

Vinylogous Cope Rearrangements.

The Thermal Isomerization of *meso*- and *rac*-5,6-Dimethyl-*trans,trans*-1,3,7,9-decatetraene¹

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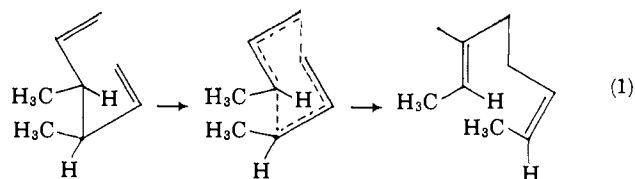
The thermal rearrangements of both *rac*- and *meso*-5,6-dimethyl-1,3,7,9-decatetraene (I) lead predominantly to a mixture of 4-vinyl-2,6,8-decatriene (two geometric isomers), 5-methyl-1,3,7,9-undecatetraene (two geometric isomers), and 2,4,8,10-dodecatetraene (three geometric isomers). From both the nature and number of the geometrical isomers produced, it is concluded that the reaction involves homolytic cleavage of I to produce two of the possible eight geometric isomers of the 1-methylpentadienyl radical followed by a recombination of these radicals. This intermolecular type mechanism has been confirmed through pyrolysis of a mixture of I and a 1,10-dideuterio derivative of I, the major products in the pyrolysate being C₁₂ hydrocarbons possessing one deuterium atom per molecule.

Introduction

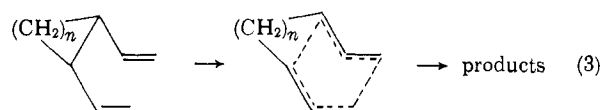
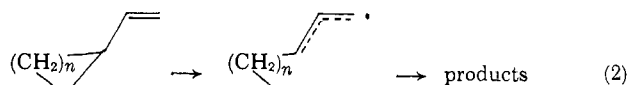
Several research groups have given attention to the mechanistic aspects of the Cope rearrangement, *i.e.*, the thermal isomerization of 1,5-hexadienes, and a fairly detailed picture of the reaction has now been established. One of the interesting features which has emerged from these studies is the significant change in mechanistic detail of the rearrangement occasioned by changes in structural features of the starting diene.

Cope and co-workers early established² through the absence of cross-products upon reaction of mixtures of substituted hexadienes that the rearrangement proceeded by an intramolecular process; in particular, their results ruled out a mechanism involving dissociation of the diene into substituted allyl radicals followed by recombination.

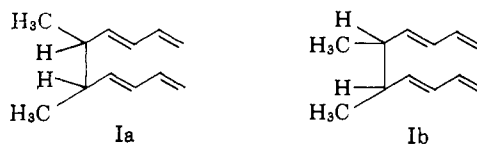
A more detailed picture of the intramolecular process has recently been provided from the studies of Doering and Roth.³ *rac*-3,4-Dimethyl-1,5-hexadiene was shown to yield mainly *trans,trans*-2,6-octadiene upon pyrolysis whereas the *meso* isomer gave predominantly *cis,trans*-2,6-octadiene. On the basis of this type of result, Doering and Roth concluded that the transition state for the reaction involves a cyclic six-membered ring in which the six carbon atoms of the ring adopt a chair-like conformation rather than one resembling a boat. This process, which may be termed the "normal" pathway, is indicated in eq. 1 for the rearrangement of the *meso* isomer.



However, experiments by Vogel^{4a} and Hammond and DeBoer^{4b} have demonstrated that steric factors present in the initial hexadiene which render a chair-type six-membered transition state unattainable can divert the course of the reaction from the "normal" path just described.^{4c} Thus, *trans*-divinylcyclopropane and *trans*-1,2-divinylcyclobutane are believed to undergo thermal rearrangements by dissociation into two allylic radical systems (eq. 2), whereas the corresponding *cis* isomers rearrange through a boat-type six-membered transition state (eq. 3). In each of these systems it is readily seen that reaction *via* the "normal" process would involve highly strained transition states.



As a consequence of other studies, we had access to the vinylogous analogs of the compounds studied by Doering and Roth, namely *rac*- and *meso*-5,6-dimethyl-*trans,trans*-1,3,7,9-decatetraene (Ia and Ib, respectively).⁵ In the light of the above discussion, it was then of interest to study the thermal isomerization



reactions of these compounds and to determine what effect, if any, the addition of the two extra double bonds to the 1,5-hexadiene system would have upon the course of the reaction.

(1) (a) A preliminary account of this work was presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 4, 1964, Organic Division Abstracts, p. 90S; (b) taken from a part of the Doctoral Dissertation of D. H. Gibson, University of Texas, Jan. 1965.

(2) For a recent review of the Cope rearrangement, see S. J. Rhodes in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 11.

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

(4) (a) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963), and references cited therein; (b) E. Vogel, *Angew. Chem.*, **74**, 829 (1962); G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, **86**, 899 (1964); (c) for further discussion of the mechanistic consequences of the thermal behavior of *cis*- and *trans*-divinylcyclopropanes, see W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963); W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963).

(5) J. E. Mahler, D. H. Gibson, and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3959 (1963).

Results and Discussion

Attempts to effect the thermal isomerization of the 5,6-dimethyldecatetraenes in sealed tubes at 300° led only to extensive polymerization of these materials. Vapor phase pyrolysis, attained by rapid passage of the compounds in an inert atmosphere through a furnace at 300°, led to very little rearrangement, but no polymerization was detected. Similar pyrolysis with the furnace at 375° converted about 70% of the starting material to a product mixture consisting of three principal components plus unreacted starting material. With the furnace at 425° all of the starting material was converted to isomeric products, but analysis of these showed one of the major components present in the products of the pyrolysis at 375° to be missing in the products of these higher temperature runs. In order to obtain the maximum number of product types the experiments described hereafter were therefore conducted at the intermediate temperature of 375°; the contact time was approximately 1 sec.

Pyrolysis of *meso* I afforded a product mixture which was cleanly separated into four components by means of preparative vapor phase chromatography (using Carbowax on Chromosorb P as the stationary phase). In the order of their elution, these fractions are referred to as I, II, III, and IV and on the basis of several runs they were found to comprise approximately 30, 20, 20, and 30%, respectively, of the pyrolysate mixture. Fractions II, III, and IV accounted for greater than 90% of the pyrolysis products. At higher temperatures, the percentage of fraction II in the product was much less while that of IV was much greater. Fraction I was found to be unreacted starting material. Similar pyrolysis of fraction II gave rise to a mixture of I, III, and IV.

Further v.p.c. analysis of fractions II, III, and IV, using columns having silver fluoroborate⁶ dissolved in Carbowax deposited on Chromosorb P as the stationary phase, indicated each fraction to be a mixture. Fraction II was comprised of two compounds present in approximately equal amounts; these are referred to hereafter as IIa and IIb in their order of elution from the column. Likewise, fraction III was separated into two components, IIIa (60%) and IIIb (40%), and fraction IV into three components, IVa (30%), IVb (60%), and IVc (10%), again labeled according to the order of their elution from the silver fluoroborate column.

Catalytic hydrogenation of each of the main fractions II, III, and IV resulted in the uptake of 4 molar equiv. of hydrogen. Fraction II was thus hydrogenated to a single compound identified as 4-ethyldecane; fractions III and IV likewise produced 5-methylundecane and dodecane, respectively, as the sole reduction products. The components of each fraction were then established to be geometric isomers (rather than double bond positional isomers) by means of the following spectral analysis.

The ultraviolet absorption spectra of II, III, and IV indicated a conjugated diene to be present in each system (λ_{\max} 228, 229, and 228 μ , respectively). From the observed extinction coefficients one such diene unit was found to be present in II while III and

(6) Silver fluoroborate in combination with Carbowax 20M has been found to be far superior to silver nitrate-Carbowax in effecting v.p.c. separations of the geometric isomers described herein.

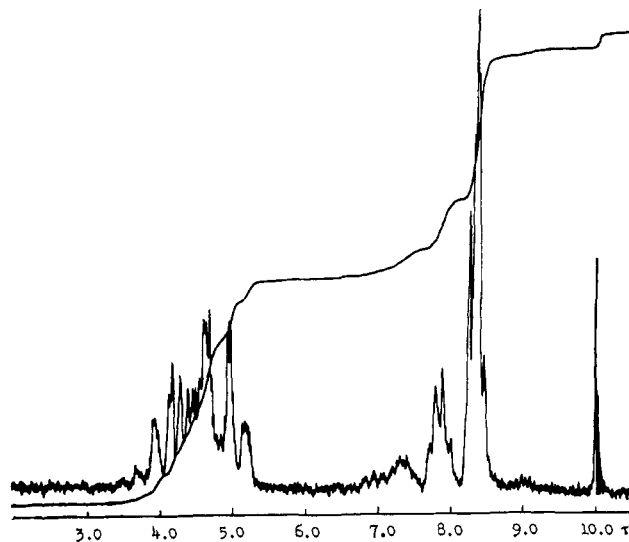
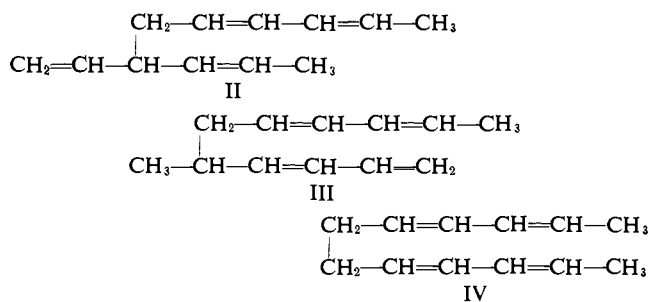


Figure 1. The proton n.m.r. spectrum of fraction II. The ratio of olefinic to saturated protons is 1:1 (9:9). The structural assignments, here and in Figures 2 and 3, are made according to the following limits given in τ -units (see ref. 7): $-(CH_2)C=C<$ (9.0-9.1); $-(CH_2)C=C<$ *cis* and *trans* (8.30-8.45); $>CH-C=C<$ and $-(CH_2)C=C<$ (7.20-8.10); $>C=CH_2$ (5.0-5.2); all other olefinic type protons absorbing at less than 5.0.

IV possessed two conjugated diene units per molecule.

The proton nuclear magnetic resonance spectrum of the fractions II, III, and IV allowed the following structural formulas to be assigned to the components of each fraction. These spectra together with the



structural assignments⁷ are given in Figures 1-3.

The nature of the geometrical isomers constituting the components of fractions II, III, and IV were then deduced from the infrared spectra of the individual compounds.

The individual components of each fraction were isolated in a pure state by means of preparative vapor phase chromatography on a silver fluoroborate-Carbowax column. The pertinent infrared data, in particular the absorptions due to C-H deformation vibrations associated with olefinic bonds, are listed in Table I. Similar data for the related *cis,trans*- and *trans,trans*-2,4-hexadienes have been obtained by Bartlett, Montgomery, and Schueller⁸ and are also listed for comparison. It was not possible to obtain sufficient quantities of compound IIa in a pure state in this manner; however, it was possible quantitatively to

(7) N. F. Chamberlain, F. C. Stehling, K. W. Bartz, C. H. Heathcock, and J. J. R. Reed, "NMR Chemical Shift and Spin Coupling Data," Research and Development, Humble Oil and Refining Co., Baytown, Texas, June 1964.

(8) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

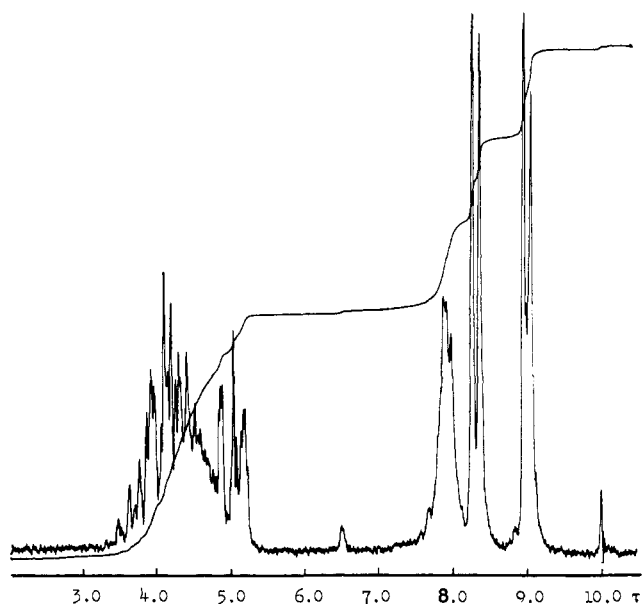
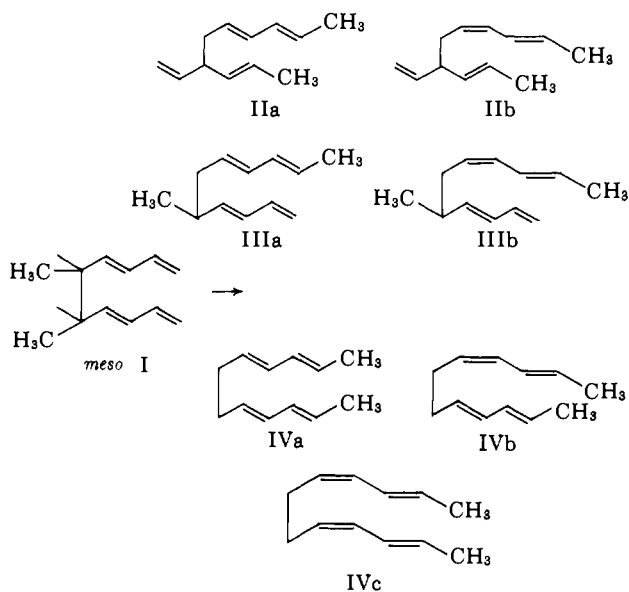


Figure 2. The proton n.m.r. spectrum of fraction III. The ratio of olefinic to saturated protons is 1:1 (9:9).

remove IIa through treatment of the mixture of IIa and IIb with tetracyanoethylene, thus providing pure IIb; the data reported for IIa were then obtained by subtracting the infrared absorption of IIb from that of II (*i.e.*, IIa + IIb).

The complete structure of the pyrolysis products are given in Scheme I.

Scheme I



A further check on these structures was provided through reaction of the various fractions or their individual components with tetracyanoethylene. *trans,trans*-Conjugated dienes form Diels-Alder adducts readily with this reagent whereas the *cis,trans* isomers react extremely sluggishly, and distinction between the two is easily established.^{8,9} The types of Diels-Alder adducts formed with the various isomers are also listed in Table I and are seen to be in complete accord

(9) R. L. Frank, R. D. Emmick, and R. S. Johnson, *J. Am. Chem. Soc.*, **69**, 2313 (1947).

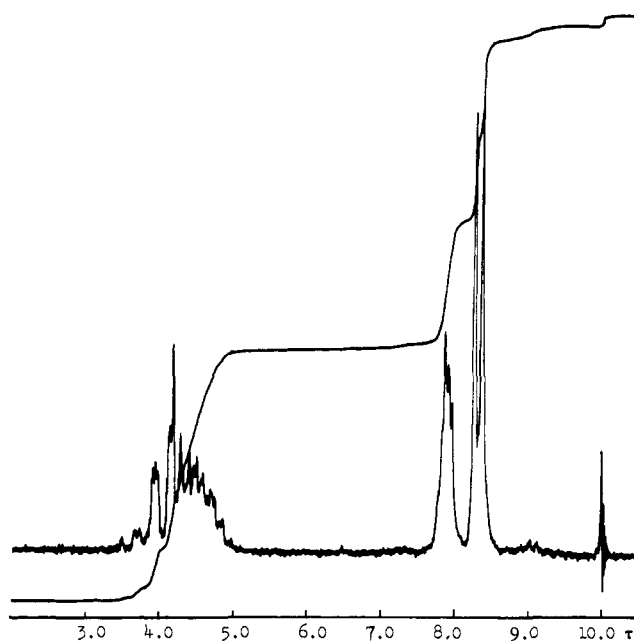


Figure 3. The proton n.m.r. spectrum of fraction IV. The ratio of olefinic to saturated protons is 4.5 (8:10).

with their structural assignments. In certain cases the infrared spectra of the adducts yielded further confirming structural evidence, and in these instances the data are given in the experimental section.

It is of interest to note that the structures are also related to the order the components of each fraction are eluted from the silver fluoroborate column; the components having the greater number of *cis* double bonds in each case have the longer retention time. This is to be expected on the basis of the greater stability of silver ion complexes of *cis* olefins over that of the isomeric *trans* olefin complexes.

The products of the pyrolysis of *rac* I are identical with those described above for the pyrolysis of *meso* I. No new products were found in the pyrolysate of *rac* I nor were any products found to be missing (the only difference in the two pyrolyses being a slightly different distribution of the components in each fraction). This lack of stereospecificity is in complete contrast to that observed by Doering and Roth for the dimethylhexadienes and immediately suggests that the two extra double bonds present in I have imposed a change in the mechanism of the rearrangement. A change in the mechanism is also suggested by the appearance of the compounds IIa and IIb in the pyrolysate; unlike the compounds of type III and IV these materials cannot be produced by any sequence of six-membered ring transition states.

Reaction Mechanism

While it is of course possible to write concerted type mechanisms leading to structures of type II, III, and IV, there is no satisfactory way of arriving at the particular isomers by such a mechanism both with respect to their number and their geometric type. Nor can this approach explain in any convincing manner why both *meso* I and *rac* I yield identical products.

An attractive alternative to the cyclic concerted mechanism is one involving thermal dissociation of I

Table I. Infrared Spectra^{a,b} of Pyrolysis Products and Related Compounds

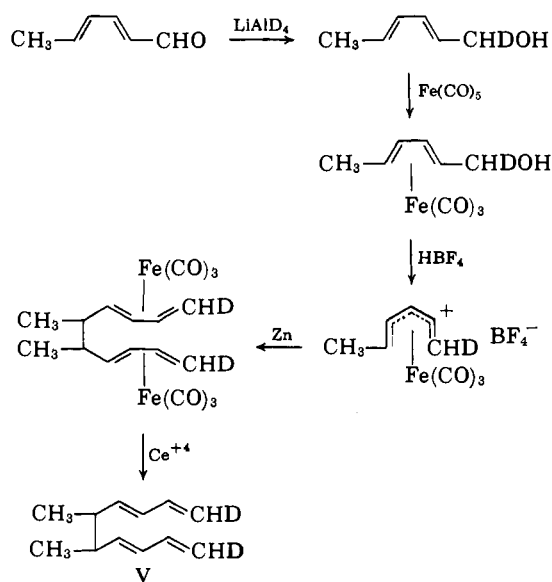
Compd.	<i>cis,trans</i> conjugated	<i>trans,trans</i> conjugated	Vinyl conjugated ^c	Vinyl non-conjugated ^c	<i>trans</i> non-conjugated	Diels-Alder adduct ^d
<i>cis,trans</i> -2,4-Hexadiene ⁸	704 s; 952 and 990 vs					...
<i>trans,trans</i> -2,4-Hexadiene ⁸		996 vs				1:1
<i>meso</i> I			895 vs; 948 m-s ^e ; 1001 vs; 3090 m			2:1
<i>rac</i> I			895 vs; 949 m-s ^e ; 1001 vs; 3090 m			2:1
IIa		983 vs ^f		910 and 990 s ^g ; 3081 m ^g	965 s ^g	1:1
IIb	714 and 730 m-s; 947 s; 983 vs			915 and 990 vs; 3081 m	967 s	...
IIIa		987 vs	900 vs; 948 m-s ^h ; 1003 vs; 3090 m			2:1
IIIb	714 s; 948 s; 987 vs		900 vs; 948 s ^h ; 1003 vs; 3092 m			1:1
IVa		987 vvs				2:1
IVb	710 m; 946 m-s; 987 vvs ⁱ	987 vvs ⁱ				1:1
IVc	710 s; 946 s; 987 s					...

^a All band positions are given in cm⁻¹. ^b For a general discussion of factors affecting out-of-plane hydrogen deformation frequencies in olefins, see W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, **9**, 679 (1959). ^c For a general discussion of C-H stretching frequencies in olefins, see K. Nakanishi, "Infrared Absorption Spectroscopy-Practical," Holden-Day, Inc., San Francisco, Calif., 1962, pp. 24-25. ^d Moles TCNE:moles hydrocarbon. ^e *trans* double bond of *trans*-vinyl conjugated diene. ^f Obtained by difference between mixture II and compound IIb. ^g Obtained from Diels-Alder adduct of IIa with TCNE. ^h *trans* double bonds of *trans*-vinyl and/or *cis,trans*-conjugated diene units (note *cis,trans*-2,4-hexadiene and *meso* or *rac* I). ⁱ *trans* double bonds of *cis,trans* and *trans,trans* conjugated diene units (note isomeric 2,4-hexadienes).

into two 1-methylpentadienyl radicals followed by recombination to give II, III, and IV. Such a mechanism would readily account for the appearance of compounds IIa and IIb and their further rearrangement to I, III, and IV and would also explain in a simple manner how the identical products arise from both *meso* and *rac* I.

Supporting evidence for such a free radical mechanism has been obtained from pyrolysis studies of 1,10-dideuterio-5,6-dimethyl-*trans,trans*-1,3,7,9-decatetraene (V). This material was prepared as shown in Scheme II.

Scheme II



An equal mixture of the dideuterated compound V and nondeuterated I was pyrolyzed, and the products were separated into the fractions equivalent to III

and IV. The mass spectral cracking pattern of these two pyrolysis fractions indicated the predominant isomers present in each case to have molecular weights of 163. The molecular weights of I and V are 162 and 164, respectively, and the predominance of products of mass 163 must arise from cross-type materials possessing one deuterium atom per molecule.

While this experiment unequivocally demonstrates the free radical nature of the thermal rearrangement the question is then raised as to why there are so few products formed in the pyrolysis reaction. There are eight geometric configurations possible for the 1-methylpentadienyl radical. These are listed in Figure 4.

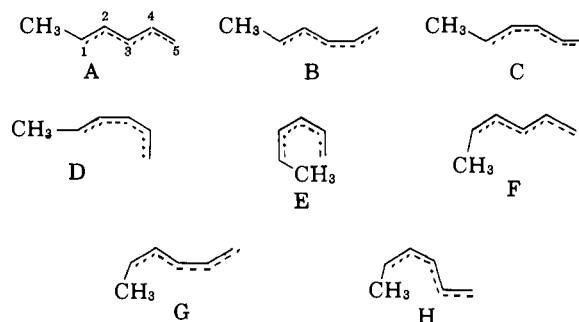


Figure 4. The configurations of the 1-methylpentadienyl radical.

Coupling processes involving all possible pairs of these radicals would result in the formation of eight geometric isomers having the general structure II, eight geometric isomers having structure III, and ten having structure IV. This clearly is not in agreement with the observed degree of stereospecificity. However, if it is assumed that only radicals A and B (Figure 4) are produced in the reaction, and that these retain

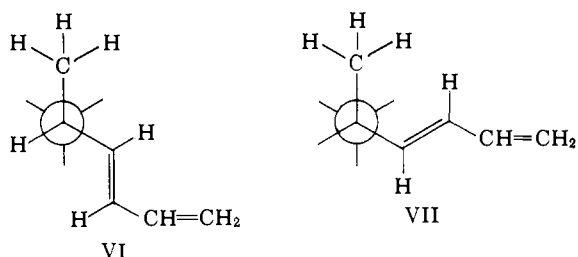
their stereochemistry before they recombine, then our mechanism predicts both the correct number of isomers that are obtained and each having the identical geometric configuration as has been established in Figure 1.

The various ways of producing compounds having the skeletal structures II, III, and IV by means of coupling radicals A and B are listed in Table II. In order that only radicals A and B be produced, it is necessary to make the reasonable assumptions that (a) the homolytic cleavage of I occurs to produce radicals in which the methyl group is *trans* about the 1,2 bond of the pentadienyl radical; (b) the *s-trans* and *s-cis* conformations of the initial tetraene are the precursors of the two radicals A and B, respectively; and (c) once formed in this way, the methylpentadienyl radicals retain their stereochemistry. Simple Hückel calculations suggest the minimum energy required for isomerism of a pentadienyl radical to be about 13 kcal. (the total π -energy of the pentadienyl radical minus the sum of the π -energy of ethylene plus the allyl radical).

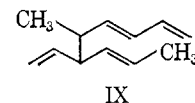
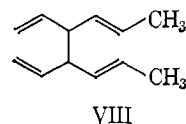
Table II. Modes of Combinations of 1-Methylpentadienyl Radicals

Skeletal structure	Radical combinations	Geometric isomer
II	A ₂ A ₅ ; A ₅ B ₂	IIa
	A ₇ B ₅ ; B ₂ B ₁	IIb
III	A ₁ A ₅ ; A ₅ B ₁	IIIa
	A ₁ B ₅ ; B ₁ B ₅	IIIb
IV	A ₅ A ₆	IVa
	A ₅ B ₅	IVb
	B ₅ B ₆	IVc

Assumption a is reasonable on the basis of internal steric factors. Comparison of the two possible conformations VI and VII suggests that as the homolytic cleavage occurs and the sp³ carbons begin to adopt the sp² configuration, then methyl-hydrogen interactions render VII, which leads to the *cis*-1-methylpentadienyl radicals, to be the least favorable.



One fact which is not in immediate accord with this mechanism is that compounds of general structure VIII and IX could, in principle, also be produced by the coupling of radicals such as A and B. The fact that such compounds are not isolated cannot be taken as evidence against the radical mechanism, however, for these two systems would be expected to be very unstable under the reaction conditions and would further react to give the compounds III and IV. It is significant that only under the minimum conditions necessary to effect rearrangement of I is it possible to isolate compounds of type II; as stated above, samples of pure II upon heating give mixtures of I, III, and IV.



Two factors might be considered responsible for the change in the mechanism of the rearrangement of the dimethyldecatetraenes compared to the dimethyl-1,5-hexadienes. The first is the greater gain in resonance energy upon formation of two pentadienyl radicals from the decatetraenes as compared to the formation of two allyl radicals from the hexadienes. The second is that a cyclic six-membered transition state for the tetraene rearrangement would presumably involve some loss in the conjugation energy of the diene units and hence would be less stable relative to the initial state than in the case of the hexadienes where no such energy loss is encountered. From the first of these considerations it seems possible that certain substituted 1,5-hexadienes, with substituents capable of strongly stabilizing free radicals, might also undergo thermal rearrangement *via* a radical mechanism. However, such substituents might also be expected to stabilize the six-membered transition state involved in the "normal" process; perhaps the most that can be said then at this point is that it would not be unreasonable to expect a change in mechanism in those cases where strong stabilization of free radicals is possible. Indeed, it has been reported by Koch¹⁰ that *meso*-3,4-diphenyl-1,5-hexadiene rearranges at 150° to a 3:2 mixture of 1,6-diphenyl- and 1,4-diphenyl-1,5-hexadiene; the latter product could result from the dimerization of 1-phenylallyl radicals.

Experimental

Vapor Phase Chromatographs. Preparative vapor phase chromatography (v.p.c.) was carried out using an Aerograph A-700 fractometer. Analytical data were obtained with this instrument as well as an Aerograph Hy-Fi (with flame ionization detector).

Vapor Phase Chromatography Columns. Apiezon column A: 3/8 in. × 20 ft., 25% Apiezon L on 45-60 mesh bicarbonate-washed Chromosorb P. Apiezon column B: 1/8 in. × 5 ft., 25% Apiezon L on 80-100 mesh Chromosorb P; Apiezon column C: 1/8 in. × 15 ft., 25% Apiezon L on 80-100 mesh Chromosorb P; Carbowax column A: 3/8 in. × 20 ft., 25% Carbowax 20M on 45-60 mesh Chromosorb P; Carbowax column B: 1/8 in. × 5 ft., 25% Carbowax 20M on 80-100 mesh Chromosorb P; silver fluoroborate column: 3/8 in. × 10 ft., 10% silver fluoroborate and 20% Carbowax 20M on 45-60 mesh bicarbonate-washed Chromosorb P.

Thermal Rearrangement of *meso*-5,6-Dimethyl-*trans*,-*trans*-1,3,7,9-decatetraene (*meso* I). A. Preparation. A solution of 160.0 g. of ceric ammonium nitrate in 400 ml. of 75 vol. % ethanol-water was added dropwise during 1 hr. to a stirred solution containing 16.0 g. of *meso*-5,6-dimethyl-*trans*,-*trans*-1,3,7,9-decatetraene-diiron hexacarbonyl⁵ in 150 ml. of acetone. The mixture was stirred an additional 20 min. and then added to water and extracted with ether.

The combined ether extracts from three such degradations were washed with saturated brine and then dried over magnesium sulfate. Removal of ether and distillation of the residual oil afforded 15.2 g. (89%) of

(10) H. P. Koch, *J. Chem. Soc.*, 1111 (1948).

meso I. The mass spectral cracking pattern of *meso* I showed the expected parent molecular ion at m/e 162.

Hydrocarbon *meso* I, 150 mg., was diluted with 2 ml. of acetone and added slowly to 300 mg. of tetracyanoethylene dissolved in 6 ml. of acetone. The mixture was allowed to stand *ca.* 30 min. and then solvent was removed under reduced pressure. The residue was then triturated several times with small portions of boiling benzene; recrystallization from benzene-acetone of the bis adduct afforded white crystals, m.p. 254–256° dec.

Anal. Calcd. for $C_{24}H_{18}N_8$: C, 68.88; H, 4.33; N, 26.79. Found: C, 68.71; H, 4.46; N, 26.92.

B. Pyrolysis. Hydrocarbon *meso* I, 14.8 g., was diluted with cyclohexane to 40 ml. and the solution was added dropwise to a vertically mounted Pyrex tube (16 mm. in diameter by 40 cm. long) which had been packed with $1/4$ in. Pyrex beads, wrapped in sheet asbestos, and enclosed in a muffle furnace maintained at 375°. The apparatus was purged with dry nitrogen at a flow rate of 3 l./min. during pyrolysis (and for *ca.* 1 hr. prior to pyrolysis). The primary collection vessel consisted of a 100-ml. round-bottom flask which was loosely packed with glass wool and cooled in a Dry Ice-acetone bath. After reaction, the collection apparatus was thoroughly washed with cyclohexane and the bulk of solvent was subsequently removed from the pyrolysate. Analysis of the pyrolysate by v.p.c. on Apiezon column B indicated three main product fractions in addition to unreacted *meso* I.¹¹ In order of elution, these four fractions accounted for 22% (*meso* I), 16% (II), 23% (III), and 34% (IV) of the pyrolysate. Preparative v.p.c. on Apiezon column A gave 1.05 g. of *meso* I, 1.45 g. of II, 1.75 g. of III, and 3.35 g. of IV; the retention times of these fractions were 28, 32, 40, and 65 min., respectively.

Pyrolysis of 10.8 g. of *meso* I, which had been prepared in the manner described previously, gave 36% of *meso* I, 17% of II, 17% of III, and 22% of IV. Preparative v.p.c. on Carbowax column A afforded 1.84 g., 0.60 g., 0.95 g. and 1.53 g. of these fractions, respectively.

C. Ultraviolet, P.m.r., and Mass Spectra of the Pyrolysis Product Fractions. The ultraviolet absorption spectrum of fraction II displayed $\lambda_{\max}^{95\% \text{ EtOH}}$ at 228 $m\mu$ (ϵ 26,600). The proton n.m.r. spectrum (CS_2) showed multiplets centered at τ 4.50, 7.40, 7.87, and 8.35 with relative areas 9:1:2:6, respectively. The mass spectrum showed the parent molecular ion at m/e 162.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.00; H, 11.10.

Fraction III displayed ultraviolet $\lambda_{\max}^{95\% \text{ EtOH}}$ at 229 $m\mu$ (ϵ 37,600). The proton n.m.r. spectrum (CS_2) exhibited multiplets centered at τ 4.30 and 7.90 and doublets centered at τ 8.30 and 9.00 with relative areas 3:1:1:1 (9:3:3:3), respectively. The mass spectrum exhibited the parent molecular ion at m/e 162.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.84; H, 11.02.

(11) Hydrocarbons *meso* and *rac* I are not separable on any of the v.p.c. columns described herein; however, the identity of recovered I was established from its infrared and n.m.r. spectra.

Fraction IV had ultraviolet $\lambda_{\max}^{95\% \text{ EtOH}}$ at 228 $m\mu$ (ϵ 35,900). The proton n.m.r. spectrum (CS_2) showed complex multiplets centered at τ 4.20 and 7.85 and a doublet centered at τ 8.30 with relative areas 4:2:3 (8:4:6), respectively. The mass spectrum exhibited the parent molecular ion at m/e 162.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.72; H, 11.02.

Thermal Rearrangement of rac-5,6-Dimethyl-trans,-trans-1,3,7,9-decatetraene (rac I). *A. Preparation.* A total of 46.6 g. of *rac*-5,6-dimethyl-trans,*trans*-1,3,7,9-decatetraenediiron hexacarbonyl⁵ was degraded in two equal portions with ceric ammonium nitrate in the manner described previously for the corresponding *meso* compound. The total yield of *rac* I was 14.8 g. (87%). The mass spectrum of *rac* I showed the parent peak at m/e 162.

The bistetracyanoethylene adduct was formed in the same manner as described for the *meso* isomer; this crystallized from benzene-acetone in white needles, m.p. 268–270° dec.

Anal. Calcd. for $C_{24}H_{18}N_8$: C, 68.88; H, 4.33; N, 26.79. Found: C, 68.85; H, 4.42; N, 26.75.

B. Pyrolysis. Hydrocarbon *rac* I, 14.0 g., was diluted with cyclohexane to a total volume of 40 ml. and added dropwise during 1 hr. to a vertically mounted Pyrex tube maintained at 375°, in the manner described previously for the pyrolysis of *meso* I. Analysis of the pyrolysate by v.p.c. on Apiezon column B indicated three main fractions in addition to unreacted *rac* I. These four fractions accounted for 26% (*rac* I), 12% (II), 23% (III), and 31% (IV) of the pyrolysate. Preparative v.p.c. on Apiezon column A gave 1.25 g. of *rac* I, 1.12 g. of II, 1.38 g. of III, and 3.00 g. of IV.

In a second similar pyrolysis 11.2 g. of *rac* I gave 18% of unreacted *rac* I, 16% of II, 22% of III, and 33% of IV. Preparative v.p.c. on Apiezon column A afforded 0.65, 1.15, 0.95, and 2.53 g. of these fractions, respectively.

V.p.c. Comparison of the Pyrolysis Fractions Obtained from meso and rac I. Fractions II, III, and IV obtained from pyrolysis of *meso* I had the same retention times on Apiezon column B and Carbowax column B as the corresponding fractions from the pyrolysis of *rac* I. Further analyses of fractions II on the silver fluoroborate column indicated that both were mixtures of two components, present in approximately equal amounts. Similar analysis of III, obtained from *meso* I, indicated two components, and the first eluted component (IIIa) accounted for 63% of the mixture. The corresponding fraction obtained from *rac* I had two components with identical retention times as those from *meso* I; however, IIIa comprised 67% of this mixture. Fraction IV, from *meso* I, was a mixture of three components: the first two, in order of elution, accounted for 27 (IVa) and 63% (IVb) of the mixture. These components accounted for 54 and 31%, respectively, of the mixture obtained from *rac* I.¹²

*Preparation of 4-Ethyldecane.*¹³ A solution containing 15.8 g. of 1-bromohexane and 10 ml. of anhydrous

(12) The stated percentages of the various geometric isomers must be taken as approximate values because of v.p.c. peak overlapping.

(13) The general method for the preparation of 4-ethyldecane is similar to that described in ref. 14 for the preparation of 5-methylundecane.

ether was added dropwise to 2.55 g. of magnesium turnings and 15 ml. of ether. After the initially vigorous reaction had subsided and addition of the 1-bromohexane solution was complete, the mixture was refluxed *ca.* 20 min. After this time, a solution containing 8.6 g. of 3-hexanone in 15 ml. of anhydrous ether was added dropwise to the stirred Grignard reagent. The mixture was stirred an additional 20 min. after ketone addition was complete and then poured into saturated ammonium chloride solution. The ether layer was extracted with two 50-ml. portions of saturated ammonium chloride solution, 50 ml. of dilute hydrochloric acid, and finally 50 ml. of dilute sodium bicarbonate solution. The ether solution was then dried over magnesium sulfate. Removal of ether and subsequent distillation of the residual oil gave 9.8 g. (61%) of 4-hydroxy-4-ethyldecane, b.p. 64° (0.25 mm.), n_{D}^{27} 1.4354.

4-Hydroxy-4-ethyldecane (9.4 g.) was heated with 1.0 g. of powdered potassium bisulfate for 4.5 hr. at 135°. The progress of the reaction was monitored by v.p.c. on Carbowax column B. After reaction, the dehydration mixture was taken up in ether and this ethereal solution was extracted with saturated sodium bicarbonate solution and then dried over magnesium sulfate. The bulk of solvent was removed under reduced pressure and a portion of the residue was subjected to preparative v.p.c. on Carbowax column A. A quantity of the collected dehydration products (0.9180 g.) was catalytically hydrogenated over pre-reduced platinum oxide in glacial acetic acid. Upon completion of the hydrogen absorption, the mixture was filtered through Celite, the filtrate was then poured into water, and the resulting mixture was extracted with pentane. Removal of pentane followed by preparative v.p.c. on Carbowax column A afforded 200 mg. of colorless oil, n_{D}^{26} 1.4219.

Anal. Calcd. for $C_{12}H_{26}$: C, 84.61; H, 15.39. Found: C, 84.50; H, 15.33.

Hydrogenation of Fraction II and Comparison of the Hydrogenation Product with 4-Ethyldecane. Fraction II, 110.6 mg., was hydrogenated over pre-reduced platinum oxide in glacial acetic acid. The hydrogen uptake (59.0 ml. at STP) indicated the presence of four double bonds (found 3.86) per molecule. The mass spectral cracking patterns of this hydrogenation product and synthetic 4-ethyldecane were in good agreement, and their retention times on Carbowax column B and Apiezon column C were identical.

*Preparation of 5-Methylundecane.*¹⁴ A solution containing 16.0 g. of 2-hexanone and 10 ml. of anhydrous ether was added to the Grignard reagent prepared from 31.6 g. of 1-bromohexane and 5.0 g. of magnesium turnings, in the manner described in the preparation of 4-hydroxy-4-ethyldecane. The reaction mixture was worked up in the usual manner. Analysis of the crude 5-hydroxy-5-methylundecane (27.8 g.) by v.p.c. on Carbowax column B indicated that the product was 88% pure. The product had b.p. 65° at 0.30 mm.

A quantity of the crude 5-hydroxy-5-methylundecane, 10.6 g., was heated with 1.0 g. of powdered potassium bisulfate for 18 hr. at 130°. The dehydration mixture was then taken up in ether; the ether solution was

extracted with saturated sodium bicarbonate solution and then dried over magnesium sulfate. After removal of ether, a portion of the dehydration mixture was subjected to preparative v.p.c. on Carbowax column A. A quantity of the dehydration products, 1.8168 g., was then catalytically hydrogenated in glacial acetic acid solution over pre-reduced platinum oxide. After hydrogenation, the mixture was filtered through Celite and the filtrate was poured into water. The resulting mixture was extracted with pentane and the pentane extracts were dried over magnesium sulfate. Removal of pentane followed by preparative v.p.c. on Carbowax column A afforded 300 mg. of colorless oil, n_{D}^{25} 1.4198 (reported¹⁴ n_{D}^{20} 1.4216).

Anal. Calcd. for $C_{12}H_{26}$: C, 84.61; H, 15.39. Found: C, 84.66; H, 15.28.

Hydrogenation of Fraction III and Comparison of the Hydrogenation Product with 5-Methylundecane. Fraction III, 104.6 mg., was hydrogenated over pre-reduced platinum oxide in glacial acetic acid. The hydrogen uptake (57.9 ml. at STP) indicated the presence of four (found 3.83) double bonds per molecule. The mass spectral cracking patterns of this hydrogenation product and synthetic 5-methylundecane were identical as were their retention times on Carbowax column B and Apiezon column C.

Hydrogenation of Fraction IV and Comparison of the Hydrogenation Product with Dodecane. Fraction IV, 86.6 mg., was hydrogenated in the manner described for fractions II and III. The hydrogen uptake (44.5 ml. at STP) indicated the presence of four (found 3.73) double bonds per molecule. The mass spectral cracking patterns of this hydrogenation product and authentic dodecane were in good agreement and their retention times were identical on Carbowax column B and Apiezon column C.

Further Characterization of the Pyrolysis Products.

A. Fraction II. Fraction II, 400 mg., was added slowly to a solution containing 160 mg. of tetracyanoethylene (TCNE) in 4 ml. of acetone. The intense red-violet color first produced faded to pale pink after the solution had remained at room temperature *ca.* 20 min. Solvent was then removed under reduced pressure and the oily residue was triturated with boiling pentane and then allowed to cool to room temperature. Analysis of the pentane layer on the $AgBF_4$ column indicated almost quantitative removal of the first eluted component (IIa) of the original mixture. Pentane was removed and the residual oil was subjected to preparative v.p.c. on the $AgBF_4$ column. The product, IIb, exhibited the infrared absorptions listed in Table I. The residue (250 mg., 70%) remaining from pentane trituration was dissolved in boiling benzene-acetone and then allowed to stand at -20° for several hours until crystallization appeared to be complete. The crystals (white needles) were collected and dried at 0.5 mm. for *ca.* 1 hr. The compound had m.p. 78-80° and its infrared spectrum (KBr disk) exhibited absorption at 910 and 990 (s) and 965 cm^{-1} (s).

Anal. Calcd. for $C_{18}H_{18}N_4$: C, 74.45; H, 6.26; N, 19.29. Found: C, 74.40; H, 6.39; N, 19.16.

B. Fraction III. Components IIIa and IIIb were collected in a pure state from the $AgBF_4$ column and

(14) V. E. Terres, L. Brinkmann, D. Fisher, D. Rullstrung, W. Lorz, and E. Weisbrod, *Brennstoff-chem.*, 40, 279 (1959).

the infrared spectra of the neat liquids were obtained. These data are listed in Table I.

Fraction III (obtained from *rac* I), 400 mg., was added slowly to 600 mg. of TCNE dissolved in 5 ml. of acetone. Reaction appeared to be complete after *ca.* 30 min. Solvent was then removed by evaporation at reduced pressure and the residue was triturated with boiling cyclohexane. The residue remaining from trituration was then washed with a small amount of boiling benzene. The crude adduct of IIIa (400 mg., 94%) was then recrystallized from benzene-cyclohexane affording white needles, m.p. 239–241° dec.

Anal. Calcd. for $C_{24}H_{18}N_8$: C, 68.88; H, 4.33; N, 26.79. Found: C, 68.83; H, 4.53; N, 26.77.

Compound IIIb, 75 mg., was added slowly to a solution containing 60 mg. of TCNE in 2 ml. of acetone. After reaction was complete (*ca.* 20 min.) the acetone was removed and the residue was then dissolved in benzene-petroleum ether. Upon standing at -20° for several days, white needles of a monoadduct (*ca.* 25 mg.), m.p. 80–82°, were obtained.

Anal. Calcd. for $C_{18}H_{18}N_4$: C, 74.45; H, 6.26; N, 19.29. Found: C, 74.45; H, 6.19; N, 19.15.

C. Fraction IV. A solid, m.p. 37.5–38.5°, was obtained by successive crystallizations (five) of IV (obtained from *rac* I) from pentane in a Dry Ice-acetone bath. The mixture melting point of this solid with one obtained similarly from *meso* I showed no depression. Both samples (neat, melts) exhibited infrared absorption at 925 (w) and 987 cm^{-1} (vs). V.p.c. analysis on the $AgBF_4$ column indicated the compound isolated in this manner to be component IVa. The proton n.m.r. spectrum (CS_2) of IVa exhibited complex multiplets centered at τ 4.30 and 7.86, and a doublet centered at τ 8.26 with relative areas 4:2:3 (8:4:6), respectively.

A sample of IVa (460 mg.) was added slowly to TCNE (730 mg.) dissolved in acetone (7.0 ml.). The reaction appeared to be complete after *ca.* 30 min. Solvent was removed and the solid residue was triturated with a small amount of boiling benzene. The crude adduct (1.15 g.) was then recrystallized from acetone-acetonitrile yielding white needles, m.p. 301–303° dec. (sealed tube).

Anal. Calcd. for $C_{24}H_{18}N_8$: C, 68.88; H, 4.33; N, 26.79. Found: C, 68.74; H, 4.49; N, 26.63.

Pentane was removed from the combined mother liquors which remained after 0.460 g. of IVa had been crystallized out of a 1.30-g. sample of IV and the residual oil, 730 mg., was slowly added to 690 mg. of TCNE (slight excess above the amount calculated to remove residual IVa and IVb) dissolved in 10 ml. of acetone. After reaction was complete the solvent was removed and the oily residue was triturated with boiling petroleum ether. The petroleum ether solution was decanted and solvent was removed by evaporation at reduced pressure, affording 170 mg. of an oil which was shown by v.p.c. on the $AgBF_4$ column to be virtually pure IVc. A pure sample was also obtained by preparative v.p.c.

The proton n.m.r. spectrum (CS_2) of IVc exhibited complex multiplets at τ 4.24 and 7.84 and a doublet centered at τ 8.32 with relative areas 4:2:3 (8:4:6), respectively.

Component IVb was obtained by preparative v.p.c.

($AgBF_4$ column) of fraction IV derived from *meso* I. A sample of IVb, 104 mg., was added slowly to 80 mg. of TCNE dissolved in 2 ml. of acetone. After 30 min. the solvent was removed and the residual oil was dissolved in boiling cyclohexane and quickly filtered through a Celite-Norit pad. All attempts to obtain a crystalline material failed; the adduct remained a viscous oil.

Anal. Calcd. for $C_{18}H_{18}N_4$: C, 74.45; H, 6.26; N, 19.29. Found: C, 72.97; H, 6.12; N, 17.48.

Preparation of 1,10-Dideuterio-meso and -rac I. A. Preparation of 5-Deuterio-syn-1-methylpentadienyliron Tricarbonyl Fluoroborate. *trans,trans*-2,4-Hexadienyliron tricarbonyl^{6,15} (20.0 g.) was diluted with 150 ml. of anhydrous ether and cooled, with stirring, to 0–5°. To this stirred solution was added 1.0 g. of lithium aluminum deuteride in 50 ml. of anhydrous ether. The addition required *ca.* 15 min. and the mixture was allowed to stir an additional hour after addition was complete. After reaction, 50 ml. of water followed by 50 ml. of dilute hydrochloric acid was slowly added to the mixture. The ether layer then was separated, washed with water, and dried over magnesium sulfate. Removal of solvent afforded 20.0 g. of crude product, 1-deuterio-*trans,trans*-2,4-hexadien-1-oliron tricarbonyl.

The crude deuterated alcohol was diluted with 25 ml. of acetic anhydride and added dropwise to a stirred solution containing 15.0 g. of 48–50% aqueous fluoroboric acid in 30 ml. of acetic anhydride which had been cooled to 5–10°. The reaction mixture was allowed to stir *ca.* 30 min. after addition was complete and was then worked up in the manner described previously for *syn*-1-methylpentadienyliron tricarbonyl fluoroborate. The product amounted to 20.5 g. (80%).

B. Zinc Reduction of 5-Deuterio-syn-1-methylpentadienyliron Tricarbonyl Fluoroborate. The deuterated salt described in part A (20.3 g.) was stirred at ambient temperature (25°) for 72 hr. with 22.0 g. of zinc dust and 150 ml. of tetrahydrofuran. The mixture was then filtered through Celite and the solvent was removed under reduced pressure. The residue was then triturated with boiling petroleum ether and the mixture was quickly filtered through Celite. Upon cooling to -78° the solution afforded 8.0 g. (55%) of a mixture of deuterated *meso* and *rac* complexes (1,10-dideuterio analogs of *meso*- and *rac*-5,6-dimethyl-*trans,trans*-1,3,7,9-decatetraenediiron hexacarbonyl). The crude product had m.p. 90–105°.

C. Degradation of the Zinc Reduction Products. 1,10-Dideuterio-*meso*- and -*rac*-5,6-dimethyl-*trans,trans*-1,3,7,9-decatetraenediiron hexacarbonyl (8.0 g.) were dissolved in acetone and degraded with ceric ammonium nitrate in the manner described previously. The yield of deuterated hydrocarbons was 2.0 g. (69%, b.p. 37° at 0.30 mm.). The mass spectral cracking pattern of the product showed the parent molecular ion at *m/e* 164; the relative intensities at *m/e* 164 and 162 indicated at least 95% of the compound possessed two deuterium atoms per molecule. An infrared spectrum of the deuterated hydrocarbons (neat) exhibited absorptions at 800 (s), 815 (m-s), 950 (m-s), 897 (vs), 1583 (m-s), and 1654 cm^{-1} (m-s). (See Table I for the major absorption bands of *meso* and *rac* I.)

(15) J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).

Pyrolysis of *meso* and *rac* I with Their 1,10-Dideuterio Analogs. A sample of the deuterated hydrocarbons, 1.5089 g., was pyrolyzed with 1.4986 g. of *meso* and *rac* I in the manner previously described for the pyrolysis of *meso* and *rac* I. Samples of pyrolysate fractions III and IV were obtained by preparative v.p.c. on Apiezon column A. The mass spectral cracking patterns (mass spectrometer inlet temperature

170°) of both fractions showed parent molecular ion peaks at *m/e* 162 (no deuterium), 163 (one deuterium atom/molecule), and 164 (two deuterium atoms/molecule); however, the peak at *m/e* 163 was the most intense peak of the three in both fractions III and IV.

Acknowledgment. We thank the Alfred P. Sloan Foundation and the Robert A. Welch Foundation for financial assistance.

The Mechanism of the Thermal Decomposition of α -Phenylethylazomethane. A Two-Step Reaction¹

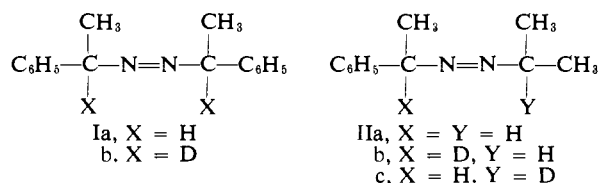
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α -Phenylethylazomethane (IIIa), α -phenylethyl- α -d-azomethane (IIIb), and α -phenylethylazomethane-*d*₃ (IIIc) were prepared. The isotope effects in the thermal decomposition, $k_{IIIa}/k_{IIIb} = 1.13$ and $k_{IIIa}/k_{IIIc} = 0.97$, were found. In addition, the C¹³ effect in the decomposition of α -phenylethylazomethane-C¹³ is $k_{12}/k_{13} = 1.0068$. From these results we conclude that the slow step involves rupture of only the α -phenylethyl carbon-nitrogen bond; the breaking of the methyl-nitrogen bond in the unstable methylazo radical occurs in a subsequent fast step. An estimate of the lower limit of the rate constant for the second step is obtained from the results. The energy and entropy of activation are discussed.

Introduction

In previous papers the use of the secondary α -deuterium isotope effect in determining whether two bonds rupture stepwise or simultaneously was pointed out.^{2,3} Azobis- α -phenylethane (Ia) and azobis- α -phenylethane- α,α' -*d*₂ (Ib) were allowed to decompose thermally in ethylbenzene; the observed isotope effect, $k_{Ia}/k_{Ib} =$



1.27, indicated that both carbon-nitrogen bonds were breaking in a simultaneous process.² Decomposition of α -phenylethylazo-2-propane presented a somewhat different picture. The secondary effects $k_{IIa}/k_{IIb} = 1.16$ and $k_{IIa}/k_{IIc} = 1.04$ led to the conclusion that here too both carbon-nitrogen bonds stretch in the same step but to unequal degrees by the time the molecule

reaches the transition state.³ Since the secondary α -effect is due, in main part, to the change in H-C-leaving group bending force constant,⁴ it was argued that a secondary α -deuterium isotope effect smaller than the usual effect of about 15% observed in unimolecular decomposition indicates a smaller than usual amount of C-leaving group bond breaking. So in the case of α -phenylethylazo-2-propane greater stretching of the benzylic-carbon-nitrogen bond than of the 2-propyl-carbon-nitrogen bond has taken place at the transition state. This is consonant with the view that the α -phenylethyl group is able to delocalize a free electron more efficiently than the 2-propyl group. "Resonance energies" of the α -phenylethyl and isopropyl radicals differ by more than 15 kcal./mole,⁵ and therefore it is not surprising that the decomposition path of lowest energy is that where unstable species are most easily stabilized. Cohen^{6b} and Overberger^{6c} and their co-workers have suggested previously that differences in rates of decomposition of dialkylazo compounds are probably due to changes in the activation energies brought about by different degrees of resonance stabilization of the particular alkyl radicals produced. The possibility of an unsymmetrical compound decomposing in a symmetrical or an unsymmetrical one-step or two-step mechanism was expressed. However, by studying only the activation energies of decomposition of unsymmetrical dialkylazo compounds, a choice between a symmetrical and an unsymmetrical one-step cleavage is difficult or impossible to make.

A new, more unsymmetrical azo compound, α -phenylethylazomethane (III), was synthesized. Its rate of decomposition was studied to gain further insight into the factors which determine the relative timing of the rupture of the two carbon-nitrogen bonds in dialkylazo compounds. From the secondary α -deuterium and C¹³ isotope effects described in this

(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 4c.

(2) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961).

(3) S. Seltzer, *ibid.*, **85**, 14 (1963).

(4) (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzaki, *ibid.*, **80**, 2326 (1958); (b) S. Seltzer, *ibid.*, **83**, 1861 (1961); (c) M. Wolfsberg and M. Stern, *J. Pure Appl. Chem.*, **8**, 225 (1964).

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