Registry No.—**1**, 33143-72-5; **2**, 33212-34-2; **3**, 33143-73-6; 1,3,7-octatriene, 1002-35-3; π-allylpalladium, 12240-87-8; 1,3,6-heptatriene, 1002-27-3; 1,3,6-octatriene, 929-20-4; 1,3,7,11-dodecatetraene, 22005-88-5.

Acknowledgment.—We wish to thank Dr. P. A. Wadsworth, Jr., for the numerous mass spectral measurements and his helpful suggestions for structure determinations.

Oligomerization and Co-oligomerizations of Allene

SHENG-HONG DAI[1a] AND WILLIAM R. DOLBIER, JR.*[1b]

Department of Chemistry, University of Florida, Gainesville, Florida 32601

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A systematic study of the oligomerization of allene was undertaken. *Via* temperature and concentration variation one could control reasonably the relative proportions of the various oligimers formed. The oligomerization was found to proceed from the dimer, 1,2-dimethylenecyclobutane, and through various [2 + 2] and [2 + 4] cycloadditions, sigmatropic rearrangements, and electrocyclic reactions. Co-oligomerizations of allene with 1,2-cyclononadiene and tetramethylallene were found to incorporate only *one* molecule of the substituted allene and they proceeded *via* pathways similar to that for allene itself.

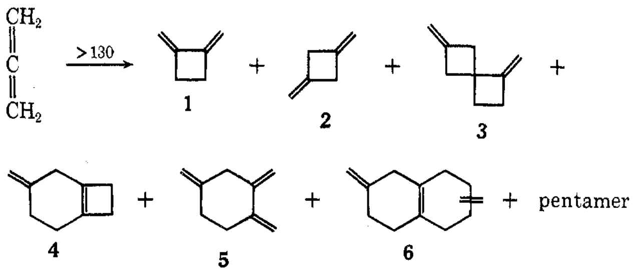
In spite of the amount of recent work which has been devoted to the dimerization and further oligomerization reactions of allene,[2] there has been little or no discussion of the detailed *pathways* to the various oligomers which are formed. Nor has any attempt been made to regulate this process so as to obtain preferentially one oligomer or another.

In order to investigate the secondary deuterium isotope effects of the allene dimerization it was necessary for us to seek conditions for a high yield (~90%) conversion of allene to 1,2-dimethylenecyclopropane. In the course of this work various data were accumulated which enable us now to be able to present a concise picture of this *very interesting* oligomerization process which apparently proceeds by a simple sequence of competitive [2 + 2] and [2 + 4] cycloadditions, sigmatropic rearrangements, and electrocyclic reactions.

It also became of interest to investigate the relative abilities of other allenic hydrocarbons, namely 1,2-cyclononadiene and tetramethylallene, to co-oligomerize with allene. There is essentially no information in the literature dealing with the relative ability of allene to codimerize or co-oligomerize with other allenic hydrocarbons. Not only were the results of these studies found to be consistent with those conclusions derived from our earlier investigation of allene itself, but much new and interesting chemical information was gleaned from these systems.

Results and Discussion

Allene Oligomerization.—The key innovation of this study as compared to those that have preceded it derived from the idea of pyrolyzing allene at relatively low concentration in benzene. Vacuum line techniques combined with gas-liquid phase chromatography (glpc) allowed quantitative analysis, isolation, and characterization of the various oligomers, which were in all cases but one proven to be identical with those described earlier by Weinstein.[2a-d]



As can be seen from Table I, 1,2-dimethylenecyclobutane, dimer **1**, is the major constituent of the oligomerization product mixture at the lower temperatures. In fact, if the weight ratio of allene to benzene was decreased to 1:3.0 at 130°, the yield of dimer after 24 hr could be increased to as high as 91%, although the conversion dropped off to 5%.

Curiously, dimer **2** was detected only in those runs at higher temperatures (>160°), and its mole fraction increased as the temperature was increased, a maximum value of >0.05 being reached, in our study, at 200°. It had been shown earlier that the process **1** → **2** did not take place even at temperatures as high as 450°.[3] Since, as it will be shown below, all higher oligomers derive solely and logically from dimer **1**, this means that >95% of all dimerizations of allene result in the formation of 1,2-dimethylenecyclobutane.

While the dimerization of allene to form 1,2-dimethylenecyclobutane (1,2-DMC) can be most consistently thought of as proceeding *via* a two-step mechanism[2e,4] very little can be said at this time about the mechanism of the process leading to 1,3-dimethylenecyclobutane (1,3-DMC). What can be said is that, since less than 1% of 1,3-DMC is formed at temperatures below 160° and yet >5% is formed at 200°, it is necessary that the entropy requirements for 1,2- and 1,3-dimethylenecyclobutane formation *cannot* be nearly the same. Moreover, the $\Delta S^{\ddagger}$ for 1,2-dimethylenecyclobutane formation must have a significantly larger negative value. This can easily be rationalized in terms of the greater

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[1] (a) Taken in part from the Ph.D. Dissertation of Sheng-Hong Dai, University of Florida, June 1971; (b) Alfred P. Sloan Foundation Fellow, 1971–1972.

[2] (a) B. Weinstein and A. H. Fenselau, *Tetrahedron Lett.*, 1463 (1963); (b) B. Weinstein and A. H. Fenselau, *J. Chem. Soc. C*, 368 (1967); (c) B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **32**, 2278 (1967); (d) B. Weinstein and A. H. Fenselau, *ibid.*, **32**, 2988 (1967); (e) a recent review discusses substituted allene dimerizations and [2 + 2] cycloadditions—J. E. Baldwin and R. H. Fleming, "Fortschritte der Chemischen Forschung," Band 15, Heft 3, Springer-Verlag, West Berlin, 1970, pp 281–310.

[3] W. v. E. Doering and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **89**, 4534 (1967).

[4] W. R. Dolbier, Jr., and Sheng-Hong Dai, *ibid.*, **92**, 1774 (1970).

Table I

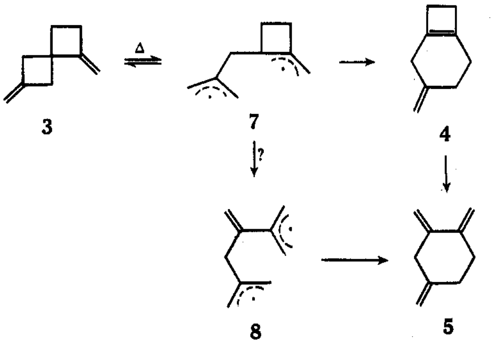
Products from Allene Oligomerizations in Benzene

Reaction temp, °C	Reaction time, hr	Wt ratio, PhH/allene	Allene, reacted, %	Mole fraction of products 1	2	3	4	5	6	Pentamer
130 ± 2	24	1.66	6–8	0.869		0.045	0.059	0.027		
135 ± 2	24	1.53	8.5	0.862		0.047	0.074	0.014		
140 ± 2	24	1.24	10	0.774		0.096	0.068	0.062		
160 ± 2	15	1.46	30	0.394	0.011	0.131	0.021	0.079	0.312	0.052
175 ± 2	24	2.20	42	0.118	0.012	0.140		0.023	0.547	0.162
200 ± 4	24	2.18	85	0.075	0.057	0.023		0.019	0.622	0.196
200 ± 5	24	3.80	80	0.108	0.052	0.050		0.026	0.582	0.176

steric requirements for C-2–C-2′ approach than for C-2–C-1′ approach in the respective rate-determining transition states.

A careful investigation of the trimer products **3**, **4**, and **5** revealed some very interesting chemistry (Scheme I). At first glance it seemed obvious that **3** and **4** are formed by competitive [2 + 2] and [2 + 4] processes, respectively, and that **5** derives from **4** *via* simple electrocyclic ring opening.

Scheme I



However, considering Table I it is apparent that things are not quite that simple. In the higher temperature runs, tetramer **6** and the pentamers have obviously increased in concentration at the expense of *all three* trimers, although tetramer **6** can logically only be obtained from [2 + 4] addition to trimer **5**. Indeed we found that, under the reaction conditions, trimer **3** could be converted quantitatively into a mixture of **4** and **5**. (See Table II.) The reaction was complete at 185° after 18 hr. Less than 1% of **4** could actually be detected in the product mixture after pyrolysis, but it was shown that conversion of **4** to **5** is very rapid under these conditions. (See Table I). The alternative possibility of the process proceeding *via* a radical ring cleavage process *via* **8** has not yet been ruled out as contributing at least partially to the mechanistic pathway. A concerted Cope rearrangement alternative pathway was not considered a realistic possibility owing to the lack of proximity of the two ends of this 1,5-hexadiene system.

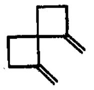
Table II

Pyrolyses of 1,6-Dimethylenespiro[3.3]heptane (**3**)

Pyrolysis temp, °C	Pyrolysis time, hr	Phase	Ratio 3	5	4
140–145	24	Acetone-d_6 solution	98.5	1.4	
160 ± 3	12	Acetone-d_6 solution	91.0	8.5	0.5
170 ± 2	12	Benzene solution	81.0	19.0	
175 ± 3	5	Acetone-d_6 solution	88.7	11.0	0.3
185 ± 5	18	Gas phase	9.0	91.0	
275 ± 5	3.5	Gas phase	0	100	

If the probable pathway *via* **4** can indeed be proven correct, this will provide a unique example of a reaction where both [2 + 2] and [2 + 4] cycloadducts are formed competitively, along with concomitant rearrangement of the [2 + 2] to the [2 + 4] adduct. This seems a likely system to be able to observe competitive [2 + 2] and [2 + 4] closure from a diradical intermediate. Such an investigation is presently underway.

Needless to say, the smooth conversion of **3** to **5** without doubt establishes the identity of the trimer **3** which Weinstein had not been able to distinguish from the isomeric structure **9**.[2b] Actually the nmr spectrum of **3** also is *much* more consistent with structure **3** than **9**.



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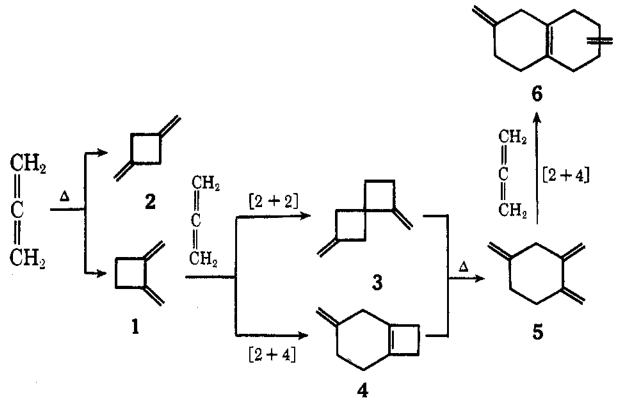
With an understanding of the thermal properties of trimer **3**, one can now rationalize easily the entire process of oligomerization of allene as a sequence of competitive [2 + 2] and [2 + 4] cycloadditions, sigmatropic rearrangements, and electrocyclic reactions with essentially all of the oligomerization beginning with the formation of 1,2-DMC (Scheme II).

Scheme II



One last point deserves mentioning. While trimer formation involved competitive [2 + 2] and [2 + 4] cycloadditions, tetramer formation from **5** apparently involves only two, competitive [2 + 4] cycloadditions. No [2 + 2] dimers could be detected by glpc. This observation has some experimental precedent, since Bartlett has shown that the interatomic distance between C-1 and C-4 of the diene system has much to do with its relative rates of [2 + 2] and [2 + 4] cycloadditions.[5] Indeed he found that the ratio of [2 + 2] to [2 + 4] cycloaddition between 1,1,2,2-dichlorodifluoroethylene and 1,2-DMC was >99, while for 1,2-dimethylenecyclohexane it was 0.8.

Co-oligomerization of Allene and 1,2-Cyclononadiene.—1,2-Cyclononadiene (CND) is the smallest cyclic allene which is relatively free of ring strain, and its properties and reactions have been studied extensively.[6] The dimerization takes place with ease at 120°, forming a remarkably pure mixture of dimers in high yield. Unlike parent allene, no higher oligomers could be detected.

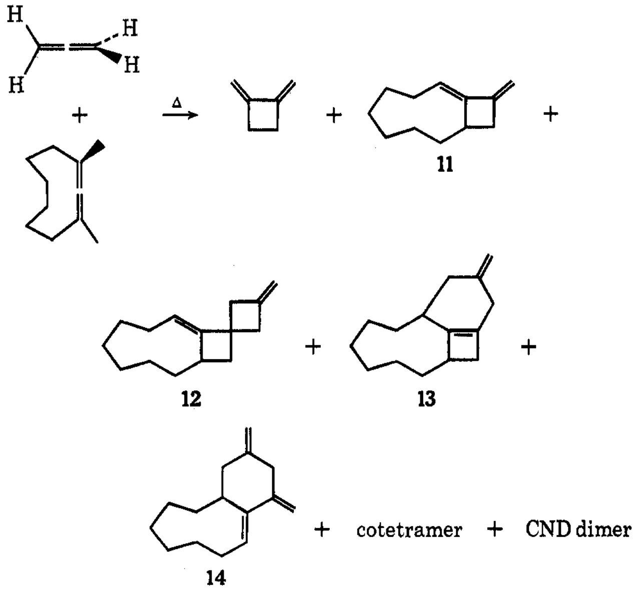
It was a desire to take advantage or the reactivity and simplicity of 1,2-cyclononadiene which prompted the study of its reaction with allene.

The reaction was carried out under a variety of conditions in a sealed tube with no solvent. After each pyrolysis, the allene was allowed to evaporate slowly, and the components in the residual liquid were separated and isolated by glpc. The results of several reactions are summarized in Table III.

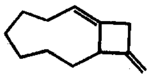
TABLE III

CO-OLIGOMERIZATION OF ALLENE AND CND

Ratio, allene/CND	Temp, °C	Time, hr	Relative ratio 11	12,13, 14	Cotetramer + CND dimer	Reacted CND, %
6.3	135 ± 2	21.5	56	10	34	82
6.0	146 ± 2	11.0	16	46	38	90
9.6	152 ± 2	8	7	38	55	100
12.0	136 ± 3	24	70	22	8	85
12.4	147 ± 3	9	16	36	48	100



Codimer **11** was formed but became the major product only under conditions where allene was used in >10-fold excess and the temperature was maintained at <140°. The structure assignment of **11** was based upon its elemental analysis and its spectral characteristics in the uv, nmr, and ir (see Experimental Section).



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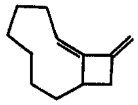

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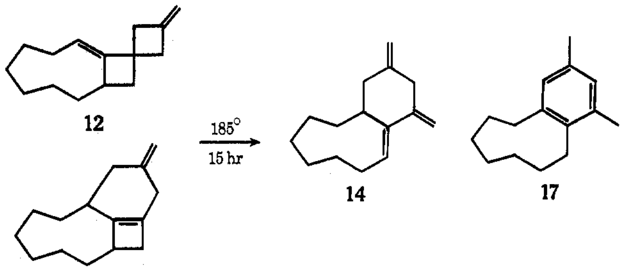
The presence of uv absorption obviously eliminates **15** as a possible structure for codimer, and geometrical isomer **16** could be ruled out by the fact that the codimer was thermally stable. Heating the codimer in a large excess of pentane at 265° for 3.5 hr led to complete recovery of the sample with negligible rearrangement having occurred.[7] A significant amount of **16** would have easily been detected by the observation of a [1,5] hydrogen shift, which is well-precedented for such systems.[8]

Three trimers eluted on the gc after the dimer and were characterized chemically and spectroscopically to have the structures **12**, **13**, and **14**.[9] A key factor in determining their structures was a pyrolytic study which showed that, similar to the case for the allene trimers **3**, **4**, and **5**, two of the cotrimers, assigned structures **12** and **13**, rearranged thermally to the third trimer, **14** (Table IV). A clean separation of the three trimers could not be achieved preparatively by glpc, but enriched samples were used to obtain the nmr spectra described in the Experimental Section. A mixture of **12** and **13** was heated at 185° for 15 hr with the result that a 50:50 mixture of the third trimer and a new compound **17** was obtained. **17** was characterized by its elemental analysis to be isomeric with the trimers. Moreover, it was shown spectroscopically to be a benzene derivative with two nonidentical methyl groups and two aromatic hydrogens. Structure **17** not only best fits the data, but is consistent with the structural assignment of **13** and **14**.

TABLE IV

PYROLYSIS OF ALLENE–CND COTRIMERS 12, 13, and 14

Pyrolysis temp, °C	Time, hr	Starting sample	Product ratio 14	21	17
185	12	Mainly 14	50		50
185	15	Mixture of 12 and 13	50		50
246	6	Mixture of three		78	22
255	5	Mainly 14		80	20
275	3.5	Mixture of three		73	27



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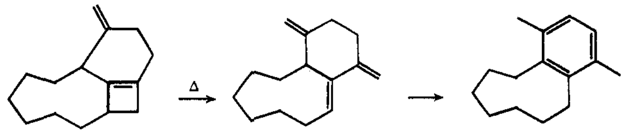
[5] P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, **90**, 6071, 6077 (1968).

[6] (a) L. Skattebøl and S. Solomon, *ibid.*, **87**, 4506 (1965); (b) W. R. Moore, R. D. Bach, and T. M. Ozretich, *ibid.*, **91**, 5918 (1969); (c) W. R. Moore and W. R. Moser, *J. Org. Chem.*, **35**, 908 (1970); (d) W. R. Moore and W. R. Moser, *J. Amer. Chem. Soc.*, **92**, 5469 (1970).

[7] Polymerization of **11** occurs quite readily in concentrated solution; *i.e.*, a total loss of **11** was observed after storage as a 30% solution in benzene at 0° for 30 days.

[8] E. F. Kiefer and C. N. Tanna, *J. Amer. Chem. Soc.*, **91**, 4478 (1969).

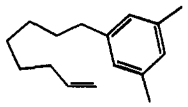
[9] A cotetramer (one CND and three allenes) was detected by glpc, as indicated in Table III, but it was not fully characterized.



18 19 20

Structures **18** and **19** can thus be ruled out as alternatives to **13** and **14**, since they could only reasonably lead to aromatic compound **20**, which has two *identical* methyl groups.

An additional pyrolysis product, interestingly, was obtained when the pyrolysis temperature was raised above 245°. This new product was formed equally well from any of the three trimers but was not found to be formed from **17**. Largely on the basis of elemental analysis and the observation in the nmr of two *identical* benzene-bound methyl groups, *three* aromatic protons, and *three* vinylic protons, the structure **21** was assigned to this product.

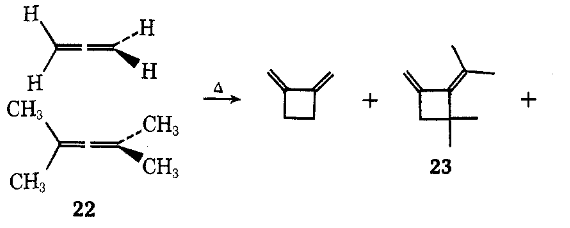


21

The picture of this co-oligomerization is now very clear, with the process being almost identical with that of parent allene oligomerization. There are, however, some key differences in the two reactions which should be mentioned. First, CND apparently is *not* an effective dienophile nor an effective [2 + 2] reagent with the codimer. Thus only *one* unit of CND becomes involved in the co-oligomerization process, and that in the initial [2 + 2] cycloaddition step. Second, in its [2 + 2] cycloadditions with allene, the codimer is reactive *only* at the unsubstituted methylene group. Most likely this is due to a steric effect on carbon–carbon bond formation at the other, substituted methylene position. Notice that the particular orientation of the [2 + 4] trimer adducts (**13** and **14**) also indicates a greater degree of bond formation in the [2 + 4] transition state at the *unsubstituted* methylene group. Finally, while the thermodynamic driving force to aromatization is unquestioned, the thermal conversion of the trimers to aromatic species **17** and **21** was not expected. The allene trimers did *not* undergo this conversion, and there is no precedent for unimolecular aromatization of such species. Certainly there is no orbital symmetry allowed pathway that can easily be envisioned.

Codimerization of Allene and Tetramethylallene.—Since tetramethylallene (TMA) is an open-chain allene and thus can have *no* ring strain, it appeared of interest to compare its reactivity in codimerization with allene with that of CND.

The reaction was carried out in essentially the same manner as the CND–allene co-oligomerization. However, in this case, only a three- to fourfold excess of allene was needed to ensure dominant codimer formation. Table V shows the results of runs under variable conditions. The analysis of the cotrimer fraction was not fully accomplished, although a good quantity of it was obtained in the run at 155°, and a mixture of cotrimers could be clearly separated from TMA dimer by glpc. Although the cotrimers were not able to be separated, nmr indicated that a cotrimer with a triene structure, most likely **24**, constituted about 70% of the cotrimer mixture. However, the definitive study in this system was limited to the chemistry of the dimer, which was established spectroscopically to have the structure **23**. Additional evidence included the formation of a 1:1 Diels–Alder adduct (**25**) with TCNE in acetone at room temperature.



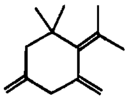
22 23

cotrimers + TMA dimer

Table V

Codimerization of Allene and TMA

Mole ratio (Allene/TMA)	Reaction temp, °C	Time, hr	TMA conversion	Codimer **23**, g (%)
3	147 ± 3	15	30	0.87 (61)
4	140 ± 2	12	21	0.41 (74)
3.7	155 ± 3	12	45	1.05 (73)
3.7	160 ± 3	12	52	1.12 (44)



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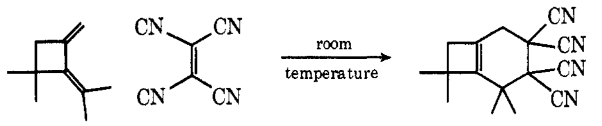
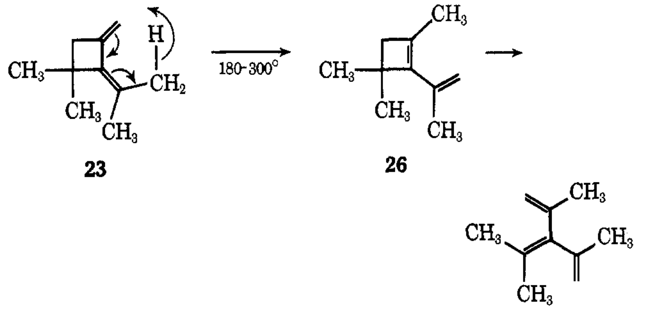


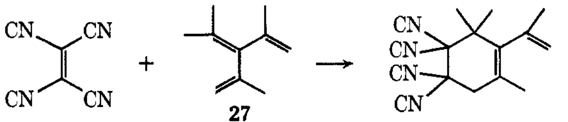
23 25

Additional interesting chemistry of the codimer **23** has been explored. As expected it undergoes a thermal 1,5-hydrogen shift to produce **26**, which then ring opens under the reactions conditions to form triene **27**.



23 26 27

As can be seen from Table VI, significant amounts of **26** can be detected at pyrolysis temperatures <210°, but at temperatures >250°, only **27** was observed. A 1:1 Diels–Alder adduct of TCNE and triene **27** could



27 28

TABLE VI

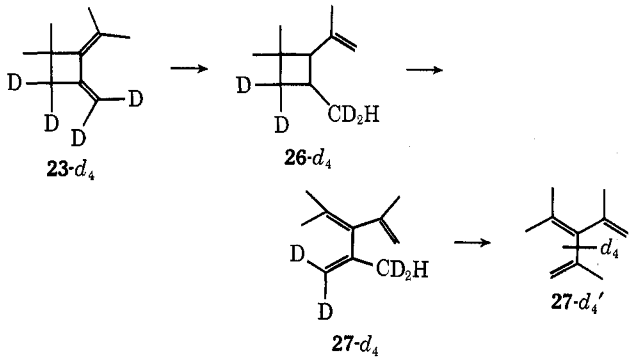
PYROLYSIS OF CODIMER **23**

Pyrolysis temp, °C	Time, hr	Solvent	Mole ratio **23**	Mole ratio **26**	Mole ratio **27**
180	12	C_6D_6	78	12	10
210	6	C_6D_6	59	13	28
270	6		0	0	100
200[a]	20	C_6D_6	72	12	16[b]
210[a]	6	C_6D_6	70	11	19[b]
300[a]	10	C_6D_6	0	0	100[c]

[a] Tetradeuterio starting material used. [b] Nmr of the trienic product showed the deuterium to be relatively unequilibrated. [c] Nmr showed *complete* equilibration of the deuteriums of the triene **27**.

be prepared at room temperature with adduct structure **28** deduced from elemental analysis and spectra.

An interesting aspect of the chemistry of triene **27** was its ability to undergo thermally degenerate 1,5-hydrogen shifts. In order to detect such a process the codimer **23**-d_4 was prepared from allene-d_4[10] and TMA. Pyrolysis of **23**-d_4 at 210° for 6 hr yielded 19% of **27**-d_4 and 11% of **26**-d_4, **27**-d_4 showing a ratio of methyl to vinyl protons in the nmr of 4.8. (A ratio of 5.0 is expected for the initially formed **27**-d_4.) After heating codimer **23**-d_4 for 10 hr at 300°, however, only triene **27**-d_4' was recovered, and the ratio of methyl to vinyl protons had attained the totally equilibrated value of 3.0. That the four deuteriums were indeed randomly distributed was verified by the formation of the Diels–Alder adduct of this triene with TCNE. The nmr integrations from this adduct were identical with those from the TCNE adduct of the undeuterated triene **27**.



Conclusions

Allenes are one of the types of reactive olefinic species which undergo thermal [2 + 2] cycloadditions. Such reactions are not common for simple olefins, and only several fluoro- and chlorofluoroalkenes can match the ability of allenes in cyclobutane ring-forming reactions.[11] The relative reactivity of allenes seems to be reflected by their relative abilities to dimerize. For instance, perfluoroallene affords a high yield of dimer at 40°,[12] CND at 130°,[6] TMA at 150°,[13] allene above 175°, and acrylonitrile above 250°.[14] Thus a qualitative order of decreasing reactivity can be arranged as follows: fluoro or fluorochloroallenes and alkenes > cycloallenes > methylated allenes > allene > activated alkenes ≫ unactivated alkenes.

Therefore any satisfactory codimerization between two different olefinic species in the above series can only be achieved by using an excess of the *less* reactive olefin; otherwise the major product will just be the dimer of the more reactive species. This idea is certainly supported by our codimerization studies.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga. Gas chromatographic separations were performed using a Model A-90-P3 Varian Aerograph gas chromatograph equipped with a Varian Model G2010 10-in. strip chart recorder. Infrared spectra were recorded on Perkin-Elmer Model 137 and Beckman IR-10 spectrometers; mass spectra on a Hitachi Model RMU-6E spectrometer; uv spectra on a Cary-15 recording spectrophotometer; and nmr spectra on a Varian A-60A spectrometer. Tetramethylsilane was used as an internal standard for the nmr spectra.

Allene Oligomerization.—A summary of the oligomerization conditions and product distributions is shown in Table I. Each reaction was carried out in a sealed thick-walled tube of 12–15 ml capacity. The detailed experimental procedure for the 175° run will serve as an example.

To a 15-ml tube was added 1.76 g of benzene, and allene (0.80 g) was transferred to the tube *via* vacuum line. The tube was sealed under vacuum, wrapped with glass wool, and heated at 175° for 24 hr in a tube furnace. Then the tube was cooled to −78°, a pin hole was opened at the point of the seal, and the unreacted allene was allowed to evaporate and transfer from −78 to −195° on the vacuum line; 0.46 g of allene was found to be unreacted (∼58% recovery). The residual liquid was characterized by glpc using a 10% 10 ft × 1/4 in. Carbowax 1500 column at 80° to estimate the relative amounts of dimers and trimers, and a 8 ft × 1/4 in. 20% SE-30 silicone oil column at 135° for estimating the trimers, tetramers, and pentamers. Benzene, dimers, and trimers were separated from less volatile tetramers and pentamers by vacuum line transfer at room temperature to −195°. The tetramers and pentamers weighed 0.24 g. Dimers were collected from gc using glass spiral traps cooled to −78°, while simple 4-mm, v-shaped tubes were used at room temperature to collect the tetramers and pentamers. The spectra of the dimers were identical with those reported in the literature,[2b] while those for the trimers and tetramers are given below.

1,6-Dimethylenespiro[3.3]heptane (3)[2b] had ir (NaCl plate) 3055, 2915, 1755, 1675, 1408, 1220, 1055, and 878 cm^{-1}; nmr (CCl_4) δ 4.68 (t, J = 2.3 cps, 1 H), 4.50 (pent, J = 2.1 cps, 3 H), 2.57 (sext, 4 H), 2.40 (m, 1 H), 2.29 (m, 1 H), and 1.60–1.97 (m, 2 H); mass spectrum (70 eV) *m/e* 120 (10) (p), 91 (85), 79 (85), and 39 (100).

3-Methylenebicyclo[4.2.0]octa-1(6)-ene (4)[2b] had nmr (CCl_4) δ 4.74 (m, 2 H), 2.65 (m, 2 H), 2.43 (s, 4 H), 2.18 (s, 4 H); mass spectrum (70 eV) *m/e* 120 (67) (p), 105 (100), 92 (40), 91 (95), 79 (64), 77 (50), 51 (45), 39 (98).

1,2,4-Trimethylenecyclohexane (5)[2b] had ir (NaCl plate) 3082, 2950, 2910, 2855, 1680, 1650, 1630, 1440, 1430, 1265, 1178, 952, 880, 802, 736, and 678 cm^{-1}; nmr (CCl_4) δ 2.24 (s, 4 H), 2.90 (pent, 2 H), 4.59 (m, 4 H), and 4.99 (m, 2 H); mass spectrum (70 eV) *m/e* 120 (p).

Dimethylene-9,10-octalins (6)[2c] had ir (NaCl plate) 3072, 2900, 2840, 1650, 1440, and 885 cm^{-1}; nmr (CCl_4) δ 4.70 (s, 4 H), 2.65 (s, 4 H), 2.22 (t, 8 H); mass spectrum (70 eV) *m/e* 160 (95) (p), 91 (100).

Pyrolyses of 1,4-Dimethylenespiro[3.3]heptane (3).—A summary of the results is shown in Table II. The gas-phase reactions were carried out under vacuum at low sample pressure in a 500-ml Pyrex tube heated in a tube furnace. Solution pyrolyses were carried out as a *ca.* 10% solution in a sealed 5-ml tube.

Allene-1,2-Cyclononadiene Co-oligomerization.—All reactions were carried out in 25-ml thick-walled tubes. A summary of the results is shown in Table III. A typical reaction and isolation of products is described below.

CND (3.4 g, 27.9 mmol) was added to a 25-ml thick-walled tube

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and 13.5 g (0.34 mol) of allene was added *via* vacuum line. The tube was sealed under N_2 and heated at 136° for 24 hr. After cooling to $-78°$, the tube was opened and the excess allene was allowed to transfer to $-195°$. The residual liquid was analyzed by glpc using the SE-30 column at 175°. The ratio of components was as follows: 1,2-dimethylenecyclobutane, 8.4; unreacted CND, 3.1; codimer **11**, 9.5; cotrimers **12**, **13**, and **14**, 3.0; cotetramer and CND dimer, 1.0. The conversion of CND was 79% and the yield of codimer **11** was 70%. Codimer **11** and the cotrimers were concentrated by distillation, the portion distilling from 50–110° (4 mm) being used for preparative glpc.

Codimer 11 (11-Methylenebicyclo[7.2.0]undec-1(2)-ene) had bp 70–80° (5 mm); ir (NaCl plate) 3040, 2890, 2815, 1730, 1660, 1645, 1462, 1440, 1344, 1264, 1075, 1040, 1008, 862, and 795 cm^{-1}; uv $\lambda_{\max}$ 255 mμ (ϵ 14,100), 240 (12,000), and 260 (10,100); nmr (CCl_4) δ 5.51 (t, J = 8.4 cps, 1 H), 4.97 (t, J = 2.5 cps, 1 H), 4.46 (t, J = 2.1 cps, 1 H), 2.70 (d, J = 9.9 cps, 2 H), 1.97 (d, J = 9.9 cps, 1 H), and 2.0–1.0 (broad, 12 H); mass spectrum (70 eV) *m/e* 162 (15) (p), 105 (50), 93 (70), 91 (72), 81 (60), 80 (75), 79 (100), 77 (50), 67 (40), 41 (50), 39 (55).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.58; H, 11.32.

Cotrimer 14 (11,13-Dimethylenebicyclo[7.4.0]tridec-1(2)-ene) had bp 90–110° (5 mm); ir 3015, 2870, 2800, 1665, 1455, 1429, 885, and 865 cm^{-1}; nmr (vinylic only) (CCl_4) δ 5.82 (t, J = 8.5 cps, 1 H), 4.93 (sext, 1 H), 4.80 (m, 1 H), and 4.09 (m, 2 H); mass spectrum (70 eV) *m/e* 202 (25) (p), 145 (25), 119 (100), 105 (75), 91 (60).

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.07; H, 10.99.

Cotrimer 13 (3-Methylenetricyclo[10.1.1.0^{5,13}]tridec-1(13)-ene) had bp 90–110° (5 mm); nmr (CCl_4) vinylic at δ 4.72 (pent, J = 2.3 cps, 2 H) and doubly allylic at δ 2.62 (m, 2 H), allylic at 1.80–2.35 (broad, 6 H) and others at 0.90–1.80 (broad, 12 H).

Cotrimer 12 (Spiro[3-methylenecyclobutane-1,11′-bicyclo-[7.2.0]undec-1(2)-ene]) had bp 90–110° (5 mm); nmr (CCl_4) vinylic protons at δ 4.74 (pent, 4 H) and 5.33 (*t*, J = 8.1 cps, 1 H).

Pyrolysis of Allene–CND Cotrimers 12, 13, and 14.—A summary of the pyrolyses is shown in Table IV. All were carried out by heating the cotrimers in a large excess of pentane (∼5% solution) sealed in a thick-walled glass tube. The products were analyzed and purified by glpc using the SE-30 column.

3,5-Dimethyl-1,2-benzocyclononane (17) had ir (NaCl plate) 2860, 2810, 1610, 1575, 1465, 1440, 1365, 1340, 1030, 855, 820, and 805 cm^{-1}; nmr δ 6.78 (s, 2 H), 2.56–2.95 (broad, 4 H), 2.26 (s, 3 H), 2.22 (s, 3 H), and 1.10–1.95 (broad, 10 H); mass spectrum (70 eV) *m/e* 202 (100) (p), 159 (60), 145 (55), 133 (65), 119 (53).

Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.43; H, 10.60.

9-(3,5-Dimethylphenyl)-1-nonene (21) had ir (NaCl plate) 3635, 2980, 2900, 2836, 1642, 1620, 1499, 1450, 1375, 1160, 996, 915, 821, and 730 cm^{-1}; nmr (CCl_4) δ 6.84 (s, 3 H), 5.45–6.01 (m, 1 H), 4.98–5.08 (m, 1 H), 4.80 (m, 1 H), 2.36–2.72 (broad t, 2), 2.25 (s, 6), 1.80–2.24 (broad, 2), 1.22–1.80 (broad, 6); mass spectrum (70 eV) *m/e* 202 (20) (p), 145 (25), 119 (100).

Pyrolysis of Allene–CND Codimer (11).—The pyrolysis was carried out as for the cotrimers, at 265° for 3.5 hr. The nmr spectrum of the recovered material showed only starting material absorptions.

Allene–Tetramethylallene Codimerization.—The results of this reaction are summarized in Table V. A typical example of reaction, isolation, and purification of codimer is described below.

Tetramethylallene (3.21 g, 33.4 mmol) was added to a thick-walled tube of ∼15 ml capacity, and 4.10 g (103 mmol) of allene was transferred to it *via* vacuum line. After sealing under N_2 and wrapping with glass wool, the tube was heated in a tube furnace at 145-150° for 15 hr. Then after cooling to $-78°$, the tube was opened and allene was transferred as before. The volatile products (3.2 g) were isolated by vacuum line transfer at room temperature and the residual oil (0.5 g) was weighed in the tube. The volatile fraction was then examined by glpc using the SE-30 column at 90°. Three major components were detected, 1,2-dimethylenecyclobutane, TMA, and codimer **23**, in a ratio of 1.0:4.2:1.5. The codimer **23**, 0.87 g (61% based on reacted TMA), was collected from the gc using a glass spiral trap cooled to $-78°$ as a colorless liquid: ir (NaCl plate) 3060, 2915, 2850, 2700, 1740, 1670, 1640, 1445, 1418, 1358, 1270, 1230, 1102, 1016, 890, and 859 cm^{-1}; uv $\lambda_{\max}$ 253 mμ (ϵ 14,300) with a shoulder at 261 (11,400); nmr (CCl_4) δ 1.24 (s, 6 H), 1.60 (s, 3 H), 1.72 (s, 3 H), 2.32 (t, J = 2.5 cps, 2 H), 4.83 (m, 1 H), and 5.14 (t, J = 2.5 cps, 1 H); mass spectrum (*inter alia*) (70 eV) *m/e* 136 (p)b.

The nmr of the tetradeuterio species, **23**-d_4, showed singlets at δ 1.26 (6 H), 1.61 (3 H), and 1.73 (3 H).

23 reacted quantitatively with TCNE at room temperature in acetone to produce the 1:1 Diels–Alder adduct: pale yellow; mp 131–132° (*n*-heptane); nmr (C_6D_6) δ 2.41 (m, 2 H), 1.90 (m, 2 H), 1.25 (s, 6 H), and 0.98 (s, 6 H); ir (KBr) 2960, 2880, 2260, 1470, 1435, 1402, 1380, 1370, 1308, 1260, 1230, 1180, 1160, 1145, 1105, 1075, 1023, 839, and 670 cm^{-1}; mass spectrum *m/e* 264 (p).

Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.72; H, 6.07; N, 21.21. Found: C, 72.62; H, 6.20; N, 21.32.

Pyrolysis of Codimer 23 (3,3-Dimethyl-2-isopropylidenemethylenecyclobutane).—Each pyrolysis was carried out using 0.15 to 0.85 g of codimer **23** in a 500-ml Pyrex tube sealed under vacuum. Table VI summarizes the results. The ratio of products was approximated from nmr spectra of product mixtures. The triene (**27**) product was isolated by glpc and characterized: ir (NaCl plate), 3050, 2895, 2710, 1880, 1620, 1428, 1363, 1098, 896, and 880 cm^{-1}; uv (EtOH) $\lambda_{\max}$ 225 mμ (ϵ 5600); nmr (C_6D_6) δ 4.98 (m, 2 H), 4.76 (m, 2 H), 1.74 (m, 6 H), and 1.70 (s, 6 H); mass spectrum *m/e* 136 (p).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.08; H, 11.84.

Triene **27** was found to react rapidly with TCNE at room temperature to form its Diels–Alder adduct **28**: pale green; mp 96–98° (benzene); ir (KBr), 3042, 2960, 2261, 1848, 1659, 1630, 1440, 1400, 1380, 1274, 1173, 1105, 1040, 940, 840, and 690 cm^{-1}; uv $\lambda_{\max}$ (*n*-hexane) 263 mμ (ϵ 3300) with a shoulder at 272; nmr (C_6D_6) δ 1.24 (s, 6 H), 2.33 (s, 2 H), 1.15 (m, 3 H), 1.44 (m, 3 H), 4.35 (m, 1 H), and 4.84 (m, 1 H).

Anal. Calcd for $C_{16}H_{16}N$: C, 72.72; H, 6.07; N, 21.21. Found: C, 72.66; H, 6.23; N, 21.26.

The vinylcyclobutene intermediate product, **26**, present only in small quantities, was not isolated but was clearly present as indicated by the nmr (C_6D_6): a singlet at δ 1.31 (6 H); a multiplet (obscured by codimer) at 1.75–1.80 (3 H); a multiplet at 1.85 (3 H); a multiplet at 1.95 (2 H); and a multiplet at 4.86–5.18 ppm (2 H) (obscured by codimer). Upon further heating this component was shown to convert to triene **27**.

Registry No.—**3**, 4696-20-2; **11**, 33487-27-3; **12**, 33487-28-4; **13**, 33487-29-5; **14**, 33487-30-8; **17**, 33487-31-9; **21**, 33487-32-0; **23**, 33487-33-1; **25**, 33487-34-2; **27**, 33487-35-3; **28**, 33487-36-4.

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