

mately  $9 \times 10^8 \text{ sec.}^{-1}$ . For this particular photolysis, the initial concentration of benzyne was estimated as  $10^{-5}$  mole/l., so that the rate constant  $k_2$  from the mass spectrometric data is  $9 \times 10^8$  l./mole sec. This figure is almost surely within a factor of three of the true rate

constant, and agrees inexplicably well with the rate determined by optical spectroscopy.

*Acknowledgments.* This work was partially supported by the U. S. Air Force Office of Scientific Research, Division of Chemical Sciences, Grant 183-63.

## The Facile Isomerization and Dimerization of 1,2,6-Cyclononatriene

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Received May 14, 1965

It is demonstrated that 1,2,6-cyclononatriene (1) undergoes a facile isomerization in the liquid phase at ca.  $135^\circ$  to give 2,3-divinylcyclopentene (2) and also dimerizes to yield both stereoisomers of tricyclo[9.7.0.0<sup>2,10</sup>]octadeca-5,9,11,15-tetraene, 7a and 7b. The configurational assignments of these dimers are based on the dimethyl acetylenedicarboxylate adducts isolated and on the Woodward-Hoffman generalized hypothesis for the steric course of electrocyclic transformations.

During our investigations directed toward syntheses of *cis,cis,cis*-1,4,7-cyclononatriene<sup>1</sup> we attempted to isomerize 1,2,6-cyclononatriene (1) with base, with acid, and thermally. The base-catalyzed isomerization of 1,2,6-cyclononatriene has been described by Gardner and co-workers.<sup>2</sup> Here we report on the structures of some of the products of the thermally induced reactions of 1,2,6-cyclononatriene.

*Isomerization of 1.* Heating 1 in a sealed tube under a nitrogen atmosphere to ca.  $150^\circ$  converts it partially to a mixture of new hydrocarbons. Starting material 1 and one of these products (2) were easily detected using g.l.p.c. analysis (isothermally at  $100^\circ$ ), and together accounted for >98% of the material detected by g.l.p.c. at this temperature. However, by using temperature programmed g.l.p.c., it was demonstrated that higher molecular weight material was also present in the thermal reaction mixtures. Table I shows the results of

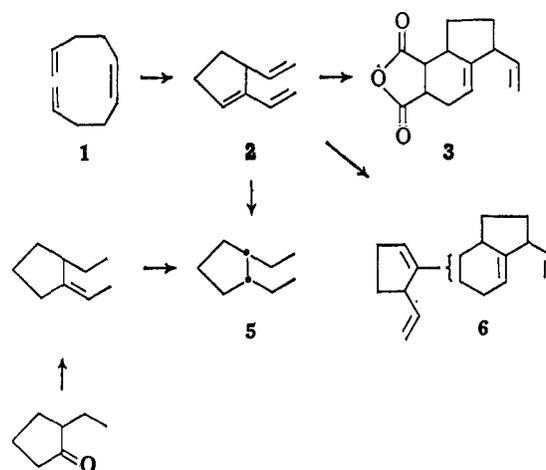
Table I. Thermal Isomerization of 1

Time, min.	Temp., °C.	Composition, %	
		1	2
30	150	73.9	25.9
60	150	26.4	72.5
30	175	4.3	94.3

three experiments in which the composition percentages were determined.

(1) K. G. Untch, *J. Am. Chem. Soc.*, **85**, 345 (1963).

(2) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *ibid.*, **85**, 1553 (1963).



Pure 2 was isolated by preparative g.l.p.c. We found by varying the heating period and temperature that highest yields of 2 resulted when 1 was heated for 40 min. at  $150^\circ$ . The elemental analysis and molecular weight of 2 showed it to be isomeric with 1. Its infrared spectrum exhibits absorptions at 3.23, 3.24, 3.28, 5.52, 10.07, and 11.04  $\mu$ , which are characteristic for a vinyl group, and at 6.10 and 6.30  $\mu$  which are typical for isolated and conjugated olefinic bonds. The ultraviolet spectrum of 2 shows absorptions at 228 m $\mu$  (sh,  $\epsilon$  24,200), 234 (27,000), and 241 (sh, 18,800) in cyclohexane at  $2.33 \times 10^{-5}$  mole/l. indicating a semi- or bicyclic diene chromophore. The n.m.r. spectrum of 2 shows three groups of absorptions: a complex set of lines between  $\tau$  3.3 and 5.3 (olefinic), a multiplet centered at ca. 6.6, and another set of lines between 7.3 and 8.5 with relative areas of 7.00:1.05:3.84, respectively (theory, 7:1:4).

Since these data showed that 2 contained a conjugated diene, the thermal reaction mixture was treated with maleic anhydride. Two crystalline Diels-Alder adducts, 3, m.p.  $93-94^\circ$ , and 4, m.p. ca.  $217^\circ$ ,<sup>3</sup> were isolated. Elemental analyses and molecular weight determinations showed 3 to be C<sub>9</sub>H<sub>12</sub> plus maleic anhydride and 4

(3) The melting point of 4 is variable. It was generally found near  $217^\circ$  (Kohler hot stage). Other samples melted at ca.  $210^\circ$ . Samples in capillary tubes melted consistently  $12-13^\circ$  higher than was found on the hot-stage apparatus.

to be  $C_{18}H_{24}$  plus maleic anhydride. The infrared spectrum of adduct **3**, indicates the presence of a vinyl group. The ultraviolet spectrum displays only end absorption.

These combined data are consistent only with 2,3-divinylcyclopentene as the assigned structure for **2**. The final piece of evidence for the structure proof of **2** was obtained by exhaustively hydrogenating **2** to give *cis*-1,2-diethylcyclopentane (**5**), which was synthesized by a different route. Treatment of 2-ethylcyclopentanone with ethylidetriphenylphosphorane (DMSO)<sup>4</sup> gave 2-ethylideneethylcyclopentane, which, without purification, was hydrogenated to give **5**. The two pure samples of **5**, obtained from the independent routes and isolated by g.l.p.c., exhibit identical infrared spectra and give identical sets of retention times on Apiezon L and Carbowax g.l.p.c. columns. Therefore, the skeletal arrangement of **2** was verified and the product of thermal isomerization of **1** is **2**.

The yield of **2** from **1**, heated at 175° for 30 min. (Table I), was determined by treating the resulting mixture with maleic anhydride and separating **3**, **4**, and **6** by differential solubility and chromatography. The amounts of **3** and **6** isolated showed that *ca.* 55% of **1** had isomerized to **2**. The structural assignment of **6** is based on its infrared spectrum, its g.l.p.c. retention time, which is similar to that of the dimer that gives adduct **4** (on the same column), and on the fact that it does not react with maleic anhydride. It is reasonable that **2** should undergo a self Diels-Alder condensation to give **6**.

We have also found that adduct **3** can be obtained, free from the dimer adduct **4**, by refluxing a solution of **1** and maleic anhydride in xylene (77% yield). The lowest temperature at which thermal isomerization of **1** was detected, by heating **1** in a sealed tube for 1 hr., is 130°.

This isomerization of 1,2,6-cyclononatriene can be considered to be another example of a Cope rearrangement.<sup>5</sup> It is an interesting case, aside from involving an allene, since Vogel has reported that an attempted isomerization of *cis*-1,2-divinylcyclopentane to 1,5-cyclononadiene was unsuccessful (even at 300°).<sup>6</sup> This result was attributed to a higher degree of ring strain in the cyclononadiene molecule than in the divinylcyclopentane. More recently Vogel and co-workers<sup>7</sup> have carried out the isomerization of *cis*-1,2-divinylcyclopentane to *cis,cis*-1,5-cyclononadiene (220°) and found that the latter compound made up 5% of the equilibrium mixture of the two components. The isomerization of **1** to **2**, reported here, apparently proceeds by a ring strain releasing process.

This same rearrangement, *i.e.*, **1** to **2**, has been independently discovered in two other laboratories. Vogel and co-workers<sup>7</sup> found that **1** gives **2** as the only product at 140° in the gas phase. Skattebol<sup>8</sup> has found the same thermal reactions of **1** in the liquid phase that we

(4) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(5) Reviews of Cope rearrangements are given by J. Hine in "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 505, and E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

(6) E. Vogel, K. H. Ott, and K. Gajek, *Ann.*, **644**, 172 (1961).

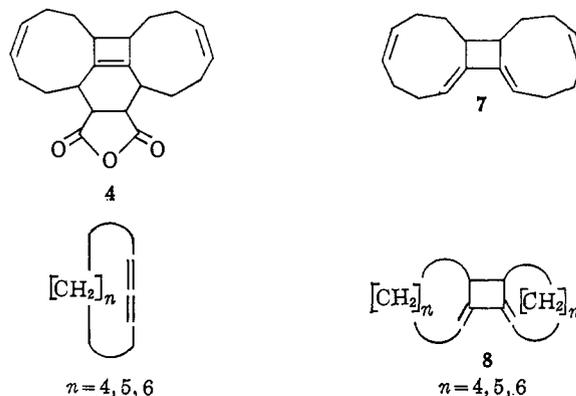
(7) E. Vogel, W. Grimme, and E. Dinne, *Angew. Chem.*, **75**, 1103 (1963).

(8) L. Skattebol and S. Solomon, *J. Am. Chem. Soc.*, **87**, 4506 (1965). We thank Dr. Skattebol for informing us of his research in this area prior to preparation of this paper.

have, and, in addition, that **1** isomerizes to **2** quantitatively in the gas phase.

**Dimerization of 1.** Having determined the structure of **2**, it was clear that the other maleic anhydride adduct **4** was not the result of the dimerization of **2** followed by condensation with maleic anhydride, but rather an initial dimerization of **1** to give a conjugated diene which reacted with maleic anhydride. We found that heating **1** in a sealed tube at 120° for 12–16 hr. gave better yields of the dimer that gave adduct **4** when treated with maleic anhydride. Under these conditions, no adduct **3** was isolated. The reaction mixture from the thermal dimerization of **1** (120° for 12 hr.) was distilled (short path) to give a viscous clear liquid hydrocarbon (**7**). The elemental analysis and molecular weight of **7** gave it a molecular formula of  $C_{18}H_{24}$ . Its infrared spectrum exhibits absorptions at 3.32, 3.42, 3.49, 6.02, 6.08, 6.84, and 13.79  $\mu$ . The ultraviolet spectrum of **7** shows an absorption maximum at 252 m $\mu$  ( $\epsilon$  8600).

By analogy with the dimerization of allene to give 1,2-dimethylenecyclobutane<sup>9</sup> and of the presumed intermediates, 1,2-cycloheptadiene and 1,2-cyclooctadiene, to give the corresponding dimers **8**,<sup>10</sup> structure **7** was assigned to the new dimer.



However, some of the evidence appeared not to agree with this assignment. The ultraviolet spectrum of **7** is unlike the seemingly characteristic ultraviolet absorption pattern for previously prepared 1,2-dimethylenecyclobutanes,<sup>8–10</sup> which show three absorption maxima or shoulders separated by *ca.* 10 m $\mu$ , with the center one most intense. The other discrepancy for the structural assignment by analogy is that only a maleic anhydride monoadduct of **7** was isolated, unlike tricyclo[7.5.0.0<sup>2,8</sup>]tetradeca-7,9-diene and tricyclo[8.6.0.0<sup>2,9</sup>]hexadeca-2,16-diene,<sup>10</sup> examples where only diadducts were isolated (an indication of a small amount of monoadduct was cited for the former compound). In addition, Skattebol has found that 1,2-cyclononadiene undergoes the allene dimerization and the resulting compound (**8**,  $n = 6$ ) gives a diadduct with maleic anhydride.<sup>8</sup> However, 1,2-dimethylenecyclobutane, when treated with maleic anhydride under conditions less vigorous than those employed here with **7** gave only monoadduct.<sup>9</sup>

Since the dimer **7** is an air-sensitive compound, derivatives were used to determine its structure. The maleic anhydride adduct **4** is insufficiently soluble in

(9) A. T. Blomquist and J. A. Verdol, *ibid.*, **78**, 109 (1956).

(10) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962).

appropriate solvents to obtain a good n.m.r. spectrum, but a saturated deuteriochloroform solution did give a spectrum with a multiplet centered at *ca.*  $\tau$  4.5 (olefinic hydrogens) and complex absorptions in the range 6.5–8.5 in a ratio of 4.0 to 22.8 (theory for **4**, 4:22). Adduct **4** is also insufficiently soluble in suitable solvents to obtain a Raman spectrum which may have exhibited a C=C stretching band characteristic for a 1,2-disubstituted cyclobutene system.

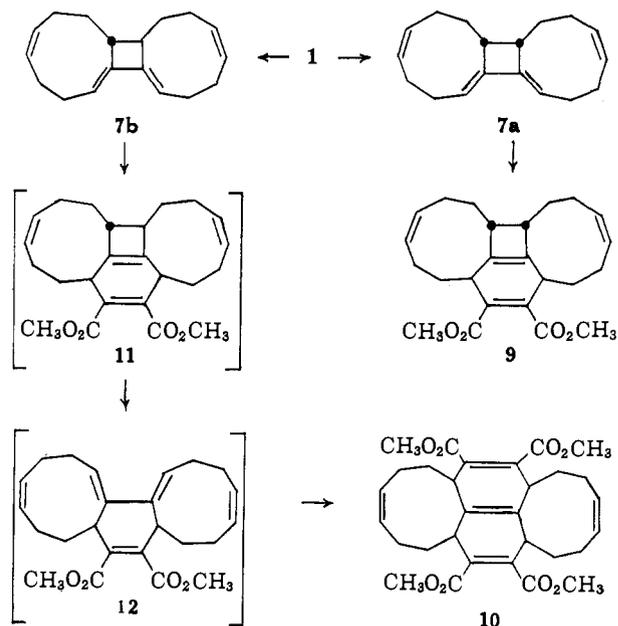
In order to obtain a derivative whose structure could be established readily by n.m.r. and Raman spectroscopy, the thermal reaction mixture from **1** (115° for 18 hr.) was treated with dimethyl acetylenedicarboxylate. Two crystalline adducts were isolated, **9**, m.p. 123–124°, and **10**, m.p. 220–222°, in *ca.* 5:1 ratio. The elemental analysis and molecular weight of **9** showed that it was an acetylenedicarboxylate mono-adduct of **7** and those of **10** showed that it was an acetylenedicarboxylate diadduct of **7**. No crystalline acetylenedicarboxylate adduct of **2**, corresponding to the maleic anhydride adduct **3**, could be isolated in this case. The n.m.r. spectrum of **9** shows a multiplet at  $\tau$  4.37 (olefinic hydrogens), a sharp singlet at 6.25 (methylene hydrogens), two multiplets at 6.87 and 7.04 (methine hydrogens), and complex absorption at 7.2–9.0 (methylene hydrogens). The ratio of the areas of the absorptions at  $\tau$  6.25 to the other nonolefinic hydrogens is 6.0:20.0 (theory, 6:20). The sharp singlet (half-width at half-height is 1 c.p.s.) at  $\tau$  6.25 due to the methyls of the carbomethoxy groups shows that they are equivalent and that the conjugated diene of **7** is symmetrically oriented. The equivalence of the methyls further suggests that the two methine hydrogens on the cyclobutene ring junctures are *syn*. Conclusive evidence that confirms the structure of **9** is obtained from its Raman spectrum, which exhibits C=C stretching vibrations at 6.10 (six-membered ring double bond conjugated with an ester carbonyl), 6.04 (nine-membered ring double bonds), and 5.89 (1,2-dialkyl substituted cyclobutene double bond<sup>11</sup>). In addition, an absorption at 5.77  $\mu$  for the  $\alpha,\beta$ -unsaturated ester C=O stretch is seen.

The structure of **10** is verified by its n.m.r. spectrum, which shows a symmetrical multiplet at  $\tau$  4.24 (olefinic hydrogens), a singlet at 6.22 (methyls of the carbomethoxy groups), a symmetrical multiplet at 6.63 (methine hydrogens), and a complex pattern at 7.6–9.0 (methylene hydrogens). The ratio of areas of the absorptions at  $\tau$  4.24, 6.22 and 6.63 combined, to those at 7.6–9.0 is 4.0:16.0:16.4 (theory, 4:16:16). Here, too, the sharp singlet shows the equivalence of the four methyl groups.

From these data, it can be concluded that **1** undergoes an allene dimerization to give both stereoisomers of **7** and these follow different courses when treated with acetylenedicarboxylate.

These stereochemical assignments of **7a** and **7b** are based on the following arguments. The n.m.r. spectrum of **9** shows that the carbomethoxy methyl groups are equivalent since they give rise to a single

(11) The C=C stretching absorption of cyclobutene observed in the Raman occurs at 6.39  $\mu$  (R. C. Lord and D. G. Rea, *J. Am. Chem. Soc.*, **79**, 2401 (1957)); that for 1-methylcyclobutene at 6.31  $\mu$  (F. F. Cleveland, M. J. Murray, and W. S. Gallaway, *J. Chem. Phys.*, **15**, 742 (1947)); that for 1,2-dimethylcyclobutene, in the infrared, at 5.92  $\mu$ , and that for a better model, tricyclo[6.4.0.0<sup>2,7</sup>]dodeca-6,8-diene, in the infrared, at 5.87  $\mu$  (K. J. Crowley, *Proc. Chem. Soc.*, 334 (1962)).



sharp line. The intermediate adduct **11** having the two methine hydrogens *anti*, might be expected to exhibit an n.m.r. spectrum with nonequivalent carbomethoxy methyl groups, *i.e.*, two distinct absorptions due to these methyl groups in slightly different environments. However, this evidence is only suggestive in the absence of the n.m.r. spectrum of **11**. The isolation of adducts **4** and **9**, recovery of **9** when treated further with dimethyl acetylenedicarboxylate, and the isolation of adduct **10** are convincing evidence that the configurations of **7a** and **7b** are as drawn when considered in conjunction with the recently presented hypothesis of Woodward and Hoffman<sup>12</sup> in which they correlate stereochemical results of "electrocyclic" transformations. According to the generalized hypothesis of Woodward and Hoffman, thermal isomerization of cyclobutenes is conrotatory.<sup>13</sup> Examples of *cis*-3,4-dicarbomethoxycyclobut-1-ene<sup>14</sup> and *cis*- and *trans*-1,2,3,4-tetramethylcyclobutenes<sup>15</sup> were cited. The stereochemical results of these cases correspond to those found by Huisgen and Seidl<sup>16</sup> for *cis*- and *trans*-1,2-diphenyl-benzocyclobutenes; *i.e.*, the *trans* derivative opened to give *trans,trans*-diphenyl-*o*-quinodimethane and the *cis* derivative gave *trans,cis*-diphenyl-*o*-quinodimethane. Accepting the electrocyclic reaction hypothesis in which thermal isomerization of cyclobutenes is conrotatory, when possible, the configurations of the dimers **7a** and **7b** can be assigned on the basis of our results. 1,2,6-Cyclononatriene (**1**) thermally dimerized to give **7a** and **7b** and both dimers react with dimethyl acetylenedicarboxylate. The adduct **9**, having *syn* cyclobutene methine hydrogens, is an isolable compound. The cyclobutene system of **9** does not isomerize because a conrotatory electrocyclic transformation would have given a *trans* double bond in one of the fused nine-membered rings and would have afforded a product **13**

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

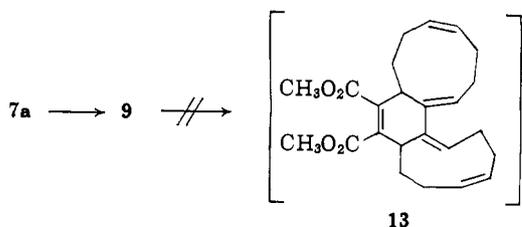
(13) See ref. 12 for the definitions of conrotatory and disrotatory.

(14) E. Vogel, *Ann.*, **615**, 14 (1958).

(15) R. Criegee and K. Noll, *ibid.*, **627**, 1 (1959).

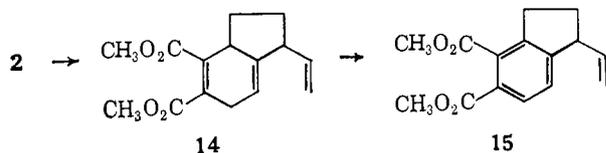
(16) R. Huisgen and H. Seidl, *Tetrahedron Letters*, No. **46**, 3381 (1964).

containing a somewhat strained *cis,trans*-cyclononadiene ring and possessing serious nonbonded interactions. The intermediate adduct **11**, however, with *anti* cyclobuteno methine hydrogens, undergoes a ready conrotatory electrocyclic transformation to give **12**, containing two, fused, strain-free *cis,cis*-cyclononadiene rings, which further reacts with dimethyl acetylenedicarboxylate to give **10**.



Using similar arguments, it might be thought that the configurations of the dimers from the seven-, eight-, and nine-membered cyclic allenes (**8**,  $n = 4, 5, 6$ ) can be deduced, since only maleic anhydride diadducts were isolated, thus showing that the cyclobutene system opened to a butadiene system. This is not the case, however, since in **8** ( $n = 6$ ) a conrotatory process could proceed with either the *syn* or *anti* isomer because a *trans* double bond is accommodated in a nine-membered ring without ring strain (the maleic anhydride diadduct would be the same from either stereoisomer). The same reasoning can be advanced for **8** ( $n = 5$ ), even though there is some ring strain in *trans*-cyclooctene. In the case of **8** ( $n = 4$ ), the *syn* isomer is not likely to undergo a conrotatory cyclobutene ring opening, but, in this instance, as well as **8** ( $n = 5$ ), less than 60% of the dimer was accounted for as maleic anhydride diadduct.<sup>10</sup>

The reason for the previously mentioned unsuccessful attempt to isolate any crystalline dimethyl acetylenedicarboxylate adduct of **2** (**14**)<sup>†</sup> may have been that none of **2** was formed at the lower temperature (115° for 18 hr.). However, when pure **2** was treated with dimethyl acetylenedicarboxylate, a clear liquid resulted (after column chromatography, 93% yield), whose infrared spectrum is consistent with **14**. After standing



overnight and rechromatography, 66% of **14** had been converted to a new liquid (**15**). The new compound shows absorption in the infrared at 6.10 (nonconjugated double bond), 6.26 (aromatic), 10.2 and 10.9 (vinyl group)  $\mu$ ; in the ultraviolet at  $\lambda_{\max}$  242 m $\mu$  ( $\epsilon$  6000), 282 (2000), and 287 (2200); in the n.m.r., an AB pattern (area 2) centered at  $\tau$  2.66, a typical pattern of a vinyl split by a methine hydrogen (area 3) between 3.9 and 5.5, two singlets (slightly nonequivalent methyls, area 6) at 6.18 and 6.22, a multiplet (area < 2) at *ca.* 6.35 (methine hydrogen), a multiplet (area 2) at *ca.* 7.1 (benzylic methylene hydrogens), and a many-lined pattern (area 2) between 7.5 and 8.4 (methylene hydrogens). These data substantiate the structures assigned to **14** and **15**.

## Experimental Section<sup>17</sup>

*Thermolysis of 1,2,6-Cyclononatriene (1)*. The general procedure employed throughout this study is as follows. A sample of **1** was placed into a thick-walled Pyrex glass tube, which was thoroughly purged with nitrogen, and sealed. The sealed tube was suspended in a stirred oil bath and kept at various temperatures (125–175°) for varying periods of time (30 min.–18 hr.). After cooling, the tube was opened and the reaction mixture was analyzed by g.l.p.c. using a 6 ft.  $\times$  0.25 in. column of 10% polyethylene glycol 400 on 35–40 mesh Chromosorb P.

*2,3-Divinylcyclopentene (2)*. The general procedure was followed. The samples of **1** (99.5% pure by g.l.p.c. on the same column as above) were heated at  $150 \pm 2^\circ$  for 40 min. Pure liquid **2** was isolated by preparative g.l.p.c. on a 10 ft.  $\times$   $\frac{3}{8}$  in. column containing the same packing as above.

*Anal.* Calcd. for  $C_9H_{12}$ : C, 89.94; H, 10.06; mol. wt., 120.19. Found: C, 90.05; H, 10.15; mol. wt., parent peak 120 (mass spectrometric determination).

The absorption spectra are described above. See the Maleic Anhydride Reactions section below for the crude yield of **2**.

*Tricyclo[9.7.0.0<sup>2,10</sup>]octadeca-5,9,11,15-tetraene (7)*. In a sealed Pyrex tube, 1.0 g. (0.083 mole) of **1** was heated at  $120 \pm 2^\circ$  for 12 hr. The sealed tube was cooled and opened; the reaction mixture was distilled (short path) under reduced pressure (0.01 mm., pot temperature  $\leq 180^\circ$ ). A colorless, air-sensitive liquid, 0.47 g., was collected. This distillate was a mixture of **7a** and **7b**.

*Anal.* Calcd. for  $C_{18}H_{24}$ : C, 89.94; H, 10.06; mol. wt., 240.38. Found: C, 89.97; H, 10.04; mol. wt., 230, 257 (Mechrolab Model 301A osmometer in benzene).

The infrared and ultraviolet absorptions are described above.

*cis-1,2-Diethylcyclopentane (5)*. *A. Hydrogenation of 2*. The reaction mixture that resulted from heating 0.167 g. (1.39 mmoles) of **1** at  $150 \pm 2^\circ$  for 40 min. was hydrogenated over 0.030 g. of 10% palladium on charcoal in *ca.* 10 ml. of pentane ( $H_2$  uptake, 40 ml.). The catalyst was removed by suction filtration through a pad of Celite, and the filtrate was analyzed by g.l.p.c. (8 ft.  $\times$  0.25 in. Apiezon L on 80–90 mesh Anakrom ABS column). Six components, which had retention times near that of diethylcyclopentane (see below), were collected using preparative g.l.p.c. This mixture, 40 mg., was again hydrogenated over 50 mg. of palladium on charcoal in pentane ( $H_2$  uptake, 6 ml.) and worked up as above, and the major component (*ca.* 70%) was collected using g.l.p.c. (10 ft.  $\times$   $\frac{3}{8}$  in. column containing 10% polyethylene glycol 400 on 35–80 mesh Chromosorb P). The resulting pure

(17) Absorption spectra were recorded with the following spectrometers: infrared, Beckman IR-9; ultraviolet, Cary, Models 14 and 15; Raman, Cary, Model 81; n.m.r., Varian Associates, Model A-60. Tetramethylsilane (TMS) was used as an internal standard in the n.m.r. samples ( $CDCl_3$ ) and the chemical shifts are given on the  $\tau$ -scale in p.p.m. relative to TMS ( $\tau$  10.00). An F & M Scientific Corporation, Model 500 and an Aerograph Autoprep, Model A-700 chromatographs were used for g.l.p.c. analyses and collections. Mass spectra were obtained from an AEI MS-9 double-focusing mass spectrometer. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill. All melting points are uncorrected.

liquid (5) exhibits an infrared spectrum which is identical with that of 5 prepared from 2-ethylcyclopentanone (see below, B) and has retention times (relative to air) 4.82 min. on a 10 ft.  $\times$  0.25 in. column (100°) containing 15% Carbowax 1500 on 60–80 mesh firebrick and 8.80 min. on a 6 ft.  $\times$  0.25 in. column (100°) containing 10% Apiezon L on 80–90 mesh Anakrom ABS.

*B. From 2-Ethylcyclopentanone.* A solution of 17.6 g. (0.047 mole) of triphenylethylphosphonium bromide and 80 ml. of dry dimethyl sulfoxide (DMSO) was added to prewashed sodium hydride (0.047 mole) to give ethylidetriphenylphosphorane.<sup>4</sup> To this solution was added 5.86 g. (0.052 mole) of 2-ethylcyclopentanone, and the resulting mixture was stirred at 60° for 20 hr. The reaction mixture was poured into 100 ml. of water (0°) and extracted with petroleum ether (b.p. 30–60°; four times, equal volumes). The combined extracts were washed three times with water and dried over MgSO<sub>4</sub>, and the solvent was removed by distillation. Fractional distillation gave 2.7 g. of a colorless liquid, b.p. 38–40° (15 mm.). This liquid fraction was exhaustively hydrogenated over 30 mg. of 10% palladium on charcoal in 25 ml. of tetrahydrofuran (THF) (H<sub>2</sub> uptake 383 ml., 72%). The catalyst was removed, and the THF solution was fractionally distilled to remove the solvent. Pure 5 was isolated from the residue using preparative g.l.p.c., and its relative retention times are identical with those obtained for the sample of 5 obtained by hydrogenating 2 (determined on the same g.l.p.c. columns); cf. A above. Its infrared spectrum shows strong absorptions at 3.38, 3.48, 6.85, and 7.24  $\mu$  and was identical with that of 5 prepared from 2.

*Maleic Anhydride Reactions. A. With the Thermal Reaction Mixture from 1.* The reaction mixture that resulted from heating 0.175 g. (1.46 mmoles, 97.7% pure) of 1 at 175  $\pm$  2° for 30 min. was treated with 0.147 g. (1.50 mmoles) of maleic anhydride in 2.0 ml. of *o*-xylene. The mixture was heated at 125° for 2.25 hr., the solvent was removed by distillation at reduced pressure (ca. 15 mm.), and the residue was triturated and decanted repeatedly, first with petroleum ether, then with ethyl acetate. The petroleum ether solution gave 0.136 g. of a semisolid, m.p. 72–77°, after removal of the solvent and heating at 60° at reduced pressure (15 mm.) to remove unreacted maleic anhydride.

The ethyl acetate solution gave 0.106 g., m.p. 214–218°, of an off-white solid. Chromatography of the ethyl acetate soluble residue, 0.106 g., on 5.0 g. of silicic acid (sample placed on column with ethylacetate-chloroform, 3:1) gave 0.104 g. of crude 4 (44.0% yield based on 1) in the first four 10-ml. fractions (chloroform elution). Recrystallization (ethyl acetate) gave 4 as a white solid, m.p. 217–218°.<sup>3</sup>

*Anal.* Calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>3</sub>: C, 78.07; H, 7.74. Found: C, 77.87; H, 7.73.

Its infrared spectrum (KBr) shows the typical anhydride absorptions, 5.42 and 5.65, and a weak absorption at 6.06  $\mu$  for a C=C stretching vibration.

The petroleum ether soluble residue was chromatographed on 5.0 g. of silicic acid. Elution with 10-ml. chloroform portions gave 0.055 g. (32.1%) of a colorless oil, 6, from fraction 1. The relative reten-

tion time of this oil, 6, on a g.l.p.c. Apiezon L column, is similar to that of 7; its infrared spectrum shows strong absorptions, characteristic for a vinyl group, at 10.12 and 11.05  $\mu$ . Fractions 3–5 gave 0.070 g. (23.3%) of crude adduct 3, m.p. 89–90°. Recrystallization from petroleum ether gave 3, m.p. 93–94°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>3</sub>: C, 71.54; H, 6.47; mol. wt., 218.24. Found: C, 71.33; H, 6.43; mol. wt., 218 (Mechrolab osmometer in benzene).

Its infrared spectrum (CHCl<sub>3</sub>) shows absorptions at 5.42, 5.66, 6.10, 9.60, 10.72, and 11.00  $\mu$ ; ultraviolet, end absorption to 208 m $\mu$ .

*B. With 1 in Refluxing o-Xylene.* A mixture of 0.240 g. (2.04 mmoles) of 1 (99.5% pure), 0.237 g. (2.42 mmoles) of maleic anhydride, and 2.0 ml. of *o*-xylene was heated at the refluxing temperature (ca. 145°, under a nitrogen atmosphere) for 3 hr. and allowed to stand overnight. The *o*-xylene and unreacted maleic anhydride were removed by distillation and sublimation at reduced pressure (ca. 0.1 mm.). The white solid residue was twice triturated with 50 ml. of petroleum ether. Evaporation of the solvent from each solution gave 0.272 g., m.p. 80–85°, and 0.066 g., m.p. 90–92.5°, of crude 3 (77% yield), respectively. The solid residue gave 0.102 g. of ethyl acetate soluble material which was a noncrystalline solid. Attempts to crystallize any adduct 4 from a saturated ethyl acetate solution of this solid failed. No adduct 4 could be detected in this unknown mixture. Recrystallization (petroleum ether) of the crude 3 (0.338 g.) gave 0.194 g. of 3, m.p. 89.5–91.5°.

*Dimethyl Acetylenedicarboxylate Reactions. A. With the Thermal Reaction Mixture from 1.* The reaction mixture, 3.805 g. (0.016 mole), resulting from heating 1 (94.9% pure) at 115  $\pm$  2° for 18 hr., was treated with 4.97 g. (0.035 mole) of dimethyl acetylenedicarboxylate dissolved in 10.0 ml. of toluene. The mixture was heated at 100° for ca. 8 hr.; the toluene was removed by distillation at reduced pressure, 15 mm.; and the crude residue, 9.05 g., was chromatographed on a 200-g. silicic acid column. Elution with chloroform (50-ml. fractions) gave two solids, 3.53 g. (fractions 14–35) of crude 9 (61%), and 1.10 g. (fractions 56–65) of crude 10 (17%). Purified 9, m.p. 123–124°, was obtained from repeated recrystallization from methanol.

*Anal.* Calcd. for C<sub>24</sub>H<sub>30</sub>O<sub>4</sub>: C, 75.36; H, 7.91; mol. wt., 382.48. Found: C, 75.12; H, 7.95; mol. wt., parent peak 382 (mass spectrometric determination).

Its infrared spectrum exhibits absorptions at 3.32, 3.41, 3.50, 5.76, and 5.79  $\mu$ . Weak absorptions can be seen in the C=C stretching vibration region, 5.8–6.2  $\mu$ , corresponding to those observed in the Raman spectrum (see above).

Recrystallization (ethyl acetate, then methylene chloride-cyclohexane) gave 10, m.p. 220–222°.

*Anal.* Calcd. for C<sub>30</sub>H<sub>38</sub>O<sub>8</sub>: C, 68.68; H, 6.92; mol. wt., 524.59. Found: C, 68.69; H, 7.09; mol. wt., parent peak 524 (mass spectrometric determination).

Its infrared spectrum shows absorption at 3.32, 3.40, 3.48, 5.74, 5.79, 5.99, 7.84, and 13.30  $\mu$ .

*B. With 9.* A mixture of 0.152 g. (0.40 mmole) of 9, 0.063 g. (0.44 mmole) of dimethyl acetylenedicar-

boxylate, and 2.0 ml. of *o*-xylene was heated at 120° for 4 hr. The solvent was removed (reduced pressure), and the resulting white solid residue was recrystallized from methanol. Adduct **9** was recovered, 0.147 g. (97%), m.p. 121–123°. This sample shows an identical infrared spectrum with that of the analytical sample of **9**.

C. *With 2*. A mixture of 0.213 g. (1.78 mmoles) of **2**, 0.251 g. (1.78 mmole) of dimethyl acetylenedicarboxylate, and 2.0 ml. of toluene was heated at the refluxing temperature (nitrogen atmosphere) for 3 hr. The solvent was removed (reduced pressure), and the resulting yellowish oil, 0.485 g., was chromatographed on 20 g. of silicic acid. Elution with 50-ml. portions of chloroform gave 0.455 g. (97.5%, fractions 1–4) of a

colorless oil. The infrared spectrum of this oil is consistent with structure **14**, *i.e.*, absorptions at 5.80, 6.10, 7.90, 10.10, and 10.95  $\mu$ .

After standing overnight, the total amount of oily product was rechromatographed on 50 g. of silicic acid. Elution with 50-ml. portions of chloroform gave 0.307 g. (66.3% based on **2**, fractions 14–24) of **15**. The absorption spectra are described above.

*Acknowledgment*. The authors are grateful to Mrs. M. S. Bentley for infrared measurements, G. L. Carlson for obtaining the Raman spectra, F. J. Michalek, C. J. Lindemann, and W. R. Freeman for the g.l.p.c. analyses and collections, and R. E. Rhodes for the mass spectrometric determinations.

## Thermally Induced Reactions of Some Novel Allenes

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Contribution from the Union Carbide Research Institute, Union Carbide Corporation, Tarrytown, New York. Received May 14, 1965

The present work describes the thermally induced reactions of both cyclic and open-chain allenes which contain an additional double bond or allenic grouping in the molecule. When heated, neat or in a hydrocarbon solvent, the allenes underwent both dimerization and isomerizations. In the vapor phase only isomerization took place. In a number of cases the isomerizations led to novel olefins in excellent yields. Particularly interesting is the formation of 3,4-diisopropylidenecyclobutene (XVIII) from 2,7-dimethyl-2,3,5,6-octatetraene (XVII). The results have been rationalized on the basis of the stability of assumed biradical intermediates.

### Introduction

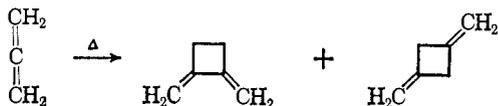
The thermally induced reactions of allenic derivatives were first investigated by Lebedev<sup>1,2</sup> more than one-half century ago. He claimed that besides other products cyclobutanes were formed by 1,2-additions, and this was later verified by other workers.<sup>3</sup> It has been shown that allene itself gives 1,2- and to a minor extent 1,3-dimethylenecyclobutane, in addition to other products, when heated at 150° in a sealed tube for 3 days<sup>2</sup> or passed through a 500–510° hot tube.<sup>4</sup> Just in recent years this reaction has been investigated more thoroughly with a wide variety of allenic derivatives,

including cycloaddition of allenes to activated olefins, such as acrylonitrile, yielding methylenecyclobutane derivatives.<sup>5</sup> Addition of allenes to normal olefins or acetylenes does not generally take place. A few examples of intramolecular cycloadditions of dienes are known,<sup>6</sup> but similar reactions of allenic derivatives have not been reported. The reason is simply that such allenes, containing two allenic groupings or an additional double bond, have until recently been virtually unknown.

With the development of the new synthesis of allenes from *gem*-dibromocyclopropanes,<sup>5–7</sup> cyclic allenes became readily available for the first time,<sup>8</sup> and a number of allenic compounds of the type described above have been prepared<sup>9,10</sup> by the same method. A study of the thermally induced reactions of these compounds appeared promising, and the present paper describes such an investigation.

### Results

Heating 1,2-cyclononadiene (I) in a sealed tube at 130° for 18 hr. afforded a crystalline mixture. This was separated by careful chromatography on alumina into two compounds, both dimers. The closely similar spectra include ultraviolet bands in the 260-m $\mu$  region, characteristic of a rigid diene chromophore,<sup>11</sup> and weak



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