

Ethyl 3-(3-Carboxycyclopentyl)propanoate. The product of the dehydration of ethyl 3-(2-hydroxy-3-carboxycyclopentyl)propanoate (34 g) was dissolved in 400 ml of ethyl acetate and hydrogenated in two 17-g portions over 1.7 g of platinum dioxide. After filtration of the catalyst and concentration of the solution, the product was used directly in the next step without further purification.

3-(3-Carboxycyclopentyl)propanoic Acid (VII). Ethyl 3-(3-carboxycyclopentyl)propanoate (32 g) was hydrolyzed in the same manner as described for methyl 3-(3-carboxycyclopentyl)propanoate to yield 20.4 g (73%) of product, mp 69–79°. One recrystallization from ether–cyclohexane raised the melting point to 79–82°. On mixture of a sample of this product with an authentic sample of the diacid (from the methyl ester series) the melting point was not depressed. The infrared spectrum of this product was identical in every respect with that of the diacid from the methyl ester series.

3-(3-Carboxycyclopentyl)propanoic Acid Chloride. A solution of 92 ml of oxalyl chloride in 100 ml of dry benzene was added dropwise to a stirred solution of 39.5 g of 3-(3-carboxycyclopentyl)propanoic acid in 200 ml of dry benzene. After the addition was completed, the solution was warmed to 40° and stirred for 1 hr. The solution was concentrated under reduced pressure, then distilled at 97–105° (0.03 mm) to yield 42.7 g (79%) of product; ν_{\max} 1795 cm^{-1} (CCl_4).

1-Carboxy-2-oxobicyclo[3.2.1]octane (IV). A solution of 30 ml of triethylamine (distilled from potassium hydroxide) in 100 ml of dry ether was added dropwise with stirring to a refluxing solution of 42.7 g of 3-(3-carboxycyclopentyl)propanoic acid chloride in 500 ml of dry ether under nitrogen pressure over a period of 0.5 hr. Reflux was continued for 1.5 hr after the addition was completed, then the reaction mixture was filtered under nitrogen pressure without exposure to air and concentrated at reduced pressure. The residue was distilled in a short-path apparatus at approximately 175° (2 mm), then redistilled at 85–90° (0.03 mm) to yield approximately 5 g of the acid chloride of 1-carboxy-2-oxobicyclo[3.2.1]octane. This product was dissolved in 50 ml of acetic acid and warmed on the steam bath for 1 hr, then concentrated by freeze drying, to yield 1 g of residue. The residue was dissolved in a small amount of benzene and placed on a chromatography column of 30 g of silica gel (powder, Baker reagent grade) prepared in

cyclohexane and eluted with cyclohexane, then mixtures of cyclohexane–benzene (3:1, 2:2, 1:3, 0:1) and then benzene–ether mixtures (9:1, 8:2, 7:3, 6:4). The fractions (20 ml) were examined by thin layer chromatography on silica gel. The plates were developed with a mixture of 80 ml of ethanol and 5 ml of 29% ammonia, then dried at 100° for 15 min and sprayed with a solution of bromocresol purple. The acids were indicated by yellow spots on a dark blue background. No acids were present in fractions prior to elution with benzene–ether. A fraction eluted with benzene–ether (8:2) gave a major spot with R_f 0.25, and crystallized (needles) on removal of the solvent, to yield 70 mg (0.2%) of product, mp 90–100°. Two sublimations at 60° (0.03 mm) raised the melting point to 109.5–112.5°. Thin layer chromatography as described above gave one spot, R_f 0.34; ν_{\max} 2950, 1750, 1710 cm^{-1} .

Anal. Calcd for $\text{C}_9\text{H}_{12}\text{O}_3$: C, 64.26; H, 7.19. Found: C, 64.14; H, 7.44.

2-Oxobicyclo[3.2.1]octane. 1-Carboxy-2-oxobicyclo[3.2.1]octane (4 mg) was heated at 260–265° for 0.5 hr in a sealed tube. The infrared spectrum of the product was identical with that of an authentic sample of 2-oxobicyclo[3.2.1]octane kindly donated by Professor H. M. Walborsky.

The Decarboxylation Studies. Weighed samples of the β -keto acids were heated for 0.5-hr periods in a stirred oil bath or a stirred Wood's metal bath at temperatures where approximately one-half of the sample was decarboxylated. The temperature was controlled to within 1° by turning the oil bath heater off and on manually as necessary. After the samples were heated, a known amount of Spectrograde chloroform was added by a pipet so that the concentration of the resulting solution was approximately 10 mg/ml, depending on the amount of decarboxylation at the chosen temperature. In all cases, the sample dissolved rapidly and completely. The amount of acid remaining in the sample after heating was determined by the intensity of the acid carbonyl band in the infrared spectrum.

The Measurement of Dihedral Angles. Dreiding models were used to construct molecular models of the compounds prepared in this work. At least two molecular models were constructed for each compound and five angle measurements were made from each model. The average value of the orbital angle is listed for each compound in Table I. The previous angle² listed for compound I is in error and the correct value is given in Table I.

Sigmatropic Reactions in the 1,4-Bis(cycloheptatrienyl)benzene Isomers

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Abstract: The preparation of the 1,4-bis(cycloheptatrienyl)benzene isomers is described. Thermal and photochemical sigmatropic reactions have been observed in these materials, and the kinetics of one of these processes have been measured. The activation energy, A factor, and transition state parameters have been calculated for this process and compared with those for similar systems. The nmr and ultraviolet spectra of the isomers are reported and discussed. An analysis of the proton spin–spin coupling in the 7,7 isomer leads to the conclusion that it exists in a preferred conformation.

As part of a continuing study of the chemistry of A compounds containing more than one diazo group,^{1–3} we have photolyzed and thermolyzed 1,4-bis(α -diazomethyl)benzene (I) in the presence of benzene in hopes of obtaining the interesting hydrocarbon, 1,4-bis(7-cycloheptatrienyl)benzene (IIa). This reac-

tion would be analogous to that reported by Gutsche, Bachman, and Coffey for phenyldiazomethane which gives phenylcycloheptatriene when photolyzed in benzene.⁴ The desired hydrocarbon (IIa) was of interest as a potential precursor to the dicarbonium ion, p -phenylenebis(cycloheptatrienylium cation) (III).

Despite numerous attempts, including a number of experimental variations, IIa was never obtained in

(1) R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).
(2) R. W. Murray and A. M. Trozzolo, *ibid.*, **29**, 1268 (1964).
(3) A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *J. Am. Chem. Soc.*, **85**, 2526 (1963).

(4) C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962).

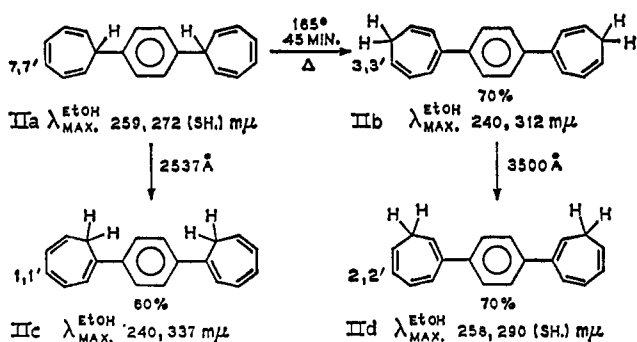
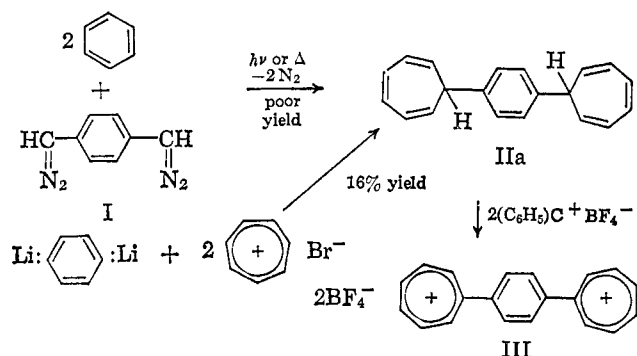


Figure 1. The 1,4-bis(cycloheptatrienyl)benzene isomers.

more than *ca.* 2% yield from the thermolysis or photolysis of I. This method was abandoned in favor of the reaction of 1,4-dilithiobenzene with 2 moles of tropylium bromide which gives IIa in 16% yield. At least part of the difficulty in the attempted synthesis of IIa from I would seem to be the number of facile thermal and photochemical hydrogen shift reactions which were subsequently discovered to occur in IIa.



The reaction of 1,4-dilithiobenzene with tropylium bromide should give the bis-7,7-cycloheptatrienyl isomer, IIa. Doering and Knox have reported⁵ the formation of a phenylcycloheptatriene from the reaction of phenyllithium with tropylium ion which they have concluded is the 7 isomer. The ultraviolet spectrum of IIa, $\lambda_{\text{max}}^{\text{EtOH}}$ 259 m μ (log ϵ 3.82), 272 (sh), is in accord with the spectrum (λ_{max} 256 m μ (log ϵ 3.56)) reported for 7-phenylcycloheptatriene by Doering and Knox.⁵

The nmr spectrum of IIa provides convincing evidence for its structure. The spectrum consists of a singlet at 2.63, a triplet at 3.25, a multiplet at 3.71, a quartet at 4.57, and a triplet of triplets at 7.21.⁶ These absorptions are assigned to the aromatic, the 3,4,3',4' olefinic, 2,5,2',5' olefinic, 1,6,1',6' olefinic, and methine protons, respectively. The comparable olefinic and methylenic absorptions in cycloheptatriene occur at 3.45, 3.88, 4.72, and 7.80, respectively.⁷

The multiplicities and relative areas of the alkyl hydrogen absorptions in the various isomers of IIa

(5) W. Von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(6) Nmr spectra were taken on a Varian Associates Model A-60 nmr spectrometer. The spin-decoupling experiments were done using a Varian DP-60 nmr spectrometer. Chemical shift values given are τ values with tetramethylsilane as external standard. Except as otherwise noted, deuteriochloroform was used as the solvent for nmr measurements.

(7) See "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 158.

provide evidence for the structures of the isomers. The methylenic absorption in the 1,1⁸ isomer must be a doublet of relative area 4. In the 7,7, 2,2, and 3,3 isomers the corresponding methylenic (2,2 and 3,3) or methine (7,7) absorptions must all be triplets.⁹ However, the relative area in the 7,7 isomer should be 2, as observed, while the 2,2 and 3,3 isomer triplets should have relative areas of 4 (see Figure 1). The possibility of mixed isomers, *i.e.*, 7,3-3,1, etc., also exists, of course, but does not appear to be a complicating factor in this work (*vide infra*).

The pure 7,7 isomer (IIa) was used to generate the dicarbonium ion (III) as reported earlier.¹⁰ It also provides the starting material for a study of thermal and photochemical sigmatropic reactions in which, formally, a hydrogen atom undergoes a series of successive shifts.

Kinetic Study

The difficulties experienced in the attempts to prepare IIa by thermal and photochemical reactions of I and the recent reports by Ter Borg and Kloosterziel¹¹⁻¹³ on thermal and photochemical hydrogen shift reactions in phenylcycloheptatriene led us to undertake a similar study in the case of IIa. Preliminary experiments demonstrated that when IIa is heated it undergoes the same series of successive 1,5-hydrogen shifts that Ter Borg and Kloosterziel had shown for 7-phenylcycloheptatriene. Similar hydrogen shift reactions have also been observed in deuteriocycloheptatriene,^{12,14-17} ethylcycloheptatriene,¹⁸ and alkoxyheptatrienes.^{19,20}

When a 5% solution of IIa in deuteriochloroform is heated in a sealed nmr tube, the triplet of the 7,7-methine hydrogens at 7.21 is seen to disappear with the concurrent appearance of a new triplet at 7.62 due to the methylene hydrogens of the 3,3 isomer (IIb). Continued heating leads to the complete disappearance of the 7,7-methine triplet and the formation of a doublet at 7.20 due to the 1,1 isomer (IIc) methylene protons, in addition to the triplet of the 3,3-isomer methylene group (Figure 2).

The hydrogen shift reaction thus appeared to be a series of consecutive 1,5-hydrogen migrations which would lead to the formation of the isomers in the sequence, 7,7 \rightarrow 3,3 \rightarrow 1,1 \rightarrow 2,2 (*i.e.*, IIa \rightarrow IIb \rightarrow IIc \rightarrow II d). The other possible hydrogen shift paths, *i.e.*, a series of 1,2 or 1,3 shifts would lead to a different sequence for the appearance of the isomers. Similar 1,5-shift sequences were observed in 7-deuteriocycloheptatriene,¹⁴ 7-phenylcycloheptatriene,¹¹ and 7-meth-

(8) The numbers used to designate the isomers of IIa refer to the positions in the cycloheptatriene rings to which the aromatic ring is attached.

(9) The observation that the 7,7 isomer methine absorption actually consists of a triplet of triplets is discussed later in this paper.

(10) R. W. Murray and M. L. Kaplan, *Tetrahedron Letters*, 2903 (1965).

(11) A. P. Ter Borg and H. Kloosterziel, *Rec. Trav. Chim.*, **82**, 741 (1963).

(12) A. P. Ter Borg and H. Kloosterziel, *ibid.*, **84**, 214 (1965).

(13) A. P. Ter Borg and H. Kloosterziel, *ibid.*, **84**, 245 (1965).

(14) A. P. Ter Borg, H. Kloosterziel, and N. Van Meurs, *ibid.*, **82**, 717 (1963).

(15) A. P. Ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962).

(16) W. R. Roth, *Angew. Chem.*, **75**, 921 (1963).

(17) W. Von E. Doering and P. P. Gaspar, *J. Am. Chem. Soc.*, **85**, (1963).

(18) K. Conrow, *ibid.*, **83**, 2343 (1961).

(19) E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 59 (1964).

(20) T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Japan*, **38**, 665 (1965).

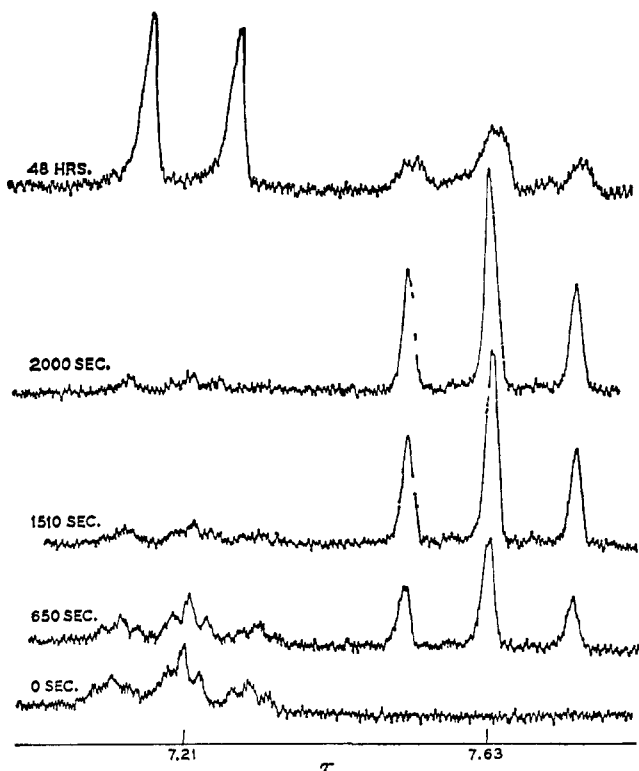
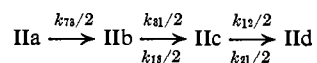


Figure 2. The effect of heating on the methine nmr absorption in 1,4-bis(7-cycloheptatrienyl)benzene.

oxycycloheptatriene.²⁰ The first step in the sequence (IIa \rightarrow IIb) appears to be essentially irreversible, while the other steps are all reversible. The kinetic system therefore, consists of the following. Again, for purposes of



simplification, we have not included the mixed-isomer possibilities. As it developed, it seems likely that the kinetics within one cycloheptatriene ring are independent of those in the other.

We have used an nmr integration method similar to that of Nozoe and Takahashi²⁰ to show that the first step in this over-all process, *i.e.*, IIa \rightarrow IIb, follows first-order kinetics (Figure 3). The total area integrated, that is, the sum of the areas for the triplet of IIa and the triplet of IIb remains essentially unchanged over the time used for the kinetic study indicating that other reactions which might consume IIa are not important during this period. Also, this method appears to be uncomplicated by the possibility of mixed isomers of the type 7,3. Either the chemical shift of the methine hydrogen in the 7,3 isomer is essentially identical with that of the 7,7 isomer or this isomer does not have sufficient lifetime to enter into the over-all scheme. At any rate, because of the method used, the rate constant measured (k_{73}) is for the conversion of a 7-substituted cycloheptatriene system to a 3-substituted system and so can be compared with rate constants for similar processes in related systems. This scheme necessarily assumes that the rate constant k_{73} is essentially the same in the 7,7 and 7,3 isomers. The structural differences between these two are far enough removed from the reaction site to make this a reasonable assumption.

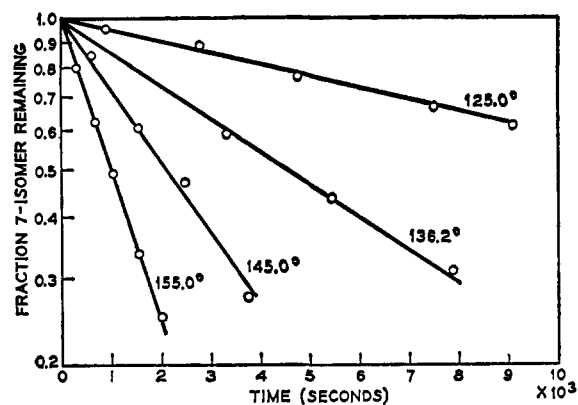


Figure 3. Plots of the logarithm of the fraction of 7 isomer present *vs.* time at several temperatures.

The rate constant k_{73} was measured at a number of temperatures (Table I). An Arrhenius plot was then

Table I. Summary of Kinetic Results for the Conversion of 1,4-Bis(7-cycloheptatrienyl)benzene to Its 3 Isomer

Solvent	1,4-Di-tropyl-benzene, wt %	Temp, °C	k_{73} , sec ⁻¹
Cl ₂ C=CCl ₂	5.5	136.2	1.61×10^{-4}
Cl ₃ C=CCl ₂	2.6	136.2	1.57×10^{-4}
CDCl ₂	5.5	136.2	1.53×10^{-4}
CDCl ₃	6.4	145.0	3.34×10^{-4}
CDCl ₃	6.4	155.0	7.20×10^{-4}
CDCl ₃	6.4	125.0	5.37×10^{-5}

drawn, and the activation energy (E_a) and log A were determined to be 30.6 kcal/mole and 12.5, respectively. The rate constant was found to be essentially independent of concentration and solvent at 136.2° (Table I). A comparison of the rate constants for the hydrogen shift reaction in a number of cycloheptatriene derivatives is given in Table II. The rate

Table II. Rate Constants for the Thermal Isomerization of Some Cycloheptatriene Derivatives^a

Compound	k_{73} , sec ⁻¹	Ref
7-Phenylcycloheptatriene	3.6×10^{-5}	11
7-Deuteriocycloheptatriene	6.0×10^{-7}	14
7-Methoxycycloheptatriene	2.48×10^{-5}	20
1,4-Bis(7-cycloheptatrienyl)benzene	3.33×10^{-5} ^a	This work

^a Estimated by extrapolation of Arrhenius plot to 121°.

constants for 7-phenylcycloheptatriene¹¹ and 7-methoxycycloheptatriene²⁰ isomerizing to the respective three isomers, and for IIa \rightarrow IIb, are quite similar and all isomerize about 50 times faster than 7-deuteriocycloheptatriene. The observed increase in rate with the addition of methoxy or aryl substituents can be rationalized if one assumes that the transition state for the isomerization involves a partial positive charge at the 7 position, which can be stabilized by these sub-

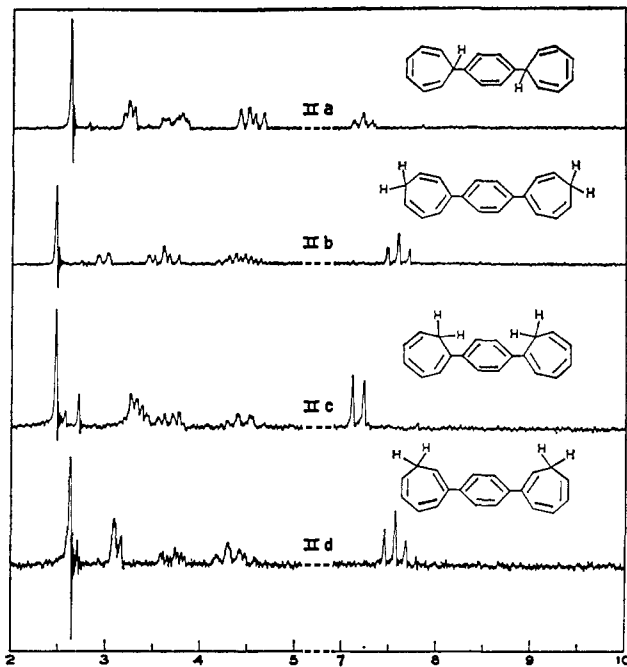


Figure 4. The nmr spectra of the 1,4-bis(cycloheptatrienyl)benzene isomers.

stituents. Such a transition state might be expected if a hydride ion were involved in the isomerization, for example.

The Eyring formulation was then used to calculate values for the transition state quantities ΔF^\ddagger , ΔH^\ddagger , and ΔS^\ddagger . The results of these calculations and the values given in the literature for deuteriocycloheptatriene, phenylcycloheptatriene, and methoxycycloheptatriene are summarized in Table III.

Table III. Transition State Parameters^a for the Thermal Isomerization of Various 7-Substituted Cycloheptatrienes to 3-Substituted Cycloheptatrienes

Compound	E_a , kcal/ mole	Log A , sec ⁻¹	ΔF^\ddagger_T , kcal/ mole	ΔH^\ddagger_T , kcal/ mole	ΔS^\ddagger_T , eu	Ref
7-Phenylcycloheptatriene	27.6	10.8	...	26.9	-11.7	11
7-Deuteriocycloheptatriene	31	10.9	...	31.6	-8.2	14
7-Methoxycycloheptatriene	26.4	10.04	...	25.7	-15.0	20
1,4-Bis(7-cycloheptatrienyl)benzene	30.6	12.5	31.4	29.8	-3.9	This work

^a The transition state parameters for 1,4-bis(7-cycloheptatrienyl)benzene are reported at 140°. The temperatures at which the values for the other compounds are given have not been specified.

The remainder of the kinetic scheme is not as accessible to analysis as is the first, essentially irreversible, step. As indicated earlier the formation of the triplet absorption of the methylene protons of the 3,3 isomer in the nmr is followed by the appearance of the doublet due to the methylene of the 1,1 isomer. The 1,1 isomer is then isomerized to the 2,2 isomer whose methylene triplet appears to be nearly coincident with that of IIb. An examination of the total nmr spectra for all of these isomers fails to disclose a region or com-

bination of regions which could reliably be used to follow the concurrent consumption or appearance of the individual isomers, IIb, IIc, and IIId. While the nmr data do indicate the over-all sequence of the isomerization processes, *i.e.*, IIa \rightarrow IIb \rightarrow IIc \rightarrow IIId, they do not permit a reliable further analysis of the kinetics.

Discussion

The establishment of the over-all kinetic scheme described above rests largely on following changes in the nmr spectrum of IIa with time as a sample is heated. This approach requires preparation of the individual isomers so that the nmr spectra of all the pure isomers are available. The 3,3 isomer (IIb) was conveniently prepared by heating a sample of IIa at 170° for 45 min in a sealed ampoule under nitrogen. The nmr spectrum of IIb consisted of a singlet at 2.48, a doublet at 2.98, a multiplet at 3.62, a multiplet at 4.43, and a triplet at 7.63. The integrated intensities were 4:1.8:4:3.9:3.5, respectively. These absorptions are assigned to the aromatic, 4,4' olefinic, 2,5,2',5' olefinic, 1,6,1',6' olefinic, and the 7,7' methylene protons, respectively. These assignments and the integrated intensities are in good agreement with the 3,3-isomer designation.

Preparation of the remaining isomers in a pure state by thermal processes is complicated by the fact that all of the hydrogen shift reactions appear to be reversible and of comparable rates. The observation of photochemical 1,7-hydrogen shifts in 7-deuteriocycloheptatriene^{12,16,17} and the report that a similar shift occurs in 7-phenylcycloheptatriene¹² suggested that a photochemical path might be a better way of synthesizing the 1,1 isomer (IIc) in the ditropylbenzene series. When a solution of IIa in pentane was photolyzed at 2537 Å for 90 min, a 60% yield of IIc was obtained. After several recrystallizations the product was obtained as pale yellow plates, mp 116–118°. The nmr spectrum consists of a singlet at 2.48, a broad multiplet at 3.48, a multiplet at 4.50, and a doublet at 7.20 with integrated areas of 4:8:1.8:4, respectively. These absorptions are assigned to the aromatic, the 2,5,2',-5',3,4,3',4' olefinic, 6,6' olefinic, and 7,7' methylene protons, respectively.

The 2,2 isomer (IIId) was also conveniently prepared by a photochemical hydrogen shift reaction. A solution of the 3,3 isomer (IIb) in pentane was photolyzed for 2 hr using 3500-Å irradiation. Several recrystallizations from ethanol gave a material with mp 124–126.5°. The nmr spectrum of this isomer consisted of a singlet at 2.63, multiplets at 3.13, 3.72, and 4.40, and a triplet at 7.58. The integrated intensities were 4:3.6:2.2:4.4:4, respectively. These absorptions are assigned to the aromatic, the 3,4,3',4' olefinic, 5,5' olefinic, 1,6,1',6' olefinic, and methylene protons, respectively. The nmr spectra of all of the isomers are shown in Figure 4.

Having the nmr spectra of all the individual isomers in hand allows one to reliably specify the sequences of isomer appearance and decay in the thermal and photochemical sigmatropic processes. The spectral features are such that they may be uniquely assigned. As mentioned earlier, the 7,7 isomer has the characteristic triplet of triplets of relative intensity 2 at 7.21 which is assigned to the 7-methine hydrogens.

The 1,1 isomer is easily recognized by the appearance of the methylene doublet of relative intensity 4 at 7.20. The 3,3 and 2,2 isomers which cannot be distinguished by the methylene triplets of relative intensity 4 because these occur at almost the same chemical shift, can be assigned on the basis of another spectral feature. The 3,4,3',4' protons which are the most deshielded of the olefinic protons, are a multiplet of relative area 4 in IIc, while the comparable absorption is a doublet of relative area 2 in IIb. These absorptions point to the assignment of IIc and IIb as the 2,2 and 3,3 isomers, respectively.

The nmr spectrum of IIa has an interesting feature which only became apparent when a more highly resolved spectrum was obtained. The methine absorption which occurs at 7.21 was found to be a triplet of triplets indicating that there was a small coupling in addition to the expected coupling with the 1,6 protons. The protons most likely to be responsible for the additional coupling are the 2,5 or the *ortho* aromatic protons, all of which are allylic to the 7-methine proton. A series of spin-decoupling experiments²¹ was used to determine the origin of this coupling. Irradiation of the 1,6 protons led to collapse of the original spectrum to a single absorption with a poorly defined fine structure. Irradiation of the 2,5 protons led to collapse of the minor triplet so that a clean triplet with $J = 5.8$ cps was obtained. Irradiation of the aromatic protons caused no change in the original spectrum. These results indicated that the major coupling ($J = 5.8$ cps) is associated with the 1,6 protons and the minor coupling ($J = 1.4$ cps) with the 2,5 allylic protons. Finally, irradiation of the 1,6 and 2,5 protons simultaneously, using two oscillators, leads to total collapse of the methine absorption to a singlet.

Nozoe and Takahashi²⁰ observed complex multiplets for the C_7 protons in 7-methoxycycloheptatriene and 7-ethoxycycloheptatriene. These authors also attributed this observation to a long-range coupling between the 7 proton and the 2,5 protons. On the other hand, Ter Borg and Kloosterziel,¹¹ who found that the C_7 proton absorption in 7-phenylcycloheptatriene consisted of a triplet of triplets, felt that the long-range coupling in their case was due to the *ortho* aromatic protons. The magnitude of their coupling constants ($J = 5.5$ cps for the coupling between the 7 proton and the 1,6 protons, and $J = 1.4$ cps for the long-range coupling) is comparable to the corresponding values of 5.8 and 1.4 cps found for IIa. It seems likely that the observed long-range coupling in 7-phenylcycloheptatriene is also due to the 2,5 allylic protons rather than the *ortho* aromatic protons which would be expected to have a much smaller coupling.

Ter Borg and Kloosterziel have presented arguments for a preferred conformation in 7-phenylcycloheptatriene,¹¹ that is, the conformer with an axial hydrogen and an equatorial phenyl substituent (*i.e.*, IVa in Figure 5). These arguments have their origin in the observed coupling constant between the 7 proton and those at positions 1 and 6. The dihedral angle between the 7 carbon-hydrogen bond and the 1 and 6 carbon-hydrogen bonds is approximately 135° in IVa, the conformer with the equatorial substituent, and would

(21) We gratefully acknowledge the assistance of Mr. E. W. Anderson in the spin-decoupling experiments.

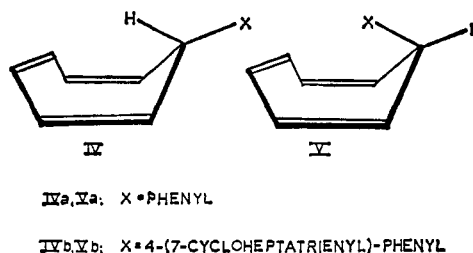


Figure 5. Conformers of 7-substituted cycloheptatrienes.

be expected to give a J value of approximately 4.6 cps,²² compared to the observed value of 5.5 cps. Were conformational isomerization occurring the observed value would be expected to be higher because of the weight of an expected higher coupling for the equatorial hydrogen.²² Similar arguments should apply to IIa where comparable couplings are observed, that is, IVb, in Figure 5, where the 7 proton occupies the axial position, should be the favored conformer.

In addition, the proposal for a single conformer also explains the long-range coupling of 1.4 cps observed in both IIa and 7-phenylcycloheptatriene. In allylic systems the long-range coupling reaches a maximum of about 3 cps when the angle between the plane containing the olefinic protons and the carbon-hydrogen bond, *i.e.*, the 7 proton, is about 90° . The coupling reaches a minimum when this angle is 0 or 180° .²³ The observed long-range coupling of 1.4 cps in IIa also suggests that a single conformer is present with the 7 hydrogen in the axial position, *i.e.*, IVb. In this conformer the angle described above is estimated to be 135° from a model so that the observed 1.4 cps is consistent with that predicted by a theoretical²⁴ or an empirical approach.²⁵ In the other conformer (IVa) with the proton in the equatorial position, the angle measured above would be very small, about 10 – 15° , and little long-range coupling would be expected. The observed coupling leads to the conclusion that no conformational isomerization is occurring since this would lead to a very small average value for the angle described above which would mean little long-range coupling could occur.²⁶ The conclusion that IIa and 7-phenylcycloheptatriene occur almost exclusively in one conformation indicates a standard free energy difference between the conformers of at least *ca.* 2 kcal/mole.

The fact that long-range coupling of the type described here is not observed in the isomers of IIa is also consistent with this explanation. In these cases the phenyl substituent is at an olefinic instead of the aliphatic carbon, and so cannot greatly influence a preferred conformation for the molecule. Conformational isomerization would be expected to be occurring with the result that the average position of the 7 protons would lead to only a small nonobservable, long-range coupling. It may be that measurements at better resolution may detect these small couplings and it is

(22) M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960).

(23) For an excellent review of the subject of long-range coupling see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(24) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(25) D. J. Collins, J. J. Hobbs, and S. Sternhell, *Australian J. Chem.*, **16**, 1030 (1963).

(26) We are grateful to Dr. F. A. Bovey for calling our attention to this possibility and for helpful discussions of the nmr spectra.

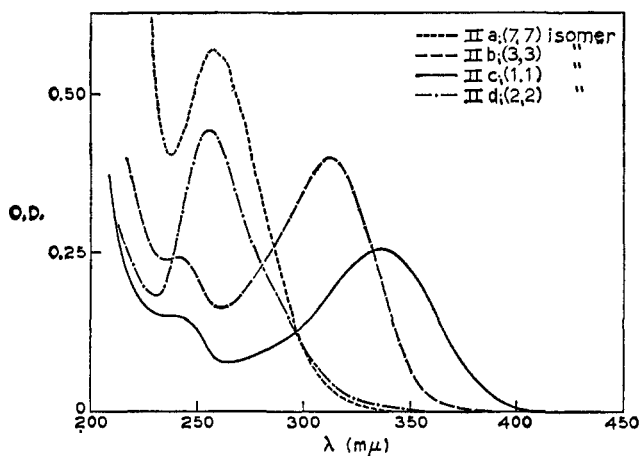


Figure 6. The ultraviolet spectra of the 1,4-bis(cycloheptatrienyl)-benzene isomers.

interesting to note that in the case of cycloheptatriene itself a line broadening in the methylene triplet has been attributed to allylic coupling.¹⁴

The basic question as to the nonplanarity of the cycloheptatriene ring which is necessary to the postulation of conformational isomerization has been settled recently. Using low-temperature nmr studies, Conrow²⁷ has shown that one cycloheptatriene derivative definitely consists of rapidly inverting conformers while Anet²⁸ has shown the same thing to be true in cycloheptatriene itself. Information on the conformation of the nonplanar cycloheptatriene is also available. Using X-ray crystallography Davis and Tulinsky²⁹ have shown that the cycloheptatriene ring in thujic acid assumes a boat conformation. Also, Traetteberg³⁰ has used the electron diffraction method to show that cycloheptatriene exists in a boat conformation. The nmr arguments presented above lend further support to the choice of the boat conformation for cycloheptatriene derivatives.

As has been pointed out by Ter Borg and Kloosterziel,¹⁴ in the case of 7-phenylcycloheptatriene these arguments concerning the conformation, such as occurs in IIa, have a bearing on the kinetic study. Since there is only one 7 proton present per cycloheptatriene nucleus in IIa and two 7 protons in cycloheptatriene itself, direct comparison of the kinetic data could have involved a statistical factor. If one assumes as seems necessary now, that the axial hydrogen is the one involved in the observed migration, then in cycloheptatriene there is always one hydrogen in the proper position for migration regardless of the conformer considered. In IIa, however, with only one 7 proton, there is, theoretically, a conformer possibility with no axial hydrogen. The conclusion reached above, based on the nmr data, that a single conformer is present with hydrogen axial, eliminates a possible complication in comparing the kinetic results.

The long wavelength ultraviolet absorption bands of the ditropybenzene isomers are also quite consistent with the assigned structures (Figure 6). The bands appear at λ_{\max} 259 shoulder at 272 m μ for IIa; λ_{\max} 312

m μ for IIb; λ_{\max} 337 m μ for IIc; and λ_{\max} 258 m μ for II d. The absorption in II d appears to be low by comparison with the other isomers. The corresponding bands in the phenylcycloheptatriene series occur at¹³ 258, 283, 295, and 238 m μ for the 7, 3, 1, and 2 isomers, respectively. Here again the absorption in the 2 isomer is unexpectedly low.

The 7,7 isomer has the shortest wavelength band as expected for the isomer with no conjugation between the cycloheptatriene and benzene ring systems. In the 3,3 isomer, where conjugation can occur, the band moves to a longer wavelength. The fact that the double bonds in the cycloheptatriene ring are cross-conjugated with the phenyl ring apparently leads to an absorption associated chiefly with two double bonds. In the 2,2 isomer, on the other hand, the cross conjugation is such that conjugation with the phenyl ring might be expected to occur with only one double bond of the cycloheptatriene ring system. The long wavelength band actually observed, however, seems to indicate a lack of any conjugation for reasons not readily apparent. The 1,1 isomer has the longest conjugated system and a correspondingly longer wavelength absorption.

The thermal and photochemical rearrangements described above fit nicely into the scheme described by Woodward and Hoffmann³¹ in which the selection rules for sigmatropic transformations are determined by orbital symmetry relationships. This elegant scheme systematizes the observed photochemical and thermal hydrogen migrations in systems, such as IIa, which contain a π -electron system into which a σ bond is to migrate. According to this scheme positive overlap must be maintained between the migrating hydrogen orbital and the framework orbital at the terminus of the migration. In the cycloheptatriene framework, such as occurs in IIa, the symmetry of the highest occupied molecular orbital is such that the migrating hydrogen, in a thermal process, must undergo a 1,5 migration. This is true because amongst the symmetry-allowed 1,3, 1,5, and 1,7 migrations only the 1,5 migration occurs *via* a suprafacial route, that is with the hydrogen atom almost on the same side of the ring, which is an additional requirement imposed on medium sized rings.³¹ This selective 1,5 migration is what was observed in the over-all migration sequence IIa \rightarrow IIb \rightarrow IIc \rightarrow II d, and has also been observed in 7-deuteriocycloheptatriene,¹⁴ 7-methoxycycloheptatriene,²⁰ and 7-phenylcycloheptatriene.¹¹

In remarkable contrast to the thermal path, photochemically induced hydrogen migrations in IIa and IIb, as well as in 7-deuteriocycloheptatriene,^{12,16,17} and possibly in 7-phenylcycloheptatriene¹² involve a highly selective 1,7 pathway. These observations are also consistent with the Woodward-Hoffmann scheme where now the first excited state orbital symmetry relationships lead to the 1,3 and 1,7 processes being symmetry allowed and suprafacial. While the selection rules suggest two possibilities for the photochemical process, the 1,7 migration seems to be the most readily observed. Woodward and Hoffmann have suggested³¹ that this observation may be due to a preference for processes with the maximum degree of linear conjugation in the transition state. It is interesting to observe, however, that in the 7-phenylcycloheptatriene case,¹² the product

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(28) F. A. L. Anet, *ibid.*, **86**, 458 (1964).

(29) A. Tulinsky and R. F. Davis, *Tetrahedron Letters*, 839 (1962).

(30) M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 458 (1964).

(31) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

obtained was not the 1,7-shift product, namely 1-phenylcycloheptatriene, but 2-phenylcycloheptatriene. While this latter product could be the result of successive 1,7-hydrogen shifts, application of the Woodward-Hoffmann selection rules now suggests that it may be a case of a symmetry-allowed 1,3 shift.

The isomers of 1,4-bis(cycloheptatrienyl)benzene have provided an interesting system for studying sigmatropic reactions. Interpretation of the nmr data obtained in these materials provides important clues as to the conformations of these molecules. Finally these materials are the precursors of an interesting and very stable dicarbonium ion. By comparing this dication with tropylium ion and substituted tropylium ions we hope to be able to determine the effect of one positive charge on the other.

Experimental Section³²

Photolysis of 1,4-Bis(α -diazomethyl)benzene in Benzene. A solution of 1,4-bis(α -diazomethyl)benzene, prepared from 1.30 g (8 mmoles) of terephthalaldehyde dihydrazone, in 350 ml of benzene was added dropwise to 1000 ml of benzene which had been stirred under nitrogen for 30 min. The solution was photolyzed using 3500-A radiation, while diazo compound was added at a rate to prevent excessive accumulation. This procedure was repeated five times using a total of 6.50 g (40 mmoles) of terephthalaldehyde dihydrazone. The combined solutions were concentrated *in vacuo*. After filtering off a yellow, insoluble material, the solution was chromatographed on Woelm neutral alumina. Elution with pentane gave 180 mg (1.75%) of a waxy, white solid. Recrystallization from ethanol gave white crystals, mp 137–140° which had ultraviolet absorption of $\lambda_{\text{max}}^{\text{EtOH}}$ 259, 272 (sh) μm . The nmr spectrum was identical with that for IIa produced from the reaction of 1,4-dithiobenzene and tropylium bromide.

Thermolysis of 1,4-Bis(α -diazomethyl)benzene in Benzene. The diazo compound was prepared in the amount and manner as for the photolysis. The benzene solution of the diazo compound was dropped through a 6-in Vigreux thermolysis tube which was maintained at *ca.* 225°, and flushed with dry nitrogen throughout the addition. The exit stream from the thermolysis tube was condensed in a series of traps cooled with Dry Ice-acetone baths. The benzene solutions collected were combined and concentrated *in vacuo*. The concentrate was chromatographed on Woelm neutral alumina. Elution with pentane gave 47 mg (0.46%) of a white, waxy solid. Recrystallization from ethanol gave white crystals, mp 135–138°, whose ultraviolet and nmr spectra were identical with those of 1,4-bis(7-cycloheptatrienyl)benzene.

1,4-Bis(7-cycloheptatrienyl)benzene (IIa). To a solution of 7.08 g (30 mmoles) of *p*-dibromobenzene in 100 ml of petroleum ether (bp 30–60°) was added 50 ml of a solution (*ca.* 10%) of *n*-butyllithium in hexane. The addition was carried out by means of a syringe which was inserted through a serum cap. The solution was refluxed for 24 hr in an atmosphere of dry nitrogen, during which period a tan solid precipitated. Tropylium bromide (10.03 g, 59 mmoles), prepared by the method of Doering and Knox,⁵ was added at one time and refluxing was continued for an additional 2 hr. Hydrochloric acid (30 ml, 2 *N*) was then added cautiously. The pale yellow organic layer was separated, and the aqueous layer was extracted three times with 50-ml portions of petroleum ether (bp 30–60°). The organic layers were washed with 20 ml of 2 *N* sodium hydroxide solution and then dried (MgSO_4). The solvent was removed on a rotary evaporator to give a pale yellow, wet solid. This material was recrystallized from ethanol to give 1.29 g (16.6%) of glistening, white plates, mp 137–139°. The ultraviolet spectrum had $\lambda_{\text{max}}^{\text{EtOH}}$ 259 μm (log ϵ 3.82), 272 μm (sh) and

(32) Ultraviolet spectra were determined on a Cary Model 15 spectrophotometer. Melting points were determined on a Kofler hot stage and are uncorrected. Photolyses were carried out in a Rayonet photochemical reactor.

the nmr spectrum consisted of a singlet at 2.63, a triplet at 3.25, a multiplet at 3.71, a quartet at 4.57, and a triplet of triplets at 7.21 with integrated intensities of 4.3:4.1:4.2:4.2:2, respectively.

Anal. Calcd for $\text{C}_{20}\text{H}_{18}$: C, 93.0; H, 7.0. Found: C, 92.5; H, 7.2.

1,4-Bis(3-cycloheptatrienyl)benzene. An ampoule was charged with 500 mg of 1,4-bis(7-cycloheptatrienyl)benzene, sealed under nitrogen, and heated at 170° for 45 min. The ampoule was opened and the crude material was chromatographed on Woelm neutral alumina. Elution with carbon tetrachloride gave white, glistening plates. Recrystallization from ethanol gave 345 mg (69%) of a material, mp 100–107°. Two additional recrystallizations from ethanol raised the melting point to 106–108°. The ultraviolet spectrum had $\lambda_{\text{max}}^{\text{EtOH}}$ 312 μm (log ϵ 3.47), 239 μm (log ϵ 3.38). The nmr spectrum had a singlet at 2.48, a doublet at 2.98, a multiplet at 3.62, a multiplet at 4.43, and a triplet at 7.63 with integrated intensities of 4:1.8:4:3.9:3.5, respectively.

Anal. Calcd for $\text{C}_{20}\text{H}_{18}$: C, 93.0; H, 7.0. Found: C, 93.32; H, 6.91.

1,4-Bis(2-cycloheptatrienyl)benzene. A solution of 100 mg (0.31 mmole) of 1,4-bis(3-cycloheptatrienyl)benzene in 100 ml of pentane was photolyzed for 2 hr with 3500-A radiation. The solution was then filtered to remove insoluble material and concentrated on the rotary evaporator to give a white, crystalline solid. This material was recrystallized from ethanol to give 70 mg (70%) of white, glistening plates, mp 110–125°. An additional recrystallization from ethanol gave a material with mp 124–126.5°. The ultraviolet spectrum had $\lambda_{\text{max}}^{\text{EtOH}}$ 258 μm (log ϵ 4.50). The nmr spectrum had a singlet at 2.63, multiplets at 3.13, 3.72, and 4.40, and triplet at 7.85 with integrated intensities of 4:3.6:2.2:4.4:4.0, respectively.

Anal. Calcd for $\text{C}_{20}\text{H}_{18}$: C, 93.0; H, 7.0. Found: C, 92.3; H, 7.03.

1,4-Bis(1-cycloheptatrienyl)benzene. A solution of 500 mg (1.55 mmoles) of 1,4-bis(7-cycloheptatrienyl)benzene in 400 ml of pentane was photolyzed for 90 min using 2537-A radiation. The reaction mixture was concentrated on a rotary evaporator and then chromatographed on Woelm neutral alumina. Elution with carbon tetrachloride gave a yellow solid. This was recrystallized from ethanol to give 300 mg (60%) of pale yellow plates. Two further recrystallizations from ethanol gave pale yellow plates, mp 116–118°. The ultraviolet spectrum had $\lambda_{\text{max}}^{\text{EtOH}}$ 240 μm (log ϵ 3.14), 337 μm (log ϵ 3.37). The nmr spectrum had a singlet at 2.48, multiplets at 3.48 and 4.50, and a doublet at 7.20 with integrated intensities of 4:8:1.8:4, respectively.

Anal. Calcd for $\text{C}_{20}\text{H}_{18}$: C, 93.0; H, 7.0. Found: C, 92.7; H, 7.2.

Kinetic Runs. The nmr technique used to determine the rate constant k_{73} was similar to that used by Nozoe and Takahashi.²⁰ Solutions of 1,4-bis(7-cycloheptatrienyl)benzene of the approximate concentration and solvent (see Table I) were placed in nmr tubes and sealed under nitrogen. The tubes were heated by complete submersion in a constant temperature bath which was regulated to $\pm 0.05^\circ$. The nmr absorption in the methylene and methine region was monitored using an expanded scale. The samples were removed from the bath and plunged into ice water, and the nmr absorption was integrated immediately. Each sample was integrated three times and the average value was used. The fraction (*f*) of 7-substituted cycloheptatriene material remaining was calculated from

$$f = \frac{2(\text{integrated area for 7 isomer})}{2(\text{integrated area for 7 isomer}) + (\text{integrated area for 3 isomer})}$$

The rate constant k_{73} was determined from a plot of log *f* vs. time (Figure 3). A summary of the data obtained is shown in Table I. The reaction exhibited first-order kinetics for about two half-lives. Further heating led to the formation of the 1,1 isomer as evidenced by the appearance of a doublet at 7.20 in the nmr spectrum.

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