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DELOCALIZATION RESONANCE ENERGY OF THE ALLYLIC RADICAL FROM THE GEOMETRICAL ISOMERIZATION OF HEXA-1,3,5-TRIENES[a]

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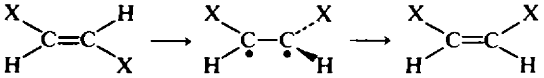
Abstract—Thermal *cis, trans* geometrical isomerization theoretically involves a 90° twisted, singlet diradical-like transition state which may serve as a base for the examination of structural perturbations. Although thermal rearrangement of hexa-1, *trans*-3,5-triene (and all-*trans* octa-2,4,6-triene) to the *cis* isomer cannot be followed directly owing to subsequent cyclization and 1,5 hydrogen shifts, activation parameters for disappearance have been determined. Experimental complications and mechanistic uncertainties which make interpretation difficult are removed in the bicyclic hexatriene, cyclopentenylidenecyclopentene. These geometrical isomers undergo uncomplicated thermal *cis, trans* isomerization in vessels of lead-potash glass: $\log k_1 = 12{\cdot}03 \pm 0{\cdot}32 - 41{\cdot}7 \pm 0{\cdot}8/(0{\cdot}004575T_{abs})$. Extraction of a value for allylic delocalization energy from the behavior of hexa-1, *trans*-3,5-triene [$\log k_1 = 12{\cdot}91 \pm 0{\cdot}47 - 44{\cdot}3 \pm 1{\cdot}2/(0{\cdot}004575\ T_{abs})$] requires corrections of the Dewar-Schmeising type for changes in hybridization of the σ bonds. Depending on whether ethylene or *trans*-butene is taken as standard, values of 12·2 and 13·1 kcal/mol are obtained (estimated uncertainty ± 2 kcal/mol).

Allylic resonance has been the subject of many investigations but continues to remain, at least in respect of its quantitative definition, the subject of dispute. In this paper the results of yet another attack on the problem are reported.

Just as the thermolysis of the carbon-carbon, sp^3-sp^3, bond has been studied to reveal the effect of changes in structure on the energies of bond dissociation and the resultant free radical, so the thermal interconversion of *cis* and *trans* geometrical isomers should also lend itself to an evaluation of the quantitative effect of structural replacement on the energy of the free radical. In rigorous terms, values derived by the two methods should not be identical and should be strictly applicable only to reactions which bear some resemblance to the model reactions.

$$CH_2X{-}CH_2X \longrightarrow \cdot CH_2X + \cdot CH_2X$$



The extraordinary richness in chemistry of systems in which X is the carbon-carbon double bond has provided the general stimulus for the broad interest in the value of the basic constant of interaction, the energy of allylic delocalization.

Experimental evaluation of the delocalization energy in the allylic radical appears to be basic not only to the assessment of the success of various theoretical approaches, but to the estimation of the activation energies of the many reactions suspected of involving an allylic radical.[1]

The primary intention of this work is an estimation of the delocalization energy of the allylic radical by observation of the effect of two vinyl groups on the energy of activation of the geometric isomerization of ethylene. The thorough studies of Douglas, Rabinovitch and Looney[2] on *trans*-dideuterioethylene, of Cundall and Palmer[3] on *cis*-butene and Flowers and Jonathan[4] on *cis*-dideuteriopropene consistently support the theory of Magee, Shand and Eyring[5] that the transition state can be represented as the singlet state twisted to 90°.[6,7,8] Most recently, theoretical work of Dewar *et al.*[9] confirms the absence of a bowl at the col and approximates in a remarkably successful manner the magnitude of the activation energy. A suggestion of Benson *et al*[10] that the mechanism involve conversion of ground state singlet ethylene to a planar diradical (presumably the first excited singlet state, rejected earlier by Magee *et al*[5]) which then must be rotated 90° at the cost of additional

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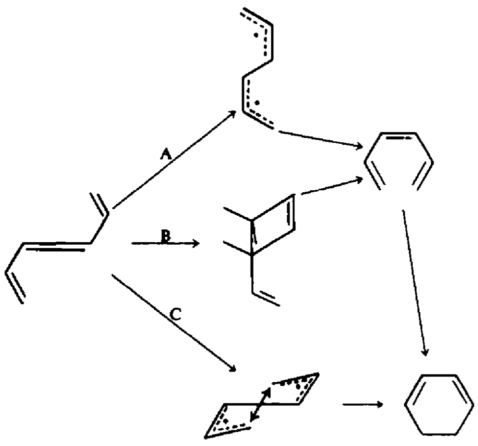
energy is less a mechanism than a model for estimation of the activation energy from thermodynamic quantities. The failure of the model by a few kcal/mol was ascribed to an implausibly high rotational barrier.

The interaction of two olefinic groups with the orthoganol transition state can be taken as a measure of the stabilization in an allylic radical, provided that the transition state be accepted to be a pair of trigonal free radicals at right angles to each other and at their equilibrium distance. Conversely, the interaction can be compared with twice the interaction of an olefin group with a free radical and used to estimate the magnitude of the perturbation between two radicals so close together in the orthogonal relationship.

In either event, it must be established that substitution by two ethylene groups is not a sufficient perturbation to change the mechanism of thermal geometrical isomerization of olefins. In the related instance of 1,2,3-trimethylbutadiene, an ethylene substituted by an isopropenyl group and two Me groups, examined by Frey *et al*,[11] the structural perturbations were sufficient to change the mechanism of *cis*, *trans* isomerization from the 90° twist to one involving conrotatory cyclization to cyclobutene and its reverse in the opposite sense.

Direct observation of the thermal geometric isomerization of acyclic hexa-1, *trans*-3,5-trienes cannot be made owing to the speed with which *cis*-hexatrienes cyclize. Parker and Goldblatt[12] working with alloöcimene, Egger and James[13] with hepta-1, *trans*-3, *trans*-5-triene and we with hexa-1, *trans*-3,5-triene and octa-*trans*-2,*trans*-4,*trans*-6-triene find only cyclohexadienes as the isolable products. These experiences are examples of the well-documented cyclization of hexa-1,*cis*-3,5-triene,[14] a concerted reaction of which the stereochemistry is known and rationalized.[15] The kinetic parameters of the cyclization of several acyclic trienes have been determined: hexa-1,*cis*-3,5-triene, log A 11·83, E_a 29·9[16] and 29·4[17] kcal/mol; octa-*trans*-2,*cis*-4,*trans*-6-triene, log A 11·4, E_a 29·4 kcal/mol;[18] and 2,6-dimethylhepta-1,*cis*-3,5-triene, log A 10·5 $E_a = 31{\cdot}8$ kcal/mol.[19]

If Arrhenius parameters are to be associated with the 90°-twisted singlet state of olefins, it must be assumed that the rate-determining step in the formation of cyclohexadienes is the *trans*,*cis* isomerization (A); that the cyclobutene mechanism is inoperative (B); and that an unsuspected element of concert is not present at the transition state (C). This latter possibility would depend on the build-up of appreciable bonding between C_1 and C_6 before achieving the dihedral angle of 90° between the two planes defined by C_2—C_3—C_4 and C_3—C_4—C_5. In this mechanism, the *cis* isomer would be bypassed as an intermediate and the conversion of *trans*-triene to cyclohexadiene could be concerted.



While Egger and James interpreted the results of their investigation of the geometric isomerization of hepta-1,*trans*-3,*trans*-5-triene without consideration of these vitiating possibilities,[13] we sought to establish the *trans*,*cis* isomerization of a triene as a directly observable reaction, free at least of these complications. As a glance at the figure will show, cyclopentenylidenecyclopentene seems eminently qualified. It may not cyclize to the corresponding cyclohexadiene from either its *cis* or *trans* configuration without the introduction of undue strain (D). Intermediates involving a cyclobutene (E), a bicyclobutane[20] (F) or any diradical derived from it are likewise excessively strained. In return for ruling so many entertaining processes off the limits of energetic accessibility, complications from the addition of four alkyl substituents and the introduction of nonbonded interactions in each half of the system have to be recognized and accepted.

Synthesis of a mixture of the two cyclopentenylidenecyclopentenes (CPCP) is effected by addition of cyclopentenylmagnesium chloride to cyclopent-2-enone followed by dehydration. The two isomers are separated by GLPC and characterized by their spectral properties and catalytic hydrogenation to bicyclopentyl.

The α-isomer has the shorter retention time, NMR absorptions at $\delta = 2{\cdot}50$ and 6·00 and 6·16 ppm and λ_{max}^{EtOH} 281 (sh), 293 and 306 (sh) nm. The β-isomer has the longer retention time, NMR absorption at $\delta = 2{\cdot}42$ and 5·90 and 6·37 ppm and λ_{max}^{EtOH} 271, 281 and 291 nm. The NMR spectra are consistent with the presence of only vinylic and allylic H atoms, while the UV spectra are characteristic of conjugated trienes.[21]

On being heated at 310°, both isomers are converted to an equilibrium mixture consisting of the β- and α-isomers in the ratio, 1·055 : 1·000 ($\Delta\Delta G =$ 60 cal/mole), respectively. This small difference in free energy makes it unlikely that differences in the Arrhenius parameters for the forward and backward reactions could be detected experimentally and makes it unnecessary for the purposes of this work to assign *cis* and *trans* structures.

In experiments preliminary to the detailed kinetic study, it was discovered that both the α- and β-isomers were isomerized at a rate too fast to be ignored to a material, γ, when heated at 285° for 30 min. This reaction is irreversible in that none of the α- or β-isomers is formed when the γ material is heated under the same conditions. The γ-material appears from its mass spectrum to be isomeric and from its UV spectrum, ($\lambda_{\max}^{\mathrm{EtOH}}$ 244 nm), which is similar to that reported for the equilibrium mixture of methylcyclopentadienes ($\lambda_{\max}^{\mathrm{heptane}}$ 247 nm),[22] may be inferred to have a conjugated system. It is assumed that the γ-material is the result of a surface-catalyzed 1,3 shift of hydrogen followed by the well-known rapid, thermal 1,5 hydrogen shifts and that it is an equilibrium mixture of the three cyclopentenes, 1-, 2- and 5-(2-cyclopentenyl)-cyclopentadienes, γ-1, γ-2, and γ-5, respectively.

Despite the unfavorable auguries, kinetic runs were carried out at low conversions in the seasoned 12-1 Pyrex flask over the range, 227–277°. Mass balances, determined by reference to durene as internal standard, were calculated by a simplified scheme in which the formation of γ was ignored. Over the small range of conversion investigated, this assumption was vindicated by the absence of fall-off of the specific rate constants. When collected in the usual form of an Arrhenius plot a line of marked downward curvature was obtained (Fig 1). such a behavior is indicative of the concurrence of at least two independent reactions of different energies of activation and is in concord with the hypothesis of a competitive, surface-catalyzed *cis-trans* geometric isomerization.

Following the discovery of J. L. Ekmanis in these laboratories that the rearrangement of methylenecyclohexane to methylcyclohexene, which occurs rapidly in Pyrex at elevated temperatures, can be virtually eliminated in tubes of Corning 0120 lead-potash glass, the thermal behavior of the β isomer was examined in a 3·5-1 flask of this glass. The difference is dramatic, almost none of the γ-material being produced and the specific rate constant at 253° being half that obtained in the Pyrex flask. Presumably both phenomena are associated with the acid-catalytic action of the Pyrex surface and are almost completely eliminated by the more nearly neutral surface of the leadpotash glass. This contribution of Ekmanis has proved useful in the eradication of the surface effects encountered by Srinivasan and Levi[23] in their kinetic investigation[24] of the thermal reactions of cycloöcta-1,5-diene.

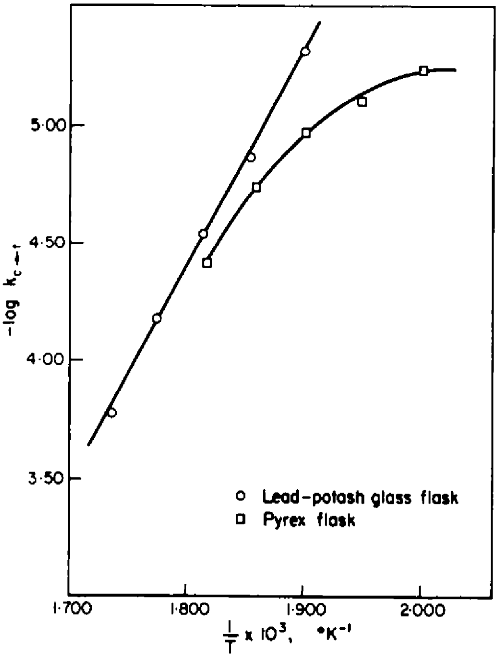
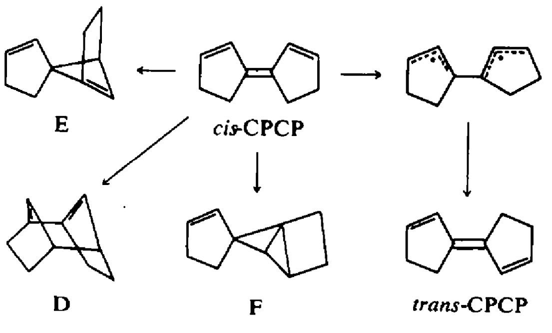


Fig 1. Arrhenius plots for interconversion of *cis*- and *trans*-1,1′-Bi (cyclopent-2-enylidene).



A test run in the presence of diphenylamine reveals a slightly faster reaction. This observation is taken as evidence that a free-radical chain mechanism is inoperative.

The results of the kinetic study of the thermal rearrangement of the β-isomer to the α are given in graphical (Fig 1) and tabular (Table 1) form. The

Table 1. Rate constants and activation parameters for the thermal isomerization of β-cyclopentenylidenecyclopentene in the lead-potash flask

Temp [°C]	$k_{t\to c}$(sec^{-1} × 10^6)[a]
253·0	4·87 ± 0·12
265·8	13·5 ± 0·35
277·6	28·8 ± 0·3
290·1	66·1 ± 0·6
303·0	166·0 ± 2·0

$\log k_{t\to c} = 12{\cdot}03 \pm 0{\cdot}32 - (41{\cdot}7 \pm 0{\cdot}8)/\theta^{b}$

$\Delta H\ddagger = 40{\cdot}6$ kcal/mole; $\Delta S\ddagger = -7{\cdot}8$ cal/deg-mole

[a] The standard deviations are those for the average of all observations, $\bar{S}(\bar{S} = S/\sqrt{n}$, where S is the standard deviation for the individual observationsS).

[b] $\theta = 4{\cdot}575T(°K) \times 10^{-3}$

Arrhenius parameters are obtained from the data in Table 1 by the method of least squares as are the standard deviations.

Although a more thorough discussion of the implications of this lowering of 23·3 kcal/mol in the activation energy *vis-à-vis* that of ethylene[2] is deferred for the moment, we suggest that this activation energy is the first which can be confidently associated with the transition state for the simple rotational geometric isomerization of a triene.

The unsubstituted parent triene, hexa-1,*trans*-3,5-triene, reacts smoothly in the gas-phase to give cyclohexa-1,3-diene as the only product. Despite the fact that liquid hexatriene polymerizes at room temperature, the mass-balance determined against cyclohexane as an internal standard was uniformly better than 90%, provided the partial pressure remained low (~ 1·5 mm/Hg) and the Pyrex vessel had been seasoned. The rate of rearrangement remained unchanged when the reaction was carried out at lower pressure (0·3 mm), with diphenylamine or in the less acidic, lead-potash flask.

An approximate correction for the small decrease in mass balance was made on the assumption that the loss occurred in the starting triene and not in the cyclohexadiene, which has been shown to be stable at these temperatures.[25] The average amount of hexatriene lost was estimated graphically and subtracted from the initial weight of hexatriene, W_H^0, to give an effective initial weight, W_H^{eff}, on the basis of which rate constants were calculated by the usual first-order expression: $k_c = 2{\cdot}303/t \log [W_H^{eff}/(W_H^{eff} - W_C)]$ where W_C is weight of cyclohexadiene produced at time, t. On the basis of a propagation of errors, weights were assigned to the individual rate constants. From these weighted rate constants, an average rate constant was obtained at each temperature (Table 2).[26]

Table 2. Rate constants and activation parameters for the thermal conversion of hexa-1,*trans*-3,5-triene to cyclohexa-1,3-diene[a]

Temp [°C]	k_1 (sec^{-1} × 10^6)
260·2	6·06 ± 0·22
271·0	12·8 ± 0·7
278·5	24·3 ± 1·3
290·0	48·1 ± 1·8
300·1	106·6 ± 4·2

$\log k_1 = 12{\cdot}9 \pm 0{\cdot}5 - (44{\cdot}3 \pm 1{\cdot}2)/\theta$[b,c]

$\Delta H\ddagger = 43{\cdot}2$ kcal/mole; $\Delta S\ddagger = -7{\cdot}2$ cal/deg. mole

[a] The preliminary results of this study were made available in *Thermal Unimolecular Rearrangements*, p. 3. A compilation by M. R. Willcott and R. L. Cargill, University of South Carolina Printing Department, August (1968)

[b] $\theta = 4{\cdot}575 \times 10^{-3}T(°K)$

[c] Too recently for more extensive recognition, S. W. Orchard and B. A. Thrush [*J.C.S. Chem. Comm.* 14 (1973)] report $\log k_1 = 12{\cdot}65 \pm 0{\cdot}18 - (43{\cdot}33 \pm 0{\cdot}48)/\theta$.

In an attempt to ascertain the effect of Me groups on the activation parameters of the rearrangement, the behavior of octa-*trans*-2,*trans*-4,*trans*-6-triene was examined. In the meantime, Egger and James[13] reported an examination of hepta-1,*trans*-3,*trans*-5-triene.

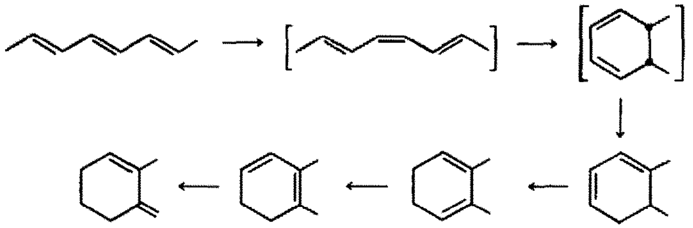
The thermal reaction of octatriene leads to nine peaks distinguishable by GLPC, one of which is recovered starting material having an NMR spectrum identical with that of authentic material and another of which is octa-*trans*-2,*trans*-4,*cis*-6-triene having the same retention time, and NMR and UV spectra as that of an authentic sample prepared according to Alder and von Brachel.[27] However, 90% of the remaining product consists of three dimethylcyclohexadienes, (DMCH), each of which is isolated by GLPC and characterized by IR, NMR and mass spectra.

DMCH-1 is identical in NMR spectrum to the 1,6-dimethylcyclohexa-1,3-diene reported by Marvell *et al.*[18] From their NMR spectra, it appears that DMCH-2 and DMCH-3 share between them the structures of 2,3- and 1,2-dimethylcyclohexa-1,3-diene. Four other unidentified products comprising less than 10% of the total are formed along with DMCH-2 and DMCH-3 when DMCH-1 is heated under the conditions required to rearrange the all-*trans* octatriene and are not direct products of the reaction of the triene.

The dimethylcyclohexadienes are formed consecutively, presumably as the result of successive migrations of the 1,5 hydrogen type. Typically, their ratio varies with the time of reaction. Thus, in a rearrangement of all-*trans* octatriene at 298·7°, the percentages of DMCH-1, DMCH-2 and DMCH-3 at 9·8, 18·0, 25·6 and 68·6% conversion are 63·1, 33·6, 3·3; 47·0, 45·2, 7·8; 39·8, 49·7, 10·5; and 27·8, 57·8, 14·5%, respectively.

No surface effect can be detected in a seasoned 12-l Pyrex vessel packed with enough glass wool to increase the estimated surface: volume ratio by a factor of 31. The specific rate constant at 259·7° is 7·85 × 10^{-6} in comparison to the average value of 8·31 × 10^{-6} sec^{-1}. Similarly a reaction in the presence of 50 μl aniline shows no change (k_1 = 7·60 × 10^{-6} sec^{-1}). Since Marvell, *et al.*[18] have found that octa-*trans*-2,*cis*-4,*trans*-6-triene cyclizes to *cis*-5,6-dimethylcyclohexa-1,3-diene which then rearranges to DMCH-1, it is understandable that at the higher temperature required for rearrangement of all-*trans* octatriene, none of the expected, initial product can be detected.

The formation of octa-*trans*-2,*trans*-4,*cis*-6-triene as a necessarily reversible product is not understood. Changing from Pyrex to lead-potash glass does not interfere with its formation (or alter the proportion of other products significantly). Its formation may be rationalized as a competitive *cis,trans* isomerization about the 6,7 double bond or as a reversible dimerization to 7,8-dimethyl-



DMCH-3 DMCH-2 DMCH-1

tetradeca-2,4,10,12-tetraen-6,9-diyl diradical. It should be noted that the same phenomenon was encountered by Egger and James. The reversible formation of octa-*trans*-2,*trans*-4,*cis*-6-triene cannot have a large disturbing effect on the kinetics since it is never present in amount greater than 20% and itself rearranges at 300° for 10 minutes to the same amount of the identical mixture of products as the all-*trans* isomer.

Accordingly the kinetics are calculated in neglect of the effect of the *cis*-6 isomer. The rate constants for the conversion of the all-*trans* isomer to the sum of compounds 1-7 are independent of the extent of reaction and are given in Table 3, as are the Arrhenius parameters obtained in the usual manner by the method of least squares.

A reliable value for allylic resonance energy should be extractable from the interconversion of *cis* and *trans* cyclopentenylidenecyclopentene. None of the doubts about mechanism which must be entertained with the acyclic trienes seems worrisome here. The transition state is almost certainly the 90° twisted arrangement and represents the upper limit of the torsional vibrational levels. Although we see no way of excluding experimentally the possibility that this geometry represents an intermediate rather than the transition state, the theoretical calculations of the π-electron energy of ethylene has so far revealed only a simple col, devoid of any suggestion of a shallow energy minimum. The analysis of energy in the starting cyclopentenylidenecyclopentene is complicated by the energy-lowering conjugative interaction of the three double bonds with each other and with their four alkyl substituents and also by the energy-raising nonbonded interaction associated with a closer approach to planarity.

Table 3. Rate constants and activation parameters for the thermal rearrangement of octa-*trans*-2,*trans*-4,*trans*-6-triene to dimethylcyclohexadienes

Temp [°C]	k_1 (sec^{-1} × 10^6)
259·7	8·55 ± 0·46
269·5	18·04 ± 0·78
284·7	55·9 ± 1·2
298·7	163·2 ± 4·5
310·1	326·8 ± 21·3

$\log k_1 = 13{\cdot}46 \pm 0{\cdot}25 - (45{\cdot}2 \pm 0{\cdot}65)/\theta^a$

$\Delta H\ddagger = 44{\cdot}1$ kcal/mole; $\Delta S\ddagger = -1{\cdot}4$ cal/deg-mole (at 285°).

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[a] $\theta = 4{\cdot}575 \times 10^{3}T$(°K).

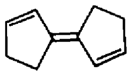
The effect of alkyl substituents can be examined in the behavior of the acyclic trienes. The methyl groups act on the energy of both the planar triene and the bis-allylic diradical-like transition state. The interaction is well and conveniently defined by the general procedure of Dewar and Schmeising.[28]

A characteristic strength is assigned to the bonds between the methyl group (sp^3) and the trigonal carbon atoms of the olefin (sp^2) [$E_{CC'}$] and the likewise trigonal carbon atom of the radical-like carbon atom in the 90° twisted transition state [$E_{CC'}$]. Since both bond types appear in theory to be similar, the difference between $E_{CC'}$ and $E_{CC'}$ might be expected to be zero or close to it.

Experimentally no consistent influence of the methyl groups is discernible in the two substituted hexatrienes. The single methyl group in the heptatriene appears to lower the activation energy by 1·9 kcal/mol while the two methyl groups in the octatriene appear to raise the activation energy by 0·9 kcal/mol. Whatever the true effect may be, it appears to fall within the relatively large experimental error associated with these complicated reactions. It should be cautioned that the reversible formation of hepta-1,*trans*-3,*cis*-5-triene and octa-*trans*-2,*trans*-4,*cis*-6-triene admits of a disturbing, alternative mechanism for the geometric isomerization of the central double bond in which a reversible 1,5-hydrogen shift becomes the means of interconversion. Were this the mechanism of the rearrangements, the two examples would be irrelevant to the question of interaction of Me group with radical-like 90°-twisted transition state. Since there is no indication of the induction period demanded by this mechanism, it is probably safe to proceed on the assumption that the alkyl substituents and the nonbonded interactions exercise only a small effect on the activation energy of the bicyclic triene.

With this assumption one can make the further inference, crucial to the significance of the ensuing discussion, that unsubstituted hexatriene is transformed to cyclohexadiene by a rate-determining geometric isomerization of the *trans*-3 double bond to *cis*-3. If some other mechanism were operative, the energy of activation of the 90° process

Table 4. Activation parameters for thermal reaction of trienes.

Triene	log A	E_a (kcal/mole)
	$12{\cdot}91 \pm 0{\cdot}5$	$44{\cdot}3 \pm 1{\cdot}2$
	$12{\cdot}28 \pm 0{\cdot}2$	$42{\cdot}4 \pm 0{\cdot}5$
	$13{\cdot}46 \pm 0{\cdot}3$	$45{\cdot}2 \pm 0{\cdot}7$
	$12{\cdot}03 \pm 0{\cdot}3$	$41{\cdot}7 \pm 0{\cdot}8$

would be lower, not higher, than that observed experimentally for cyclopentenylidenecyclopentene.

The ensuing theoretical interpretation will be developed around *trans*- and *cis*-hexa-1,3,5-triene (instead of the cyclopentenylidenecyclopentenes) since their heats of hydrogenation are known[29] and their structures have been determined by electron diffraction.[30] The significant structural features are planarity of the *trans* isomer and near planarity (10° twist of the central double bond) of the *cis* isomer; and a longer distance in the central double bonds (1·368 Å in the *cis* isomer) than in the terminal double bonds (1·336 Å).

The enthalpy of activation (ΔH‡) of the conversion of hexa-1,*trans*-3,5-triene to cyclohexa-1,3-diene is 43·0 kcal/mol. It can be compared with the enthalpies of activation for the geometrical isomerizations of ethylene,[2] propylene[4] or *cis*-[31] or *trans*-[3] butene which are 63·5 kcal/mol, 60·8 kcal/mol, 61·3 kcal/mol (*cis*) and 62·2 kcal/mol (*trans*), respectively.

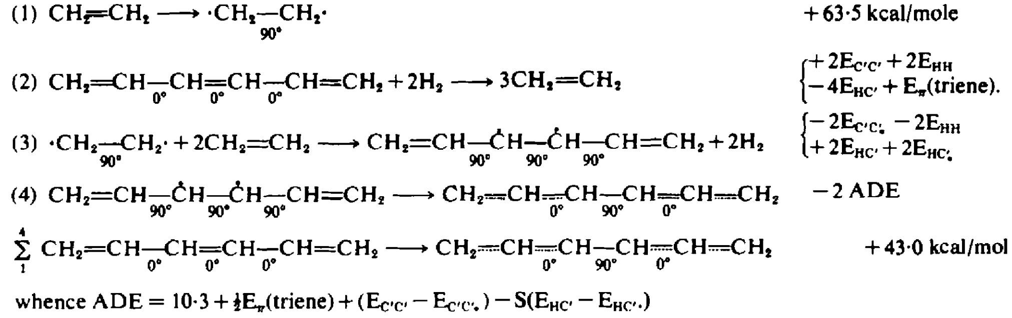
The replacement of two vinylic H atoms by two vinyl groups thus results in a lowering of the enthalpy of activation by 20·5 kcal/mol whence the effect of the vinyl group *vis-à-vis* hydrogen is 10·3 kcal/mol. This value is useful, for example, in predicting the enthalpy of activation for thermal geometrical isomerization in butadiene: 63·5 − 10·3 = 53·2 kcal/mol. If *trans*-butene be taken as the standard (62·2 kcal/mol) the effect of replacement of the two Me groups by two vinyl groups is a lowering of 19·2 kcal/mol. With this standard, the predicted enthalpy of activation of the hypothetical isomerization of butadiene becomes 52·6 kcal/mol. Both values are in close agreement with the value of 52·8 kcal/mol found for penta-1,*cis*-3-diene by Frey, Lamont and Walsh.[11]

Extraction of the magnitude of allylic delocalization energy from the difference between the activation energies for geometrical isomerization of ethylene and hexa-1, *trans*-3,5-triene does not appear to be achievable in a simple manner. A thermodynamic scheme based on Dewar and Schmeising[28] allows the difficulties to be appreciated (Fig 2).

A model relating allylic delocalization energy to the heats of hydrogenation and activation energies for the geometrical isomerizations of ethylene and *trans*-hexatriene may be constructed in stages. For this purpose allylic delocalization energy is defined as the energy released in an sp² radical when an orthogonally oriented vinyl substituent rotates 90° into the co-planar orientation. In the first stage the cost of replacing two H atoms in ethylene and its 90° twisted transition state by two vinyl groups is evaluated.

In the second stage, an experimentally independent expression for E_π(triene) is derived from heats of hydrogenation and represents the cost of transforming ethylene into the central double bond of hexatriene (Fig 3).

In an entirely similar fashion, an expression for ADE based on *trans*-butene can be derived ($\Delta H_{H,}$



$$(1)\ \mathrm{CH_2{=}CH_2 \longrightarrow {\cdot}CH_2\underset{90^\circ}{-}CH_2{\cdot}} \qquad +63{\cdot}5\ \text{kcal/mole}$$

$$(2)\ \mathrm{CH_2{=}CH\underset{0^\circ}{-}CH\underset{0^\circ}{=}CH\underset{0^\circ}{-}CH{=}CH_2 + 2H_2 \longrightarrow 3CH_2{=}CH_2} \qquad \begin{cases} +2E_{C'C'} + 2E_{HH} \\ -4E_{HC'} + E_\pi(\text{triene}). \end{cases}$$

$$(3)\ \mathrm{{\cdot}CH_2\underset{90^\circ}{-}CH_2{\cdot} + 2CH_2{=}CH_2 \longrightarrow CH_2{=}CH\underset{90^\circ}{-}\dot{C}H\underset{90^\circ}{-}\dot{C}H\underset{90^\circ}{-}CH{=}CH_2 + 2H_2} \qquad \begin{cases} -2E_{C'C'^{\bullet}} - 2E_{HH} \\ +2E_{HC'} + 2E_{HC'^{\bullet}} \end{cases}$$

$$(4)\ \mathrm{CH_2{=}CH\underset{90^\circ}{-}\dot{C}H\underset{90^\circ}{-}\dot{C}H\underset{90^\circ}{-}CH{=}CH_2 \longrightarrow CH_2{=}CH\underset{0^\circ}{=}CH\underset{90^\circ}{-}CH\underset{0^\circ}{=}CH{=}CH_2} \qquad -2\,\text{ADE}$$

$$\sum_1^4 \mathrm{CH_2{=}CH\underset{0^\circ}{-}CH\underset{0^\circ}{=}CH\underset{0^\circ}{-}CH{=}CH_2 \longrightarrow CH_2{=}CH\underset{0^\circ}{=}CH\underset{90^\circ}{-}CH\underset{0^\circ}{=}CH{=}CH_2} \qquad +43{\cdot}0\ \text{kcal/mol}$$

$$\text{whence ADE} = 10{\cdot}3 + \tfrac{1}{2}E_\pi(\text{triene}) + (E_{C'C'} - E_{C'C'^{\bullet}}) - S(E_{HC'} - E_{HC'^{\bullet}})$$

Fig 2. The hypothetical thermodynamic scheme for the definition of Allylic Delocalization Energy (ADE) in which subscript angles refer to sp² planes and E_{HH}, $E_{HC'}$, $E_{HC'^{\bullet}}$, $E_{C'C'}$, $E_{C'C'^{\bullet}}$ and E_π(triene) refer to the energy of the σ bonds between H and H, H and sp²C of a double bond, H and sp²C of a free radical, two sp²C in a double bond, the sp²C of a double bond and the sp²C of a free radical, and the π electron delocalization energy of hexatriene, respectively.

(1) $\underset{\text{A}}{\text{hexa-1,5-diene}} + 2H_2 \longrightarrow \text{n-hexane}$

$$-60{\cdot}2\ \text{kcal/mol} = -10E_{HC} - E_{CC} + 2E_{HH} + 6E_{HC'} + 2E_{CC'} + 2E_{\pi}(\text{ethene})$$

(2) $\underset{\text{B}}{\text{ethene}} + H_2 \longrightarrow \underset{\text{C}}{\text{ethane}}$

$$-32{\cdot}8\ \text{kcal/mol} = -6E_{HC} - E_{CC} + E_{HH} + 4E_{HC'} + E_{\pi}(\text{ethene})$$

(3) $\underset{\text{D}}{\textit{trans}\text{-hexa-1,3,5-triene}} + 3H_2 \longrightarrow \text{n-hexane}$

$$-79{\cdot}4\ \text{kcal/mol} = -14E_{HC} - 5E_{CC} + 3E_{HH} + 8E_{HC'} + 2E_{C'C'} + 3E_{\pi}(\text{ethene}) + E_{\pi}(\text{triene})$$

(1) + (2) − (3):
$A + B \longrightarrow D + C$

$$E_{\pi}(\text{triene}) = 13{\cdot}6\ \text{kcal/mol} + 2(E_{C'C} - E_{C'C'}) - 2(E_{HC} - E_{HC'})$$

$$\text{ADE} = 17{\cdot}1\ \text{kcal/mol} + (E_{C'C} - E_{C'C'\cdot}) - (E_{HC} - E_{HC'\cdot})$$

Fig 3. The hypothetical thermodynamic scheme for the evaluation of the π-electron delocalization energy in *trans*-hexa-1,3,5-triene (D) and an alternative expression for allylic delocalization energy (ADE). Reference should be made to Fig 2 for definitions of symbols.

for *trans*-butene = − 27·6 kcal/mol; ΔH‡ for *trans*-butene = + 62·2 kcal/mol);

$$\text{ADE} = 13{\cdot}8\ \text{kcal/mol} + (E_{C'C} - E_{C'C'\cdot}) - (E_{CC} - E_{CC'\cdot}).$$

This is the value of ADE to be compared with the immediately following literature values of ΔΔH‡.

In this Dewar-Schmeising type of analysis, allylic delocalization energy takes the form, ADE = ΔΔH‡ + f(C′C/CC′·). Depending on the model taken as the localized standard, the precise Dewar-Schmeising terms will vary but their nature is clear. They represent the secondary changes worked on the strengths of the sigma bonds by the changes made in the π-system. In all the previous literature, ADE has been identified with ΔΔH‡ on the implicit assumption that the Dewar-Schmeising terms vanish.

Three of the estimates of ΔΔH‡ in the literature are derived from reactions in which these terms relate to the common trigonal free radical (C·) and are defined by f(C′C/CC·) = $(E_{C'C} - E_{C'C\cdot}) - (E_{CC} - E_{CC\cdot})$.

Egger *et al*,[32] for example, compare the activation energy for the abstraction by iodine atoms of the secondary hydrogen atom in propane with that of the allylic hydrogen atom in butene-1 and find ADE = 12·6 kcal/mol + f(C′C/CC·). In a second approach[33] involving abstraction of an allylic hydrogen atom in propylene by iodine atoms, a value for ADE = 10·2 kcal/mol + f(C′C/CC·) is obtained. These values are based on an unsupported assumption that the activation energy for the reaction of an allylic radical with hydrogen iodide is 1 kcal/mol and are tied to a strength of 98 kcal/mol for the primary H-bond in propane. A third evaluation,[34] based on the pyrolysis of allyl methyl sulfone in a flow system using toluene as the carrier gas and radical trap, leads to a value of ΔΔH‡ = 13·4 kcal/mol. The evaluation involves the assumption of no activation energy for the recombination of allyl and methylsulfonyl radicals and is also tied to the bond strength in propane.

Attempts to measure ADE-f(C′C/CC·) by the cleavage of hexa-1,5-diene are numerous and include values of 17·8 kcal/mol,[35] 12 kcal/mol,[36] 9·6 kcal/mol[37] and 15·5 kcal/mol.[38]

To obtain a value for ADE from the equation governing the geometrical isomerization of hexa-1, *trans*-3,5-triene,

$$\text{ADE} = 17{\cdot}1\ \text{kcal/mol} + (E_{C'C} - E_{C'C'\cdot}) - (E_{HC} - E_{HC'\cdot}),$$

the latter terms need to be estimated. Equating the common free radical, C·, with C′· in the diradical-like transition state for geometric isomerization and both with the trigonal olefinic carbon atom [the same as setting f(C′H/CC′·) = f(C′H/CC·) = f(C′H/CC′)], allows values for the four types of bonds to be evaluated according to Dewar and Schmeising:

$$\begin{aligned} E_{C'C'\cdot} = E_{C'C\cdot} = E_{C'C'} &= 100{\cdot}4\ \text{kcal/mol} \\ E_{HC} &= 97{\cdot}2\ \text{kcal/mol} \\ E_{HC'\cdot} = E_{HC\cdot} = E_{HC'} &= 100{\cdot}9\ \text{kcal/mol} \\ E_{C'C} &= 91{\cdot}8\ \text{kcal/mol}^{*} \end{aligned}$$

Substitution gives a value for ADE equal to 12·2 kcal/mol. Similar estimates of f(C′C/CC′·) allow a value of ADE = 13·1 kcal/mol to be extracted from the expression based on *trans*-butene as standard.

The term E_{π}(triene) in the initial expression for allylic delocalization energy given in Fig 2,

$$\text{ADE} = 10{\cdot}3 + 0{\cdot}5E_{\pi}(\text{triene}) + (E_{C'C'} - E_{C'C'\cdot}) - (E_{HC} - E_{HC'\cdot}),$$

has recently been calculated by Dewar and de Llano[39] to be zero. If the assumption is made again

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*By calculation according to their relationship between bond energy and bond length (assumed to be 1·515 Å).[28]

that the strengths of bonds of olefinic sp^2 C atoms and to the diradical-like C atoms of the transition state are equal, then $f(C'H/C'C'\cdot)$ becomes $f(C'H/C'C')$, all terms vanish and ADE becomes 10·3 kcal/mol.

Although there is no immediate way of resolving the difficulties at the required level of quantitative refinement, their existence should be recognized. In general when the effect of a group (X) on geometric isomerization of the carbon-carbon double bond is being compared with that of hydrogen, the delocalization energy will take the form $DE = \Delta H\ddagger_{unsubt} - \Delta H\ddagger_{subt} + E_{\pi}(XC = C) + f(XH/C'C'\cdot)$. The difference in the enthalpies of activation needs to be corrected by a function of the sigma bond strengths of hydrogen and the group X, $[f(XH/C'C'\cdot) = (E_{XC'} - E_{XC'\cdot}) - (E_{HC'} - E_{HC'\cdot})]$, and by any energy of conjugative interaction in the substituted olefin. The form can be changed if an independent evaluation of conjugative interaction is available from heats of hydrogenation, heats of combustion, or the like.

EXPERIMENTAL

Air thermostat. This thermostat is patterned after the design of Clark.[40] Its use has already been reported in other works.[24,41] Although a more detailed description of its construction is available in Beasley's dissertation,[42] it may be noted that the smaller of the two heaters (2 coils of No. 26 Nichrome wire wound on glass rods connected in parallel, total resistance 45 ohms) is controlled by Thermotrol Temperature Controller, Model 1053 A, Hallikainen Instruments, Richmond, Calif. and a platinum resistance thermometer, Air Temperature Sensor, Model 9899, Burns Engineering, Inc., Minneapolis, Minn. The all-glass vacuum system, to which the air thermostat was attached, employed Teflon stopcocks to avoid absorption of organic material in stopcock grease. From top to bottom of the heating well a temperature gradient of 1° was recorded. At a given spot temperature variation was less than 0·1°.

The reliability of the apparatus was checked by determining rate constants for pyrolysis of methylenecyclobutane to ethylene and allene, a reaction which has been studied independently in three laboratories.[43] The results are shown in the Table 5.

Table 5. Activation parameters for pyrolysis of methylenecyclobutane

log A	E_a [kcal/mol]	Author
15·68	63·3	Chesick[43a]
15·15	61·8	This work
15·09	61·5	Brandaur *et al.*[43b]
15·03	61·0	Burkhardt[43c]

In the general procedure, sample and internal standard are degassed and transferred *in vacuo* into the source and recovery cold finger of the vacuum system. After being warmed to room temperature, the contents are allowed to diffuse into the previously evacuated reaction vessel—in this instance a 12-l Pyrex flask. One minute before the time recorded as the end of the run, the reaction mixture is returned to the cold-finger by cooling with liquid nitrogen and opening the stopcock. Although five minutes is allotted to this transfer one minute has been shown to suffice for collection of 95% of the contents. Subsequent transfer to a detachable ampoule is normally followed by analysis by GLPC with the aid of a disc integrator. The amount of recovered starting material or products is calculated by reference to the unreacted internal standard and is corrected for differences in the thermal responses of molecules according to the procedure of McNair and Bonelli[44] (correction factors (CF) are determined from reference standards and are arbitrarily referred to the internal standard.)

In the specific reaction of methylenecyclobutane, a sample obtained through the courtesy of J. L. Ekmanis was purified by GLPC (¼″ × 4 m, 7% dimethylsulfolane on 60/70 Anakrom P at 40°) and shown by its NMR spectrum and GLPC on this column and that used for the analysis (column A: ¼″ × 4 m 16% Carbowax 600–4% $AgBF_4$ on 60/80 Chromosorb P) to contain less than 1% impurity. Purified cyclopentane served as the internal standard. In these reactions ~ 11 mg each of methylenecyclobutane and cyclopentane in a 1-l Pyrex flask provided a total pressure of ~ 6 mm/Hg at 435°. The rate constants are collected in Table 6.

Table 6. Specific rate constants for the pyrolysis of methylenecyclobutane.

T [°C]	$k_1(sec^{-1} \times 10^5)$	Calculated $k_1(sec^{-1} \times 10^5)$		
	This work	Chesick[43a]	Brandaur *et al.*[43b]	Burkhardt[43c]
411·1	2·54 ± 0·10	2·88	2·82	3·55
422·6	5·59 ± 0·33			
433·6	10·9 ± 0·3			
446·2	23·8 ± 0·7			
460·8	55·8 ± 3·6	67·6	60·3	74·1

α- and β-Cyclopentenylidenecyclopentene

A. 1(*Cyclopent-2-en-1-yl*)*cyclopent-2-en-1-ol.* Cyclopentenyl magnesium chloride, prepared according to Branner-Jørgensen and Berg[45] from 41 g 3-chlorocyclopentene in THF solution, was treated with 10·2 g cyclopent-2-enone. After 12 hr, the mixture was neutralized with just enough sat NH_4Cl aq to precipitate mg salts. The THF soln was decanted, the salts were leached several times with THF, and the combined THF solns were dried (Na_2SO_4). Distillation removed THF and afforded a fraction, bp 63–64°/15 mm, consisting mainly of 1,1-bi(cyclopent-2-enyl) (> 90% on column B: ¼″ × 2 m, 16% XF-1150 on 60/80 mesh Chromosorb P at 117°) and a second fraction, 15·2 g, bp 75–77°/7 mm, of the carbinol (~ 90% by GLPC; same column).

B. *α- and β-Cyclopentenylidenecyclopentene.* Distillation of 6·0 g of the second fraction at 75°/15 mm with a small amount of $KHSO_4$ gave 3·4 g of a mixture of products from which 1·0 g of α-CPCP and β-CPCP was obtained. These two products could be separated on column B at 117°, α-CPCP having the shorter retention time.

α-CPCP had the following spectral properties: NMR (δ): 2·50 (s, 4·0 H) and a symmetrical pair of multiplets at

5·90 (1·0 H) and 6·37 (1·0 H), centered at 6·13; IR (cm^{-1}): 3130 (w), 3050 (m, olefinic) and 720 (s, *cis*-disubst olefin);[46] UV (nm); λ_{max}^{EtOH} 281 (sh), 293, 306 (sh); *m/e*: 132·094176 (calc for $C_{10}H_{12}$, 132·093896).[47]

β-CPCP: NMR (δ): 2·42 (s, 4·0 H); symmetrical multiplets, 5·85 (1·1 H) and 6·35 (1·1 H), centered at 6·10; IR (cm^{-1}): 3120 (w), 3050 (m), 722 (s); UV (nm): λ_{max}^{EtOH} 271 (sh), 281 and 291; *m/e*: 132·094176.

C. *Catalytic hydrogenation of α- and β-CPCP.* Hydrogenation of α-CPCP (31·7 mg) in 7·0 ml glacial AcOH with 30·7 mg prereduced PtO_2 at 31° for 68 min led to absorption of 3·22 molar equiv H_2. Diluted with water, extracted with ether and purified by GLPC on column C, (¼″ × 0·6 m, 8% Carbowax 20 M on 50/60 Anakrom ABS) at 60°, the reaction mixture afforded bicyclopentyl having an IR spectrum identical with that of an authentic sample. In similar fashion, β-CPCP (19·2 mg) absorbed 3·04 molar equiv hydrogen and afforded bicyclopentyl.[48]

Kinetics of the cis-trans *equilibration of cyclopentenylidenecyclopentenes*

A. *In the* 12-1 *Pyrex flask.* For all kinetic runs, α-CPCP and β-CPCP were purified by GLPC on column B at 117°, dissolved in pentane, dried over Na_2SO_4, freed of pentane by evaporative distillation at −78°, transferred *in vacuo* and stored under N_2 at −80°. The standard, durene (Eastman Organic Chemical), was pure by GLPC and NMR, but was subjected to transfer *in vacuo* before use.

With few modifications the general procedure was followed: the dead volume outside the thermostat was heated at 60° with heating tape to prevent condensation; the time for transfer out of the reaction flask was extended to ten minutes; approximately 2 mg each of durene and α-CPCP were used; since neat samples of CPCP polymerized at an appreciable rate at room temp, weight of sample was the difference between the weighing tube and sample before and after the vacuum transfer into the reaction flask; seasoning (37 mg β-CPCP at 310° for 40 hr) was required for reproducible results.

Preliminary reactions indicated the formation of a third substance (γ). Isolated and purified on column B at 155°, this material showed *m/e* 132, 117, 104, 91 and 67 at 16 ev and λ_{max}^{EtOH} 244 nm. When heated at 285° for 35 min in the 12-1 Pyrex flask no trace of α- and β-CPCP (18%) while β-CPCP rearranged to α-CPCP (18%) and both rearranged to the third substance (γ) to the extent of 6%.

GLPC analysis of reaction mixtures was effected on Column B at 117°. Correction factors for α- and β-CPCP relative to durene were 0·969 and 0·966, respectively. That of the third substance was assumed to be unity. Mass balance in all runs was at least 95%.

Position of equilibrium was determined in both directions: 2·242 mg β-CPCP and 1·948 mg durene was heated to 650 min at 310°. The ratio of β to α as determined on column B was 1·066. The reverse reaction, 2·871 mg α-CPCP and 2·130 mg durene gave a ratio of 1·057. Application of the correction factors gave an equilibrium ratio of 1·055.

The specific first-order rate constants were calculated on the assumption that the effect of the formation of the third substance at low conversion could be ignored and that a simplified expression would serve: $k_{\alpha\to\beta} = (C_e^\beta/C_0^\alpha t) \ln[C_e^\beta/(C_e^\beta - C_t^\beta)]$ where $k_{\alpha\to\beta}$ is the specific first-order rate constant for the conversion of α-CPCP to β-CPCP, C_e^β and C_t^β are concentrations of β at equilibrium and time, t, in sec., respectively, and C_0^α is the concentration of α at the beginning of the reaction. In terms of fractional concentrations, this expression becomes $(0{\cdot}5134/t)\ln[0{\cdot}5134/(0{\cdot}5134 - C)]$ where C is fraction of α rearranged to β at time, t. The data and the results of calculation appear in Table 7.

B. *In the* 3·5-1 *Corning* 0120 *lead-potash flask.* Following the discovery by Ekmanis that the thermal rearrangement of methylenecyclohexane to methylcyclohexene, which occurs rapidly in Pyrex glass (76% after 30 hr at 331°), is virtually eliminated in Corning 0120 lead-potash glass (0·7% after 72 hr at 340°), a 3·5-1 flask for use in the air-thermostat was blown by hand from the commercially available tubing.

When a single run at 253° and 140 min gave a considerably smaller rate constant ($k_{\alpha\to\beta} = 5{\cdot}11 \times 10^{-6}\ sec^{-1}$) than had been obtained in an identical run in the seasoned 12-1 Pyrex reaction vessel ($k_{\alpha\to\beta} = 9{\cdot}9 \times 10^{-6}\ sec^{-1}$) and the formation of γ was virtually eliminated, the kinetics was examined thoroughly in the lead-potash flask.

Specific first-order rate constants for the conversion of β-CPCP to α-CPCP were calculated on the basis of the equation, $k_{\beta\to\alpha} = (0{\cdot}487/t)\ln[(0{\cdot}487/0{\cdot}487)—C]$, where C is the fractional amount of α formed from β at time, t. The following corrections were applied: (a) for the presence of 1% α in the starting sample of β, 1% of the total area under α, β and γ was subtracted from the area under α; (b) for the presence of 1·5% of the impurities in starting β, the amount of α was multiplied by 1·015, (c) for deficiency in mass balance (always better than 91%) by ascribing entire loss to decomposition of β which in most runs was

Table 7. The kinetic data on thermal reaction of α-CPCP in 12-*l* Pyrex flask

W_D [mg]	W_α [mg]	A_α/A_D^a	A_β/A_D	A_γ/A_D	t [sec × 10^{-3}]	$k_{\alpha\to\beta}$ [sec^{-1} × 10^6]	Temp [°C]
1·864	2·297	1·052	0·0485	0·0340	7·20	5·87	227·0
2·225	3·394	1·353	0·0607	0·0481	7·20	5·87	227·1
1·616	2·613	1·481	0·0467	0·0200	3·60	8·44	240·0
2·234	2·193	0·887	0·0235	0·0156	3·60	7·09	239·9
1·868	3·628	1·671	0·0898	0·037	4·20	11·7	253·0
2·299	2·182	0·828	0·0377	0·0182	4·38	9·76	252·9
2·224	2·986	1·175	0·0686	0·0218	2·82	19·3	264·6
2·268	2·528	0·965	0·0499	0·0096	2·82	17·2	264·6
2·142	2·246	0·916	0·0772	0·012	2·10	38·9	276·9
2·596	2·099	0·922	0·0580	0·0074	2·10	38·1	276·9

[a] A_α, A_D, A_β and A_γ are the areas under the GLPC traces of α-CPCP, durene, β-CPCP and γ, respectively.

Table 8. Kinetic data for thermal reaction of β-CPCP in lead-potash flask

W_D^a [mg]	W_β^a [mg]	A_α/A_D^b	A_β/A_D	A_γ/A_D	t [sec × 10^{-3}]	$k_{\beta\text{-}\alpha}$ [sec^{-1} × 10^6]	Temp [°C]	C^c
2·634	1·930	0·0349	0·645	0·016	8·40	5·11	253·0	0·0415
2·477	3·194	0·117	1·068	0·033	21·3	4·60	253·0	0·0890
2·516	2·456	0·110	0·774	0·014	21·3	6·10	252·9	0·1137
2·560	2·120	0·0954	0·640	0·024	28·7	4·72	252·9	0·1182
2·642	2·360	0·130	0·607	0·059	42·0	5·05	253·0	0·1720
2·122	2·110	0·0922	0·794	0·0066	7·20	14·2	265·9	0·0924
2·238	1·590	0·0824	0·554	0·0065	10·5	13·1	265·8	0·1189
2·808	2·431	0·120	0·651	0·0104	13·3	12·7	265·8	0·1430
2·696	2·134	0·139	0·585	0·0119	16·5	13·8	265·7	0·1830
2·031	3·148	0·205	1·240	0·0052	5·40	28·3	277·6	0·1319
1·784	3·248	0·322	1·329	0·0084	8·10	28·2	277·6	0·1823
1·839	3·031	0·370	1·164	0·0172	10·8	29·0	277·6	0·231
1·620	2·081	0·321	0·876	0·0155	12·7	28·9	277·6	0·258
2·186	2·034	0·270	0·595	0·0126	16·2	29·8	277·6	0·306
2·210	2·999	0·196	1·060	0·0023	2·70	64·5	290·0	0·1460
1·698	1·792	0·200	0·803	0·0024	3·60	67·5	290·1	0·1917
2·150	1·065	0·123	0·341	—	5·40	66·3	290·1	0·2540
2·674	2·798	0·298	0·649	0·0215	7·20	66·0	290·1	0·3035
1·890	1·410	0·165	0·545	0·0020	1·80	169	303·1	0·226
2·077	2·534	0·292	0·862	0·0014	2·10	161	302·9	0·244
1·965	1·912	0·291	0·646	0·0021	2·88	167	302·9	0·306
2·751	1·746	0·204	0·394	0·0018	3·37	166	303·0	0·334
2·546	2·002	0·271	0·473	0·0031	3·90	167	303·0	0·358

[a] W_D and W_β are the weights of standard durene and β-CPCP at the beginning of the reaction. [b] A_α, A_D, A_β and A_γ are the average areas of the GLPC traces of α-CPCP, durene, β-CPCP and γ. [c] C is the corrected molar fraction of α-CPCP produced; i.e., A_α/A_D.

Table 9. Kinetic data on the thermal rearrangement of hexa-1,*trans*-3,5-triene

W_S^b [mg]	S_S^b [mg]	L_H^c [mg]	W_{He}^{eff} [mg]	A_H/A_S	A_C/A_S	t [sec × 10^{-3}]	k_C [sec^{-1} × 10^6]	T [°C]
7·259	7·066	0·262	6·997	0·945	0·088	15·00	6·37	260·2
7·500	7·254	0·419	7·081	0·804	0·168	33·00	5·77	260·2
6·758	6·945	0·547	6·211	0·654	0·247	54·00	6·10	260·2
8·083	7·854	0·808	7·275	0·584	0·348	79·20	6·09	260·1
7·446	7·457	0·850	6·596	0·454	0·419	110·40	5·99	260·1
7·458	7·702	0·373	7·085	0·806	0·124	10·80	13·7	271·0
6·785	6·796	0·528	6·257	0·694	0·235	21·60	13·9	271·0
7·020	7·154	0·618	6·402	0·606	0·300	33·00	12·7	271·0
6·328	7·107	0·570	5·758	0·475	0·361	46·80	12·9	271·0
6·929	7·139	0·638	6·291	0·414	0·467	61·20	12·6	271·0
7·976	8·054	0·390	7·586	0·816	0·140	7·20	23·0	278·5
7·306	8·049	0·534	6·772	0·595	0·244	14·70	23·8	278·5
7·583	7·358	0·673	6·910	0·591	0·370	21·60	23·6	278·5
6·606	8·268	0·581	6·025	0·352	0·374	28·80	25·7	278·5
6·519	7·631	0·587	5·932	0·285	0·490	39·90	25·9	278·5
7·218	6·587	0·209	7·009	0·920	0·162	3·60	46·0	290·1
8·378	7·737	0·410	7·968	0·744	0·298	7·20	48·6	290·0
7·660	7·220	0·513	7·147	0·544	0·456	12·60	50·5	290·0
7·876	8·914	0·543	7·333	0·349	0·468	18·00	48·4	290·0
6·507	7·026	0·507	5·994	0·256	0·578	25·20	46·8	290·0
7·567	7·451	0·348	7·219	0·690	0·300	3·60	105·0	300·1
6·748	7·404	0·391	6·357	0·442	0·416	6·00	114·0	300·1
7·710	7·478	0·494	7·216	0·384	0·576	9·00	104·0	300·1
7·276	6·485	0·480	6·796	0·310	0·742	12·00	106·0	300·1
6·690	6·758	0·461	6·229	0·200	0·714	15·00	104·0	300·1

[a] Weight of starting hexatriene. [b] Weight of cyclohexane added as standard. [c] Average weight of hexatriene lost, from which the effective weight of starting material, W_H^{eff} is calculated.

recovered in greater than 70%; and (d), in runs marked by an asterisk where more than 2% γ is formed, for this product by adding an arbitrary 0·6 of the ratio of γ to β at the end of each run to the amount of α produced. The corrected rate constants were independent of the extent of reaction. The data are given in Table 8.

Hexa-1,*trans*-3,5-*triene*

Hexa-1,*trans*-3,5-triene[49] was purified by GLPC on column D (¼″ by 5 m 15% β,β'-oxydipropionitrile on 60/80 mesh Keiselguhr) at 63°, found to contain no detectable impurities on this and two other columns (A and B) and stored over Na_2SO_4 at $-78°$. The internal standard, cyclohexane (Aldrich Chem.), was pure by GLPC (column C).

The general procedure for kinetic runs was followed. To obtain reproducible results, the 2-l Pyrex flask had to be seasoned by heating with ~ 100 mg of the triene at 278° for periods of 18–40 hr. Analysis of products was effected by GLPC on column D at 50°. Cyclohexadiene, the only product, was identified by retention time and its IR spectrum. Mass balance was uniformly better than 90% of theory. Relative areas were determined with the aid of a disc integrator. Correction factors for hexa-1,*trans*-3,5-triene and cyclohexa-1,3-diene were 1·04 and 0·98, respectively, relative to cyclohexane.

The rate of rearrangement was determined in the Corning 0120 lead-potash flask at 300·1°. The specific rate constant, $0{\cdot}99 \times 10^{-4}\,sec^{-1}$, was only slightly lower than the average of five runs in the Pyrex flask, $1{\cdot}07 \times 10^{-4}\,sec^{-1}$. In the presence of 34 mg diphenylamine, a rate constant, $1{\cdot}02 \times 10^{-4}\,sec^{-1}$, was obtained. Since the kinetic runs were carried out at ~ 1·5 mm/Hg, two runs were carried out at 0·3 mm/Hg. The average first-order constant, $2{\cdot}59 \times 10^{-5}\,sec^{-1}$, compared with $2{\cdot}44 \times 10^{-5}\,sec^{-1}$ at the higher pressure (both at 278·5°). The data are collected in Table 9.

Table 10. Cyclohexadienes from thermal rearrangement of octa-*trans*-2,*trans*-4,*trans*-6-triene at 297·8°

% Reaction	DMCH-1/DMCH-2	DMCH-2/DMCH-3
9·8	1·88	10·0
18·0	1·04	5·8
25·6	0·80	4·8
68·6	0·48	4·0

Octa-trans-2,trans-4,trans-6-*triene*

Octa-*trans*-2,*trans*-4-dien-6-ol was prepared from Et-MgBr and sorbinaldehyde (Aldrich) according to the procedure of Kuhn and Grundmann.[50] The mixture was neutralized with sat NH_4Cl aq to precipitate the Mg salt. Distillation of the yellow ether layer afforded the carbinol (bp 80°/12 mm). Dehydration was effected by distillation through an alumina column (Alcoa, 8 mesh, grade F-1), at 300° according to Alder and von Brachel.[27] The all-*trans* isomer was separated by crystallization at $-70°$ and purified by GLPC on Column A at 68°. Purified triene, mp 52° under N_2, was dried, transferred *in vacuo* and stored at $-80°$ under N_2.

The internal standard for the kinetic runs was mesityl-

Table 11. Kinetic data for thermal rearrangement of octa-*trans*-2,*trans*-4,*trans*-6-triene

W_0^a [mg]	W_S^b [mg]	A_B/A_S^c	A_3/A_S	A_7/A_S	A_O/A_S	A_X/A_S	t [sec × 10^{-2}]	k_1 [$sec^{-1} \times 10^6$]	T [°C]
6·007	8·244	0·0065	0·0375	0·0276	0·706	0·0226	120·0	8·92	259·7
3·497	5·632	0·0036	0·0312	0·0239	0·608	0·0145	135·0	7·60	259·7
3·921	6·173	0·0029	0·0323	0·0270	0·590	0·0182	136·2	7·85	259·7
5·770	6·489	0·0114	0·0473	0·0465	0·820	0·0300	150·0	8·67	259·7
6·151	4·541	0·0203	0·0800	0·0821	1·238	0·0431	180·0	8·47	259·7
4·530	6·940	0·0104	0·0413	0·0489	0·598	0·0273	210·0	8·21	259·6
6·980	6·381	0·0238	0·0752	0·0971	0·967	0·0468	240·6	8·46	259·7
9·518	8·576	0·0100	0·0572	0·0426	1·074	0·0229	60·0	17·86	269·5
8·675	7·724	0·0141	0·0642	0·0585	1·044	0·0227	73·8	18·22	269·5
5·348	6·801	0·0132	0·0517	0·0545	0·742	0·0182	90·0	18·97	269·5
7·415	5·792	0·0226	0·0860	0·101	1·121	0·0282	108·0	17·10	269·5
7·751	6·435	0·0138	0·0649	0·0494	1·142	0·0110	21·0	55·3	284·7
3·791	5·797	0·0139	0·0454	0·0446	0·626	0·0115	31·8	56·3	284·8
4·947	7·602	0·0176	0·0536	0·0640	0·576	0·0119	42·0	57·4	284·7
4·647	7·538	0·0261	0·0635	0·0990	0·468	0·0126	69·0	54·7	284·7
10·578	7·668	0·0141	0·0758	0·0402	1·406	0·0167	6·00	170·8	298·7
7·026	6·744	0·0211	0·0816	0·0788	0·949	0·0183	12·0	165·0	298·7
8·116	10·052	0·0274	0·0768	0·0967	0·656	0·0175	18·0	164·3	298·7
5·797	7·883	0·0371	0·0826	0·129	0·507	0·0186	27·0	158·5	298·7
7·796	7·537	0·0672	0·136	0·235	0·622	0·0269	36·0	158·7	289·8
9·398	8·579	0·0225	0·0891	0·0874	1·014	0·0166	6·00	346·6	310·1
7·261	5·584	0·0469	0·132	0·171	1·006	0·0249	9·60	345·5	310·1
7·201	7·465	0·0406	0·103	0·151	0·721	0·0233	12·0	314·9	310·1
8·988	5·855	0·0933	0·193	0·331	0·936	0·0248	18·0	296·7	310·1
7·655	6·239	0·114	0·199	0·392	0·550	0·0269	27·0	330·1	310·2

[a] Weight of octatriene. [b] Weight of standard mesitylene. [c] A_B is the rel. area of the by-products; A_S is the rel. area of standard; A_3 the rel. area of 1,6-dimethylcyclohexa-1,3-diene; A_7 that of 1,2-dimethylcyclohexa-1,3-diene; A_O that of recovered starting octatriene; A_X that of octa-*trans*-2,*trans*-4,*cis*-6-triene.

ene which was purified on column A. When 30 mg of octatriene was heated in the 12-l Pyrex flask at 300° for 30 min, a mixture of products was obtained which could be separated by GLPC on column A: cpd 1, 0. 157 (retention time relative to mesitylene); 2, 0·193; 3, 0·228; 4, 0·283; 5, 0·294; 6, 0·350; 7, 0·415; 8, 0·63; and 9, 0·73.

Cpd **3** is 1,6-dimethyl-1,3-cyclohexadiene by identity of its NMR and UV spectra as reported by Marvell.[18] Cpd **5** revealed the following spectral data: λ_{max}^{EtOH} 262 nm; *m/e* (16 ev) 108 and 93; NMR (δ): 1·73 (s); 1·98 (br t); 5·50 (br s); allyl: vinyl ratio, 5·00: 1·03; IR (cm^{-1}): 3030, 3000, 1590 (vw), 1450, 1380 (d) and 880. Cpd **7**: λ_{max}^{EtOH} 264 nm *m/e* (20 ev): 108, 93, 91, 77; NMR (δ): 1·70 (s, 3·50 H); 2·03 (s, 1·99); and 5·62 (s, 1·05); IR (cm^{-1}): 3040, 1650, 1596, 1440, 1380 and 700. Cpd **6**; λ_{max}^{EtOH} 236 nm; NMR (δ): 1·85 (s); 2·2 (m); 4·85 (m); 5·65 (m); IR (cm^{-1}): 3080, 1650, 1580, 1440, 1370, 1360 and 880. Cpd **9** had NMR and UV spectra identical with those of an authentic sample of octa-*trans*-2,*trans*-4,*cis*-6-triene prepared according to the method of Alder and von Brachel.[27] Cpd **8** was identified as starting material. Cpds **1**, **2**, **4** and **6** were present in small amount and were not identified.

When a purified sample of cpd **7** was heated in the 12-l Pyrex flask at 300° for 30 min, the same mixture of products (but for the absence of cpds **8** and **9**) was obtained.

When octa-*trans*-2,*trans*-4,*trans*-6-triene was heated in a 460-ml ampoule of lead-potash glass for 90 min at 285°, cpd **9** was formed in essentially the same ratio to cpds **1**–**7** as had been obtained in the Pyrex flask.

The kinetic runs were carried out in the usual manner in the 12-l Pyrex flask which had been seasoned by being heated with 75–100 mg of a mixture of octa-*trans*-2,*trans*-4,*trans*-6-triene and octa-*trans*-2,*trans*-4,*cis*-6-triene at 300° for 12 hr. Analysis was effected on column A. Relative to mesitylene, correction factors of all-*trans* octatriene, DMCH-1, 2 and 3 are 1·10, 0·954, 0·986 and 1·00, respectively. Early in the run DMCH-1 is the major product and the ratio of DMCH-2 to DMCH-3 is high. As the reaction proceeds this ratio drops. The results of four runs at 297·8° is shown in Table 10 and the data on which the kinetic parameters are based are given in Table 11.

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