Anal. Calcd for $C_{16}H_{20}N_2S$: C, 70.59; H, 7.35; N, 10.29; S, 11.77. Found: C, 70.47; H, 7.44; N, 10.06; S, 11.69.

The nmr spectrum (in carbon tetrachloride) showed singlets at τ 8.40 (methyl protons), 7.13 (methylene protons), and a multiplet centered on 2.28 (aromatic protons). The infrared spectrum showed absorptions at 3100, 1550, and 1570 cm^{-1}.

4,5-Di-*t*-butylimidazole (IX).—The Raney nickel necessary for the desulfurization reaction was prepared by dissolving 50% nickel–aluminium alloy in concentrated sodium hydroxide solution at 50°.[22] After all the alloy had been added, stirring was continued for 45 min and the Raney nickel was washed four times with distilled water and three times with dioxane. To this still basic Raney nickel (60 g) in 200 ml of dioxane was added 4 g of the sulfur-containing imidazole VI. The mixture was stirred by a vibrator and refluxed for 7 hr. The warm solution was filtered and the Raney nickel was refluxed twice with 200 ml of dioxane to remove all the absorbed imidazole. The combined dioxane filtrates were concentrated in a rotatory evaporator and the residue recrystallized from carbon tetrachloride to give 1.2 g (yield 35%), mp 150–151°.

Anal. Calcd for $C_{11}H_{20}N_2$: C, 73.33; H, 11.11; N, 15.56. Found: C, 72.99; H, 11.28; N, 15.54.

The nmr spectrum (in carbon tetrachloride at 70°) gave singlets at τ 8.55 (*t*-butyl protons), 2.90 (aromatic proton), and 0.42 (N–H proton).

4,5-Di-*t*-butyloxazole (VIII, Picrate).—The desulfurization reaction was carried out as described for the imidiazole VI. The residue from the dioxane filtrates was dissolved in 50% ethanol and picric acid in 50% ethanol was added. Crystals of the picrate were collected, mp 150–151°.

Anal. Calcd for $C_{17}H_{22}N_4O_8$: C, 49.80; H, 5.41; N, 13.67. Found: C, 49.80; H, 5.47; N, 13.65.

For spectral data see the Discussion of Results.

2,3-Di-*t*-butyl-5,6,7,8-tetrahydroquinoxaline (X) and 2,3-Di-*t*-butyl-1,2-dihydroquinoxaline (XVII).—The desulfurization reaction of quinoxaline VII was carried out as described for the imidazole VI. The residue obtained by concentration of the dioxane filtrates was dissolved in hot methanol. Upon cooling bright, white needles began to crystallize and after filtration and recrystallization from methanol analytically pure 2,3-di-*t*-butyl-5,6,7,8-tetrahydroquinoxaline (X) was obtained, yield 25%, mp 79–80°.

Anal. Calcd for $C_{16}H_{26}N_2$: C, 78.11; H, 10.65; N, 11.39. Found: C, 78.34; H, 10.65; N, 11.11.

The methanol filtrates were concentrated and the residue was dissolved in petroleum ether (bp 40–60°). Upon cooling 2,3-di-*t*-butyl-1,2-dihydroquinoxaline (XVII) crystallized as a microcrystalline compound, yield 25%, mp 110–116°.

Anal. Calcd for $C_{16}H_{24}N_2$: C, 78.75; H, 9.91. Found: C, 79.07; H, 9.96.

Concentration of the petroleum ether filtrates yielded a residue consisting of a mixture of the two compounds X and XVII. These compounds were separated by chromatography over basic aluminium oxide. Each compound was thus obtained in 35% yield. For spectral data see the Discussion of Results.

2,3-Di-*t*-butylquinoxaline (XI).—The Raney nickel obtained after the four washings with water was refluxed for 0.5 hr with 200 ml of acetone and the acetone was replaced by 200 ml of dioxane, the sulfur-containing quinoxaline VII was added, and the desulfurization reaction was carried out further as described for the imidazole VI. The residue obtained by concentration of the dioxane filtrates was dissolved in petroleum ether (bp 40–60°) and chromatographed over basic aluminium oxide. Elution with petroleum ether (bp 40–60°) gave the desired quinoxaline, yield 50%, mp 53–54°.

Anal. Calcd for $C_{16}H_{22}N_2$: C, 79.34; H, 9.09; N, 11.57. Found: C, 79.43; H, 9.05; N, 11.50.

For spectral data see the Discussion of Results.

The syntheses of 2,3-diisopropylquinoxaline, 2,3-dimethylquinoxaline, and 2-mono-*t*-butylquinoxaline were carried out as described for quinoxaline VII by condensing the appropriate α-diketones with *o*-phenylendiamine in acetic acid. The nmr spectrum of 2,3-diisopropylquinoxaline (in carbon tetrachloride) showed a doublet centered on τ 8.63, heptet centered on 6.53 (isopropyl protons), and a multiplet centered on 2.25 (aromatic protons).

The nmr spectrum of 2-*t*-butylquinoxaline (in carbon tetrachloride) indicated a singlet at τ 8.50 (*t*-butyl protons), a multiplet centered on 2.13 (5,6,7,8-aromatic protons) and 1.15 (3-aromatic proton). Ultraviolet spectra are shown in Figure 1.

The ultraviolet spectra of 2,3-dimethylquinoxaline [λ_{max} 237, mμ (ϵ_{max} 25.7 $\times 10^3$), 316 mμ (ϵ_{max} 7.1 $\times 10^3$)], and of 2-*t*-butylquinoxaline [λ_{max} 235 mμ (ϵ_{max} 30.2 $\times 10^3$), 307 (5.8 $\times 10^3$), 317 (6.6 $\times 10^3$)] show the normal characteristics for these compounds.

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(22) See also H. R. Billica and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 176.

Reaction of the Cyclooctatetraenyl Dianion with Methyl Iodide[1]

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The reaction of the cyclooctatetraenyl dianion with methyl iodide gives, as initial products, 7,8-dimethyl-1,3,5-cyclooctatriene (**3**) and 5,8-dimethyl-1,3,6-cyclooctatriene (**2**). These products are thermally sensitive, the first dimerizing *via* its valence tautomer, 7,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**4**), and the second undergoing 1,5-hydrogen shift to 3,8-dimethyl-1,3,5-cyclooctatriene (**5**) which equilibrates with its valence tautomer, 3,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**6**), which decomposes to toluene at still higher temperature. The structures were initially inferred from the products of ozonolysis and pyrolysis of Diels–Alder adducts of the original product mixtures. The 7,8-dimethyl-1,3,5-cyclooctatriene (**3**) was never isolated in a pure state because of its ease of polymerization, but each of the other products was isolated and its structure confirmed by spectral analysis.

The chemistry of the cyclooctatetraenyl dianion has received considerable attention ever since the initial report that cyclooctatetraene in ether will dissolve 2 g-atoms of lithium metal.[3] In accord with Hückel's hypothesis predicting that a planar monocyclic conjugated system containing $4n + 2$ electrons ($n = 2$, here) will have resonance stabilization, Katz and coworkers have shown that cyclooctatetraenyl dianion is a planar, highly resonance stabilized species.[4,5] The high electron density and negative charge of the dianion suggest that it should be a highly basic, nucleophilic species and accordingly it has been shown to react with a number of substrates, including proton sources,[3,6]

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(1) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, p 63S.

(2) From the dissertation of David A. Bak, submitted in partial fulfillment of the requirements for the Ph.D. degree, Kansas State University, 1966.

(3) W. Reppe, O. Schlichting, K. Klager, and T. Topepel, *Ann. Chem.*, **560**, 1 (1948).

(4) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3735 (1960).

(5) T. J. Katz, W. H. Reimuth, and D. E. Smith, *ibid.*, **84**, 802 (1962).

(6) A. C. Cope and F. A. Hochstein, *ibid.*, **72**, 2515 (1950).

carbon dioxide,[7] aldehydes and ketones,[8-13] and alkyl halides.[7,8] With *gem*-dihalides[14,15] and acid halides,[16] bicyclic derivatives result. In addition to its reactivity as a nucleophile, the dianion also is reactive as a reducing agent, transferring its electrons to a substrate and being reoxidized to cyclooctatetraene.[17,18]

This work began with the idea that cyclooctatetraenyl dianion might be a good precursor to bicyclic systems in which the eight-membered ring of the dianion is fused to some number of other atoms by nucleophilic attack on some difunctional substrate. Attempts with such substrates as benzil, biacetyl, methyl oxalate, phenacylbromides, and phthalolyl chloride gave only intractable materials or products which seemed to arise from electron transfer from the dianion. We decided to study the reaction of dianion with a simpler substrate, methyl iodide, in order to avoid reduction and obtain products which would be relatively easily identified.

Since the preparations of the cyclooctatetraenyl dianion in the literature give, in our hands, solutions which are considerably darkened, indicating polymerization concurrent with dianion formation, we refined the preparation of dianion by using a potassium dispersion in glyme at −70°, which results in a slightly yellow reaction mixture. The reaction with methyl iodide, too, was permitted to occur at this low temperature, resulting in a much increased yield (84%, by vpc analysis) of dimethylcyclooctatriene isomers, and a minimum of polymerization.

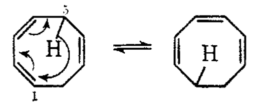
Because Cope[6] obtained both the 1,2- and 1,4-addition products (1,3,5-cyclooctatriene and 1,3,6-cyclooctatriene) in the reaction of dianion with proton sources, we expected two products from the reaction of dianion with methyl iodide, namely, 5,8-dimethyl-1,3,6-cyclooctatriene (**2**) and 7,8-dimethyl-1,3,5-cyclooctatriene (**3**).

However, the ultraviolet spectrum of the material collected from preparative vpc through a METHPED column showed three maxima. Cope[6] showed that the 1,3,5-cyclooctatriene gave a single absorption at 265 mμ and the 1,3,6 isomer gave only tail absorption. There is no reason to expect that the dimethyl derivatives from simple 1,2 and 1,4 addition should give more complex spectra than the parent substances. Therefore the three ultraviolet maxima were an indication that our mixture contained more than these two products, *i.e.*, that isomerization of the initial products had occurred.

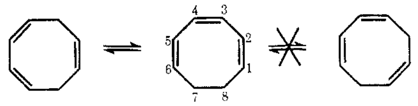
Two different mechanisms by which thermal isomerizations of cyclooctatrienes occur have been reported.

Cope, *et al.*,[19] have studied the formation of bicyclo[4.2.0]octa-2,4-diene from 1,3,5-cyclooctatriene. At temperatures of 80–100° they found an equilibrium mixture of 85% mono- and 15% bicyclic isomers starting with either of the pure isomers. Both isomers formed the same Diels–Alder adduct with maleic anhydride but under quite different temperature conditions.

The mechanism of the thermal transformation of the 1,3,6 to the 1,3,5 isomer involves a 1,5-hydrogen shift.



Roth[20] has studied 1,5-hydrogen shifts using 1,3,5-cyclooctatriene labeled in the 7,8 positions with deuterium. 1,3,5-Cyclooctatriene-d_2 was heated at 225° to establish the 1,3,5- and 1,3,6-isomer equilibrium. The deuterium was shown to be statistically distributed only in the 3, 4, 7, and 8 positions rather than over the whole 1,3,5-cyclooctatriene system. This establishes 1,5-hydrogen shift and rules out 1,3 shifts in going from the 1,3,6 to the 1,3,5 isomer.



Since we had ultraviolet evidence that more than two products were present, we searched for a vpc column which would give separation of the components. We were able to separate what seemed to be a three-component mixture on a $^1/_8$ in. × 6 ft 5% silver nitrate–5% Apiezon L column. This column gave good separation with small injections and was used as the analytical column to estimate the yields from later reactions, but there was considerable overlap of the peaks when injections larger than 1 μl were used. (Hereafter the components will be identified as peak 1, peak 2, and peak 3 in order of their increasing retention times on this column.) We found that we were able to use fractional distillation to obtain samples which were enriched in the various components. The conditions (low pressure and temperature, collecting the distillate in a cold bath) of the distillations were chosen to prevent the polymerization reported in earlier work on the cyclooctatriene system.

We attempted to separate peak 1 in a pure condition by preparative vpc using a larger silver nitrate–Apiezon L column. The sample used had been enriched in peak 1 by distillation. Reinjection of the collected sample showed that peak 1 had developed a small shoulder (hereafter referred to as peak 1 shoulder) and a third component in major amount which corresponded in retention time with peak 3. The formation of peak 3 from a collected sample of peak 1 indicated that peak 3 must be related to peak 1. Peak 1 shoulder, however, could not be confidently correlated with peak 1 at this time since it might have arisen by isomerization of peak 2 during the initial injection.

After this experience, we thought it would be impossible to separate the isomers by preparative vpc because of the isomerization which was observed in these

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(7) W. Reppe and H. Schlenck, German Patent 857,376 (Nov 27, 1952); *Chem. Abstr.*, **50**, 4207*h* (1956).

(8) N. D. Azatyan, *Dokl. Akad. Nauk*, SSSR, **98**, 403 (1954).

(9) N. D. Azatyan and R. S. Gyuli-Kevkhyan, *Dokl. Akad. Nauk Arm. SSSR*, **20**, 81 (1955); *Chem. Abstr.*, **50**, 4051*a* (1965).

(10) N. D. Azatyan and R. S. Gyuli-Kevkhyan, *Izv. Akad. Nauk Arm. SSR, Khim. Nauk*, **14**, 451 (1961); *Chem. Abstr.*, **58**, 3327 (1963).

(11) T. S. Cantrell and H. Shechter, *J. Am. Chem. Soc.*, **87**, 136 (1965).

(12) T. S. Cantrell and H. Shechter, Abstracts of 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964, p 71S.

(13) G. Wittig and D. Wittenberg, *Ann. Chem.*, **606**, 1 (1957).

(14) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2858 (1963).

(15) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 4816 (1964).

(16) T. S. Cantrell and H. Shechter, *ibid.*, **85**, 3300 (1963).

(17) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963).

(18) K. Conrow and P. C. Radlick, *J. Org. Chem.*, **26**, 2260 (1961).

(19) A. C. Cope, A. C. Hoven, Jr., F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

(20) W. R. Roth, *Ann. Chem.*, **671**, 25 (1964).

first attempts. We decided to try to infer their identity by identification of the oxidative ozonolysis products of the reaction mixtures. Although it would be easier to identify pure samples of each isomer it is possible to make the identification from a mixture if the components give different ozonolysis products.

Ozonolysis of the isomeric mixture obtained by preparative vpc gave acids after oxidative work-up which could be obtained from the aqueous solutions by continuous extraction. When the mixtures of acids obtained were found to be too complex for thin layer chromatography identification, the acids were esterified and the esters were identified by vpc retention time comparisons and by mass spectrometry. *meso*-Dimethyl 2,3-dimethylsuccinate was identified by vpc retention comparison with an authentic sample. Dimethyl methylsuccinate was identified from its mass spectral fragmentation pattern and molecular weight and its identity was confirmed by its vpc retention time comparison with an authentic sample. Dimethyl 3-methylcyclobutane-1,2-dicarboxylate and dimethyl 3,4-dimethylcyclobutane-1,2-dicarboxylate were identified solely by their mass spectral molecular weight and fragmentation patterns. The mass spectra were run on samples collected from preparative vpc.

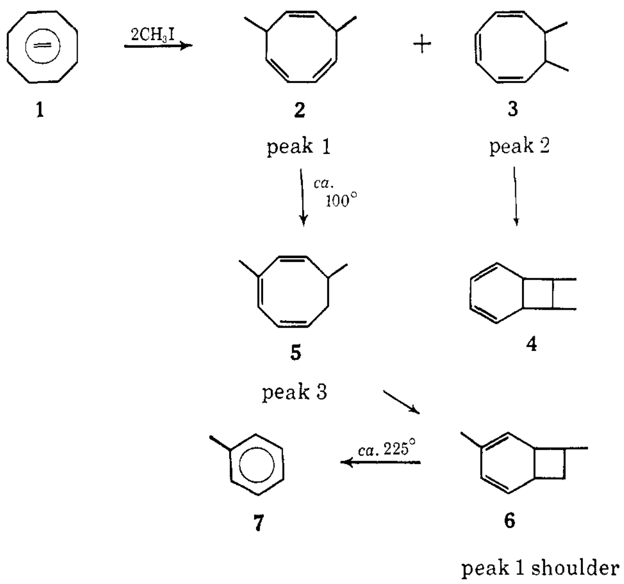
On the assumption that only 1,2- and 1,4-addition products occurred and that no subsequent skeletal rearrangement occurred which would move the methyl groups from their original positions, the identification of these oxidation product esters shows that the dimethyl cyclooctatriene mixtures contained 3,8-dimethyl-1,3,5-cyclooctatriene (**5**), 7,8-dimethyl-1,3,5-cyclooctatriene (**3**), 3,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**6**), and 7,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**4**). The composition of the starting material was unknown because we had not yet adopted the analytical silver nitrate column at this time, but the oxidation product ratios indicated that there was about 80% 1,4-addition products and 20% 1,2-addition products in the sample. The presence of such a variety of products in the sample which was ozonized probably is the result of thermal isomerizations occurring during its vpc separation.

In order to obtain ozonolysis products which more nearly represented the initial reaction mixture with a minimum of subsequent isomerization, a sample of dimethylcyclooctatriene mixture which had never been heated above 60° was ozonized. The starting material contained 40% peak 1, 47% peak 2, and 13% peak 3 as determined by vpc analysis. A different set of esters was obtained which were identified by retention time comparisons with authentic samples. This time no indication of cyclobutane derivatives was found. Methyl acetate, methyl oxalate, dimethyl methylmalonate, dimethyl methylsuccinate, and *meso*- and *dl*-dimethyl 2,3-dimethylsuccinate (in a 4:1 ratio) were identified.

The composition of the oxidation products corresponded to 53% 1,4- and 47% 1,2-addition products. Since peak 2 and the ozonolysis products corresponding to 1,2 addition, *meso*- and *dl*-dimethyl dimethylsuccinate, both are present in equivalent amount it would seem that peak 2 must be 7,8-dimethyl-1,3,5-cyclooctatriene (**3**). Peaks 1 and 3, which were already known to be interrelated, must both therefore be derived from 1,4 addition. The large amount (23%) of dimethyl methylmalonate indicates that peak 1 corresponds to 5,8-dimethyl-1,3,6-cyclooctatriene (**2**), and the quantity (11%) of dimethyl methylsuccinate indicates that peak 3 is 3,8-dimethyl-1,3,5-cyclooctatriene (**5**). Thus, this sample contained a quantity of the initial 1,4 adduct, 5,8-dimethyl-1,3,6-cyclooctatriene (**2**), a substance absent from the sample which had been exposed to a higher temperature.

The ozonolysis data implied that methyl iodide reacts with cyclooctatetraenyl dianion to give both the 1,2- and 1,4-addition products in analogy with Cope's work with the parent cyclooctatrienes. The heat supplied by the vpc conditions seemed to cause the 1,5-hydrogen shift and valence tautomerism. Although these experiments provided evidence for the assignment of structure to the chromatographic peaks and comparison of the ozonolysis products obtained in different cases confirmed the expected sequence of events in the isomerization, we sought additional experimental verification of these conclusions. (See Scheme I.)

SCHEME I



In an attempt to confirm the identity of peak 2 as the 7,8-dimethyl isomer (**3**), a sample containing 20% peak 1, 70% peak 2, and 10% peak 3 was placed in an nmr tube in preparation for taking the spectrum of the mixture. After being in the tube for about 5 min, a vigorous exothermic reaction occurred. The nmr spectrum showed, and vpc analysis confirmed, that toluene was formed in the reaction.

A series of experiments was initiated to discover the cause of this spontaneous reaction and the source of the toluene. It developed that acidic, basic, and free-radical catalysts were all ineffective in inducing the formation of toluene, but that simple thermolysis was effective in interconverting isomers and bringing about the formation of toluene. These experiments also further confirmed the sequence of events in the thermal isomerization of the primary products and eventually led to a degree of understanding which permitted isolation of pure samples of most of the compounds.

The first attempt at the thermal reaction involved a sample containing 73% peak 1, no peak 2, and 27%

peak 3. Small, sealed tubes of the samples were placed in baths at 100, 150, and 200°. In 10 min the two hottest baths gave samples containing about 70% peak 1 and 30% peak 3. This same ratio persisted throughout the experiment. The 100° samples reached this equilibrium mixture only after 1 hr. The equilibrium composition is so close to that of the starting material that it seems that the 1,5-hydrogen shift equilibrium was already set up before the experiment was run. The experiment was repeated with a sample containing peak 2. The sample also had 1% toluene present. This experiment was carried out in the same manner at room temperature, 92, 154, and 198°, and equal quantities of the contents of each tube were injected for vpc analysis so that some estimate of losses to polymerization was available. After 30 min the two higher temperature samples showed that the same equilibrium mixture of peaks 1 and 3 had arisen as in the previous experiment. Peak 2 had disappeared, but the area of the toluene peak had not increased from that of the starting material showing that peak two does not form toluene with its disappearance. The disappearance of peak 2 was more gradual in the 92° case, still being present after 1 hr but gone after 10 hr. Peaks 1 and 3 gradually disappeared at the higher temperatures, presumably owing to polymerization, but always maintained their 70:30 ratio.

Toluene was finally produced thermally by using a temperature of 225°. Peak 2 had disappeared after 15 min. Although toluene was also formed during this period, an insufficient amount of toluene was formed to have resulted from the disappearance of peak 2. During 15 min at 225°, toluene had begun to form and peaks 1, one shoulder, and 3 had decreased. The total area of toluene and these three peaks was the same as their total area had been in the starting material, showing they were being interconverted. At 30 min the amount of toluene increased at the expense of the other three peaks but the total area was still the same. The following samples began to show a decrease in the total area probably owing to polymerization.

A polymer peak was observed at longer retention time whose retention time was such that the material was most likely dimeric as is the case with the parent triene thermal dimerization studied by Sanne.[21]

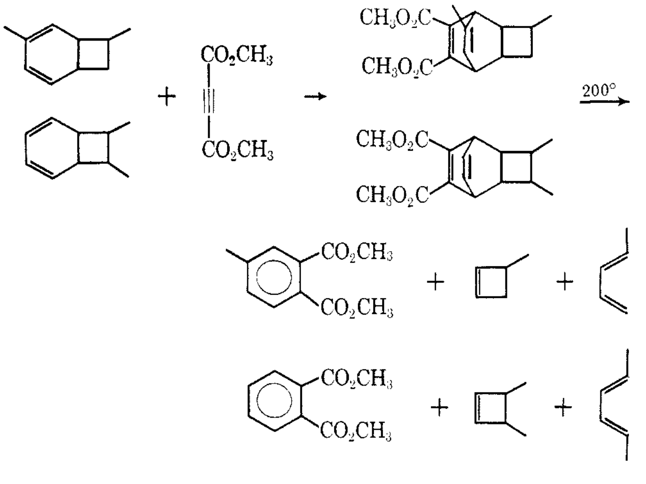
This thermal work indicated that the reaction in the nmr tube must have been initiated by some exothermic reaction, perhaps polymerization of 1,2 adduct, which gave off enough heat to raise the temperature above 225° thus converting some of the 1,4-addition isomers to toluene.

The fact that the three peaks which disappeared slowly were interdependent and toluene was formed from them means they must be the three possible 1,4-addition isomers, 5,8-dimethyl-1,3,6-cyclooctatriene (**2**), 3,8-dimethyl-1,3,5-cyclooctatriene (**5**), and 3,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**6**). This means that the remaining peak (peak 2) which disappears rapidly under thermal conditions is the 7,8-dimethyl-1,3,5-cyclooctatriene (**3**), confirming the earlier assignments.

In order to verify that the toluene comes from 3,8-dimethylbicyclo[4.2.0]octa-2,4-diene rather than the 2,7-dimethyl isomer, which would arise from a more extensive sequence of isomerization, we formed the Diels–Alder adduct with a mixture of the isomers and dimethyl acetylenedicarboxylate. The adduct was pyrolyzed[19] to form the phthalic esters. As expected dimethyl 4-methylphthalate and dimethyl phthalate were obtained. These must come from the 3,8-dimethyl- and 7,8-dimethylbicyclic isomers, respectively. The dimethyl phthalate was identified by comparison of its retention time with an authentic sample. Dimethyl 4-methylphthalate was identified by saponification and formation of the anhydride, and by its nmr spectrum. No trace of dimethyl 3-methylphthalate was observed.

The volatile products from the pyrolysis of the dimethyl acetylenedicarboxylate adduct were collected and analyzed by vpc. The retention time for the most abundant peak was identical with 1,3-pentadiene. Woodward's work[22] with cyclobutene shows that this product arises by opening of the cyclobutene ring. The remaining three peaks were assigned as 3-methylcyclobutene, 3,4-dimethylcyclobutene, and 2,4-hexadiene. The basis of these assignments is that the ratio (about 9:1) of the sum of the areas of the two largest peaks, at lowest retention times, to the sum of the areas of the two smaller peaks corresponds to the ratio (about 9:1) of dimethyl 4-methylphthalate and dimethyl phthalate found in the less volatile fraction. (See Scheme II.)

SCHEME II



Cope's work[19] with 1,3,5-cyclooctatriene showed that the bicyclic isomer reacts more rapidly with maleic anhydride to form a Diels–Alder adduct. The different reactivity of the isomers toward maleic anhydride enabled us to see which component of the 1,4-adduct isomer mixture is the bicyclic isomer.

We gradually increased the temperature of a mixture of all four isomers as well as 1,3,5- and 1,3,6-cyclooctatriene and maleic anhydride from 0 to 106° over a 48-hr period. No reaction occurred at 0° in 12 hr. After 6 hr at room temperature, the 1,3,5-cyclooctatriene peak was gone. No further change was observed until after 9 hr at 88° the 1,3,6-cyclooctatriene and 7,8-dimethyl-1,3,5-cyclooctatriene (**3**, peak 2) had disappeared. After 12 hr at 106° the peak 1 shoulder area had diminished greatly indicating it to be the bicyclic isomer

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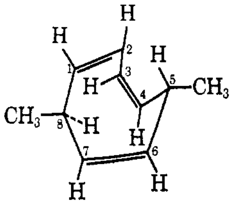
(21) W. Sanne and O. Schlichting, *Angew. Chem.*, **75**, 156 (1963).

(22) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(6) from 1,4 addition. The other component of this two-component peak is the 5,8-dimethyl-1,3,6 isomer (2), as was indicated by the ozonolysis products.

These thermolysis experiments suggested that we would be able to separate the three 1,4-addition products by vpc by reducing the detector temperature to 60° to avoid isomerization of the material as it came off the column. The 5,8-dimethyl-1,3,6-cyclooctatriene (2, peak 1) was first isolated pure by this technique from a sample distilled through a spinning-band column which was 92% pure before the vpc. The infrared spectrum shows the characteristic bands for unsaturation and methyl groups. The ultraviolet spectrum also is characteristic of the 1,3,6-cyclooctatriene system having the same extinction coefficient at 265 mμ (log ϵ 2.30) as Cope reports[6] for the parent compound.

The nmr spectrum of the material fits the assigned structure when its conformation **8** is considered. The methyl groups show a doublet at δ 1.15 (J = 7 cps). The methynes (H-5 and H-8) show a five-component multiplet centered at δ 2.94. The multiplet has only five components because there is no spin–spin interaction with the hydrogens in positions 6 and 7 because, assuming the methyl groups to be equatorial, the dihedral angle of 100° between H-5 and H-6 (or H-7 and H-8) indicates a virtually zero splitting constant.[23,24] Thus the methyne hydrogen atoms give spin–spin interaction only with the methyl groups and with the protons on positions 1 and 4.



8

Protons H-1 and H-4 occur as a split doublet centered at δ 5.03 owing to interactions with the protons on positions 5 and 8 (J = 6.5 cps) and the protons on positions 2 and 3 (J = 9 cps). These splitting constants conform to the Karplus relation[24] at the dihedral angles measured from Drieding models. The protons on positions 2 and 3 occur as a doublet at δ 6.01 (J = 9 cps). The protons on positions 6 and 7 occur as a singlet at δ 5.25. No splitting of these identical protons with H_5 and H_6 occurs because of the 100° dihedral angle as explained above.

The spectrum indicates that a single, *trans* (diequatorial) isomer is present. Inspection of models shows that axial methyl groups would have strong interaction with the π-electron cloud of the transannular double bond, so the *trans* isomer is expected to be conformationally homogeneous.

The 5,8-dimethyl-1,3,6-triene (peak 1) could be separated from the other two 1,4-addition isomers (peaks 1 shoulder and 3) on a 1/4 in. × 20 ft 5% silver nitrate–5% Apiezon L column, but this column would not separate peak 1 shoulder and peak 3. The peak composed of these isomers was collected and rechromatographed through the 1/8 in. × 6 ft column. This gave the pure samples of **6** and **5** in amounts sufficient for infrared and ultraviolet analysis. The infrared of both isomers show typical unsaturation and methyl bands but only the bicyclic isomer has a band at 960 cm^{-1} which is characteristic[25] of cyclobutane compounds. The ultraviolet data for the monocyclic triene, $\lambda_{\max}$ 263 mμ (log ϵ 3.56), and for the bicyclic diene, $\lambda_{\max}$ 275 mμ (log ϵ 3.43), correspond to the literature values of the corresponding unsubstituted olefins.[6,11,19,23,26]

Not enough of the separated materials was obtained for nmr analysis so we had to make assignments of nmr absorptions on the basis of spectra of samples with varying amounts of the two isomers. The nmr spectra of the mixtures show the methyl absorptions of **6** and **5** without contribution from **2**. The monocyclic isomer (**5**) shows a doublet at δ 1.00 (J = 7 cps) for the methyl group in the 8 position. The methyl group in the 3 position shows a rather broad singlet at δ 1.80. The bicyclic isomer (**6**) shows a doublet at δ 1.08 (J = 6.5 cps) for the methyl group on the four-membered ring. The 3-methyl absorption centered at δ 1.68 shows five components indicating long-range spin–spin splitting. Splitting by the vinyl proton on the same double bond is common[27] but there seems to be splitting here by other protons in the conjugated diene system.

The methyl groups on 7,8-dimethyl-1,3,5-cyclooctatriene (**3**) absorb in the nmr at δ 1.08 (J = 7 cps) as determined from a sample containing a mixture of all the isomers with only a small amount of **5** and **6**. Since we found it impossible to obtain a pure sample of this isomer, because of its very ready dimerization, we have no further physical data for it. In fact in order to isolate pure samples of the isomers of 1,4 addition we deliberately destroyed peak 2 since it overlapped with the other peaks too badly to permit vpc collection of pure samples.

In two preparations of the dimethylcyclooctatriene, the reaction time with methyl iodide was shortened from the usual 3-hr period to 30 min in the hope that intermediates of the methylation reaction might be observed. Upon work-up we found that 1,3,5- and 1,3,6-cyclooctatriene were present as shown by vpc retention time comparisons and by nmr spectra. The isolation of unsubstituted trienes produced by hydrolysis of unreacted dianion after a short reaction time indicates that the reaction of methyl iodide with dianion is slow. However, no monomethyl cyclooctatrienes were observed in the short reaction time preparations.

The reaction between dianion and methyl iodide thus is a slow reaction but the reaction of the intermediate with a second molecule of methyl iodide must be quite rapid.

This is quite easily explained since the reaction with the first methyl iodide has to overcome the aromatic stabilization of the dianion. The resulting monoanion, which is relatively localized due to the rehybridization to a tetrahedral carbon at the position of the first methyl group, is then an intermediate of relatively high

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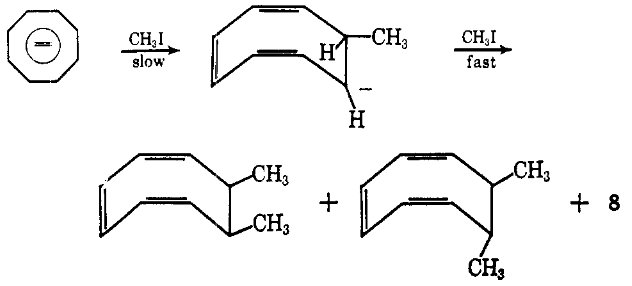
(27) "Nuclear Magnetic Resonance Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 135.



energy which reacts immediately with a second molecule of methyl iodide.

The relative amounts of *meso-* and *dl*-dimethyl succinic acid from ozonolysis of the 7,8-dimethyl-1,3,5-cyclooctatriene (**3**) indicates that the *trans* and *cis* isomers are present in a 1:4 ratio. The lack of stereochemical specificity is not unexpected in view of the mechanism of the reaction and the relatively hindered nature of both the *trans-* (one methyl necessarily axial) and the *cis*-7,8-dimethyl (eclipsed equatorial methyl) isomers. The contrasting stereochemical specificity observed (nmr spectra) for the diequatorial 5,8-dimethyl-1,3,6 isomer may be understood on the basis of the less crowded nature of the diequatorial isomer which is not, in this case, offset by the eclipsing of adjacent diequatorial methyl groups.

If it is assumed that the 1,5-hydrogen shift in the 5,8-dimethyl-1,3,6-cyclooctatriene occurs in the diequatorial conformer, than the immediate product of the 1,5-hydride shift will be the 3,8-dimethyl-1,3,5-cyclooctatriene in which the 8-methyl group is axial. However, this will rapidly equilibrate with the equatorial conformer. The sharpness of the methyl doublet of **5** and its position at δ 1.00 (*cf.* δ 1.15 for the doublet of **2**) suggest that the methyl group in **5**, too, exists in the equatorial conformation.

The relatively rapid dimerization of the 7,8-dimethyl-1,3,5-cyclooctatriene as compared to the 3,8-dimethyl isomer and its bicyclic valence tautomer (which could each be isolated) must be due to the hindrance to dimerization offered by the methyl group on unsaturated atoms in the latter cases. The 5,8-dimethyl-1,3,6 isomer does not have a coplanar diene system (see **8**) and considerable strain is introduced in attaining coplanarity; thus its failure to dimerize is understandable.

Experimental Section

The vapor phase chromatography (vpc) columns used in this work are (1) $^1/_8$ in. × 6 ft 5% silver nitrate–5% Apiezon L on 60–80 mesh Chromosorb W, (2) $^1/_4$ in. × 6 ft 5% silver nitrate–5% Apiezon L on 60–80 mesh firebrick, (3) $^1/_4$ in. × 20 ft 5% silver nitrate–5% Apiezon L on 60–80 mesh firebrick, (4) $^3/_8$ in. × 10 ft 30% METHPED (monohydroxyethyltrihydroxypropylethylenediamine) on 60–80 mesh firebrick, (5) $^1/_4$ in. × 6 ft 20% dioctyl phthalate on 60–80 mesh firebrick, (6) $^1/_4$ in. × 6 ft 20% GE-SF-96 on 60–80 mesh firebrick, (7) $^1/_4$ in. × 6 ft 9% silver nitrate–21% glycerin on 60–80 mesh firebrick.

The conditions under which the chromatography was run are reported as follows: column number (injector port temperature, column temperature, detector temperature, and flow rate).

The infrared spectra were taken on a Perkin-Elmer Infracord or a Perkin-Elmer 137 spectrophotometer at the fast scan rate. The spectra were corrected to a polystyrene reference.

The ultraviolet spectra were taken on a Cary 11 spectrophotometer in absolute ethanol solvent.

The mass spectra were taken on Bendix time-of-flight mass spectrometers. Details of the mass spectra will be submitted in a separate paper.

The nuclear magnetic resonance (nmr) spectra were taken on a Varian Associates A-60 instrument with a tetramethylsilane reference at δ 0.

The boiling points are uncorrected. The melting points are corrected.

Preparation of Cyclooctatetraenyl Dianion.—Freshly cut potassium metal (11.7 g, 0.3 g-atom) was dispersed in 300 ml of glyme (1,2-dimethoxyethane), which had been twice distilled from lithium aluminum hydride, by heating the glyme above the melting point of the potassium and then stirring vigorously by means of a vibrating mixer. The hot dispersion was then cooled rapidly with a Dry Ice–isopropyl alcohol bath. The dispersion was transferred with the aid of 200 ml of glyme to a dry, three-neck flask equipped with a nitrogen gas inlet, a paddle stirrer, and a pressure-equalizing dropping funnel. After flushing the apparatus and the dispersion with deoxygenated and dried nitrogen gas and cooling to a Dry Ice bath temperature, a solution of cyclooctatetraene (15.6 g, 0.15 mole) in 300 ml of glyme was added dropwise to the stirred dispersion. When the addition was complete the mixture was stirred until the potassium had all reacted, the time varying from 4 to 24 hr.

Preparation of Dimethylcyclooctatriene at Low Temperature (Run 3).—A solution of methyl iodide (51.27 g, 0.362 mole) in 50 ml of glyme was added dropwise to a dianion solution prepared from cyclooctatetraene (18.85 g, 0.181 mole) and potassium metal (14.18 g, 0.362 g-atom) in 1 l. of glyme under a nitrogen atmosphere at Dry Ice bath temperature. The solution was stirred for 3 hr at this temperature. The solvent was distilled through a 30-cm Vigreux column. The residue contained 16% cyclooctatetraene, 41% 5,8-dimethyl-1,3,6-cyclooctatriene (peak 1), 37% 7,8-dimethyl-1,3,5-cyclooctatriene (peak 2), and 6% 3,8-dimethyl-1,3,5-cyclooctatriene (peak 3) as found by analytical vpc through column 1 (150, 80, and 250°, 50 cc/min). The reaction mixture was distilled through the 30-cm Vigreux column at low temperature and pressure to minimize polymerization. Five fractions were obtained containing different ratios of the three methyl isomers and cyclooctatetraene.

An attempted preparative vpc separation through column 2 (150, 100, and 250°; 50 cc/min) of the third distillation fraction containing 2% cyclooctatetraene, 62% 5,8-dimethyl-1,3,6-cyclooctatriene (**2**), 32% 7,8-dimethyl-1,3,5-cyclooctatriene (**3**), and 4% 3,8-dimethyl-1,3,5-cyclooctatriene (**5**) was unsuccessful. Only enough of peak 1 was isolated for further work and its reinjection showed it contained 73% peak 1 and 27% peak 3.

A sample of the mixture was distilled at room temperature (0.5 mm) into a liquid nitrogen cooled trap.

Anal. Calcd for $C_{10}H_{14}$: C, 89.55; H, 10.45; mol wt, 134 Found: C, 89.33; H, 10.60; mol wt (vapor pressure osmometer), 141.

Isolation of 5,8-Dimethyl-1,3,6-cyclooctatriene (2).—Vpc analysis of the products from another run (column 1, as above) showed 0.5% 1,3,6-cyclooctatriene, 1.8% 1,3,5-cyclooctatriene, 77.1% **2**, 14% **3**, and 6.5% **5**.

This mixture was distilled through a 36-in. polymer-coated spinning-band column. Five fractions were obtained containing varying amounts of the components.

Fraction 4 [bp 49–50° (6–8 mm)], containing 92.2% **2**, 3.6% **3**, and 1.8% **5**, was preparatively gas chromatographed through column 2 (155, 85, and 220°; 50 ml/min). Collection of peak 1 (nominally **2**) gave a sample containing 73.5% **2** and 26.5% **5**. Further preparative vpc through column 2 with the detector temperature at 60° gave a sample containing 99.7% 5,8-dimethyl-1,3,6-cyclooctatreine (**2**).

The infrared spectrum of 5,8-dimethyl-1,3,6-cyclooctatriene showed bands at 3065 (vinyl CH), 1625 (C=C), 1375, 1460, 2900, and 2985 cm^{-1} (all methyl CH). The ultraviolet spectrum showed λ_{max} 265 mμ (log ε 2.30); n^{20}_{D} 1.4870.

The nmr spectrum showed a doublet centered at δ 1.15 (J = 7 cps, six hydrogens), a five-component multiplet at 2.94 (J = 6.5 cps, two hydrogens), a split doublet centered at 5.03 ($J_{1,2}$ = 9 cps, $J_{1,8}$ = 6.5 cps, two hydrogens), a singlet at 5.25 (two hydrogens), and a doublet centered at 6.01 (J = 9 cps, two hydrogens).

Isolation of 3,8-Dimethylbicyclo[4.2.0]octa-2,4-diene (6) and 3,8-Dimethyl-1,3,5-cyclooctatriene (5).—Vpc analysis of the reaction mixture from another run through column 1 showed 15.3% cyclooctatetraene, 6.8% 1,3,6-cyclooctatriene, 36.3% 1,3,5-cyclooctatriene, 28.8% **2**, 10.7% **3**, and 2.1% **5**.

A preliminary preparative vpc through column 2 (150, 100, and 60°; 50 cc/min) served to remove most of the nonmethylated substances in the product mixture and (presumably) to effect some 1,5-hydrogen shift and valence tautomerism. Analytical vpc through column 2 showed this fraction to contain 0.5% toluene, 0.6% cyclooctatetraene, 2.3% 1,3,6-cyclooctatriene, 0.8% 1,3,5-cyclooctatriene, 79.3% **2** and **6**, 3.7% **3**, and 12.2% **5**. Preparative vpc of this material through column 3 (150, 90, and 60°; 60 cc/min) separated **2** from the other isomers which came off the column in one peak. Vpc through column 1 of the mixture of 1 shoulder, 2, and 3 showed that no **3** was present. The remaining two isomers (**5** and **6**) were separated through column 1 (150, 68, and 60°; 30 cc/min). Separations could not be accomplished when an appreciable amount of **3** was present since there was too much overlap of the peaks.

The infrared spectrum of 3,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**6**) shows bands at 3050 (vinyl CH), 1600 and 1665 (C=C), 1370 and 1445 (methyl CH), and 960 cm^{-1} (cyclobutane system). The ultraviolet spectrum showed $\lambda_{\max}$ 275 mμ (log ϵ 3.43).

The nmr spectrum showed a doublet centered at δ 1.08 (J = 6.5 cps), a five-component multiplet centered at 1.68, two sets of multiplets between 2 and 3.2, and multiplets between 5.2 and 5.9. The only nmr spectra available are those of mixtures with 3,8-dimethyl-1,3,5-cyclooctatriene (**5**) below.

The infrared spectrum of 3,8-dimethyl-1,3,5-cyclooctatriene (**5**) showed bands at 3010 (vinyl CH) and 1655 cm^{-1} (methylene CH). The ultraviolet spectrum showed $\lambda_{\max}$ 263 mμ (log ϵ 3.56).

The nmr spectrum showed a doublet centered at δ 1.00 (J = 7 cps), a singlet at 1.80, two sets of multiplets between 2 and 3.2, and multiplets between 5.2 and 5.9. The only nmr spectra available are those of mixtures with 3,8-dimethylbicyclo[4.2.0]octa-2,4-diene (**6**) above.

Ozonolysis of Dimethylcyclooctatriene Mixture Collected after Vpc at Elevated Temperature.[28]—A solution of dimethylcyclooctatriene mixture from run 1 (1.17 g, 8.8 mmoles) in 20 ml of ethyl acetate was cooled to Dry Ice–isopropyl alcohol bath temperature in a 25 × 190 mm test tube with a side arm. An ozone–oxygen gas mixture was passed into the solution *via* a sintered glass gas bubbler and then out the side arm into a saturated potassium iodide solution. After 10 min the potassium iodide solution began to be oxidized to iodine as indicated by the appearance of a red color. The ozone–oxygen mixture was passed through the olefin solution for a total of 1 hr. The ethyl acetate was removed through a rotary evaporator under aspirator vacuum. The residue in the flask was dissolved *immediately* in 20 ml of acetic acid. The ozonide weighed 2.12 g.

Hydrogen peroxide (15 ml of 30%) was added to the acetic acid solution of ozonide. The peroxide solution of ozonide was heated in a steam cone for 4.25 hr. The oxidized mixture was concentrated under vacuum and the residue was dissolved in sodium carbonate solution. The aqueous solution was extracted with ether, acidified with dilute hydrochloric acid, and extracted again with ether. The remaining aqueous solution was continuously extracted with ether for 4 days. The ether extraction of the basic solution gave no residue upon concentration. The extract from the acid solution gave about 1 ml of light orange liquid smelling strongly of acetic acid. The continuous extraction gave about 2 ml of residue. Thin layer chromatography of the acids obtained from the continuous extraction gave three poorly defined spots on silica gel G with a solvent of ethyl alcohol–ammonium hydroxide–water in the ratios 80:4:16, respectively. The indicator used was bromocresol green.

The acids obtained from the continuous extraction were esterified with an ether solution of diazomethane. The excess diazomethane was decomposed with benzoic acid. The ether solution was washed with sodium bicarbonate solution and dried over magnesium sulfate, and the ether was distilled.

Vpc analysis through column 5 (210, 168, and 300°; 50 cc/min) showed seven components: (1) 19.4 min, 1.5% unknown; (2) 21 min, 41.6%, dimethyl methylsuccinate; (3) 24 min, 1.5% *meso*-dimethyl 2,3-dimethylsuccinate; (4) 30.7 min, 13.3%, methyl benzoate; (5) 39.5 min, 3.8% unknown; (6) 59.9 min, 28.1%, dimethyl 3-methylcyclobutane-1,2-dicarboxylate; and (7) 69.8 min, 10.3%, dimethyl 3,4-dimethylcyclobutane-1,2-dicarboxylate. Identification was made by comparison of retention times with authentic samples or by mass spectroscopy.

Preparative vpc through column 1 gave enough of the dimethyl methylsuccinate and dimethyl 3-methylcyclobutane-1,2-dicarboxylate–dimethyl 3,4-dimethylcyclobutane-1,2-dicarboxylate mixture to obtain their mass spectra. The parent ions have the same mass as the calculated molecular weights 160, 182, and 196, respectively.

Ozonolysis of Dimethylcyclooctatriene Mixture Never Subjected to High Temperature.—A solution of dimethylcyclooctatrienes from run 4 (1.0 g, 74.6 mmoles) containing 40.2% **2**, 46.8% **3**, and 13% **5** in 175 ml of methylene chloride was cooled to Dry Ice–isopropyl alcohol bath temperature in a 250-ml erlenmeyer flask with a side arm. An ozone–oxygen gas mixture was passed into the solution *via* a gas bubbler and then out the side arm into a saturated potassium iodide solution. Ozone was passed through the solution for 1 hr after the potassium iodide solution began to oxidize to iodine.

A solution of 15 ml of 30% hydrogen peroxide in 20 ml of acetic acid was added and the mixture was heated to reflux in an oil bath. Hydrochloric acid (2 ml, 3 *N*) was added and the solution was maintained at reflux for 3 more hr. The methylene chloride was distilled and the residue was taken up in ether, which was dried over magnesium sulfate and filtered.

The aqueous layer and an insoluble material were treated with 50% sodium hydroxide solution and 10 ml of 30% hydrogen peroxide. The solution was heated to boiling, cooled, acidified, and continuously extracted with ether.

The ether solutions of acids were combined and esterified with an ether solution of diazomethane. An excess of diazomethane was destroyed with a little dilute hydrochloric acid. The ether solution was dried over magnesium sulfate and filtered, and the ether was distilled through an 18-cm glass helixes column.

Vpc analysis of the ester mixture through column 5 (200, 160, and 300°; 50 cc/min) showed 9.6% methyl acetate, 1.41 min; 1.3% unknown, 6.0 min; 1.2% unknown, 6.75 min; 2.5% dimethyl oxalate, 7.6 min; 22.9% dimethyl methylmalonate, 12.2 min; 6.2% dimethyl methylsuccinate, 21.8 min; 20.3% *meso*-dimethyl 2,3-dimethylsuccinate, 23.3 min; and 4.7% *dl*-dimethyl 2,3-dimethylsuccinate, 28 min.

Retrocyclization of 3,8-Dimethylbicyclo[4.2.0]octa-2,4-diene.—A portion of the dimethylcyclooctatriene mixture from run 3, containing 18.2% **2**, 71% **3**, and 10.8% **5** was placed in an nmr tube. After 5 min a vigorous, exothermic reaction occurred. The nmr spectrum of the resultant mixture showed the presence of toluene, which was confirmed by vpc retention time comparison with an authentic sample of toluene.

Vpc analysis of the nmr tube residue through column 2 (120, 85, and 240°) showed 50.5% toluene, 31% **2** and **6**, 8.3% **3**, and 10.2% **5**. The percentage of each component here is misleading (perhaps because of extensive polymerization) as it seems to indicate that toluene arises from the 7,8-dimethyl-1,3,5-cyclooctatriene. The thermal treatments below, however, show this not to be the case.

Attempts to induce this retrocyclization and/or isomerization with acids (sulfuric, hydrochloric, acetic, and *p*-toluenesulfonic), free-radical catalysts (azobisisobutyronitrile at 80°), and base (potassium *t*-butoxide in refluxing *t*-butyl alcohol) effected either polymerization or no change in the composition of typical mixtures.

Thermal Treatment of Dimethylcyclooctatriene Mixture. Determination of Equilibrium Concentration.—Nine capillary tubes (Kimax No. 34505) were purged with nitrogen gas. Into each was put 8 μl of dimethylcyclooctatriene mixture containing 73.2% **2** (and **6**?) and 26.8% **5**. The tubes were centrifuged to bring all of the liquid to the bottom of the tubes, flushed again with nitrogen, and immediately sealed with an oxygen-gas torch. Three oil baths were brought to temperatures of 100, 150, and 200°. Three tubes were put into each bath. A tube was removed from each bath at the time intervals 10 min, 1 hr, and 12 hr, and plunged into a cold bath to quench any reaction still occurring. The reaction mixtures were then analyzed by vpc using column 1. (See Table I.)

Table I

Thermal Equilibration of 2 and 5

Time, min	Substance	% 100°	150°	200°
10	2	75	69	69
	5	25	31	31
60	2	78	69	70
	5	22	31	30
720	2	71	69	70
	5	29	31	30

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(28) A. C. Cope and W. I. Bailey, *J. Am. Chem. Soc.*, **70**, 2305 (1948).

TABLE II

THERMAL TREATMENT OF DIMETHYLCYCLOOCTATRIENE MIXTURE

Time, min	Compd	R.T.[a] Area	R.T.[a] %	92° Area	92° %	154° Area	154° %	198° Area	198° %
30	**7**	0.2	1	0.2	1	0.2	1	0.2	1
	2	10.9	58	11.0	60	11.9	67	9.2	70
	3	4.9	25	4.2	23	0.0	0	0.0	0
	5	3.0	16	3.0	16	5.6	32	5.6	29
60	**7**			0.2	1	0.2	1	0.2	3
	2			12.9	66	10.4	68	6.2	68
	3			2.8	14	0.0	0	0.0	0
	5			3.8	19	4.8	31	2.6	29
600	**7**	0.2	1	0.2	1	0.2	5	0.0	0
	2	10.9	58	15.1	68	3.1	68	Tr	
	3	4.6	25	0.0	0	0.0	0	0.0	0
	5	3.1	16	7.0	31	1.3	28	Tr	

[a] Room temperature (ambient).

TABLE III

THERMAL TOLUENE FORMATION

Substance	0 min Area	0 min %	15 min Area	15 min %	30 min Area	30 min %	45 min Area	45 min %	60 min Area	60 min %
7	0.7	3.2	2.2	18.3	4.4	25.4	3.1	26.3	2.8	47.5
5	4.0	17.4	6.0	50.3	4.4	25.3	2.5	21.2	1.4	23.7
6	3.0	13.1	2.7	22.6	2.2	12.6	1.7	14.4	0.5	8.5
2	3.9	17.2	1.1	9.3	1.2	7.9	0.4	3.4	0.0	0
3	11.3	49.2	0.0	0	0.0	0	0.0	0	0.0	0
4	0.0	0			5.2	29.8	4.1	34.8	1.2	20.4

Thermal Treatment of Dimethylcyclooctatriene Mixture. Decomposition of the 7,8-Dimethyl Isomer.—Eleven capillary tubes were purged with nitrogen gas. Into each was put 8 μl of a dimethylcyclooctatriene mixture containing 1% toluene, 58% **2** (and **6**?), 25% **3**, and 16% **5**. The tubes were centrifuged to bring all of the liquid to the bottom of the tubes, flushed again with nitrogen gas, and sealed with an oxygen-gas torch. Three oil baths were brought to temperatures of 92, 154, and 198° and three tubes were put into each bath. A tube was withdrawn from each bath at the time intervals 30 min, 1 hr, and 10 hr, and plunged into a cold bath to quench any reaction still occurring. The reaction mixtures were then analyzed by vpc through column 1. One-microliter injections were made of each sample. (See Table II.)

Thermal Treatment of Dimethylcyclooctatriene Mixture. Formation of Toluene.—Ten microliters of a mixture of dimethylcyclooctatriene isomers was placed in each of eight capillary tubes. The tubes were sealed after flushing with nitrogen gas and immersed in an oil bath at 225 ± 1°. A tube was removed every 15 min and analyzed by vpc using column 7. (See Table III.)

Peak identification: **7**, toluene, **4**, dimeric material.

Diels–Alder Reaction of the Dimethylcyclooctatriene Mixture. Dimethyl Acetylenedicarboxylate Adduct.—A solution of dimethylcyclooctatrienes from run 4 (47 mmoles) in 250 ml of glyme and dimethyl acetylenedicarboxylate (9 g, 63 mmoles) was deoxygenated by bubbling nitrogen gas into the solution for 1 hr. The solution was refluxed under the nitrogen atmosphere for 24 hr on a steam bath. The solvent was distilled through a 30-in. Vigreux column. The excess dimethyl acetylenedicarboxylate was removed by heating the residue at 60° under full pump vacuum overnight. The residue was washed with ether and insoluble material was filtered off. Evaporation of the ether gave a light orange oil.

The infrared spectrum showed bands at 1710 and 1740 (C=O), 1625 and 1665 (C=C), and 950 cm^{-1} (cyclobutane system).

Pyrolysis of the Diels–Alder Adduct.[29]—The Diels–Alder adduct (6.65 g) was placed in a 5-ml flask equipped with a nitrogen inlet and a 6-in. water-cooled condenser leading to two liquid nitrogen cooled traps. The system was flushed with nitrogen and the gas inlet was closed off. The system was evacuated to 100 mm, the traps were immersed in the liquid nitrogen baths, and the reaction flask was immersed in an oil bath at 195°. The reaction was heated at this temperature for 20 min whereupon the flask was cooled to below room temperature as rapidly as possible. The vacuum was released by passing in a nitrogen gas sweep, sweeping the reaction flask for 30 min. The traps were then sealed and stored in Dry Ice.

Vpc analysis of the pot residue through column 6 (240, 230, and 330°; 50 cc/min) showed 1.6% of an unknown material at 3.2 min, 10.4% dimethyl phthalate at 5.4 min, and 88% dimethyl 4-methylphthalate at 7.2 min.

The infrared spectrum of an enriched sample of the 4-methylphthalate showed bands at 1730 (C=O), 1585 and 1625 (aromatic C=C), 1070, 1130, and 1210 cm^{-1} (1,2,4-aromatic substitution).

The nmr spectrum shows a singlet at δ 2.30 (3 H), a singlet at 3.88 (6 H), and a singlet at 7.45 straddled by a typical aromatic AB quartet, each wing centered at 7.27 and 7.62 (J = 8 cps, Δ chemical shift = 22 cps, 3 H). The identity of the 4-methylphthalic ester was further secured by saponification and conversion to its anhydride, mp 93.5–95° (lit.[30] mp 88–94°) after crystallization from Skelly B and vacuum sublimation.

Vpc analysis of the volatile components through column 6 (113, 102, and 230°; 50 cc/min) showed 17.4% 3-methylcyclobutene (?), 71% 1,3-pentadiene, 8.9% 3,4-dimethylcyclobutene (?), and 2.8% 2,4-hexadiene (?). The identity of 1,3-pentadiene was obtained by retention time comparison on the vpc through column 6. The identity of the other components is postulated by comparison to the amounts of phthalates formed and knowledge of their relative boiling points.

Maleic Anhydride Treatment of the Dimethylcyclooctatriene Mixture.—An aliquot of the mixture containing 0.5% toluene, 0.6% cyclooctatetraene, 2.3% 1,3,6-cyclooctatriene, 0.8% 1,3,5-cyclooctatriene, 79.5% **2** and **6**, 3.7% **3**, and 12.2% **5** was combined with maleic anhydride. After 12 hr in the refrigerator there was no change in the composition. After 6 hr at room temperature only the 1,3,5-cyclooctatriene peak had disappeared. After 13 hr at room temperature, 1 hr at 53°, and 1 hr at 80°, no further change in composition had occurred. After 9 hr at 88° the 7,8-dimethyl-1,3,5-cyclooctatriene (**3**) had disappeared. After 12 hr at 106° the combination peak of 5,8-dimethyl-1,3,6-cyclooctatriene and 3,8-dimethylbicyclo[4.2.0]octa-2,4-diene had diminished greatly.

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