was confirmed by examination of its nuclear magnetic resonance (NMR) spectrum and by its conversion on careful hydrogenation into bicyclo[2,2,0]hexane (II). The structure was also determined by synthesis: "Dewar benzene" was obtained by oxidising the anhydride of bicyclo[2,2,0]hex-2-ene-5,6-dicarboxylic acid (III) with lead tetra-acetate. It is of interest to note that the anhydride is formed by the photo-initiated valence-isomerisation of 1,2-dihydrophthalic anhydride (IV):



Valence isomerisations, like non-valence isomerisations, may be classified as reversible or irreversible. The isomerisation of the hydrocarbon (I) to benzene is an example of irreversible valence isomerisation. Isomerisations of this kind are very numerous (see reviews [2-4,6] and some original papers of recent years [7-37]).

Irreversible valence isomerisation occurs when two valence isomers differ greatly in their thermodynamic stability. When this difference is not great, dynamic equilibrium may be established between the valence isomers. This type of valence isomerism is termed reversible. An example that may be quoted is the recently described reversible valence isomerisation of *trans*-1,2-diphenylbenzocyclobutene (V) to *trans-trans*-5,6-dibenzylidenecyclohexadiene ($\alpha\alpha'$-diphenyl-*o*-quinodimethane) (VI) [38] (see also Freedman and coworkers [39]):



We shall give a number of other examples of this type of isomerisation below.

In recent years the term "valence tautomerism" has been increasingly used in publications outside the Soviet Union to describe the phenomenon of equilibrium valence isomerism. According to Rhodes [4], for the correct use of this term the following condition should be observed: "the corresponding isomers must be converted into each other under normal working conditions and the energy barrier to be overcome must be relatively small. If the latter condition is not fulfilled, it is better to call the compounds valence isomers".

The author does not say what is to be understood by normal working conditions. A study of the literature shows that other authors do not adhere to this kind of limitation in the definition of valence tautomerism. It is clear from papers we shall refer to later that valence-tautomeric conversions may include conversions that occur at widely different temperatures and pressures, and under widely different conditions of illumination, etc. The position of equilibrium between the valence tautomers can also have any value. As is pointed out below, at present systems are known in which equilibrium is largely displaced in the direction of one of the tautomers‡. Hence it follows that the energy barrier to be overcome when one tautomer is converted into another may vary appreciably from case to case.

Notwithstanding what has just been said, it must be recognised that the term "valence tautomerism" is not a good one. Firstly, although this term was proposed a long time ago, the concept of valence tautomerism itself was invested with a somewhat different meaning (see, for example, Ingold [40]).

The idea that valence tautomerism can occur was first put forward by Kekulé, who proposed a dynamic formula for the structure of benzene in 1872. [41] The term "valence tautomerism" itself was first used by Wieland in 1920–1922, who, like many other chemists of that time, regarded valence tautomerism as the rapid intramolecular oscillation of valence bonds [42,43]. Later, a meaning not differing substantially from the modern concept of resonance began to be applied to the concept of "valence tautomerism". As is known, the concept of resonance is based on the idea that the real state of a given molecule may be described by the superposition of several limiting structures, none of which occurs alone in the unexcited state. It is characteristic of the limiting structures that they have the same distances between corresponding atomic nuclei and the same angles between the atoms; they differ only in the arrangement of the π-electrons. Resonance structures do not have the significance of structural formula of real compounds and

† At present only three review articles on the subject of valence-isomeric conversions can be cited, and these have appeared in foreign journals [2-4]. These articles are, to a certain extent, already out-of-date, because many new experimental papers have been published since they appeared. No reviews of this kind have yet appeared in Soviet literature.

‡ In this connection it should be noted that a sharp line cannot be drawn between reversible and irreversible isomerisation. Processes that are now regarded as irreversible may in the future turn out to be reversible when new sources of energy are used or more sensitive methods of analysis are applied.

are only arbitrary constructs which may be used for molecular calculations by the method of valence diagrams. In contrast, valence tautomers, which are being considered here, are structures that really exist. Moreover, they differ from one another not only in the order of alternation of single and double bonds, as, for example, the oscillating benzene structures proposed by Kekulé and by Dewar, but also in the distances between atoms, in the valence angles, and in free energy content.

Secondly, the use of this term may give rise to the idea that the concept of valence tautomerism is related to, or even identical with, the concept of electronic tautomerism[44,45]. In fact both concepts differ in their content.

Notwithstanding what has been said above, the term "valence tautomerism" is now widely used in the literature. For this reason, and also because there is no other suitable name for this phenomenon, we are forced to retain this term in our review.

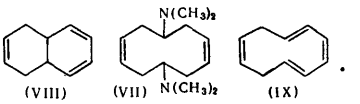
Since valence tautomerism is associated with reversible-valence-isomerisation phenomena, it should be possible to make a suitable change of terms and use the term "reversible valence isomerisation" instead of "valence tautomerism". To this, however, it must be objected that the new term is longer than the old one and therefore less convenient in use. The idea of tautomerism does not always fully correspond with the idea of reversible isomerisation. The difference lies in that in tautomerism a state of dynamic equilibrium is established, but this is not a necessary condition for reversible isomerisation. As confirmation of this we may cite as an example those reversible valence isomerisations (they are considered below) in which the direct reaction occurs under some conditions, for example, with ultraviolet irradiation, and the reverse reaction occurs under other conditions, for example, with heating. There is no state of equilibrium between valence isomers in such instances (and therefore these isomers cannot be regarded as valence tautomers), although this state could be achieved under certain conditions of irradiation and heating (and then a system of this kind should be regarded as tautomeric). Thus, the idea of reversible valence isomerisation embraces the idea of valence tautomerism, but the converse is not true. The question whether one term should be replaced by the other must therefore be answered in the negative.

The present review is devoted to a description of the phenomena of reversible valence isomerisation, which here also covers the field of valence tautomerism. Another no less interesting field, that of valence (intramolecular) rearrangements, is not considered. We might well have limited our remarks on valence rearrangements to this observation, if the error[4] was not frequently encountered that isomerisations can be called rearrangements and conversely. In this connection, it would be useful to consider what is meant by intramolecular rearrangement and how it differs from isomerisation.

In a number of available theoretical handbooks on organic chemistry a definition of the concept of rearrangement is either not given (see, for example, Ingold[46]) or the proposed definitions are not sufficiently rigorous and reliable[47,48]. Some authors[49-51], however, are agreed that the term molecular rearrangement should only be applied to a special group of reactions, be they substitutions, eliminations, or additions, in which the principle of minimal structural change is violated. Although this formulation of the concept of a new type of reaction must be considered somewhat vague (because of the vagueness of the principle itself), nevertheless at the present time it best meets the requirements of reality. On the other hand, it is quite clear that this definition is not applicable to the concept of isomerisation. Thus, it would be absurd to consider the question whether the principle of minimum structural change is preserved in isomerisation reactions. In these reactions only the structure changes, and not the composition, since only one molecule of final product is formed from one reacting molecule. In reactions of the intramolecular-rearrangement type a change always occurs not only in structure but also in composition, although in isolated instances the number of molecules reacting may be the same as the number of molecules formed.

The question of the mechanism of rearrangements requires special consideration. It is difficult to draw any conclusion on this point from the actual definition of these reactions (see above). However, there is now convincing published evidence (see p. 511 of the book by Temnikova[51]) that rearrangements may proceed in two ways, either by way of an active reaction complex (brought about by a so-called reaction with reaction-centre transfer), or by the rapid isomerisation in the course of the reaction of the initial compound or one of its intermediates. The fact that the reaction can proceed in the first way is a further argument against identifying rearrangements with isomerisations.

Everything that has been said here on reaction mechanism is also valid for valence rearrangements. It should be noted, however, that the experimental investigation of the mechanism of valence rearrangements presents great difficulties, because of the absence of appreciable displacement of the atomic nuclei in the conversion process. Only one example of valence rearrangement will be given here. The dioxide of the diamine (or the diquaternary ammonium salt) obtained from 1,6-bis(dimethylamino)-cyclodeca-3,8-diene (VII) undergoes thermal decomposition (120–150°) with the formation of *trans*-1,4,9,10-tetrahydronaphthalene (VIII). According to Grob and Schies[52], the latter is formed by valence isomerisation of the unstable tetraene (IX), a product of the normal cleavage of the diamine dioxide (VII) or quaternary salt. Since the intermediate tetraene (IX) has not been isolated, the proposed mechanism cannot be considered proved. It is possible that the tetrahydronaphthalene (VIII) is formed directly from the diamine dioxide (or the diquaternary ammonium salt), without an intermediate stage (see, however, Grob and coworkers[53]).

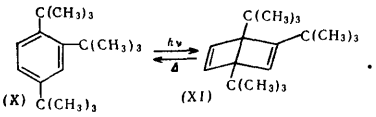


(VIII) (VII) (IX)

After the foregoing discussion on valence isomerisation (reversible and irreversible), valence tautomerism, and finally, molecular rearrangements including valence rearrangements, we may proceed to a more detailed examination of the phenomena of reversible valence isomerisation, which in fact is the main theme of the present paper.

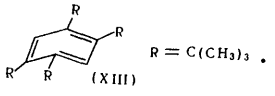
In recent years the valence-isomeric conversions of benzene and its homologues have attracted particular attention. It is curious to note that the structures of the valence isomers of benzene have a formal similarity to the benzene structures proposed in their time by Dewar and by Ladenburg (hence the names "Dewar benzene" and "Ladenburg benzene"). An example of the irreversible valence

isomerisation of "Dewar benzene" into ordinary benzene was given on p. 559 (see also Criegee and Zanker[54]). An example of reversible valence isomerisation of this kind is the conversion of 1,2,4-tri-t-butylbenzene (X) into 1,2,4-tri-t-butylbicyclo[2,2,0]hexa-2,5-diene (XI), which proceeds under the action of light[55]. The isomer (XI) can be separated from the remaining products of photoconversion by thin-layer chromatography and purified by distillation under high vacuum at room temperature. It has been proved that the hydrocarbon (XI) is monomeric; its structure has been confirmed by ultraviolet and NMR spectra. When heated to 200° for 15 min, it is converted into the initial tri-t-butylbenzene (X):



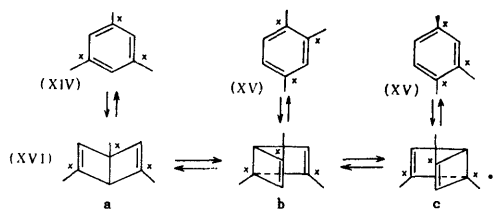
There is no dynamic equilibrium between the isomers, but it may be supposed that this equilibrium would be achieved under suitable conditions (illumination + heating).

In this instance the formation of the bicyclic isomer (XI) from tri-t-butylbenzene is promoted by the steric effect of the substituents. There are grounds for supposing that the carbon atoms in the 1,2,4-tri-t-butylbenzene ring are not coplanar, because of the proximity of bulky substituents. A similar phenomenon occurs, for example, with 2,4,6-tri-t-butyltoluene (XII), [56] or 1,2,4,5-tetra-t-butylbenzene (XIII), [57] which have the form of a tub:

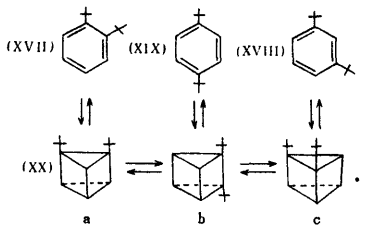


The non-planar structure of the molecule (X) must lower the stability of this hydrocarbon in comparison with other aromatic compounds that do not contain sterically hindered alkyl groups and thereby facilitate its conversion into the strained bicyclic form (XI).[6]

A number of papers deal with the displacement of alkyl groups in benzene homologues under the action of ultraviolet light[58-60]. Using an isotope marker, Kaplan and coworkers[60] established that isomerisation of 1,3,5-trimethylbenzene (XIV) to 1,2,4-trimethylbenzene (XV) (30°, λ = 2537 Å) proceeds not as a result of 1,2-shift of the methyl group, as it might well do, but by a change in the positions of the carbon atoms in the ring — in (XV), as well as in (XIV), the methyl groups are attached to labelled carbon atoms in the ring. This change is said to be effected by the equilibrium compound (XIV) and the three "Dewar isomers" (XVI, a, b, and c) which is rapidly established under ultraviolet irradiation; the "Dewar isomers" are, in turn, in equilibrium with the initial and final compounds.

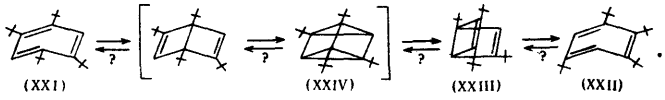


Because of the great strain set up in the molecule by the proximity of the t-butyl radicals, when *o*-di-t-butylbenzene (XVII) is irradiated with ultraviolet light, it is converted into an equilibrium mixture of the *meta*- and *para*-isomers (XVIII) and (XIX) (in the ratio 1 : 4):



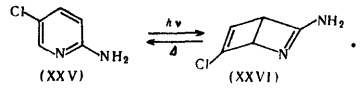
Burgstahler and coworkers[59,61], who described this phenomenon, suggest that the conversion of (XVII) into (XVIII) and (XIX) is accomplished by valence isomerisation of the initial molecule, at first into homologues of "Ladenburg benzene" (XX, a, b, and c) and then into the observed reaction product.

Later, Arnett and Bollinger[62] observed that when 1,2,4,5-tetra-t-butylbenzene (XXI) is irradiated with ultraviolet light, 1,2,3,5-tetra-t-butylbenzene (XXII) is formed, together with the "Dewar isomer" 1,2,3,5-tetra-t-butylbicyclo[2,2,0]hexa-2,5-diene (XXIII).[62] In the opinion of these workers, the fact that irradiation of the highly strained compound (XXI) gives the still more highly strained compound (XXII) excludes any other isomerisation mechanism except intramolecular reorganisation of bonds with the intermediate formation of the homologue of "Ladenburg benzene", "tetra-t-butylprismane" (XXIV) according to the following scheme:

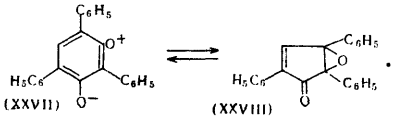


The reversibility of the valence isomerisation (XXI) ⇌ ⇌ (XXII) in this example has not yet been demonstrated.

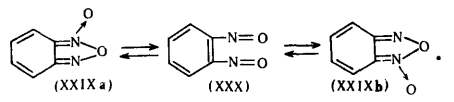
Reversible valence isomerisation similar to the isomerisation of benzene homologues to bicyclohexadiene homologues is observed in a number of heterocyclic compounds. Thus, illumination with sunlight converts 2-amino-5-chloropyridine (XXV) into the bicyclic isomer (XXVI), which was characterised by its ultraviolet and NMR spectra[63,64]. When set aside at room temperature, the isomer (XXVI) is reconverted into the initial compound; this is indicated by the reappearance of the characteristic absorption spectrum of the aminochloropyridine in the ultraviolet region:



Another type of valence isomerisation occurs with triphenylpyrilium oxide (XXVII),[65] which is converted on irradiation with light of wavelength greater than 4500 Å into 1,2,4-triphenylcyclopentadienone oxide (XXVIII) (see also other work[66-68]). On irradiation with light of wavelength 3200–3930 Å, the latter is converted into the starting compound (XXVII).



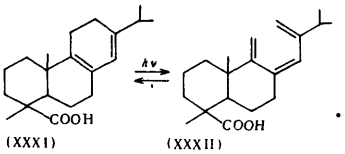
Instances of ring-chain valence tautomerism of heterocycles are known[69-72]. Thus, it was established[70,71] from the temperature dependence of the NMR spectrum of ^{17}O in benzofurazan oxide (XXIX) between -60° and +100° that this compound is in a state of rapid valence-tautomeric conversion, which includes an *o*-dinitrosobenzene (XXX) stage:



(XXIXa) (XXX) (XXIXb)

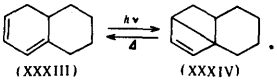
The life period of each tautomer is so short that none of them can be isolated in the pure state.

Under the action of light, compounds that have the 1,3-cyclohexadiene-ring system as a component undergo reversible valence isomerisation, which may proceed in two directions[73]. In the first, the six-membered ring containing two conjugated double bonds opens to form a hexa--1,3,5-triene grouping. In the other, a second smaller ring is formed inside the cyclohexadiene ring. An example of a conversion of the first type is the equilibrium between palustric acid (XXXI) and the triene (XXXII), which is set up by the action of light[74] (see also other work[26,75-81]):



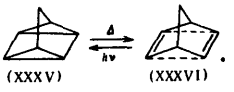
(XXXI) (XXXII)

A conversion of the second kind occurs when 1,2,3,4,9,10--hexahydronaphthalene (XXXIII) is irradiated with ultraviolet light; this compound then isomerises to the tricyclic hydrocarbon (XXXIV). When (XXXIV) is heated to 150°, (XXXIII) is regenerated[77] [see above, conversion (IV) → (III), also Dauben and Fonken[82], and Prinzbach and coworkers[83]]:



(XXXIII) (XXXIV)

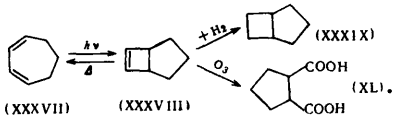
There is great interest[84-87] in the reversible isomerisation of quadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]heptane (XXXV) to norbornadiene (XXXVI):



(XXXV) (XXXVI)

The existence of interaction between the 2 and 6, and between the 3 and 5 carbon atoms of the excited norbornadiene molecule facilitates this reaction[88].

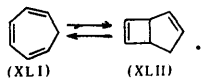
On ultraviolet irradiation, cyclopenta-1,3-diene (XXXVII) is converted into bicyclo[3,2,0]hept-6-ene (XXXVIII), the structure of which has been proved in an exhaustive manner (see scheme). When the photoisomer (XXXVIII) is heated to 400°, the reversible conversion (XXXVIII) → (XXXVII) occurs[89]:



(XXXVII) (XXXVIII) (XXXIX) (XL).

Some derivatives of cycloheptadiene undergo an analogous reversible photoisomerisation[90-93].

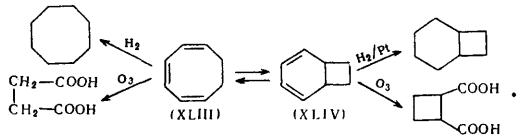
Under the action of light, cycloheptatriene, or tropilidene (XLI), isomerises to bicyclo[3,2,0-[hepta-2,6--diene (XLII);[89] tropilidine derivatives behave in the same way[30,94-96]. At high temperature, the bicyclic isomer (XLII) is converted into tropilidene:



(XLI) (XLII)

A great many cyclic polyenes undergo the so-called intracyclic diene synthesis, in which one double bond plays the part of a dienophile, and the other that of a conjugated diene system[97]. In turn, the bicyclic "adducts" obtained by this reaction can undergo retrodiene decomposition to give the starting compound; it not infrequently happens that both these reactions of cyclic polyenes occur under the same conditions, and as a result two valence-isomeric compounds are found to be in a state of tautomeric equilibrium.

The most striking example of valence tautomerism is intracyclic diene synthesis and decomposition is the equilibrium between bicyclo[4,2,0]octa-2,4-diene (XLIV) and cyclo-octa-1,3,5-triene (XLIII), which is established at 100°.[97-101] The equilibrium position corresponds to a concentration of 15% of the bicyclic and 85% of the monocyclic tautomer. Both tautomers can be obtained in the pure state, and their structures have been proved conclusively (see scheme); when heated to 100° each of the tautomers gives the same mixture, (XLIII) + (XLIV):



(XLIII) (XLIV)

The activation energy for this conversion is 27.1 kcal × × mole^{-1}.[102]

The cyclo-octatetraene (XLV)–bicyclo[4,2,0]octatriene (XLVI) system is an example of widely displaced equilibrium:

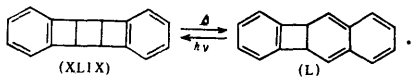
(XLV) (XLVI) (XLVII) (XLVIII).

It has long been known that cyclo-octatetraene reacts in two ways[103-109]. Thus, hydrogenation of (XLV) gives cyclo-octane, but halogenation and diene synthesis give the derivatives (XLVII) and (XLVIII) respectively, the formation of which would be expected on the basis of the tautomeric bicyclo-octatriene (XLVI). However, up to recently no reliable proofs that this tautomer really existed could be adduced. In 1964, the kinetics of the diene synthesis of cyclo-octatetraene with a number of dienophiles of different activity was studied[110]. The results showed that valence tautomerism does in fact exist between cyclo-octatetraene and bicyclo-octatriene, but the concentration of the bicyclic form is only about 0.01%. Nevertheless it is this form that determines the course of the diene-synthesis reaction.

Later, Vogel and coworkers succeeded in obtaining bicyclo-[4,2,0]octatriene (XLVI) in the pure state[111] by elimination of bromine from the dibromide (XLVII) at -78° with the aid

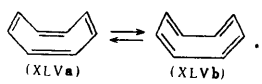
of the disodium derivative of phenanthrene. The structure of the hydrocarbon (XLVI) obtained in this way was confirmed by a number of chemical and spectroscopic data. At room temperature this hydrocarbon spontaneously isomerises to (XLV); the activation energy of the isomerisation is 18.7 kcal mole^{-1}.

Derivatives of bicyclo[4,2,0]octatriene that are stable at room temperature are known [112,113]. On irradiation, some of them undergo valence isomerisation to the corresponding tricyclo[4,2,0,$0^{2,5}$]octadiene (XLIX) derivatives, for example [103]:



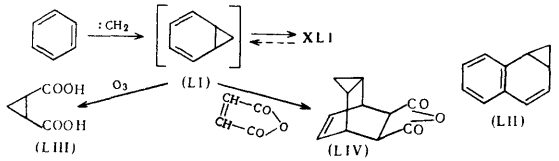
See also Wittig and Weinlich [112], Criegee and coworkers [113], and Keller and coworkers [114]. When (XLIX) is heated to 200°, (L) is regenerated.

The results of a recent study of the temperature dependence of the NMR spectrum of cyclo-octatetraene led Anet and coworkers to the conclusion that there is a rapid displacement of single and double bonds within the cyclo-octatetraene ring [115]:



The conversion (XLVa) ⇌ (XLVb) does not lead to the formation of a new compound; it is an example of what is termed degenerate valence tautomerism. It is doubtful if degenerate valence tautomerism could be recognised by a chemical method, but it nevertheless has a real existence. Other examples of this kind of tautomerism will be given below. The activation energy of the conversion is 12 kcal × × mole^{-1}.

The problem of the existence of valence tautomerism in the tropilidene (XLI)–norcaradiene (LI) system has still not been solved [116,117]. Unsubstituted norcaradiene should be formed by the action of methylene on benzene, in the same way as benzonorcaradiene (LII) is obtained in the analogous reaction with naphthalene [118]:

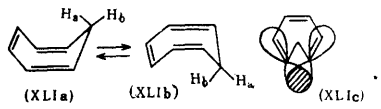


However, when diazomethane was decomposed in benzene, tropilidene was obtained instead of norcaradiene [119]. This may be explained by the isomerisation of norcaradiene to tropilidene immediately it is formed.

It was further noted that tropilidene has some anomalous properties: in oxidations it gives the compound (LIII), and in the diene-synthesis it gives the compound (LIV), both of which contain the three-membered ring [120-123]. Two possible explanations of the results of these reactions have been put forward [120]: either the reagent causes isomerisation of tropilidene to norcaradiene, which then reacts in the normal way, or even in the absence of the reagent the initial tropilidene contains norcaradiene as impurity, with which it is in a state of valence tautomerism. Up to now the presence of norcaradiene has not been detected in the reactions enumerated above, nor could it be shown that it is formed as an intermediate.

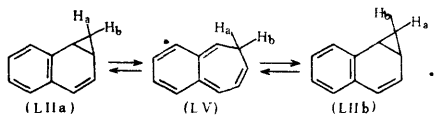
Spectroscopic data [123-128] indicate that if the equilibrium of the two forms actually exists, it must be almost wholly displaced in the direction of tropilidene; in any case, the concentration of the bicyclic tautomer does not exceed 0.01%. The preponderance of tropilidene can easily be accounted for: approximate calculations show that this hydrocarbon must be more stable than norcaradiene by 12 kcal mole^{-1}.[129]

A study of the NMR spectrum of tropilidene at different temperatures [125,126,130], and X-ray studies of (XLI) and some of its crystalline derivatives [131,132] have shown that this hydrocarbon has a non-planar molecule in the form of a tub, with alternate single and double bonds. Even at room temperature tropilidene undergoes ring inversion (XLIa) ⇌ ⇌ (XLIb).



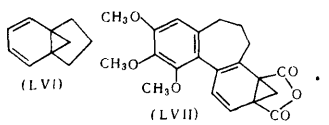
The shape of the ring in this compound is such that the π-electrons of the carbon atoms at positions 1 and 6 partly overlap under the "tub", giving rise to an unusual π-bond (XLIc). [132] The existence of such a bond might explain the dual reactivity of tropilidene (reactions with transfer of reaction centre); however, the existence of valence tautomerism between the quasiaromatic compound (XLI) and norcaradiene is considered to be possible in principle [133]. It is clear that the detection of the bicyclic tautomer when it is present in insignificant concentration is no easy task.

Under ordinary conditions, the benzonorcaradiene (LII) mentioned above is stable. This appears to be due to the high energy content of the valence-isomeric benzocycloheptatriene (LV), resulting from the formation of an *ortho*-quinoid structure [134]:



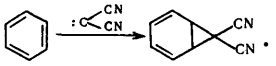
Nevertheless, at temperatures of the order 150–180° a change of position is noted in the signals of the methylene-group protons in the NMR spectrum of benzonorcaradiene. According to Vogel and coworkers [135,136], this indicates that at high temperature a state of equilibrium is set up between the *exo*- and *endo*-forms of benzonorcaradiene, (LIIa) and (LIIb), the compound (LV) being formed as an intermediate [135,136]. The activation energy for the conversion of (LII) into (LV) was calculated from the temperature dependence of the chemical shifts of H_a and H_b; the value found was 19.4 kcal mole^{-1}.

Norcaradiene derivatives fully resistant to isomerisation into the corresponding tropilidene derivatives may be obtained by linking the 1- and 6-carbon atoms of norcaradiene by a three-atom bridge, as in (LVI) [15] or (LVII) [137] (compare Knox and coworkers [138]):



Recently it was found that the introduction of two nitrile groups at the seventh carbon atom of norcaradiene also makes

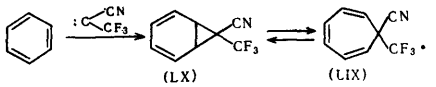
this system stable [139]. The synthesis of 7,7-dicyanonorcaradiene (LVIII) is shown by the following scheme:



(LVIII)

The structure of (LVIII) has been proved by ultraviolet and NMR spectra and by chemical methods.

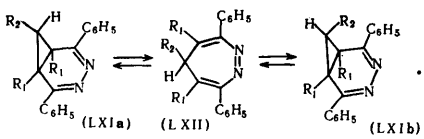
In contrast to (LVIII), 7-cyano-7-trifluoromethylcycloheptatriene (LIX), which is obtained by reaction of the corresponding carbene with benzene, is in equilibrium at room temperature with 7,7-disubstituted norcaradiene (LX): [140]



(LX) (LIX)

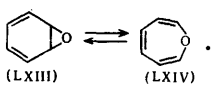
The preparation of stable derivatives of norcaradiene, and the existence of valence tautomerism between (LII) and (LV), and between (LIX) and (LX), definitely confirm the hypothesis of valence tautomerism in the norcaradiene–tropilidene system.

In 1963, Maier prepared nitrogen-containing analogues of norcaradiene (LXI) [141] and was subsequently [142,143] able to show the existence of a tautomeric equilibrium between (LXI) (R_1 = H, R_2 = CH_3) and the monocyclic form (LXII). The concentration of the latter, however, is so low that the compound (LXII) cannot be detected by chemical or by spectroscopic methods. The existence of equilibrium in the system (LXI) $\rightleftharpoons$ (LXII) can only be deduced on the basis of *exo/endo*-transfer of the 7-methyl group in the system (LXIa) $\rightleftharpoons$ (LXIb), which has been demonstrated by means of NMR spectroscopy:



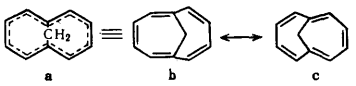
(LXIa) (LXII) (LXIb)

Valence tautomerism, analogous to the conversion (LXI) $\rightleftharpoons$ (LXII) has also been described in a number of three-membered heterocycles [144,145]. The position of the NMR signals and the ultraviolet absorption spectrum of benzene oxide (LXIII) [1a,5a-dihydrobenzoxiran] suggest that this compound is in a state of mobile equilibrium with oxepin (LXIV) (compare Vogel and coworkers [146]):



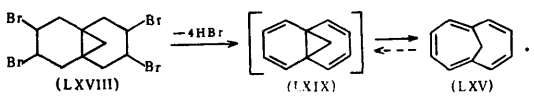
(LXIII) (LXIV)

Vogel and Roth [147] (see also Vogel and coworkers [146]) utilised the ability of norcaradiene to undergo spontaneous valence isomerisation with opening of the three-membered ring in the synthesis of 1,6-methanocyclodecapentaene§ (LXV). This hydrocarbon is of interest because it contains 10 π-electrons and according to Hückel's rule should be aromatic in character¶. In this case its structure would be represented by formula (LXVa) with delocalised double bonds, or, in terms of resonance theory, by the superposition of the two structures (LXVb) and (LXVc):



a b c (LXV).

The synthesis of (LXV) is effected according to the following scheme:



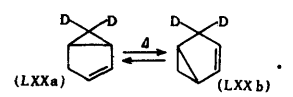
(LXVIII) (LXIX) (LXV)

When alkali acts on the tetrabromo-compound (LXVIII), 9,10-dihydro-9,10-methanonaphthalene (LXIX) should be obtained. However, this hydrocarbon contains the unstable norcaradiene grouping and might be expected to isomerise to (LXV) immediately it is formed. Moreover, the possibility of the formation of an equilibrium mixture of both compounds must be considered.

The ultraviolet and NMR spectra of the reaction product provide evidence against the structure (LXIX). The presence of a ring current in the molecule [147] and the chemical properties of the reaction product, for example, its tendency to undergo substitution reactions [151], are some indications of its aromatic character. However, the possibility of valence tautomerism between (LXIX) and (LXV) cannot be entirely ruled out.

The tendency of norcaradiene and related structures to isomerise to tropilidene and its derivatives is due to strain on the three-membered ring [2,3]: the energy for the breaking of the C–C bond of cyclopropane is less by 19 kcal mole^{-1} than the energy required to break the single bond in ethanol (81 kcal mole^{-1}). A further reduction in the C_1–C_6 bond energy in norcaradiene in comparison with saturated hydrocarbons occurs, because after this bond has been broken, two allyl radicals, capable of conjugation and therefore relatively stable, are formed. This reduces the C_1–C_6 bond energy by a further 2.22 kcal mole^{-1} (where 22 kcal mole^{-1} is the stabilisation energy of one allyl radical). As a result, the activation energy for the isomerisation of norcaradiene to tropilidene is only ~20 kcal mole^{-1}. [3,135]

Because of the favourable occurrence of a three-membered ring in conjunction with a double bond, valence isomerisation of compounds containing the vinylcyclopropane grouping is found to be very common [31,76,83,152–155]. An interesting example of this kind is the conversion of 6,6-dideuterobicyclo[4,1,0]hex-2-ene (LXXa) into 2,2-dideuterobicyclo-[4,1,0]hex-3-ene (LXXb) by heating to 225°. [3] It may be noted that this conversion only occurs because one of the carbon atoms of the initial molecule is labelled with deuterium; the isomerisation is degenerate. The NMR spectrum may be used to distinguish the initial molecule (LXXa) from the mixture of valence isomers (LXXa) and (LXXb) obtained after heating:

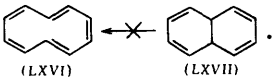


(LXXa) (LXXb)

Compounds containing two double bonds and a three-membered ring undergo valence isomerisation still more easily [118,156–165], as shown, for example, by the isomerisation of 1,2-divinylcyclopropane (LXXI) to cyclohepta-1,4-diene (LXXII); [3,33] the *cis*-isomer of this hydrocarbon is

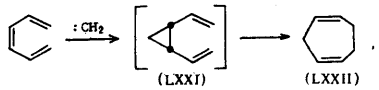
§ Bicyclo[4,4,1]undeca-1,3,5,7,9-pentene (Ed. of Translation).

¶ Attempts to prepare unsubstituted cyclodecapentaene (LXVI) by valence isomerisation of 9,10-dehydronaphthalene (LXVII) were not successful [148–150]:



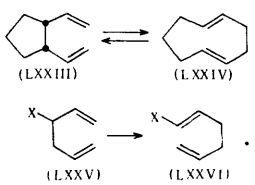
(LXVI) (LXVII)

converted into (LXXII) immediately it is formed from hexatriene and methylene at -40°:



In most instances the conversion turns out to be irreversible, because of the great difference in free energy between the initial and final compounds. This difference is less for divinylcyclobutane than for divinylcyclopropane [33], but the free energy of divinylcyclopentane (LXXIII) is found to be even somewhat less than that of the valence-isomeric cyclononadiene (LXXIV). Vogel and coworkers found that at 200° (LXXIII) and (LXXIV) are in a state of dynamic equilibrium [191]. The equilibrium position corresponds to a concentration of 95% of divinylcyclopentadiene and 5% of cyclononadiene.

The valence isomerisation of divinylcycloalkanes is a special case of the well-studied thermal isomerisation of 1,5-dienes called the Cope rearrangement [166,167] (LXXV)–(LXXVI):

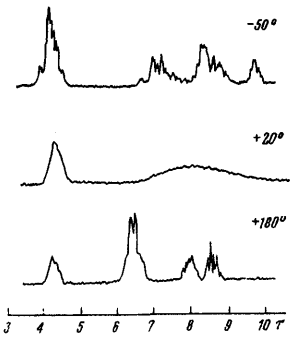


It is known that neither ionic nor radical intermediates are formed in the course of this reaction [2,3]: the reaction is effected via a cyclic transition state in which old bonds are broken and new bonds are simultaneously formed. Atoms or atomic groups do not migrate during the reaction; the Cope rearrangement is a typical example of valence conversion. However, in accordance with the definitions of rearrangement and isomerisation (see p. 560), these reactions should not be called rearrangements but isomerisations. The Cope isomerisation has been the subject of several reviews [2-4,33,168]; for this reason, we shall confine ourselves to a reference to some new examples of valence conversions of this type [52,53,169-179].

The valence tautomerism of homotropilidene, or bicyclo[5,1,0]octa-2,5-diene (LXXVII), and of other compounds containing the homotropilidene grouping occupies a special position among valence isomerisations. A special feature of these conversions is that they are degenerate (the initial and final stages of the conversion are indistinguishable) and that they occur very rapidly. It is concluded that tautomerism actually occurs, because the NMR spectra of homotropilidene and its derivatives undergo reversible changes with change of temperature, while the infrared spectra remain unchanged.

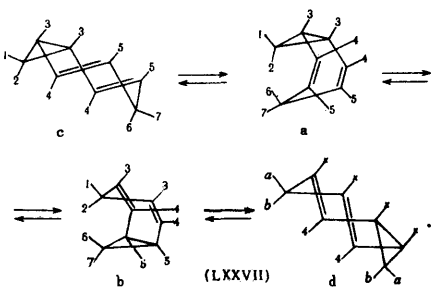
At -50° the NMR spectrum of homotropilidene [3,168,180] shows signals corresponding in position and intensity to the seven types of protons in homotropilidene (see Figure); at this temperature the rate of valence tautomerism of homotropilidene is relatively low.

When the temperature is increased, the conversion (LXXVIIa) ⇌ (LXXVIIb) is accelerated. Tautomerism leads to an exchange of the positions of protons, H_1 with H_7, H_2 with H_6, and H_3 with H_5. With very rapid mutual transfers (+180°), the half-life of each tautomer does not exceed 0.004 s; the H_1 and H_7 protons become indistinguishable in the NMR spectrum and give only one signal of type $2H_a$. Similarly,



NMR spectrum of homotropilidene.

H_2 and H_6 form one signal $2H_b$. Rapid mutual conversions of $2H_3$ and $2H_5$ lead to one new $4H_x$ signal. Only the $2H_4$ signal retains its position corresponding to two vinyl protons. Thus, from the point of view of NMR spectroscopy, the fairly rapid valence tautomerism of homotropilidene leads from a compound with seven types of protons to a compound with four types.



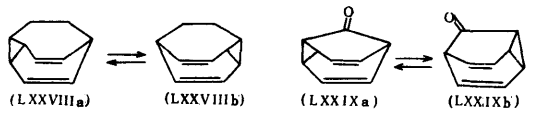
Because of the existence of rapid degenerate valence tautomerism, a single formula does not represent the structure of homotropilidene over a long time interval. Homotropilidene belongs to a group of compounds with what is termed a fluctuating structure [180].

Quite a number of compounds with fluctuating structures are now known; these include: tricyclo[3,3,2,$0^{4,6}$]deca-2,7-diene (LXXVIII), [181] tricyclo[3,3,1,$0^{2,8}$]nona-3,6-dien-9-one or barbaralone (LXXIX), [182] tricyclo[3,3,2,$0^{1,8}$]deca-2,5,9-triene or bullvalene (LXXX), [181,183-185] and also some derivatives of these [186-191].

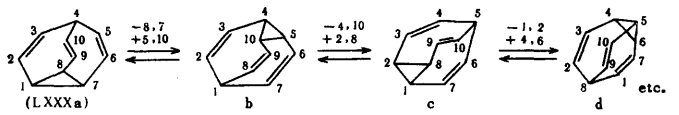
Homotropilidene exists in two forms, the cisoid (LXXXVIIa) and the transoid (LXXVIIc), and only the cisoid form undergoes isomerisation [180], but with barbaralone and bullvalene the unsuitable transoid conformation of the molecule is excluded, and valence isomerisation may be expected to occur still more readily. The question than arises whether a limit has been reached at which two separate classical structural formulae cease to correspond to two separate potential energy minima (each with its own set of vibrational levels) and are converted into two limiting structures representing the same compound. Here the concept of tautomerism would have to be equated with the concept of mesomerism.

A study of the NMR spectrum of barbaralone has shown that at -60° this ketone exists in the form of two tautomers. At higher temperatures, the spectrum shows some intermediate proton positions, which are occupied during the

rapid transformation from one tautomer to the other. The activation energy of the valence-tautomeric conversion of barbaralone is only 8.1 kcal mole^{-1}.



As would be expected, bullvalene (LXXX), which was predicted in 1962 by Doering [168] and synthesised in 1963 by Schröder [183,184], has only one signal in its NMR spectrum at 100°. This means that, at this temperature, because of very rapid valence-tautomeric conversions, all the protons, and therefore all the carbon atoms, of the molecule become, as it were, equivalent. It can be shown by means of successive Cope isomerisations, associated with the rupture of any of the three C–C bonds of the three-membered ring (the molecule has a threefold axis of symmetry), that each carbon atom can occupy the position of any other atom, for example:



It has been calculated that there are more than a million different mutual arrangements of the carbon atoms in bullvalene, and all these combinations (permutations [186]) occur in the molecule over a short time interval, comparable with the relaxation period of the nuclear spins of the protons linked with these carbon atoms. Thus, the carbon atoms of bullvalene are not in "fixed" positions but move at relatively high speed over the "surface" of the molecule [168]. These displacements of atoms do not, however, lead to a change in the structure of the compound.

It should be noted that the high rate of bullvalene valence-tautomeric conversions must, however, not be regarded as evidence that all the 1 209 600 tautomers that undergo mutual conversion can be obtained one from the other at the same rate, since the conversion of one into another occurs in many stages — for example, (LXXXa) into (LXXXd). [186]

The question whether bullvalene is an equilibrium mixture of a tremendous number of valence isomers undergoing rapid conversion or an individual compound which is a resonance hybrid of a number of electronic structures has been decided with the aid of the theory of groups: ten points cannot be arranged on the surface of a sphere in such a way that a geometrical figure completely symmetrical in three dimensions is obtained. It is quite clear that only with such a construction would bullvalene have ten really equivalent carbon atoms. Since this construction is impossible, it follows that even at high temperature bullvalene is a mixture of 1.2 million irregular polyhedra, rapidly being converted into one another. The minimum energy of this system is represented not by one average state but by 1.2 million states identical in energy (degenerate), but separated from one another by an energy barrier (11.8 kcal mole^{-1} [185]). In other words, in bullvalene we also have an instance of valence tautomerism, and not of mesomerism.

The number of examples of reversible valence isomerism has increased to such an extent in recent years that it would be difficult to give all the examples in a single review. However, even the foregoing presentation will be quite sufficient to attract the attention of chemists to this new interesting type of isomerisation†.

1. C.A.Grob and P.Schiess, Angew.Chem., 70, 502 (1958).
2. E.Vogel, Angew.Chem., 74, 829 (1962).
3. W.von E.Doering and W.R.Roth, Angew.Chem., 75, 27 (1963).
4. "Molecular Rearrangements" (Edited by P.De Mayo), Wiley, New York, 1963, Vol.1, Ch.4, p.11.
5. E.E.van Tamelen and S.P.Pappas, J.Amer.Chem.Soc., 85, 3297 (1963).
6. D.Seebach, Angew.Chem., 77, 119 (1965).
7. O.L.Chapman, H.G.Smith, and R.W.King, J.Amer.Chem.Soc., 85, 803 (1963).
8. M.Stiles and U.Burekhardt, J.Amer.Chem.Soc., 86, 3396 (1964).
9. E.H.White and H.C.Dunathan, J.Amer.Chem.Soc., 86, 453 (1964).
10. H.Tanida, J.Hata, I.Matsui, and I.Tanaka, J.Org.Chem., 30, 2259 (1965).
11. K.F.Bangert and V.Boekelheide, J.Amer.Chem.Soc., 86, 905 (1964).
12. G.J.Fonken and W.Moran, Chem.and Ind., 1841 (1963).
13. K.F.Bangert and V.Boekelheide, Chem.and Ind., 1121 (1963).
14. T.J.Katz and P.J.Garratt, J.Amer.Chem.Soc., 86, 5194 (1964).
15. E.Vogel, W.Wiedermann, H.Kiefer, and W.F.Harrison, Tetrahedron Letters, 673 (1963).
16. W.R.Roth and B.Peltzer, Angew.Chem., 76, 378 (1964).
17. J.Zirner and S.Winstein, Proc.Chem.Soc., 235 (1964).
18. O.L.Chapman, G.W.Borden, R.W.King, and B.Winkler, J.Amer.Chem.Soc., 86, 2660 (1964).
19. W.C.Herndon and L.L.Lowry, J.Amer.Chem.Soc., 86, 1922 (1964).
20. H.Prinzbach, W.Eberbach, and G.von Veh, Angew.Chem., 77, 454 (1965).
21. S.F.Chapell III and R.F.Clark, Chem.and Ind., 1198 (1962).
22. J.W.H.Wattney and S.Winstein, J.Amer.Chem.Soc., 85, 3715 (1963).
23. P.J.Kropp, Tetrahedron Letters, 3647 (1964).
24. R.Srinivasan, J.Amer.Chem.Soc., 84, 3432 (1962).
25. S.Masamune and N.T.Castelluci, Angew.Chem., 76, 569 (1964).
26. R.Srinivasan, J.Amer.Chem.Soc., 84, 3982 (1962).
27. L.A.Paquette, J.Amer.Chem.Soc., 86, 500 (1964).
28. H.Prinzbach, W.Eberbach, and G.von Veh, Angew.Chem., Internat.Edn., 4, 436 (1965).
29. O.L.Chapman and E.D.Hoganson, J.Amer.Chem.Soc., 86, 498 (1964).
30. O.A.Neumüller, H.J.Kuhn, G.O.Schenk, and F.Santavy, Annalen, 674, 122 (1964).
31. C.A.Wellington, J.Phys.Chem., 66, 1671 (1962).
32. D.E.Applequist and R.Searle, J.Amer.Chem.Soc., 86, 1389 (1964).
33. E.Vogel, K.-H.Ott, and K.Gajek, Annalen, 644, 172 (1961).
34. R.Criegee, D.Seepach, R.E.Winter, B.Börretzen, and H.-A.Brune, Chem.Ber., 98, 2339 (1965).
35. E.N.Marvell, G.Caple, and B.Schatz, Tetrahedron Letters, 385 (1965).

† In connection with the hundredth anniversary of Kekulé's benzene formula, reviews devoted to several types of reversible valence isomerisation appeared in the International Edition of Angewandte Chemie [192–194].

36. D.S.Glass, J.W.H.Wattney, and S.Winstein, Tetrahedron Letters, 377 (1965).
37. E.Vogel, W.Grimme, and E.Dinne, Tetrahedron Letters, 391 (1965).
38. R.Huisgen and H.Seidel, Tetrahedron Letters, 3381 (1964).
39. H.H.Freedman, G.A.Doorakian, and V.R.Sandel, J.Amer. Chem.Soc., 87, 3019 (1965).
40. C.K.Ingold, in Collected Papers, "Elektronnaya Teoriya v Organicheskoi Khimii" (Electronic Theory in Organic Chemistry) (Edited by V.S.Malinovskii), ONTI, Leningrad, 1936, p.173.
41. A.Kekulé, Annalen, 162, 86 (1872).
42. H.Wieland, Ber., 53, 1318 (1920).
43. H.Wieland, Ber., 55, 1806 (1922).
44. V.V.Razumovskii, "Voprosy Stroeniya i Reaktsionnoi Sposobnosti Organicheskikh Soedinenii" (Problems of the Structure and Reactivity of Organic Compounds), Trudy Leningrad.Elektrotekh.Inst.Svyazi, No.8 (45), Leningrad, 1956, Ch.6.
45. V.V.Razumovskii, Zhur.Obshch.Khim., 34, 1693 (1964).
46. C.K.Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Inostr.Lit., Moscow, 1959.
47. W.Hückel, "Theoretische Grundlagen der organischen Chemie" (Translated into Russian), Inostr.Lit., Moscow, 1955, Vol.1, p.298.
48. D.J.Cram and G.S.Hammond, "Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1964, p.451.
49. C.D.Nenițescu, "Chimie Organică" (Translated into Russian), Inostr.Lit., Moscow, 1962, Vol.1, p.450.
50. O.A.Reutov, "Teoreticheskie Problemy Organicheskoi Khimii" (Theoretical Problems of Organic Chemistry), Izd. Moskov.Gos.Univ., Moscow, 1964, p.538.
51. T.I.Temnikova, "Kurs Teoreticheskikh Osnov Organicheskoi Khimii" (Course on Theoretical Bases of Organic Chemistry), GNTI KhL, Leningrad, 1962, p.496.
52. C.A.Grob and P.W.Schies, Helv.Chim.Acta, 47, 558 (1964).
53. C.A.Grob, H.Link, and P.W.Schiess, Helv.Chim.Acta, 46, 483 (1963).
54. R.Criegee and F.Zanker, Angew.Chem., 76, 716 (1964).
55. E.E.van Tamelen and S.P.Pappas, J.Amer.Chem.Soc., 84, 3789 (1962).
56. W.A.Gibbons and H.Fischer, Tetrahedron Letters, 43 (1964).
57. C.Hoogzand and W.Hübel, Tetrahedron Letters, 637 (1961).
58. K.E.Wilzbach and L.Kaplan, J.Amer.Chem.Soc., 86, 2307 (1964).
59. A.W.Burgstahler and Ping Lu Chien, J.Amer.Chem.Soc., 86, 2940 (1964).
60. L.Kaplan, K.E.Wilzbach, W.C.Brown, and Shii Shu Yang, J.Amer.Chem.Soc., 87, 675 (1965).
61. A.W.Burgstahler, Ping Lu Chien, and M.O.Abdel-Rahman, J.Amer.Chem.Soc., 86, 5281 (1964).
62. E.M.Arnett and J.M.Bollinger, Tetrahedron Letters, 3803 (1964).
63. E.C.Taylor, W.Pandler, and J.Kuntz, J.Amer.Chem.Soc., 83, 2967 (1961).
64. E.J.Corey and J.Streith, J.Amer.Chem.Soc., 86, 950 (1964).
65. E.F.Ullman, J.Amer.Chem.Soc., 85, 3529 (1963).
66. E.F.Ullman and J.E.Milks, J.Amer.Chem.Soc., 84, 1315 (1962).
67. E.F.Ullman and W.A.Henderson, Jnr., J.Amer.Chem.Soc., 86, 5050 (1964).
68. J.M.Dunston and P.Yates, Tetrahedron Letters, 505 (1964).
69. J.J.Delpuech, Bull.Soc.chim.France, 2697 (1964).
70. P.Diehl, H.A.Christ, and F.B.Mallory, Helv.Chim.Acta, 45, 504 (1962).
71. G.Englert, Z.Elektrochem., 65, 854 (1961).
72. S.Sarel and J.Rivlin, Tetrahedron Letters, 821 (1965).
73. P.de Mayo, in "Advances in Organic Chemistry, Vol.II" (Edited by R.A.Raphael, E.C.Taylor, and H.Wynberg) (Translated into Russian), Izd.Mir, 1964, p.368.
74. W.G.Dauben and R.M.Coates, J.Org.Chem., 29, 2761 (1964).
75. W.G.Dauben and R.M.Coates, J.Amer.Chem.Soc., 86, 2490 (1964).
76. H.Prinzbach and H.Hagemann, Angew.Chem., 76, 600 (1964).
77. G.J.Fonken and K.Mehratra, Chem.and Ind., 1025 (1964).
78. G.J.Fonken, Tetrahedron Letters, 549 (1962).
79. E.Vogel, Angew.Chem., Internat.Edn., 2, 1 (1963).
80. K.E.Lewis and H.Steiner, J.Chem.Soc., 3080 (1964).
81. R.L.Autrey, D.H.R.Barton, and W.H.Reusch, Proc. Chem.Soc., 55 (1959).
82. W.G.Dauben and G.J.Fonken, J.Amer.Chem.Soc., 81, 4060 (1959).
83. H.Prinzbach, H.Hagemann, J.H.Hartenstein, and P.Kitzing, Chem.Ber., 98, 2201 (1965).
84. G.S.Hammond, N.J.Turro, and A.Fischer, J.Amer.Chem. Soc., 83, 4674 (1961).
85. G.S.Hammond, P.Wyatt, C.D.DeBoer, and N.J.Turro, J.Amer.Chem.Soc., 86, 2532 (1964).
86. W.G.Dauben and R.L.Cargill, Tetrahedron, 15, 197 (1961).
87. H.M.Frey, J.Chem.Soc., 365 (1964).
88. C.F.Wilkox, S.Winstein, and W.G.McMillan, J.Amer. Chem.Soc., 82, 5450 (1960).
89. W.G.Dauben and R.L.Cargill, Tetrahedron, 12, 186 (1961).
90. G.Büchi and E.M.Burgess, J.Amer.Chem.Soc., 82, 4333 (1960).
91. O.L.Chapman, D.J.Pasto, G.W.Borden, and A.A.Grinwald, J.Amer.Chem.Soc., 84, 1220 (1962).
92. O.L.Chapman and D.J.Pasto, Chem.and Ind., 53 (1961).
93. D.I.Schuster, M.J.Nash, and M.L.Kantor, Tetrahedron Letters, 1375 (1964).
94. R.Gruve and W.Wulf, Chem.Ber., 84, 621 (1951).
95. E.J.Forbes, J.Chem.Soc., 3865 (1955).
96. O.L.Chapman and G.W.Borden, Proc.Chem.Soc., 221 (1963).
97. K.Alder and H.A.Dortman, Chem.Ber., 87, 1492 (1954).
98. A.C.Cope, A.C.Haven, F.L.Ramp, and E.R.Trumbull, J.Amer.Chem.Soc., 74, 4867 (1952).
99. E.Vogel, O.Roos, and K.-H.Disch, Angew.Chem., 73, 342 (1961).
100. E.Vogel, O.Roos, and K.-H.Disch, Annalen, 653, 55 (1962).
101. W.Ziegenbein, Angew.Chem., 77, 42 (1965).
102. R.Huisgen, F.Mietsch, and G.Boche, Angew.Chem., 77, 353 (1965).
103. M.Avram, I.G.Dumlescu, D.Dinn, G.Matescu, and C.D.Nenitzescu, Tetrahedron, 19, 309 (1963).
104. W.Reppe, O.Schichting, K.Klager, and T.Toepel, Annalen, 560, 1 (1948).
105. S.L.Friess and V.Boekelheide, J.Amer.Chem.Soc., 71, 4145 (1949).
106. E.H.White and R.L.Stern, Tetrahedron Letters, 193 (1964).
107. K.Ziegler and H.Wilms, Annalen, 567, 1 (1950).
108. M.Avram, G.Matescu, and C.D.Nenitzescu, Annalen, 636, 174 (1961).
109. R.A.Raphael, in "Non-Benzenoid Aromatic Compounds" (Edited by D.Ginsburg) (Translated into Russian), Inostr. Lit., Moscow, 1963, Ch.8.
110. R.Huisgen and F.Mietzch, Angew.Chem., 76, 36 (1964).
111. E.Vogel, H.Kiefer, and W.R.Roth, Angew.Chem., 76, 432 (1964).
112. G.Wittig and J.Weinlich, Chem.Ber., 98, 471 (1965).
113. R.Criegee, W.-D.Wirth, W.Engel, and H.A.Brune, Chem. Ber., 96, 2230 (1963).

114. C. E. Keller, G. F. Emerson, and R. Pettit, J. Amer. Chem. Soc., 87, 1388 (1965).
115. F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, J. Amer. Chem. Soc., 86, 3576 (1964); see also D. E. Gwynn, G. M. Whitesides, and J. D. Roberts, *ibid.*, 87, 2862 (1965).
116. R. Darms, Dissertation, Zurich, 1963.
117. W. Wiedermann, Dissertation, Cologne, 1963.
118. W. von E. Doering and M. J. Goldstein, Tetrahedron, 5, 53 (1959).
119. W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 73, 828 (1951).
120. K. Alder and G. Jacobs, Chem. Ber., 86, 1528 (1953).
121. G. Juppe and A. P. Wolf, J. Amer. Chem. Soc., 83, 337 (1961).
122. E. J. Corey and H. J. Burke, J. Amer. Chem. Soc., 76, 5257 (1954).
123. E. J. Corey, H. J. Burke, and W. A. Remers, J. Amer. Chem. Soc., 78, 180 (1956).
124. E. J. Corey, H. J. Burke, and W. A. Remers, J. Amer. Chem. Soc., 77, 4941 (1955).
125. C. LaLau, Spectrochim. Acta, 19, 1559 (1963).
126. F. A. L. Anet, J. Amer. Chem. Soc., 86, 458 (1964).
127. F. R. Jensen and L. A. Smith, J. Amer. Chem. Soc., 86, 956 (1964).
128. M. V. Evans and R. C. Lord, J. Amer. Chem. Soc., 82, 1876 (1960).
129. K. N. Klump and J. P. Chezick, J. Amer. Chem. Soc., 85, 130 (1963).
130. M. Traetteberg, J. Amer. Chem. Soc., 86, 4265 (1964).
131. J. D. Dunitz and P. Pauling, Helv. Chim. Acta, 43, 2188 (1960).
132. R. E. Davis and A. Tulinsky, Tetrahedron Letters, 839 (1962).
133. K. Conrow, M. E. H. Howden, and D. Davis, J. Amer. Chem. Soc., 85, 1929 (1963).
134. R. Huisgen and G. Juppe, Chem. Ber., 94, 2332 (1961).
135. E. Vogel, D. Wendisch, and W. R. Roth, Angew. Chem., 76, 432 (1964).
136. E. Vogel, D. Wendisch, and W. R. Roth, Angew. Chem., Internat. Edn., 3, 443 (1964).
137. J. Schreiber, W. Leimgruber, M. Pesaro, P. Schudel, T. Threlfall, and A. Eshenmoser, Helv. Chim. Acta, 44, 540 (1961).
138. L. H. Knox, E. Velarde, and A. D. Cross, J. Amer. Chem. Soc., 85, 2533 (1963).
139. E. Ciganek, J. Amer. Chem. Soc., 87, 652 (1965).
140. E. Ciganek, J. Amer. Chem. Soc., 87, 1149 (1965).
141. G. Maier, Angew. Chem., 75, 920 (1963).
142. G. Maier, Chem. Ber., 98, 2438 (1965).
143. G. Maier, Chem. Ber., 98, 2446 (1965).
144. E. Vogel and W. A. Boell, Tetrahedron Letters, 609 (1965).
145. E. Vogel, R. Schubart, and W. A. Boell, Angew. Chem., 76, 535 (1964).
146. E. Vogel, M. Biskup, W. W. Pretzer, and W. A. Boell, Angew. Chem., 76, 785 (1964).
147. E. Vogel and H. D. Roth, Angew. Chem., 76, 145 (1964).
148. J. J. Bloomfield and W. T. Quinlin, J. Amer. Chem. Soc., 86, 2738 (1964).
149. E. E. van Tamelen and B. Pappas, J. Amer. Chem. Soc., 85, 3296 (1963).
150. E. Vogel, W. Meckel, and W. Grimmé, Angew. Chem., 76, 786 (1964).
151. E. Vogel and W. A. Boell, Angew. Chem., 76, 784 (1964).
152. W. von E. Doering and J. B. Lambert, Tetrahedron, 19, 1989 (1963).
153. C. G. Overberger and A. E. Borchert, J. Amer. Chem. Soc., 82, 1007 (1960).
154. H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, Angew. Chem., 76, 922 (1964).
155. J. R. Ellis and H. M. Frey, Proc. Chem. Soc., 221 (1964).
156. E. L. Stogryn and S. J. Brois, J. Org. Chem., 30, 88 (1965).
157. R. A. Braun, J. Org. Chem., 28, 1383 (1963).
158. J. Meinwald and C. Wahl, Jnr., Chem. and Ind., 425 (1965).
159. P. K. Freeman and D. G. Kuper, Chem. and Ind., 424 (1965).
160. E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, Annalen, 682, 1 (1965).
161. R. Erb, Dissertation, Cologne, 1963.
162. H. A. Staab and F. Vögtle, Chem. Ber., 98, 2701 (1965).
163. C. Cupas, W. E. Watts, and P. von R. Schleyer, Tetrahedron Letters, 36, 2503 (1964).
164. E. Vogel and R. Erb, Angew. Chem., 74, 76 (1962).
165. E. L. Stogryn, M. H. Gianni, and A. J. Passanante, J. Org. Chem., 29, 1275 (1964).
166. A. C. Cope and E. M. Hardy, J. Amer. Chem. Soc., 62, 441 (1940).
167. G. R. Aldridge and G. W. Murphy, J. Amer. Chem. Soc., 73, 1158 (1951).
168. V. Döring, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 308 (1962).
169. J. A. Berson and M. Jones, Jnr., J. Amer. Chem. Soc., 86, 5017 (1964).
170. J. A. Berson and J. J. Gajewski, J. Amer. Chem. Soc., 86, 5019 (1964).
171. G. Wilke, Angew. Chem., 75, 10 (1963).
172. H. Minato and K. Takeda, Angew. Chem., 76, 789 (1964).
173. P. Heimbach, Angew. Chem., 76, 859 (1964).
174. W. von E. Doering and W. R. Roth, Tetrahedron, 18, 67 (1962).
175. C. Walling and M. Naiman, J. Amer. Chem. Soc., 84, 2628 (1962).
176. H.-R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux, and V. Boekelheide, J. Amer. Chem. Soc., 87, 130 (1965).
177. G. S. Hammond and C. D. DeBoer, J. Amer. Chem. Soc., 86, 899 (1964).
178. D. J. Trecker and J. P. Henry, J. Amer. Chem. Soc., 86, 902 (1964).
179. W. R. Roth, Annalen, 671, 10 (1964).
180. W. von E. Doering and W. R. Roth, Tetrahedron, 19, 715 (1963).
181. R. Merényi, J. F. M. Oth, and G. Schröder, Chem. Ber., 97, 3150 (1964).
182. J. B. Lambert, Tetrahedron Letters, 1901 (1963).
183. G. Schröder, Angew. Chem., 75, 722 (1963).
184. G. Schröder, Chem. Ber., 97, 3140 (1964).
185. M. Saunders, Tetrahedron Letters, 1699 (1963).
186. G. Schröder, Chem. Ber., 97, 3131 (1964).
187. J. F. M. Oth, R. Merényi, J. Nielsen, and G. Schröder, Chem. Ber., 98, 3385 (1965).
188. G. Schröder, R. Merényi, and J. F. M. Oth, Angew. Chem., 76, 607 (1964).
189. G. N. Schranzer, P. Gockner, and R. Merényi, Angew. Chem., 76, 498 (1964).
190. G. Schröder, Angew. Chem., 77, 682 (1965).
191. E. Vogel, W. Grimme, and E. Dinné, Angew. Chem., 75, 1103 (1963).
192. E. E. van Tamelen, Angew. Chem., Internat. Edn., 4, 738 (1965).
193. G. Schröder, J. F. M. Oth, and R. Merényi, Angew. Chem., Internat. Edn., 4, 752 (1965).
194. H. G. Viehe, Angew. Chem., Internat. Edn., 4, 746 (1965).

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