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A RAPIDLY REVERSIBLE DEGENERATE COPE REARRANGEMENT

BICYCLO[5.1.0]OCTA-2,5-DIENE

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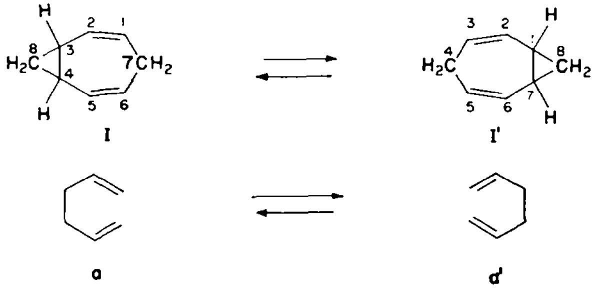
Abstract—The occurrence of a structurally degenerate Cope rearrangement which proceeds rapidly at room temperature is revealed by the examination, at varying temperatures, of the N.M.R. spectrum of bicyclo[5.1.0]octa-2,5-diene (I). This molecule is made by the cyclopropanation of cycloheptatriene in the 3, 4 position according to Gaspar-Roth. Its structure is assigned by virtue of its conversion to bicyclo[5.1.0]octane on catalytic hydrogenation and its failure to absorb U.V. light at $\lambda > 210$ mμ.

At 225°, its double-bond isomer, bicyclo[5.1.0]octa-2,4-diene (II), rearranges to cycloöcta-1,3,5-triene which is subsequently transformed to benzene (and ethylene ?) and a substance tentatively assigned the structure, tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (III). This latter material appears to arise from and be in equilibrium with 5-vinylcyclohexa-1,3-diene (IV) through the relationship of an intramolecular Diels-Alder reaction.

The hypothetical tricyclo[3.3.2.$0^{4,6}$]deca-2,7,9-triene (VII) is a uniquely interesting molecule in which individual carbon atoms must circulate freely about the structure quite independently of each other if the Cope rearrangement operates.

"Bicyclo[5.1.0]octa-2,5-diene (I)" brings a new combination of familiar features to the set of transition states which comprises the Cope rearrangement of hexa-1,5-dienes.[2–6] The most obvious feature of the Cope rearrangement is its inherent symmetry, a characteristic so striking that the simplest, albeit unrealized,[7] rearrangement



I I'

a a'

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[1] We are deeply grateful to the Aaron E. Norman Fund, Inc. for the award of the 1960 and 1961 Hickrill Chemical Research Foundation Postdoctoral Fellowship in Organic Chemistry to Dr. Wolfgang R. Roth.

[2] A. C. Cope and E. M. Hardy, *J. Amer. Chem. Soc.* **62**, 441 (1940).

[3] A. C. Cope, C. M. Hofmann and E. M. Hardy, *J. Amer. Chem. Soc.* **63**, 1852 (1941).

[4] A. C. Cope, K. E. Hoyle and D. Heyl, *J. Amer. Chem. Soc.* **63**, 1843 (1941).

[5] H. Levy and A. C. Cope, *J. Amer. Chem. Soc.* **66**, 1684 (1944).

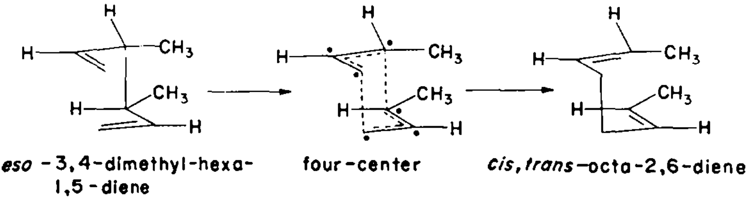
[6] E. G. Foster, A. C. Cope and F. Daniels, *J. Amer. Chem. Soc.* **69**, 1893 (1947).

[7] Although a study of the kinetics of the disappearance of hexa-1,5-diene on heating has been reported by D. J. Ruzicka and W. A. Bryce, *J. Can. Chem.* **38**, 827 (1960), the measured activation energy of 31. 3 kcal/mole probably refers to the combination of several reactions and not to the primary breaking to two allyl radicals. We hope to shed light on the primary step by examining the behavior of a dideuterohexa-1,5-diene.

of hexa-1,5-diene (α) to itself (α′) involves no structural change. One consequence of this symmetry is the intrinsic reversibility of the rearrangement which is often masked by an excessive thermodynamic bias in favor of one or the other of the conjugate pairs. Although Levy and Cope[6] have satisfactorily demonstrated reversibility in the system 1- and 3-methylhexa-1,5-diene, no fully symmetrical example is to be found in the literature.[8] The interconversion of bicyclo[5.1.0]octa-2,5-diene (I) to the superimposable mirror image of itself (I′) represents such a fully symmetrical, completely reversible Cope rearrangement.

Among the many types of reactions which can be assigned to the set of transition states comprising the uncatalyzed homolysis of sp^3–sp^3, carbon–carbon bonds, the Cope rearrangement represents the influence of two conjugated double bonds on the breaking bond, while the pyrolysis of butene-1[9] represents the effect of conjugation with one double bond. The activation energy for the homolysis of butene-1 to a methyl radical and an allyl radical is 61·5 kcal/mole, or 21·8 kcal/mole lower than the activation energy of 83·3 kcal/mole reported for the homolysis of ethane.[10] By an hypothesis of additivity, one estimates the activation energy for the breaking of the central bond in hexa-1,5-diene to two allyl radicals to be about 39·7 kcal/mole [83·3 kcal/mole less 2(21·8 kcal/mole)].[7] To obtain an estimate of the activation energy of the Cope rearrangement (of hexa-1,5-diene), one must subtract from 39·7 kcal/mole the energy of overlap of two allyl radicals, the factor which converts a comparatively facile but otherwise uninteresting homolysis of a carbon-carbon bond to the highly organized, intramolecular Cope rearrangement.

Although the magnitude of the force holding two, more or less parallel allyl radicals together is not known at the present time,[7] the geometry of the complex of two allyl radicals comprising the transition state of the Cope rearrangement has recently been specified in some detail.[11] The favored arrangement is a four-center state involving overlap between the ends of the two allyl radicals, but not between the middle carbon atoms. From the fact that *meso*-3,4-dimethylhexa-1,5-diene rearranges to *cis,trans*-octa-2,6-diene, it has been estimated that the four-center state is preferred over the six-center by at least 6 kcal/mole.



The contribution of strain in the cyclopropane ring to the breaking of the carbon–carbon bond has been evaluated quite ingeniously by Rabinovitch, Schlag and Wiberg[12]

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[8] Cf. the relevant examples of R. B. Woodward and T. J. Katz, *Tetrahedron* **5**, 70 (1959) and R. P. Lutz and J. D. Roberts, *J. Amer. Chem. Soc.* **83**, 2198 (1961).

[9] A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* **A202**, 263 (1950).

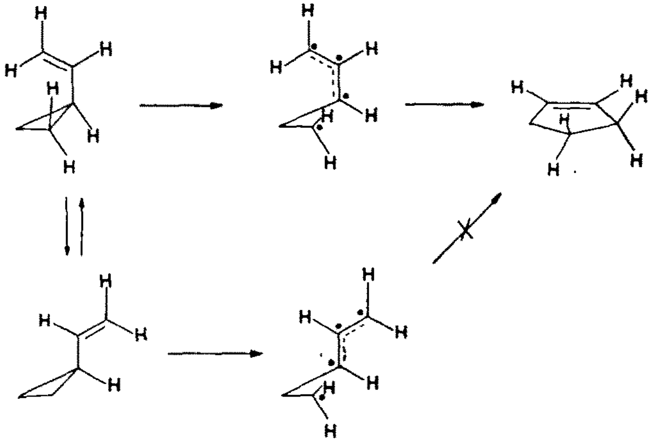
[10] T. L. Cottrell, *The Strengths of Chemical Bonds* p. 201. Academic Press, New York (1954). In view of the uncertainties in our much simplified approach and in many of the bond energies themselves, it is best to make ethane the reference standard in this paper and worry later about possible corrections and refinements.

[11] W. von E. Doering and W. R. Roth, *Tetrahedron* **18**, 67 (1962).

[12] B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.* **28**, 504 (1958).

by measuring the activation energy of the epimerization of *cis*,-1,2-dideuteriocyclopropane. The difference (19·1 kcal/mole) between this activation energy (64·2 kcal/mole) and the activation energy of breaking ethane into two methyl radicals (83·3 kcal/mole)[10] is a measure of the fraction of the total strain in cyclopropane (27 kcal/mole)[13] available for lowering the energy of the bond-breaking transition state.

The consequence of combining the effects of the strain of a three-membered ring and the delocalization energy of one double bond on the breaking of the carbon–carbon bond is manifest in the rearrangement of vinylcyclopropane to cyclopentene, discovered by Overberger and Borchert.[14] The activation energy (49·6 kcal/mole) of this rearrangement, measured by Flowers and Frey,[15] is to be compared with a value of 42·4 kcal/mole calculated by subtracting the contributions of ring strain (19·1 kcal/mole) and allyl delocalization (21·8 kcal/mole) from the value (83·3 kcal/mole) of the bond strength of ethane. The agreement is good enough to give some encouragement to the further exploration of the hypothesis of additivity. The calculated value doubtless applies to the process in which opening of the cyclopropane bond produces the *trans* allyl radical of lower energy, from which closure to cyclopentene is not possible without further geometrical readjustment. Opening to the fruitful *cis* allyl radical must require a little more energy, perhaps 1–2 kcal/mole. In addition, the strain-free arrangement which brings the methylene groups of the two radicals closest together is actually one in which they are perpendicular and not essentially parallel to each other as they must be in the final product, cyclopentene. How much additional activation energy, if indeed any, is needed to overcome this unfavorable disposition, seems impossible to estimate at the present time



The combination of two double bonds and one cyclopropane ring has been investigated most elegantly in its simplest form by Vogel *et al.*[16–18] Of the two stereoisomers

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[13] S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.* **71**, 261 (1952).

[14] C. O. Overberger and A. E. Borchert, *J. Amer. Chem. Soc.* **82**, 1007, 4891 (1960).

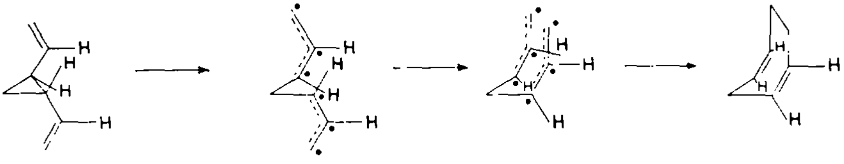
[15] M. C. Flowers and H. M. Frey, *J. Chem. Soc.* 3547 (1961).

[16] E. Vogel, *Angew. Chem.* **72**, 4 (1960).

[17] E. Vogel, K.-H. Ott and K. Gajek, *Liebigs Ann.* **644**, 172 (1961).

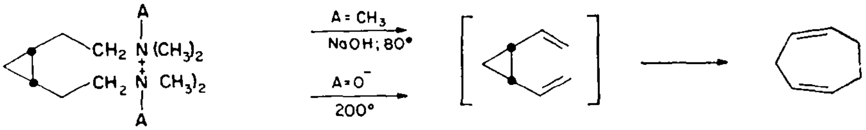
[18] E. Vogel and R. Erb, *Angew. Chem.* (*Inter. Ed.*) **1**, 53 (1962).

studied by them, *trans*-1,2-divinylcyclopropane[18] is especially interesting since the rigid geometry of the cyclopropane ring obliges the central bond to break without assistance from the allyl overlap so vital to the very existence of the Cope rearrangement. Both the preferred four-center overlap and a pure six-center overlap are precluded. To be fruitful, bond-opening in the *trans*-isomer must generate both allyl components in the *cis*-geometrical configuration; and these two *cis* allyl radicals must then rotate from a *trans* to a *cis* relationship which, at best, permits overlap of the two allyl radicals in the unfavored six-center arrangement. Only then may the reaction be concluded by closure to cyclohepta-1,4-diene. Aside from the complication that double bonds must be generated *cis* in the fruitful transition state, this reaction is a simple homolysis in which two allyl delocalizations and the partial relief of the strain of one cyclopropane contribute to the lowering of the activation energy. The estimated activation energy of 20·6 kcal/mole [83·3–2(21·8)–19·1], although somewhat low for a reaction occurring at 190°,[18] is in the right range, and should be raised by twice the amount by which allyl radicals are more difficult to form in the *cis* configuration than in the *trans*.



The relative of *trans*-divinylcyclopropane in which the intramolecular characteristics of the Cope rearrangement might be expected to add their influence to the lowering of the energy of the transition state is *cis*-divinyl cyclopropane. Unfortunately, this substance has not as yet been isolated.

Vogel *et al.*[17] have attempted its synthesis from *cis*-(1,2-*bis*-β-dimethylaminoethyl) cyclopropane by the pyrolysis of the amine oxide and by the Hofmann elimination of trimethylamine from the corresponding *bis*-quaternary ammonium salt. In both reactions, including the latter at 80°, the product was cyclohepta-1,4-diene instead of *cis*-1,2-divinylcyclopropane. This event was rationalized by the hypothesis, among other reasonable ones,[19] that *cis*-1,2-divinylcyclopropane had indeed been formed initially, but had been transformed to the cyclohepta-1,4-diene by a very rapid Cope rearrangement. The contribution of this extraordinarily facile conversion to the mechanism would be considerably enhanced were direct experimental investigation of *cis*-1,2-divinylcyclopropane to become possible.



In another try at the isolation of *cis*-1,2-divinylcyclopropane, we have applied

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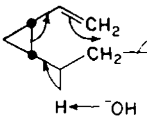
[19] For example, it is conceivable that the first intermediate anticipated in the Hofmann elimination might undergo a concerted opening of the cyclopropyl ring and displacing of trimethylamine in which cyclohepta-1,4-diene was produced directly.



the Gaspar-Roth recipe to *cis*-hexa-1,3,5-triene.[20] In this procedure a dried stream of diazomethane in nitrogen is passed into a suspension of cuprous chloride in the substrate. The chemistry of this method of cyclopropanation is not new. Copper-catalyzed decomposition of diazoacetic ester as a method of forming cyclopropane carboxylic esters from olefins goes back to Loose,[21] although credit for the first structurally unequivocal example is due to Ebel *et al.*[22] Several recent examples of the reaction have been given by D'yakonov *et al.*,[23] who have also reported two examples of the copper-catalyzed addition of diphenyldiazomethane.[24] Stereochemically the addition is *cis* and largely *exo*.[25] The first copper-catalyzed addition of diazomethane itself to olefins seems to have been reported by Dull and Abend.[26]

Although benzene and its derivatives are not converted to tropilidenes by the copper-catalyzed decomposition of diazoacetic ester,[27,28] it has been discovered, independently in three laboratories, that benzene is subject to attack by the intermediate in the copper-catalyzed decomposition of diazomethane.[29–31] Gaspar found this to be the only method of preparing structurally homogeneous 7,7-dideuterotropilidene, since the light needed to effect the photochemical addition of dideuterodiazomethane causes secondary rearrangement of deuterium. Gaspar's method involves passing gaseous diazomethane, carried by a stream of nitrogen into a suspension of copper powder in benzene. Roth shortly thereafter developed the method into a convenient, small-scale, general procedure for cyclopropanation of olefinic double bonds and found cuprous chloride to be an excellent catalyst. Although the procedure lacks chemical novelty, it may be commended for its convenience.

Among the products of the application of the Gaspar-Roth recipe to *cis*-hexa-1,3,5-triene, are *cis*-1-cyclopropylbutadiene, *cis*-1-cyclopropyl-2-vinylcyclopropane, *cis*-1,2-dicyclopropylethylene and *cis*-1,2-dicyclopropylcyclopropane, molecules whose properties and behavior on thermal reorganization will be discussed elsewhere in a paper on the vinylcyclopropane rearrangement. *cis*-1,2-Divinylcyclopropane could not be detected among the products of the reaction, either at room temperature or at −45°. Instead there appeared cyclohepta-1,4-diene and the products of its further cyclopropanation. Cyclohepta-1,3-diene, hypothetically the product of 1,6-addition of methylene to *cis*-hexa-1,3,5-triene, was not among the products.

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[20] J. C. H. Hwa, P. L. de Benneville and H. J. Sims, *J. Amer. Chem. Soc.* **82**, 2537 (1960).

[21] A. Loose, *J. Prakt. Chem.* **79**, 505 (1909).

[22] Fr. Ebel, R. Brunner and P. Mangelli, *Helv. Chim. Acta* **12**, 19 (1929).

[23] I. A. D'yakonov, *Zh. Obsh. Khim.* **19**, 1734, 1891 (1949); **20**, 2289 (1950); I. A. D'yakonov and N. A. Lugovtsova, *Ibid.* **21**, 839 (1951); I. A. D'yakonov and N. D. Pirogova, *Ibid.* **21**, 1979 (1951); I. A. D'yakonov and N. B. Vinogradova, *Ibid.* **22**, 1349 (1952); I. A. D'yakonov and V. F. Myznikova, *Sbornik Statei Obsh. Khim. Akad. Nauk S.S.S.R.* **1**, 489 (1953); I. A. D'yakonov, I. N. Somnin and M. I. Komendantov, *Zh. Obsh. Khim.* **23**, 1641 (1953).

[24] I. A. D'yakonov, *Zh. Obsh. Khim.* **21**, 1986 (1951); I. A. D'yakonov and O. V. Guseva, *Ibid.* **22**, 1355 (1952).

[25] W. von E. Doering and T. Mole, *Tetrahedron* **10**, 65 (1960); P. S. Skell and R. M. Etter, *Proc. Chem. Soc.* 443 (1961).

[26] M. F. Dull and P. G. Abend, *J. Amer. Chem. Soc.* **81**, 2588 (1959).

[27] Ch. Grundmann and G. Ottmann. *Liebigs Ann.* **582**, 163 (1953).

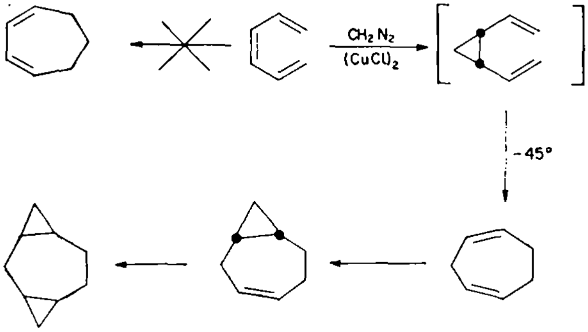
[28] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **78**, 4947 (1956).

[29] E. Müller, H. Fricke and W. Rundel, *Z. Naturforsch.* **15b**, 753 (1960).

[30] P. P. Gaspar, Doctoral Dissertation, Yale (1961), in collaboration with W. von E. Doering.

[31] G. Wittig and K. Schwarzenbach, *Liebigs Ann.* **650**, 1 (1961).

Cyclohepta-1,4-diene was identified by comparison of its I.R. spectrum with that reported by Vogel *et al.*[17] and synthesized quite conveniently by the reduction of cycloheptatriene with sodium in alcohol. The products of further cyclopropanation were synthesized independently by applying the Gaspar–Roth recipe to cyclohepta-1,4-diene.



The structure of the monocyclopropanation product bicyclo[5.1.0]oct-3-ene follows from the method of synthesis, the presence in the I.R. spectrum of a band at 1020 cm^{-1} corresponding to a cyclopropane ring and a band at 1640 cm^{-1} corresponding to a *cis*-double bond (—CH═CH—) and the presence in the N.M.R. spectrum of peaks at $\tau = 4{\cdot}55$ p.p.m. corresponding to vinyl hydrogen and peaks at $\tau = 9{\cdot}2$ p.p.m. corresponding to the methylene group of cyclopropane. The two doubly cyclopropanated derivatives *cis*- and *trans*-tricyclo[6.1.0.0^{3,5}]nonane have no vinyl hydrogen atoms in the N.M.R. spectrum and show strong absorption in the region $\tau = 10$ p.p.m. by the cyclopropyl methylene group. This structural feature is confirmed by the presence in the I.R. of absorption at 1020 cm^{-1}.

To be quite sure that migration of double bonds during the Gaspar–Roth cyclopropanation was not invalidating the method of synthesis as one of the bases for assigning the structure, cyclohepta-1,3-diene was treated in the same way. The three products, bicyclo[5.1.0]oct-2-ene and *cis*- and *trans*-tricyclo[6.1.0.0^{2,4}]nonane, were distinctly different in gas chromatographic retention times, infrared spectra and N.M.R. spectra.

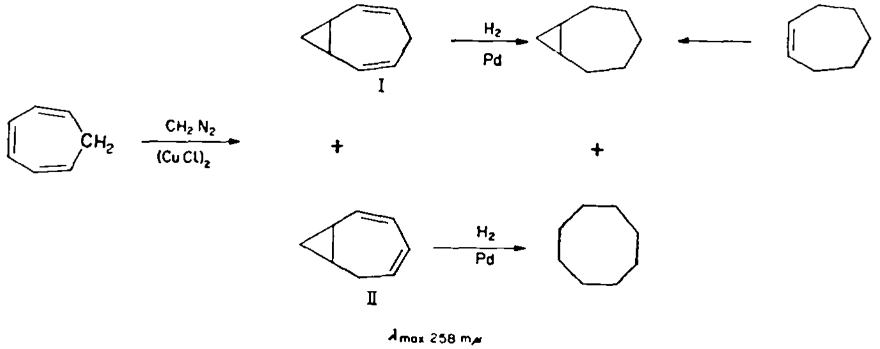
It seems reasonable to consider *cis*-1,2-divinylcyclopropane as the precursor of cyclohepta-1,4-diene. This hypothesis requires that the active species in the copper-catalyzed reaction of diazomethane be able to react with the twice conjugated double bond of the triene. As some support of this condition, one can adduce the fact that *trans*-hexa-1,3,5-triene reacts, among other ways, at its similarly conjugated double bond to give *trans*-1,2-divinylcyclopropane.

Granting that *cis*-1,2-divinylcyclopropane is the precursor does not then justify the further assumption that the rate of its rearrangement at −45° is too rapid to allow isolation. The immediate product of the addition of methylene to the triene must contain the doubtlessly large exothermicity of the reaction and might rearrange rapidly as a thermally excited, "hot" cyclopropane before the excess energy is dissipated. Normally, excess vibrational energy is lost very rapidly in solution and the fact that *trans*-1,2-divinylcyclopropane can be isolated is a counterargument to the hypothesis of a "hot" intermediate, but not a very strong one. The state of affairs concerning the rate of the Cope rearrangement of *cis*-1,2-divinylcyclopropane remains virtually unchanged: until the molecule can be isolated and examined *per se*, our observations and those of Vogel *et al.*[17] indicate strongly but not conclusively that the rearrangement is too fast at 80° and, perhaps even at —45°, to permit isolation.

If the rearrangement of *cis*-1,2-divinylcyclopropane is indeed fast at room temperature or thereabouts, incorporation of the system into a ring might accelerate the rearrangement and make estimation of the rate accessible to study by the N.M.R. technique. Bicyclo[5.1.0]octa-2,5-diene or 3,4-homotropilidene (I) is such a molecule and, indeed, has been recognized by Vogel as an interesting extension of his work with the divinylcyclopropanes.[32] Cope rearrangement within this molecule generates the starting structure and leads to no permanent change.

A reasonable route to its synthesis, the photolysis of diazomethane in tropilidene, has recently been investigated by Alder and Krane.[33] G.l.p.c. indicated the formation of two components, of which the major one was separated by fractional distillation and claimed to be bicyclo[5.1.0]octa-2,4-diene (II) on the basis of hydrogenation to bicyclo[5.1.0]octane and conversion to a crystalline adduct with maleic anhydride, while the minor one was not isolated in pure state. It was concluded to be a methylcycloheptatriene from the fact that catalytic hydrogenation of a 40% mixture with the major product (60%) gave a product showing the infrared absorption (1375 cm^{-1}) characteristic of methyl groups. Despite the use of g.l.p.c. to analyze the mixture of products, the absence of details makes it impossible to decide whether I was formed at all in the reaction.

Application of the Gaspar–Roth recipe to tropilidene leads to a simple, convenient synthesis of both I and II.[34] Although it is not possible to avoid entirely the formation of di- and tri-cyclopropanated derivatives, methylated products arising by insertion into carbon-hydrogen bonds are not formed. The presence of a cyclopropane ring in I is indicated by bands at 1005 and 1040 cm^{-1} in the I.R. spectrum, and the isolation of bicyclo[5.1.0]octane from the products of catalytic hydrogenation. II is likewise hydrogenated to bicyclo[5.1.0]octane. Whereas I does not absorb light



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[32] Communicated publicly by Professor E. Vogel, University of Cologne, during the discussion of a paper, *The Cope Rearrangement*, presented April 25, 1961 by W. von E. Doering at the Heidelberg Chemischen Gesellschaft.

[33] W. Krane, Inaugural-Dissertation, Universität, Köln in collaboration with the late Professor K. Alder, 1960.

[34] This work was presented on 14 December 1961 at the A. M. Butlerov Centennial Symposium on Theoretical Organic Chemistry in Leningrad, U.S.S.R. [W. Doering, *Zh. Vsesoyuz. Khim. Obshchestva im D. I. Mendeleeva* 7, 308 (1962)].

above 215 mμ, its conjugated counterpart II absorbs at 258 mμ (ϵ 4200), in much the same manner as cyclohepta-1,3-diene.[35]

The most important property of 3,4-homotropilidene (I) is revealed by its N.M.R. spectra (Fig. 1). At room temperature, the only clearly discernible feature is a peak of relative area 4 centered at $\tau = 4{\cdot}2$ p.p.m. This peak arises from the four hydrogen atoms in I of the vinyl type. For the rest, the spectrum is uselessly broad and ill-defined. At lower temperature (−50°) the spectrum becomes well-resolved and rich in fine structure. The gross interpretation is clear and unequivocal: the spectrum at room temperature is that of two or more molecules in equilibrium. As the temperature is raised the spectrum becomes sharper again until, at 180°, a well-resolved spectrum with considerable fine structure has been achieved. Cooled to −50°, the previous spectrum reappears without modification.

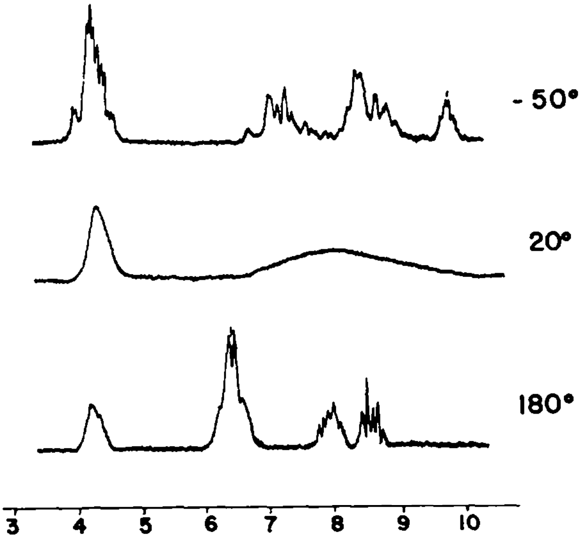

FIG. 1. N.M.R. spectra of bicyclo[5.1.0]octa-2,5-diene (3,4-homotropilidene, I) in carbon tetrachloride solution at −50°, 20° and 180°, respectively, in p.p.m. with tetramethylsilane taken as $\tau = 10{\cdot}0$ p.p.m.

The temperature dependence of the N.M.R. spectrum may be caused by a change in position of equilibrium between two molecules, one of which is thermodynamically favored at low temperature, the other at high. Thus, 3,4-homotropilidene (I) may exist in a *trans*-like and a *cis*-like conformation (see Fig. 2) of which the latter can reasonably be expected to be the less stable thermodynamically. However, this explanation is inconsistent with the fact that the infrared spectrum does not change when the temperature is raised from 20° to 185°. Thus, the instantaneous structure of the molecule is independent of temperature within the range, 20–185°, and probably, within the range, −50 to 185°. The conclusion is clear: at all temperatures the observed N.M.R. and I.R. spectra pertain to the same molecule.

The temperature dependence of the N.M.R. spectra may be consistently explained in terms of a Cope rearrangement. Were this reaction sufficiently rapid at the higher temperature, the N.M.R. spectrum would be "averaged" over the two valence

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[35] E. Pesch and S. L. Friess, *J. Amer. Chem. Soc.* 72, 5756 (1950).

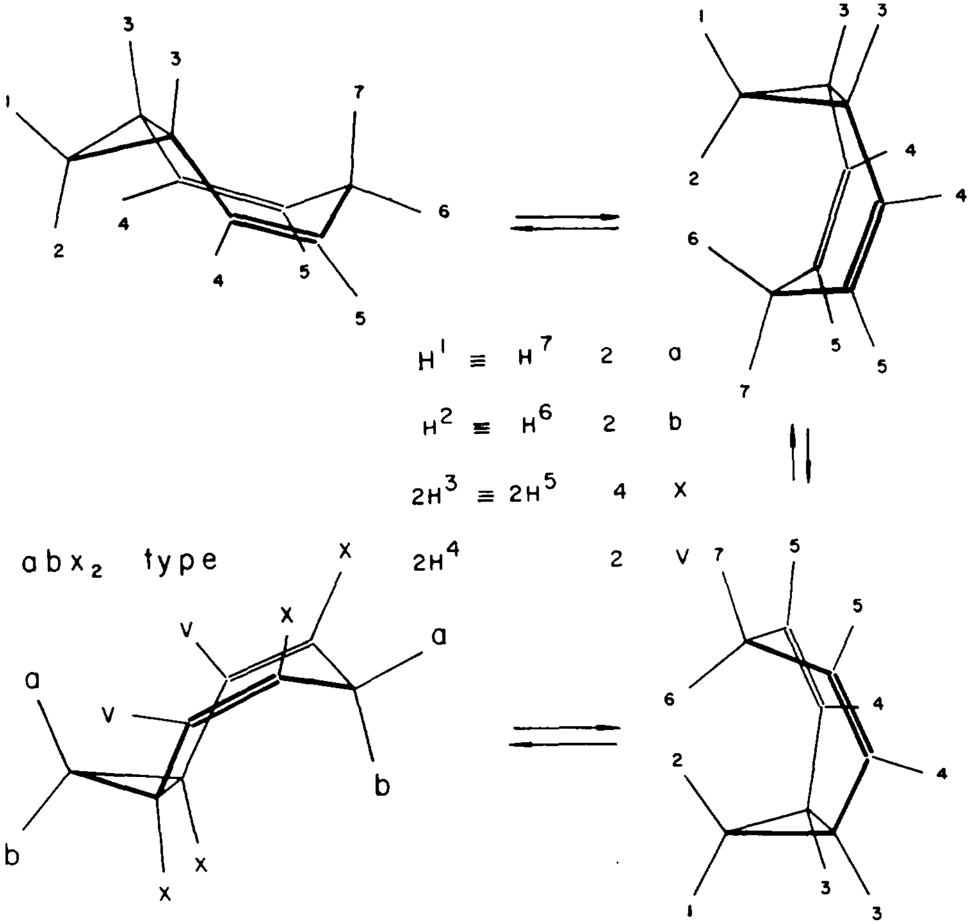

FIG. 2. 3,4-Homotropilidene (I): *trans* and *cis* conformations and structural consequences of the Cope rearrangement.

tautomeric forms[36] and the shape of the spectrum would depend on temperature, provided the rate of the Cope rearrangement were slow enough at the lower temperature to give one form of the molecule a half-life longer than ca. 1 sec.

The *trans*-like and *cis*-like conformations of 3,4-homotropilidene are shown in Fig. 2. In the *cis* form, the proximity of hydrogen atoms 2 and 6 must give rise to considerable interpenetration or transannular non-bonded repulsion and, as a consequence, the *trans*-like structure is considered to be favored over the entire range of temperature. If the rate of the Cope rearrangement is slow enough, the *trans* form will have an N.M.R. spectrum at −50° arising from seven different kinds of hydrogen atoms. In fact, one can discern four vinylic hydrogen atoms at about 4·3 p.p.m., two different methylenic hydrogen atoms of the allylic type in the region about 7·2 p.p.m. and a single cyclopropyl hydrogen, possibly H^1, at 9·7 p.p.m. The two tertiary cyclopropyl hydrogen atoms, $2H^3$, appear in the region between 8–9 p.p.m. with the

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[36] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York (1959).

other secondary cyclopropyl hydrogen, H^2, which has apparently been shifted down-field by the double bonds.

The Cope rearrangement, which becomes increasingly rapid as the temperature is raised, cannot occur economically of activation energy in the *trans* conformation because the dihedral angle between carbon-hydrogen bonds 3 and 4 is about 80° and far from the 0° it assumes in the strain-free form of the rearranged molecule. In the *cis* conformation the dihedral angle is 10°, close to the optimum of 0°. Although the *trans* form is probably favored thermodynamically over the *cis*, we guess that the kinetic factor is decisive and that the rearrangement occurs over the *cis* conformation. On the assumption that the interconversion of the *trans* conformation to the *cis* has an activation energy lower than that of the Cope rearrangement, the free energy of activation of the Cope rearrangement of the *trans* conformation is given by the sum of the free energy of activation of the rearrangement of the *cis* conformation and the difference in free energy of the *cis* and *trans* conformations.

Cope rearrangement occurring in the *cis* form (Fig. 2) leads to the conversion of H^1 of the cyclopropyl type to H^7 of the methylene type and *vice versa*; at the same time H^2 and H^6 are interconverted. In a pair of "Cope" tautomers, H^1 and H^7 and H^2 and H^6 become equivalent and may be relabeled 2H^a and 2H^b, respectively. The pair of cyclopropyl hydrogen atoms, 2H^3, becomes 2H^5, of the vinylic type, and *vice versa*. These four hydrogen atoms may then be relabeled 4H^x. Only the two vinylic hydrogen atoms, 2H^4, remain unaltered by the rearrangement (2H^v). In terms of the N.M.R. spectrum, sufficiently rapid Cope rearrangement changes 3,4-homotropilidene from a molecule described by seven different types of hydrogen atom to one described by four.

The actual changes in the N.M.R. spectrum which occur on raising the temperature from $-50°$ to $+180°$ are identical with those predicted by the hypothesis of a rapid Cope rearrangement. The number of vinylic hydrogen atoms in the region of 4·3 p.p.m. has dropped from four (2H^4 + 2H^5) to two (2H^v); two of these hydrogen atoms (2H^5) have mixed with two of the cyclopropyl hydrogen atoms (2H^3) in the region of 8·9 p.p.m. to give a new group of area four (4H^x) in the region about 6·4 p.p.m.; at the same time each one of the methylenic hydrogen atoms of the cyclopropyl ring (H^1 and H^2) has mixed with its opposite number in the allylic methylene (H^7 and H^6) to give a new absorption of area 4(2H^a and 2H^b) centered at 8·2 p.p.m. These two pairs are coupled with the hydrogen atoms of the x type to produce two independent groupings of the abx$_2$ type. The near mirror symmetry of the ab part of this spectrum about 8·2 p.p.m. is typical of this type of system. It need only be mentioned that in some of the higher temperature spectra the expected triplet character of the 2H^v group at 4·2 p.p.m. could be discerned.

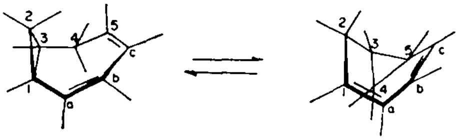
The rate of the Cope rearrangement at 180° is high enough to effect the mixing of 2H^3 and 2H^5. In the low temperature spectrum these pairs are separated by about 4·4 p.p.m. or 260 c.p.s. Thus, for complete mixing the half-life of an individual molecule of 3,4-homotropilidene in a fixed structure must be less than about $\frac{1}{260}$ sec. It is clear that this rate of rearrangement has not been achieved at room temperature but is reached by about 150°. It is also clear that by $-50°$ the half-life has increased to the order of 1 sec or longer. In principle, the kinetics of the rearrangement can be worked out by a closer examination of the dependence of the spectrum on temperature. In practice, the complexity of both the low temperature (unmixed) and the high temperature (mixed) spectra make this analysis an arduous task.

Over a large temperature range, the qualitative conclusion is clear: a single structure does not fairly represent 3,4-homotropilidene over a reasonable time average. From a classical point of view, the parent molecule does not have a single structure and the number and behavior of its substituted derivatives will be conditioned by this fact.

It is interesting to ask how much farther one will be able to go in the direction of accelerating the rate of the Cope rearrangement. The freedom of 3,4-homotropilidene to assume the thermodynamically favored *trans* conformation when the *cis* conformation is the more conducive to rearrangement is an unfavorable factor which can easily be removed by replacing hydrogen atoms 2 and 6 with a carbon bridge. Whether such a modification will suffice to achieve the limit in which the two classical structures no longer represent separate mimima in potential energy, each with its own set of vibrational modes, but the two extremes of a normal vibration mode of a single molecule, remains to be seen.[37,38] In this direction the two valleys of "tautomerism" merge into the single valley of "resonance" and the point of merging loses its definition in the uncertainty principle.

The central problem of "no-mechanism" reactions is concerned with the origin of activation energies. That 1,2-homotropilidene does not undergo a rapid valency tautomeric reorganization is somewhat surprising and therefore relevant to the general problem. The unchanging nature of the N.M.R. spectrum of II between −50° and +180° indicates the absence of a low pass comparable in energy to that available to the *cis* conformation of 3,4-homotropilidene (I).[39] Examination of Dreiding models of 1,2-homotropilidene reveals a *cis* and a *trans* conformation. Although the *cis* conformation (defined as the conformer in which the methylene group of the cyclopropyl ring is *cis* to the transannular double bond) has the proper dihedral angle between carbon–hydrogen bonds 1 and a, to stabilize the odd electron by allyl resonance and to accommodate the double bond in the rearranged product, it is also the conformation in which the two methylene groups are essentially *trans*. It appears that more drastic adjustments of bond angles and bond distances are demanded by 1,2-homotropilidene than by its more symmetrical 3,4-isomer.

When 1,2-homotropilidene is heated at higher temperature to probe the upper



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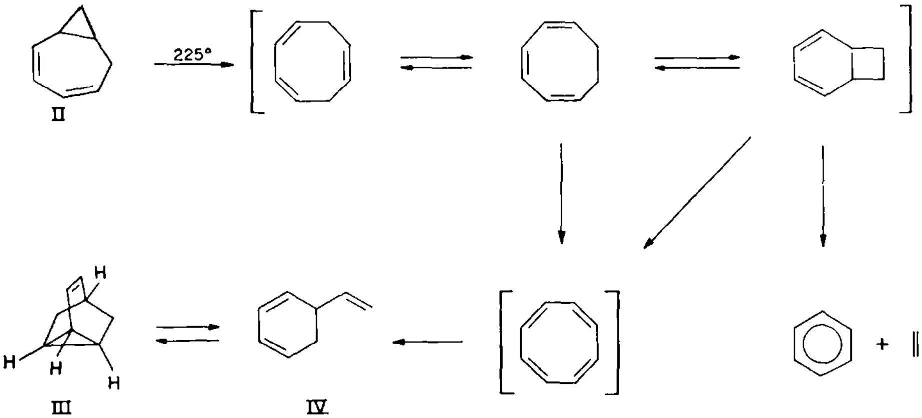
[37] Indeed, there is nothing in the present work to say that the *cis* form of 3,4-homotropilidene has not already reached such a limit, in which the lowest energy equilibrium structure is the pair of allyl radicals overlapping in the six-center arrangement. The parallel extreme of this arrangement was considered earlier[11] to be one of the possible transition states or unstable intermediates in the Cope rearrangement, but was rejected in favor of the four-center arrangement. Thus, a *trans* arrangement of allyl radicals overlapping in the four-center manner is a better candidate for the role of permanently non-classical molecule than the *cis* arrangement with six-center overlap which necessarily prevails in the *cis* conformation of 3,4-homotropilidene or one of its bridged relatives.

[38] Very recently, a molecule of the gross structure tricyclo[3.3.1.$0^{4,6}$] nona-2,7-dien-9-one has been synthesized from cycloheptatriene-7-carboxylic acid in these laboratories by Dr. Barbara M.Ferrier and has been found to have an N.M.R. spectrum corresponding, even at −50°, to that expected from the two valency tautomeric forms averaged by rapid Cope rearrangement.

[39] 8,8-Dideuteriobicyclo[5.1.0]octa-2,4-diene, presently under investigation by Dr. W. Grimme, Yale, offers a potentially more sensitive means of detecting the rearrangement.

slopes of the energy surface for new routes of escape, a pass out of the valley is encountered at a level of activation energy which, though undetermined at present, corresponds to a convenient rate of reaction at 225°. This pass leads to cycloöcta-1,3,5-triene [or to cycloöcta-1,3,6-triene or bicyclo[4.2.0]octa-2,4-diene, a question which hasn't been resolved since these three isomers are interconverted rapidly at 100°].

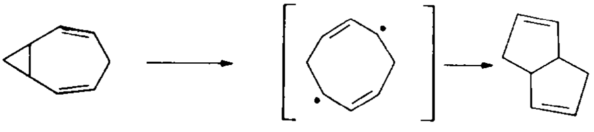


Out of this trio of valleys, two new passes, kinetically accessible at 225°, lead to benzene and a molecule III, C_8H_{10}, to which the tentative structure, tricyclo[3.2.1.$0^{2,7}$]-oct-3-ene, is assigned.

III shows two vinylic hydrogen atoms in the N.M.R. spectrum, absorbs precisely two equivalents of hydrogen catalytically to give pure bicyclo[3.2.1]octane, and is in equilibrium at 270° with an isomer IV, tentatively assigned the structure 5-vinylcyclohexa-1,3-diene. This latter molecule shows seven vinyl and three allylic hydrogen atoms in its N.M.R. spectrum and is hydrogenated catalytically to ethylcyclohexane. At 270° over nickel catalyst, the equilibrium may be approached from either direction and has a composition of 13% vinylcyclohexadiene and 87% tricycloöctene. Equilibrium is also established at 225° where the tricycloöctene (III) is even more highly favored.

The decomposition of bicycloöctene to benzene has been reported by Alder and Krane[33] and presumably follows the breaking of the C_1–C_8 bond in an unexceptional fashion. The formation of the vinylcyclohexadiene (IV)-tricycloöctene (III) pair is most easily imagined to occur by the breaking of C_7–C_8 in cycloöcta-1,3,5-triene to form octatetraene. Unexceptional triene-cyclization would afford 5-vinylcyclohexa-1,3-diene which could go on to tricyclo[3.2.1.$0^{2,7}$]oct-3-ene by an intramolecular Diels-Alder reaction. The question of the reality of these hypothetical steps is under investigation.

When 3,4-homotropilidene (I) is heated to higher temperature, a new reaction proceeding at a convenient rate at 305° is encountered of which bicyclo[3.3.0]octa-2,6-diene (V) is thought to be the product. Catalytic hydrogenation to *cis*-bicyclo-[3.3.0]octane and the N.M.R. spectrum constitute the basis for the tentative assignment of structure. Despite the fact that the formation of this molecule can be visualized so attractively in two dimensions, it appears to involve a high activation energy. Here again, models reveal the need for extensive changes in bond angles and distances in the transformation.



V

Finally, it may be mentioned that this rearrangement to bicyclo[3.3.0]octa-2,6-diene (V) proceeds quite rapidly over a supported nickel catalyst at 270° and that this same catalyst is able to divert 1,2-homotropilidene from its rearrangement to cycloocta-1,3,5-triene to a mixture of bicyclo[3.3.0]octa-2,6-diene (V) and bicyclo[3.3.0]-octa-2,7-diene (VI) in which the latter predominates.

By virtue of its potentially extraordinary properties, tricyclo[$3.3.2.0^{4,6}$]deca-2,7,9-triene (VII) or "bullvalene," as it has been colloquially named, deserves mention even though it is at present no more than an hypothetical molecule. This structure is formally derived from 3,4-homotropilidene by replacing the two offending hydrogen atoms 2 and 6 in the *cis* conformation (Fig. 2) by a third, *cis* double bond. The resulting molecule can be expected to undergo the Cope rearrangement even faster than 3,4-homotropilidene, since the freedom to change to the thermodynamically favored, but kinetically prohibitive, *trans* conformation has been permanently removed.[38] Rapid Cope rearrangement can be expected to produce the simplest of N.M.R. spectra consisting of a single, sharp band.

In Figure 3, it is seen how three reversible Cope rearrangements, each identical to the other by virtue of the three-fold axis of symmetry, successively convert each cyclopropyl atom (C_{10},C_5 and C_4) into a bridgehead atom, simultaneously with the conversion of each of the carbon atoms adjacent to the original bridgehead atom (C_1)

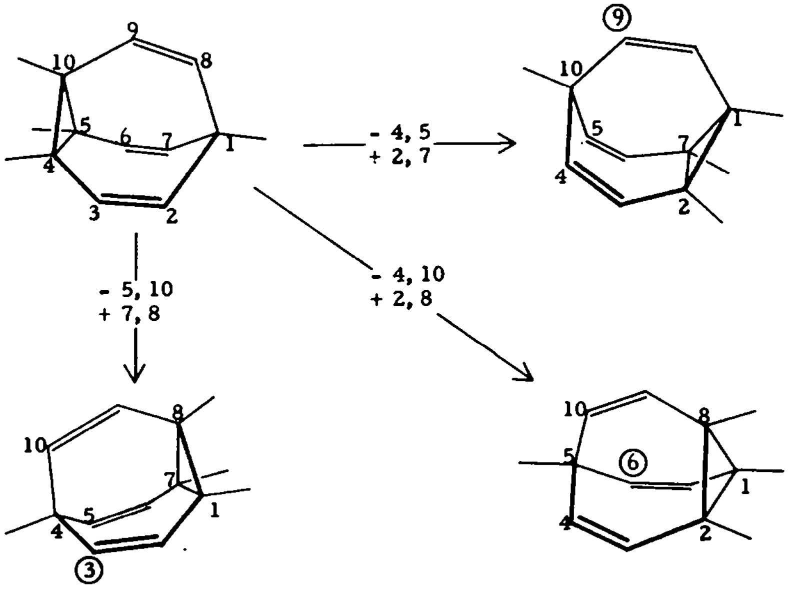


FIG. 3. The Cope rearrangement in bullvalene showing the conversions of bridgehead carbon into cyclopropyl (C_1) and conversely of cyclopropyl into bridgehead carbon atoms (C_{10}, C_5 and C_4), of carbon atoms adjacent to bridgehead (type I vinylic) into cyclopropyl (C_7 and C_2, C_8 and C_2, and C_7 and C_8), and of carbon atoms adjacent to cyclopropyl (type II vinylic) into carbon atoms adjacent to bridgehead (type I vinylic) (C_9, C_6 and C_3).

into cyclopropyl atoms (C_7 and C_2, C_8 and C_2, and C_7 and C_8, respectively). It is thus a property of a cyclopropyl carbon atom of bullvalene that one Cope rearrangement can transform it into a bridgehead atom and it is the property of carbon atoms adjacent to bridgehead atoms that they are thereby transformed into cyclopropyl carbon atoms. Since carbon atoms C_3, C_6 and C_9 (type II vinylic) are transformed into atoms adjacent to bridgehead atoms (type I vinylic) in the first wave of Cope rearrangements, they may become cyclopropyl carbon atoms in the second wave and bridgehead atoms in the third. Carbon atoms C_2, C_7 and C_8, (type I vinylic) which become cyclopropyl atoms in the first wave may become bridgehead in the second. Thus, by the occurrence of a relatively small number of Cope rearrangements every one of the ten atoms of bullvalene may be transformed into the bridgehead type. On the average, each hydrogen atom will have $\frac{1}{10}$ bridgehead character, $\frac{3}{10}$ cyclopropyl character, $\frac{3}{10}$ the character of type I vinylic and $\frac{3}{10}$ the character of type II vinylic hydrogen.

The unique, unprecedented feature of the molecule lies not so much in the expectation of only a single N.M.R. band as in the necessary consequence of this property that each of the more than 1·2 million possible arrangements of carbon atoms will be undergoing mutual interconversion. This feature of bullvalene can be followed in Fig. 4 which develops the "rotational" operation (either clockwise or counter clockwise, "cw rot" being illustrated in Fig. 4) as the consequence of a particular sequence of two Cope rearrangements, and the operation of α, γ exchange ("α, γ") as a consequence of a particular sequence of seven Cope rearrangements (1 "Cope" followed by three cw or ccw rotational operations), and in the Fig. 5 showing the operation of α, β exchange ("α, β") as a consequence of a sequence of forty-seven Cope rearrangements. It is obvious that the possibility of interchanging adjacent carbon atoms allows the interconversion of any one of the more than 1·2 million arrangements into any other. If bullvalene turns out to be protected by sufficiently high barriers from escaping down

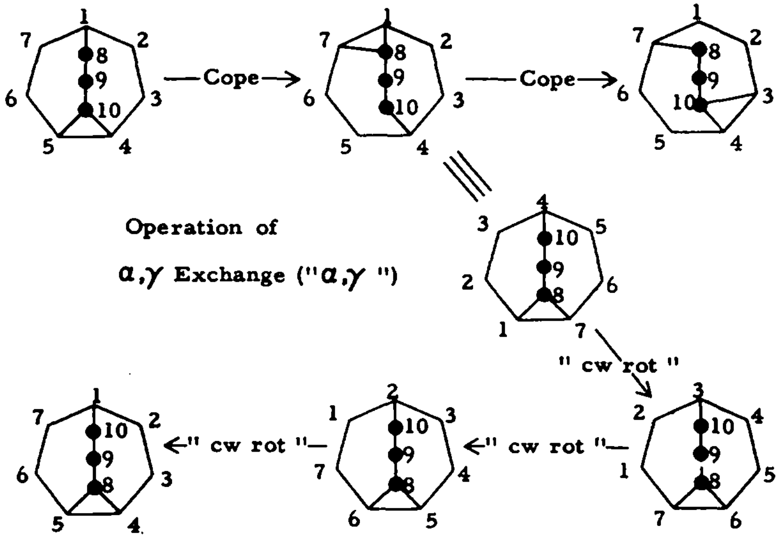


FIG. 4. Clockwise Rotational Operation ("cw rot") across the top line; the Operation of α, γ Exchange ("α, γ").

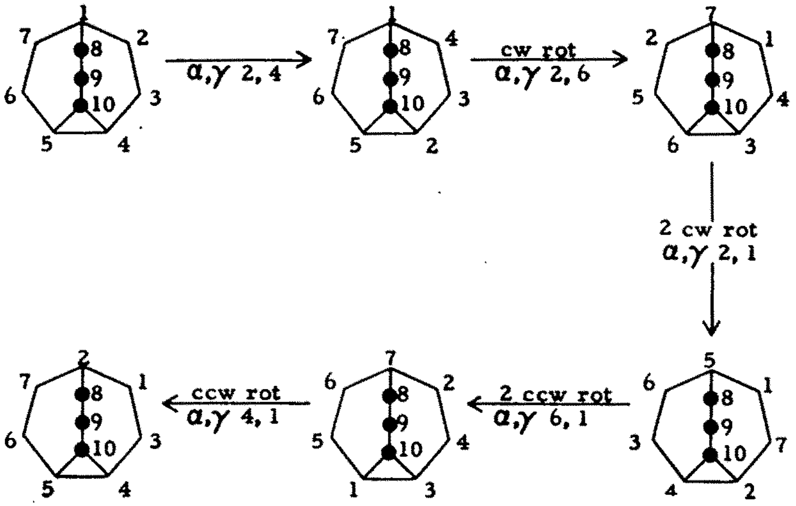


FIG. 5. Operation of α,β Exchange ("α,β").

the various paths one can visualize for it and if then it shows a single N.M.R. band, it will of necessity be a molecule in which no two carbon atoms remain bonded to each other, and all ten carbon atoms inevitably wander over the surface of a sphere in ever changing relationship to each other. Such a fluxional structure will have had no precedent in organic chemistry.

EXPERIMENTAL

Almost all the new substances obtained in this work are liquids. They have been isolated and purified by gas–liqud partition chromatography (g.l.p.c.). The various columns, described in more detail below, were tested roughly for efficiency by the procedure outlined in Kaiser.[40]

Silicone column A consisted of a 60″ column, ¼″ in diameter, of 40–60 mesh firebrick with 10% by weight of Dow–Corning silicone 550 and having about 1000 plates.

Silicone column B was a 100″, 1″-preparative column having 15% Dow-Corning silicone 550 on 40–60 mesh kieselguhr.

Silicone column C: ¼″ × 160″; 40–60 mesh kieselguhr; 20% Dow–Corning silicone 550; ca. 1850 plates.

Silicone column D: ¼″ × 215″; 40—60 mesh kieselguhr; 10% Dow–Corning silicone 550; ca. 2600 plates.

Silicone column E: ¼″ × 160″; 40–60 mesh firebrick; 15% Dow–Corning silicone 550.

Carbowax column A: ¼″ × 160″; 40–60 mesh kieselguhr; 20% Carbowax 400.

Silver nitrate column A: ¼″ × 160″; 40–60 mesh kieselguhr; 30% by weight of a 30% solution of silver nitrate in glycerine; ca. 600 plates.

General procedure for cyclopropanation of olefins with diazomethane, catalyzed by anhydrous cuprous chloride (the Gaspar-Roth recipe).[30] In this procedure, the dried olefin, either neat or in solution in pentane and in amount varying from 0·5 g to 15·0 g, is treated with gaseous diazomethane in nitrogen. The apparatus permits a stream of diazomethane to be blown below the surface of the magnetically stirred liquid. The escaping gas, which often foams, passes through a widened portion, where the bubbles collapse, and thence through a spiral reflux condenser, which may be cooled to −70° or higher as required. Such an apparatus is constructed by sealing a small Erlenmeyer flask (serving as the reaction vessel) to the bottom of a distilling flask, the sidearm of which is bent upwards to accommodate the reflux condenser. Diazomethane is most conveniently prepared separately in a 500-ml, three-necked flask of the ordinary type without ground glass joints. It is fitted by rubber stoppers with an inlet tube through which a stream of nitrogen can be introduced to the bottom of the flask. This stream serves both to stir the reaction and to carry out the diazomethane. There is an outlet tube through which the

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[40] R. Kaiser, *Chromatographie in der Gasphase* p. 12. Bibliographisches Institut, Mannheim (1961).

gas passes into the reaction vessel by way of a drying section filled with pellets of potassium hydroxide. The third stoppered opening may be opened at 10-min intervals to introduce 1·0-g portions of N-methyl-N-nitro sourea until the desired amount of diazomethane has been introduced. The flask is conveniently filled with 100 ml 50% aqueous potassium hydroxide and 25 ml decalin. By dissolving the liberated diazomethane, the latter serves as a temporary reservoir from which the nitrogen may sweep diazomethane at a more constant rate than would otherwise be achieved. About 100 mg catalyst consisting of cuprous chloride of Mallinckrodt Analytical Reagent Grade is used. Cuprous chloride of the purity obtained by the published procedure is somewhat more active.[41]

Whenever the tube carrying the nitrogen and diazomethane becomes plugged in the reaction vessel or the diazomethene is introduced too rapidly (80–100 ml/min is a generally satisfactory rate), explosions occur. These invariably destroy the generator but rarely, if ever, damage the reaction vessel. These explosions involve relatively small amounts of diazomethane and lead to interruptions of the reaction which can be kept quite short if spare generators are on hand.

With the present catalyst one should always operate above −50°. Below this temperature, diazomethane is not decomposed, accumulates in the reaction vessel and eventually explodes with singularly dangerous and destructive violence. Explosions in the reaction vessel can also be caused by failure of the catalyst. It is quite deactivated by moisture and care should be taken to dry all materials in the reaction vessel. During the reaction the catalyst gradually turns black, loses activity and appears to be consumed. Accumulations of diazomethane are then indicated by the turning yellow of the drops of condensate on the tip of the reflux condenser. Experienced operators normally withdraw and continue flushing the apparatus with nitrogen in the occasionally vain hope that the diazomethane will thus be removed without event.

The products, generally obtained in 50–70% of the theoretical yield based on N-methyl-N-nitrosourea, are usually isolated by fractional distillation or by g.l.p.c.

Cyclopropanation of cis-*hexa*-1,3,5-*triene*. The Gaspar-Roth recipe was applied to 5 ml pure *cis*-hexa-1,3,5-triene, prepared and purified according to the procedure of Hwa *et al.*[20] The reaction was carried out at 0° with 100 mg cuprous chloride with the reflux condenser cooled to −30°. G.l.p.c. (silicone A; 20 lb He; 90°) afforded eight products given in order of increasing retention time. The relative amounts are shown for two experiments in which 20 and 50 g N-methyl-N-nitrosourea were used, respectively: *cis*-hexa-1,3,5-triene: 40%, 6%; product A: 2·4 min, 31%, 8%; B: 2·9 min, 6%, 3%; C: 3·6 min, 8%, 12%; D: 5·0 min, 8%, 12%; E: 5·8 min, 2%, 5%; F: 7·5 min, 4%, 48%; G: 10·5 min, 0·5%, 3%; H: 12·0 min, 0·5%, 3%. Products A, C, D and F are shown elsewhere to be *cis*-1-cyclopropylbutadiene, *cis*-1-cyclopropyl-2-vinylcyclopropane, *cis*-1,2-dicyclopropylethylene and *cis*-1,2-dicyclopropylcyclopropane, respectively.[42]

Product B had an I.R. spectrum identical in all respects with that of the sample prepared below and with that reported by Vogel *et al.*[17] Product E has an I.R. spectrum identical with that of bicyclo[5.1.0]oct-3-ene (see below). The two products G and H have the same retention times and the same I.R. spectra as those of the *cis* and *trans*-tricyclo[6.1.0.0^{3,5}]nonane prepared below.

When the cyclopropanation of *cis*-hexa-1,3,5-triene (50% solution in pentane) was carried out at −45° by surrounding the reaction vessel with a cooling bath at −50°, the same eight products were produced. The quantities of F, G and H were very small and these products were identified by retention time only. E was isolated and shown to have the same infrared spectrum as bicyclo[5.1.0]oct-3-ene below.

Preparation of cyclohepta-1,4-*diene and cyclohepta*-1,3-*diene*. Over a period of 20 min, 11·5 g sodium was added to a solution of 15 g cycloheptatriene (Shell Development Co., 93% containing 7% toluene) in 150 ml absolute alcohol. In the preparation of cyclohepta-1,4-diene, the reaction mixture was cooled as the sodium reacted and was poured into 1 l. ice water. An ether extract of the aqueous solution was dried over anhydrous calcium chloride and concentrated. The residue was taken up in 50 ml xylene and heated under reflux for 5 hr with 20 g maleic anhydride. The olefins were removed by distillation *in vacuo* and redistilled in a spinning band column (80-cm Piros-Glover column; H. S. Martin and Co.) to separate cycloheptene and cyclohepta-1,4-diene (95% of purity). This material could be separated from toluene and cycloheptene by preparative g.l.p.c. (silicone column B; 1·5 lb H_2; 100°) and had the same I.R. spectrum as that reported by Vogel *et al.*[17]

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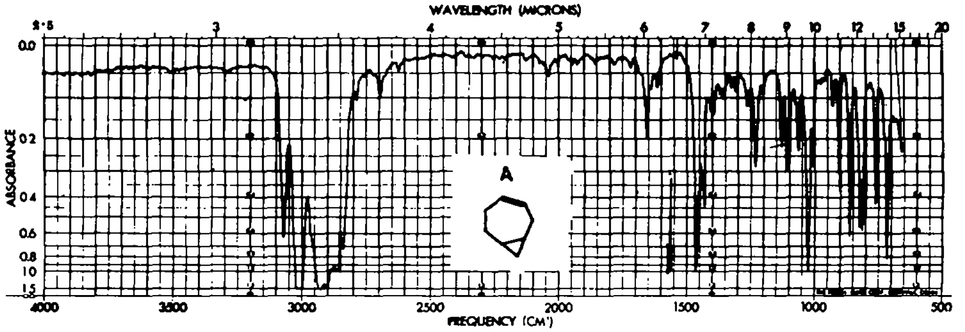
[41] R. N. Keller and H. D. Wycoff, *Inorganic Syntheses*, (Edited by W. C. Fernelius) Vol. II, p. 1. McGraw-Hill, New York (1946).

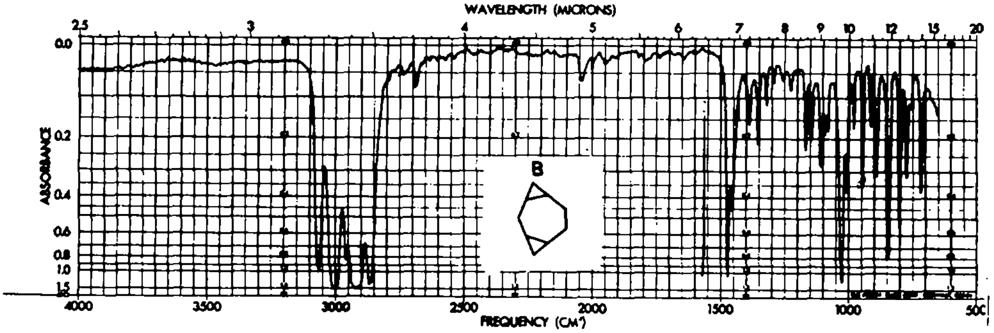
[42] W. von E. Doering and W. R. Roth, in preparation.

In the preparation of cyclohepta-1,3-diene, the reaction mixture was boiled under reflux for 24 hr to effect the rearrangement of cyclohepta-1,4-diene to cyclohepta-1,3-diene discovered by Schroeder.[43] The mixture was then poured into water and extracted with pentane. The pentane extract was washed thoroughly with water, dried over anhydrous calcium chloride and fractionally distilled with the spinning band column. The resulting diene could be freed of about 10% cycloheptene by g.l.p.c. on preparative silicone column B and was then identified by comparison with an authentic sample.

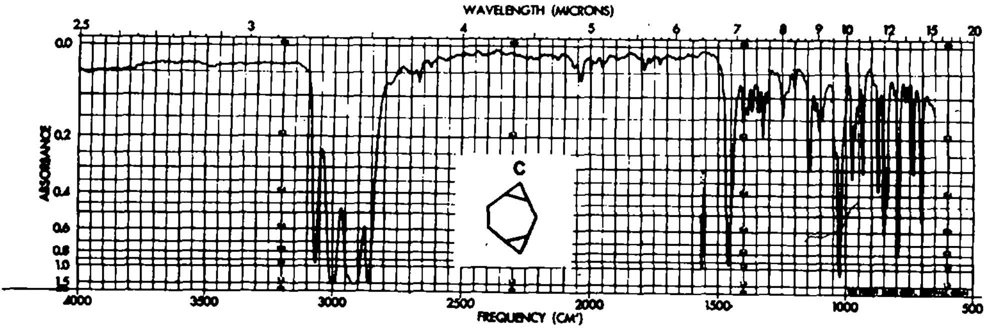
Cyclopropanation of cyclohepta-1,4-diene. Treated by the Gaspar-Róth procedure, 5·0 g cyclohepta-1,4-diene reacted at 0° with the diazomethane generated from 30 g N-methyl-N-nitrosourea.



G.l.p.c. (silicone column C; 11 lb H_2; 130°) afforded starting material and three products: cyclohepta-1,4-diene: 3·0 min (15%); bicyclo[5.1.0] oct-3-ene (A), 6·5 min (45%); *trans* (or *cis*) -tricylo-[6.1.0.0^{3,5}] nonane (B), 11·0 min (20%); *cis* (or *trans*) -tricyclo[6.1.0.0^{3,5}]nonane (C), 12·5 min (20%).



Although the ratio of the latter two products, one to the other, did not change during the course of the reaction, their ratio to that of monocyclopropanated product increased steadily. A has an N.M.R. spectrum containing peaks about τ = 4·55 p.p.m. (relative area 1·8) indicative of two vinylic hydrogen atoms and a complicated series of peaks about τ = 7·8 p.p.m. indicative of allylic hydrogen atoms, a second complicated series between 8 and 9·3 p.p.m. and finally peaks at 9.9 p.p.m. indicative of the



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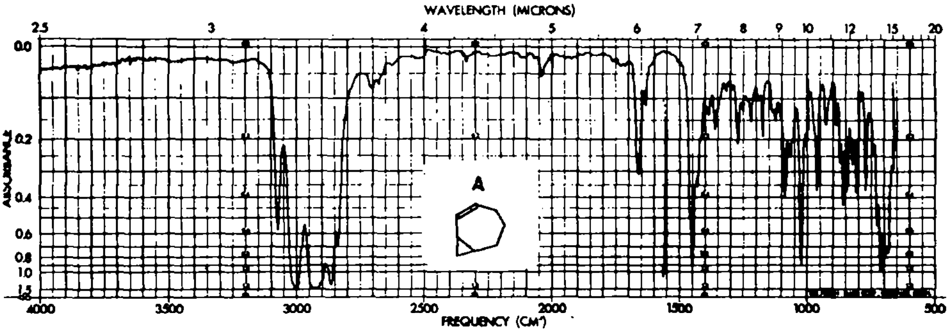
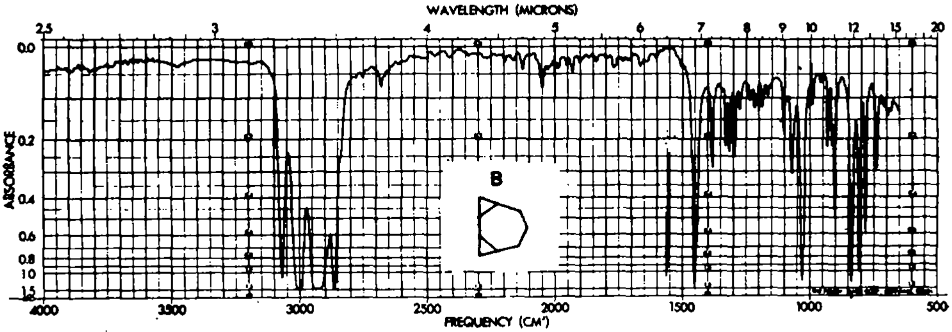
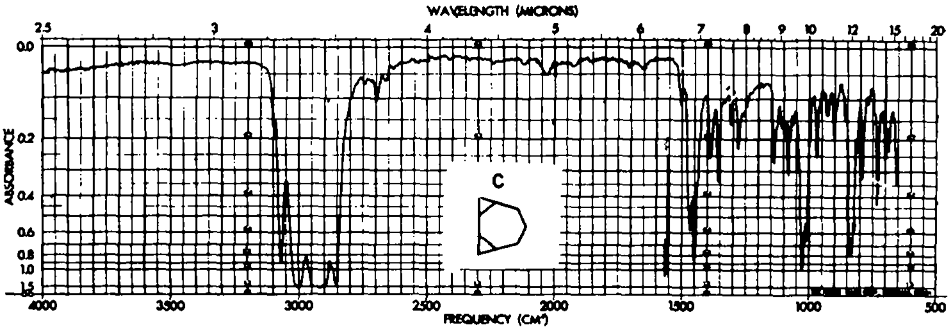
[43] W. von E. Doering and G. Schroeder, in preparation.

methylene group of a cyclopropyl ring. In the I.R. spectrum (q.v.) bands at 1650 and 1020 cm^{-1} confirm the presence of a *cis* double bond and a cyclopropyl ring, respectively. Neither compound B nor C shows peaks in the N.M.R. below about 8·5 p.p.m. and both are therefore free of vinylic hydrogen atoms; both show peaks in the region, $\tau = 9{\cdot}9$–$10{\cdot}0$ p.p.m., characteristic of cyclopropane. Consistently neither shows absorption in the I.R. region about 1600 cm^{-1}, although both absorb strongly at 1020–1025 cm^{-1}.

Cyclopropanation of cyclohepta-1,3-*diene.* A solution of 2·0 g cyclohepta-1,3-diene in 3·0 ml pentane was treated at 0° with diazomethane generated from 20·0 g N-methyl-N-nitrosourea. The products were separated on silicone column C: cyclohepta-1,3-diene, 3·5 min (19%); bicyclo[5.1.0]-oct-2-ene (A), 6·5 min (45%); *trans* (or *cis*) -tricyclo [6.1.0.$0^{2,4}$]nonane (B), 10·0 min (35%); *cis* (or *trans*) -tricyclo [6.1.0.$0^{2,4}$]nonane (C), 15·5 min (10%). During the reaction the ratio of B to C remained constant while that of B + C to A increased. Comparison of the I.R. spectrum of these three substances with the I.R. spectra of three related products obtained from cyclohepta-1,4-diene shows differences in all cases. Otherwise the substances are quite similar: in the N.M.R., A shows vinylic absorption at τ = 4·6 p.p.m. (relative area 1·6), allylic at 7·8 p.p.m. and cyclopropyl at 10·0 p.p.m., while B and C show no absorption below 8·5 p.p.m. and strong absorption at 9·9–10·1 p.p.m.; in the







I.R. attention is called to the bands at 1665 and 1025 cm^{-1} in A and to the bands at 1030 and 1035 cm^{-1} in B and C, respectively.

Cyclopropanation of tropilidene. Tropilidene (kindly given by the Shell Development Co., Emeryville, California) containing 7% toluene was subjected to the Gaspar-Roth procedure. G.l.p.c. analysis of the crude reaction mixture from the treatment of 5 g tropilidene with diazomethane [(from 40 g N-methyl-N-nitrosourea) silcone A, 10 lb He; 95°] led to the separation of six peaks: tropilidene, 4 min, 6%; A, 10 min, 21%; B, 15 min, 24%; C, 20 min, 21%; D, 30 min, 9%; E, 35 min, 19%. More careful chromatography was able to separate fractions A, B and C into two components each. The further identification of the components of fraction A is treated in more detail below.

The second band of products, B, can be shown by g.l.p.c. (silicone column D, 7 lb H_2; 80°) to consist of two components, B′ and B″, although complete separation is not possible with this column. The N.M.R. spectrum of the mixture shows only two vinylic hydrogen atoms. From this fact one concludes that the products are dicyclopropanated derivatives of tropilidene. Catalytic hydrogenation of the mixture gives a complicated mixture of which only the fifth and major component (10·6 min, 15%), was isolated (silicone column C; 11 lb H_2; 130°) and identified as the dicyclopropanated product (B) of the shorter retention time obtained above from cyclohepta-1,3-diene; that is, the product tentatively called *trans* (or *cis*) -tricyclo[6.1.0.0^{2,4}]nonane.

Chromatography on silicone column D managed to effect a partial separation of fraction C into two components: C′ (66 min, 50%) and C″ (69 min, 50%). The N.M.R. spectrum of the mixture showed two vinylic hydrogen atoms, while catalytic hydrogenation (palladium-black in tetrahydrofuran) led to the absorption of 3 equivalents of hydrogen. Although g.l.p.c. indicated the presence of at least six products of the hydrogenation, no one of them could be identified with one of the four products of the dicyclopropanation of cycloheptadiene 1,3 and 1,4.

Fractions D and E showed no absorption between 1600 and 1760 cm^{-1} and were considered to be products of the tricyclopropanation of tropilidene.

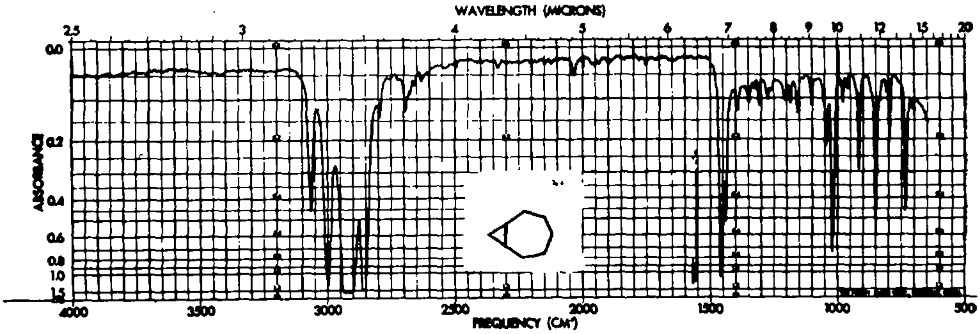
Bicyclo[5.1.0]*octa-2,5-diene* (I) *and bicyclo*[5.1.0]*octa-2,4-diene* (II). Separation of the monocyclopropanated products of tropilidene from fraction A was achieved with a column of about 2500 plates (silicone column E; 10 lb H_2; 90°). II with a retention time of 60 min was obtained in 5 times the amount of I with retention time of 65 min. Although II could be obtained in useful quantity by this procedure, additional concentration steps were needed for the convenient preparation of I.

The whole reaction mixture was distilled *in vacuo* at 50 mm. The fraction boiling below 80° was diluted with an equal volume of toluene and treated at 110–120° with an excess of maleic anhydride (calculated as if the entire fraction were C_8 diene). By checking the composition every 3–4 hr by g.l.p.c., it was determined that 12 hr sufficed to remove all of the tropilidene and the bulk of II and to change the ratio of II to I to 2:3. The unreacted products were removed by distillation *in vacuo* and separated from toluene on the silicone column A. Refractionation on the longer column (silicone column D; 5 lb He; 80°) afforded samples of pure II and I.

II showed absorption in the U.V., λ_{max} 258 (ε 4200) in ethanol [reported for cycloheptadiene[35] λ_{max} 248 (ε 3700)], while I showed no absorption above 215 mμ. The I.R. spectra of I and II are shown below.

Each substance (50 mg) was hydrogenated in 4 ml tetrahydrofuran which had been prereduced with 50 mg palladium-black. After 1 hr 2·5–2·7 equivalents of hydrogen had been absorbed, although the reaction was still proceeding slowly. The reaction mixture was poured into 10 ml water, filtered, extracted with 0·5 ml pentane; the pentane extract was then washed three times with water, dried over anhydrous calcium chloride and separated into its components by g.l.p.c. (silicone column E; 9 lb H_2; 90°). Both I and II gave three substances, an unknown of retention time 12 min, bicyclo[5.1.0]-octane (18 min) and cycloöctane (22 min). These substances were obtained in relative amounts, 20:65:15 from II and 20:20:60 from I. Cycloöctane was isolated in each case and identified by comparison of the infrared spectrum with that of an authentic sample, prepared by catalytic hydrogenation of cycloöcta-1,5-diene. Bicyclo[5.1.0]octane was isolated in both cases and identified by comparison of the I.R. spectra with that of an authentic sample synthesized from cycloheptene by the Gaspar–Roth recipe (only one substance was produced in this reaction). The unknown substance with the shortest retention time was not identified further.

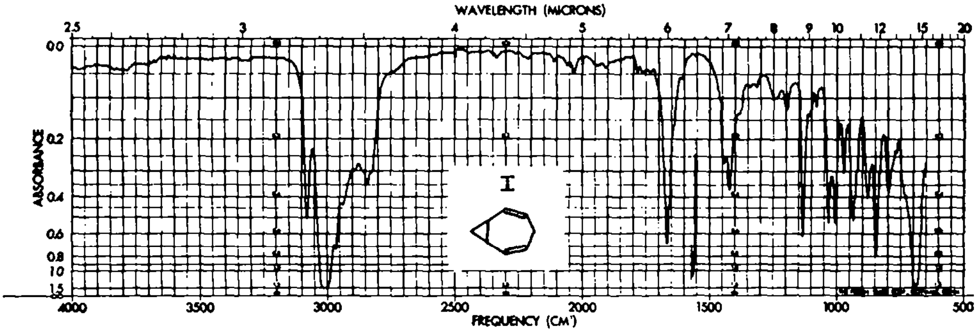
A more convenient preparation of I and II involves the use of a larger excess of tropilidene. Diazomethane from 35 g N-methyl-N-nitrosourea was passed into 15 ml tropilidene containing cuprous

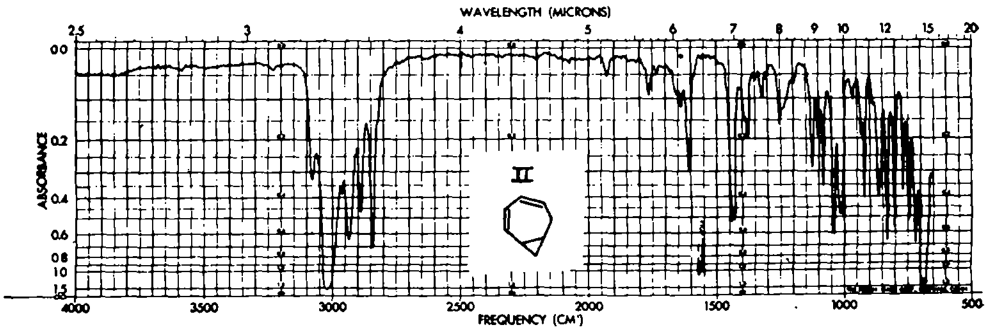


chloride in the usual fashion. The reaction product was distilled fractionally at 50 mm in a 15-cm Vigreux column. The fraction, b.p. 70–75°/50 mm (2 ml) was immediately separated in a freshly prepared silver nitrate column A (5 lb He; 75°) into pure samples of I and II which had retention times of 8·5 and 5·0 min, respectively.

N.M.R. and I.R. spectra of I and II. In the temperature range from −50° to 180°, II (1,2-homotropilidene) shows no change in N.M.R. spectrum. The spectrum of I shows marked changes which are entirely reversible and which are depicted in Fig. 1. The I.R. spectrum of I was determined in a 10-cm gas cell by pumping to 10^{-3} mm and filling the cell with 50 mg I. Over a 2 hr period the temp was gradually raised to 185° while I.R. spectra were taken intermittently. There were no differences between the spectra measured at room temp and those measured at 185°. After being heated, the substance was recovered, the I.R. of the empty cell was retaken to show that nothing had deposited on the windows of the cell, and the I.R. of the recovered material in carbon tetrachloride found to be unchanged.

Thermal reorganization of 3,4-*homotropilidene* (I) *at higher temperature.* A sample of I purified over a freshly prepared silver nitrate column A was heated for 24 hr at 260° in the gas phase and





recovered unchanged (g.l.p.c. on Carbowax column A). At 305° for 24 hr, I is largely (85%) converted to a single substance (V) which was isolated by g.l.p.c. on Carbowax column A (10 lb He; 125°) and tested for homogeneity on silver nitrate column A.

Nickel-catalyzed rearrangement of 3,4-*homotropilidene* (I). The catalyst was prepared by mixing 33 g 40–60 mesh kieselguhr with a solution of 16 g nickel nitrate hexahydrate in 120 ml water and adding 45 ml 30% aqueous sodium carbonate at 70° with stirring. After being filtered, washed thoroughly with water and dried at 100°, the catalyst was packed into a column, ¼″ I.D. × 156″ long, and reduced by passing through hydrogen gas at 250° for 2 hr. The operation was carried out conveniently in the Aerograph gas chromatographic apparatus in which the rearrangements and catalytic hydrogenation reported below were also carried out.

Rearrangement was effected by injecting 20-mg portions of I into the column at 270° with 3 lb helium as the carrier gas. The residence time under these conditions was about 2.5 min. The single product (V) was isolated on silver nitrate column A and had the same I.R. spectrum as the product of thermal reorganization.

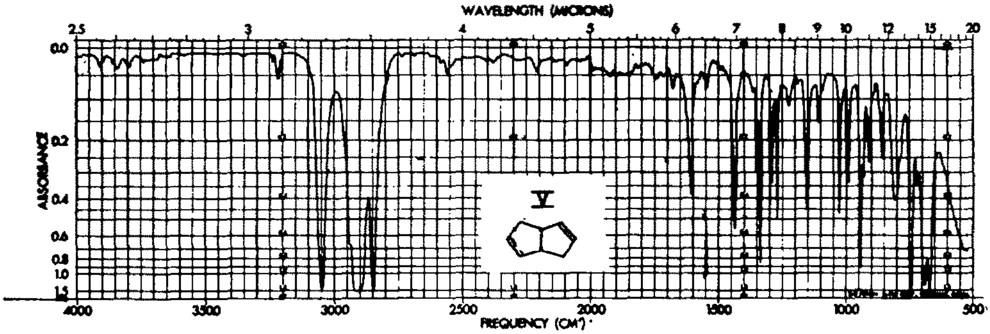
Catalytic hydrogenation of V was effected on the nickel column at 75° under 1 lb hydrogen and a contact time of about 1 min. The retention time of the product on Carbowax column A (8 lb He; 125°) was 2·5 min. The I.R. spectrum was identical with that reported for bicyclo[3.3.0]octane.[44]

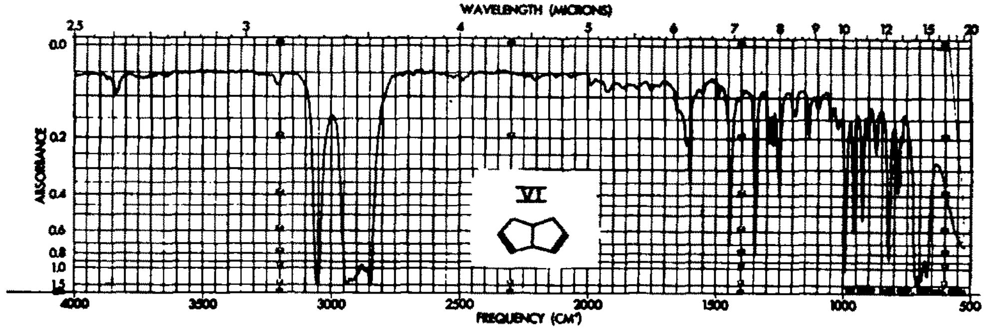
Nickel-catalyzed rearrangement of 1,2-*homotropilidene* (II). Injection of 20-mg samples of II, which had been freshly purified on silver nitrate column A, into the nickel column at 270° (*vide supra*) afforded product which was separated from small amounts of by-product on a silicone column A. This material was then separated on silver nitrate column A (5 lb He; 75°) into two products: VI of retention time 2·8 min (58%) and V, 8·9 min (42%). This latter product had the same I.R. spectrum as that of the product obtained above from I. This mixture of V and VI is not changed either by heating for 24 hr at 305° or by repassing over the nickel column at 270°.

The product VI may be hydrogenated as was V above to give pure bicyclo[3.3.0]octane having the same infrared spectrum as that obtained from V and reported in the literature.[44]

A mixture of I and II in the ratio 1:5, treated in the same manner, gave a mixture of V and VI in the ratio 5:3.

The I.R. spectra of V and VI are shown below.





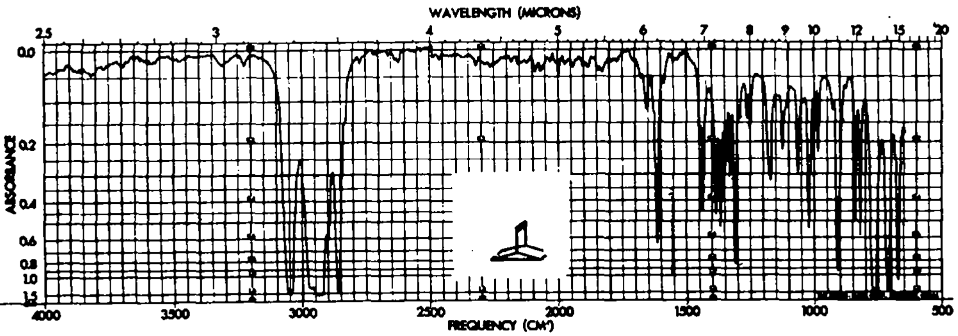
[44] American Petroleum Institute Project 44: I.R. spectrum 1251.

The N.M.R. spectra of V and VI have the following feature: both show 4 hydrogen atoms in the vinylic region at $\tau = 4{\cdot}48$ and 4·45 p.p.m. V shows two hydrogen atoms at $\tau = 6.64$ p.p.m., consistent with tertiary allylic hydrogen; whereas VI shows a single hydrogen at $\tau = 6{\cdot}37$ p.p.m., not inconsistently located for a tertiary, doubly allylic hydrogen; in both molecules, the remaining hydrogen atoms appear in a complicated pattern with the highest peak in VI being at $\tau = 8{\cdot}15$ p.p.m. and in V at 8·02 p.p.m.

Thermal reorganization of 1,2-*homotropilidene* (II). Heating 100 mg pure II at 225° for 18 hr in a 200-ml ampoule sealed *in vacuo* afforded a mixture of products resolved into two components on a silicone column and three products on silver nitrate column A. At 5 lb He and 75°, these products had the following retention times: benzene, 1·5 min (4%); tricyclo[3.2.1.0^{2,7}]oct-3-ene (III) (6%); 1,2,-homotropilidene (II), 5·0 min (70%); cycloöcta-1,3,5-triene, 18·5 min (20%); and a shoulder at 4·0 min. Longer heating of II (48 hr) caused benzene and III to increase to 15 and 25%, 1,2-homotropilidene (II) to decrease to 30% and cycloöcta-1,3,5-triene to increase to 30%.

Benzene was identified by its I.R. spectrum. The tricyclo [3.2.1.0^{2,7}] oct-3-ene (III) has the same I.R. spectrum as the material obtained below. Cycloöcta-1,3,5-triene was identified by comparison of its I.R. spectrum with that of an authentic sample prepared from cycloöctatetraene according to the prescription of Jones.[45] G.l.p.c. on silver nitrate column A (5 lb He; 75°) easily separates cycloöcta-1,3,5-triene (retention time, 18·5 min) from its inevitable companion, bicyclo[4.2.0]octa-2,4-diene (retention time, 4·0 min).

Thermal reorganization of cycloöcta-1,3,5-*triene*. After having been heated for 24 hr at 225°, cycloöcta-1,3,5-triene was partly transformed to benzene (19%; 3·4 min retention time) and tricyclo-[3.2.1.0^{2,7}] oct-3-ene (12%; 7·0 min) while its equilibrium mixture with bicyclo [4.2.0]octa-2,4-diene was recovered in 69% of theory (11·3 min ret. time on Carbowax column A; 10 lb He; 125°). III appears homogeneous on both a silicone and a silver nitrate column. Catalytic hydrogenation in tetrahydrofuran over palladium on charcoal leads to the absorption of two equivalents of hydrogen in 15 min and the formation of bicyclo[3.2.1] octane: ret. time 7·5 min on the Carbowax column A at 7 lb He and 105°. As isolated, the hydrocarbon melted at 133°, but after sublimation from sodium the m.p. was 134–136°(reported 133°, 133°, 141°, 139–141°). This material had the same I.R. spectrum as that reported by Goldstein.[46]



Nickel-catalyzed rearrangement of cycloöcta-1,3,5-*triene*. Passed over the 1-m nickel column at 270° in 20-μl quantities with 2 lb He and a contact time of about 30 sec, cycloöcta-1,3,5-triene was converted to three products which were separated by g.l.p.c. (silicone column A; 10 lb He; 125°): benzene (4%; 3·4 min), 5-vinylcyclohexa-1,3-diene (13%; 5·2 min) and tricyclo[3.2.1.0^{2,7}]oct-3-ene (16%; 7·0 min), 67% cycloöct-1,3,5-triene being recovered (11.3 min).

5-Vinylcyclohexa-1,3-diene has λ_{max} 260 mμ and is hydrogenated over the 1-m nickel column at 75° to ethylcyclohexane, identified by comparison of the I.R. spectrum with that reported.[47] The N.M.R. spectrum of 5-vinylcyclohexa-1,3-diene showed complicated areas of absorption: one of rel.

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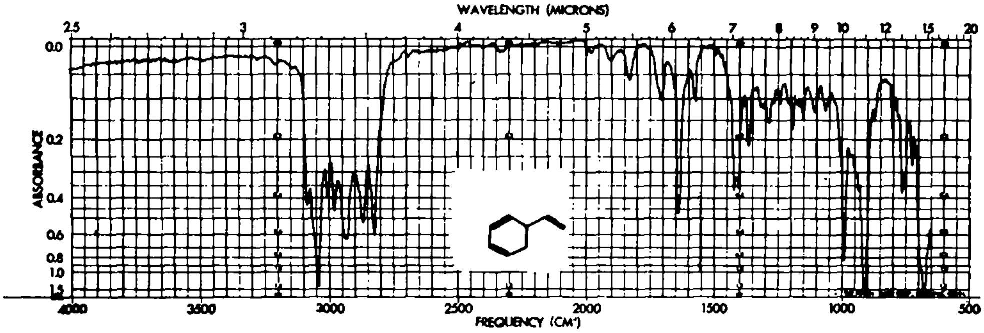
[45] W. V. Jones, *J. Chem. Soc.* 1808 (1954).

[46] M. J. Goldstein, Ph.D. Dissertation, Yale University, 1957.

[47] American Petroleum Institute Project 44: *I.R. spectrum* 384.



area 5 centered at $\tau = 4{\cdot}19$ p.p.m., a second of rel. area 2 centered around $\tau = 4{\cdot}87$ p.p.m.,[48] a third of rel. area 1 centered at $\tau = 7{\cdot}74$ p.p.m.

At 270° over the nickel catalyst, tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (III) and 5-vinylcyclohexa-1,3-diene (IV) reached the equilibrium ratio 87:13. When III is heated in the absence of a catalyst for 24 hr at 225°, a band having the correct retention time for 5-vinylcyclohexa-1,3-diene appeared, but in quantity too small to isolate.

[48] The fine structure of this absorption is similar to that ascribed to the methylene group of a vinylic group [J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, pp. 238-246, McGraw-Hill, New York (1959)].