Linear Dimerization and Codimerization of 1,3,7-Octatriene

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The linear dimerization of 1,3,7-octatriene *via* π-allylpalladium complexes in homogeneous reactions yields in high selectivity *n*-hexadecapentaenes. The same catalysts also prove active for the codimerization of 1,3,7-octatriene with various other polyolefins such as 1,3,6-heptatriene, 1,3,6-octatriene, 1,3,7,11-dodecatetraene, and 1,5,7,10,15-hexadecapentaene producing linear olefins in the C_{16}–C_{24} carbon range. The addition of phosphine ligands alters the course of the reaction and branched dimers are formed.

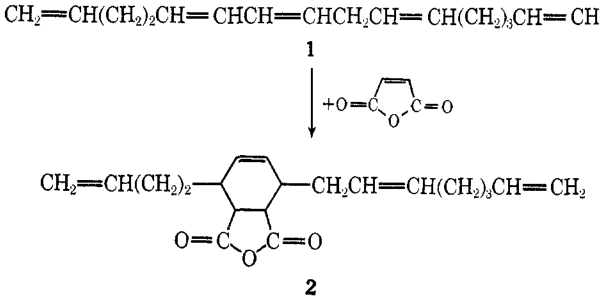
Over the last decade, oligomerization reactions of olefins *via* π-allylic intermediates of various transition metal complexes have seen a prodigious growth.[1,2] Although often not too well understood, they represent an exciting development in coordination chemistry and are finding increasing interest in both the academic and industrial world. Especially the linear and cyclic oligomerization of 1,3-dienes has demonstrated great usefulness for the synthesis of numerous novel and known organic compounds.[3] Many attempts to oligomerize other dienes such as isoprene, piperylene, dimethylbutadiene, and chloroprene have been disclosed. It can be generalized that catalysis with dienes other than butadiene directed at open chain or cyclic oligomers is complicated by the concomitant formation of the various, possible isomers. The products and their distribution often can be altered by modifying the catalysts with ligands such as phosphines or phosphites. However, very few cases are known in which dienes other than butadiene have cleanly been oligomerized to predominantly one product.

In this paper, a remarkably selective dimerization reaction of trienes to predominantly linear products in the n-C_{12}–C_{24} range will be described. This dimerization represents a facile route to a variety of novel linear compounds. Long straight carbon chains play an important role in nature, especially in fatty acids, fatty alcohols, sphingosines, and pheromones. It can be envisaged that linear natural products may be synthesized by utilizing the described type of oligomers as starting materials for further chemical reactions. Our major experimental research efforts were focused on the dimerization of 1,3,7-octatriene, which was available in large quantities in our laboratory.[4]

Results and Discussion

The addition of catalytic amounts of bis-π-allylpalladium[5] to a cis,trans mixture of 1,3,7-octatriene yielded four linear hexadecapentaenes containing one major isomer in >70% selectivity. Microanalysis and molecular weight measurements indicated an empirical formula of $C_{16}H_{24}$. Proof of linearity rested on hydrogenation of the dimer mixture giving *n*-hexadecane in 97% selectivity. For a structure assignment, the major isomer was arduously trapped by glc fractionation. All attempts to locate spectroscopically (nmr, ir, uv) the exact position of the five double bonds proved impossible in our hands. These spectroscopic data fit various possible double bond isomers. However, they clearly indicated the presence of two terminal and three internal double bonds of which two are conjugated. Additional evidence was needed for a correct structure assignment.

An ozone analysis was attempted; however, the results obtained did not unambiguously distinguish among the various possible isomers. At this point, it became obvious that the location of the position of the conjugated diene fragment would be helpful for an exact structure assignment. Therefore, a Diels–Alder reaction with maleic anhydride was carried out. The nmr data in addition to ir and high-resolution mass spectral analysis of both the hydrogenated and nonhydrogenated product have led to the structure assignment 3-(octadienyl-2,7)-6-(butenyl-3)-1,2,3,6-tetrahydrophthalic anhydride (2) pointing at a diene conjugation in 5–7 position.



Having located the conjugated diene unit in the predominant isomer of the dimerization of 1,3,7-octatriene, the nmr and ir data were in agreement with the structure 1,5,7,10,15-hexadecapentaene (1).

Definitive structure assignment is lacking for the three minor *n*-hexadecapentaene isomers. All attempts of separating and trapping by glc failed because of nearly identical retention times; however, spectroscopic evidence (nmr, uv, ir) of the combined mixture suggested that only different cis and trans isomers have been formed. This is not too surprising. The presence of various cis and trans isomers in oligomerization products of 1,3-dienes has frequently been observed.[6]

During the course of our studies to increase conversions of the dimerization reaction which never exceeded 60%, it was noted that the unreacted 1,3,7-octatriene[7] consisted of predominantly cis isomer. In this way, it was possible to synthesize pure cis-1,3,7-octatriene

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(1) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Logos Press, London, 1967.

(2) J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes," Elsevier, New York, N. Y., 1968.

(3) P. Heimbach, P. W. Jolly, and G. Wilke, *Advan. Organometal. Chem.*, **8**, 29 (1970).

(4) E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1967).

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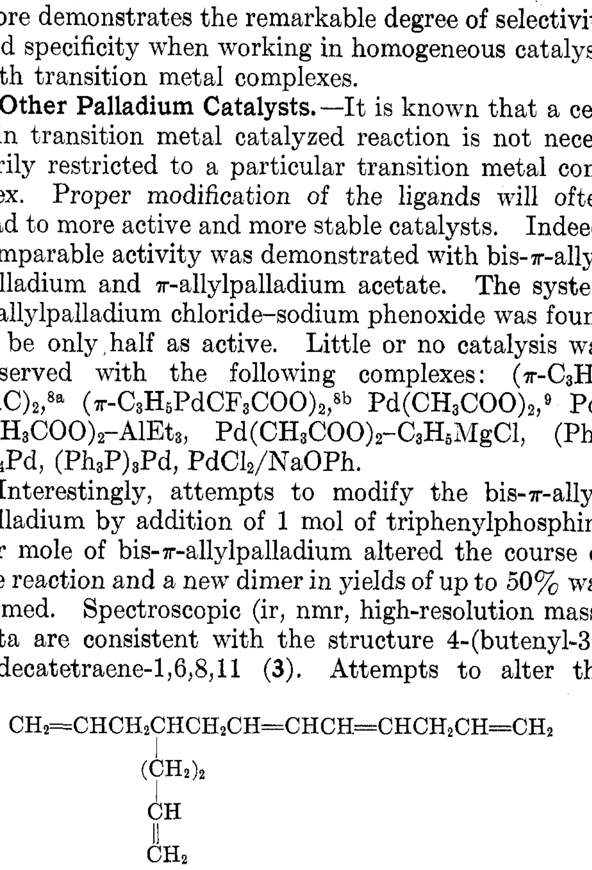
(6) G. Wilke, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963).

(7) The octatriene-1,3,7 used for the dimerization was composed of ~60% *trans*-1,3,7-octatriene and 40% *cis*-1,3,7-octatriene.

starting from the trans and cis mixture. Further investigation of this interesting finding confirmed that pure *cis*-1,3,7-octatriene did not undergo dimerization or isomerization under the catalytic influence of bis-π-allylpalladium. Unfortunately, experimental evidence regarding the inhibiting effect of the cis isomer is lacking due to unavailability of sizable amounts of *pure trans*-1,3,7-octatriene. The above observation once more demonstrates the remarkable degree of selectivity and specificity when working in homogeneous catalysis with transition metal complexes.

Other Palladium Catalysts.—It is known that a certain transition metal catalyzed reaction is not necessarily restricted to a particular transition metal complex. Proper modification of the ligands will often lead to more active and more stable catalysts. Indeed, comparable activity was demonstrated with bis-π-allylpalladium and π-allylpalladium acetate. The system π-allylpalladium chloride–sodium phenoxide was found to be only half as active. Little or no catalysis was observed with the following complexes: $(\pi\text{-}C_3H_5\text{-}PdC)_2$,[8a] $(\pi\text{-}C_3H_5PdCF_3COO)_2$,[8b] $Pd(CH_3COO)_2$,[9] $Pd(CH_3COO)_2\text{–}AlEt_3$, $Pd(CH_3COO)_2\text{–}C_3H_5MgCl$, $(Ph_3P)_4Pd$, $(Ph_3P)_3Pd$, $PdCl_2/NaOPh$.

Interestingly, attempts to modify the bis-π-allylpalladium by addition of 1 mol of triphenylphosphine per mole of bis-π-allylpalladium altered the course of the reaction and a new dimer in yields of up to 50% was formed. Spectroscopic (ir, nmr, high-resolution mass) data are consistent with the structure 4-(butenyl-3)-dodecatetraene-1,6,8,11 (**3**). Attempts to alter the dimerization of 1,3,7-octatriene toward the branched dimer exclusively failed. The addition of alkylphosphines and triphenylarsins was found to have a deleterious effect. The various ligands studied and the order of their effectiveness is as follows: diphenylphosphinoethane ≈ triphenylphosphine > phenol >>> pyridine, acetic acid, dipyridyl, triphenylarsine.

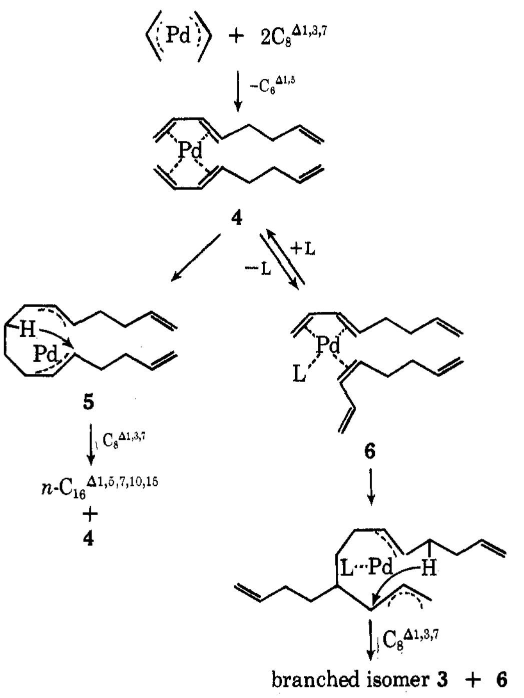


$$\begin{array}{l} CH_2{=}CHCH_2\underset{\displaystyle \begin{array}{c} | \\ (CH_2)_2 \\ | \\ CH \\ \| \\ CH_2 \end{array}}{CH}CH_2CH{=}CHCH{=}CHCH_2CH{=}CH_2 \end{array}$$

3

The mechanism proposed for the dimerization of 1,3,7-octatriene is depicted in Scheme I. The initial step is the coordination of two 1,3,7-octatrienes to bis-π-allylpalladium yielding intermediate **4**. Simultaneously, the two π-allyl groups in bis-π-allylpalladium are displaced by forming 1,5-hexadiene, a product identified in the reaction mixture. A carbon–carbon coupling of the C_8 units in **4** gives the bis-π-allyl intermediate **5**, which is coordinatively unsaturated and coordinates to incoming 1,3,7-octatriene under concomitant displacement of 1,5,7,10,15-hexadecapentaene (**1**). In this way, the intermediate **4** is regenerated and the catalytic cycle completed. An arrow in **5** indicates the allylic hydrogen shift which is necessary for the displacement of the C_{16} chain. Carbon–carbon couplings accompanied by allylic hydrogen shifts have frequently been discussed to explain oligomerization reactions of conjugated dienes.[10-14]

SCHEME I



The formation of the branched C_{16} isomer **3** can also be derived from the intermediate **4**. Ligands such as triphenylphosphine coordinate to palladium in **4**, thus displacing a coordinated olefin as depicted in **6**. Again, a carbon–carbon coupling and allylic hydrogen shift is needed to form the branched isomer **3**. The fact that, in the presence of triphenylphosphine, the linear dimer is also formed can be explained by the donor properties of triphenylphosphine. It is well established in the literature that triphenylphosphine is not very strongly bonded to a transition metal complex and the equilibrium **4** $\rightleftarrows$ **6** can be considered. The proposed scheme explains in a reasonable manner the formation of the products. It is in agreement with current aspects of transition metal catalyzed oligomerization of conjugated dienes but should not be taken too literally.

Codimerization of 1,3,7-Octatriene.—The proposed mechanism indicated the feasibility of codimerization of 1,3,7-octatriene with other polyolefins possessing a conjugated diene unit as in 1,3,6-octatriene, 1,3,7,11-dodecatetraene, and 1,5,7,10,15-hexadecapentaene. Indeed, bis-π-allylpalladium is an active catalyst for the linear codimerization of 1,3,7-octatriene with various polyolefins as listed in Table I. In view of the immense difficulties encountered in locating the double bonds in the 1,3,7-octatriene dimer, no attempts have been made to characterize the olefinic dimerization products. Identification and characterization were carried out by hydrogenation. Table I summarizes

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(8) (a) A. J. Wilkinson, *et al.*, *J. Chem. Soc.*, 1585 (1964); (b) B. L. Shaw and S. D. Robinsons, *J. Organometal. Chem.*, **3**, 367 (1965).

(9) G. Wilkinson, *et al.*, *J. Chem. Soc.*, 3632 (1965).

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(13) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifugi, and S. Ikeka, *J. Organometal. Chem.*, **6**, 572 (1966).

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TABLE I

LINEAR CODIMERIZATION OF 1,3,7-OCTATRIENE WITH POLYOLEFINS CONTAINING A 1,3-DIENE UNIT

	Reactants		Reaction				Products		
Reaction	Olefin A (ml)	Olefin B (ml)	Pd catalyst, mg	Time, days	Temp, °C	Concn, % $C_8H_{12}^{\Delta 1,3,7}$	Before hydrogen	After hydrogen	Distribution
a	n-$C_8H_{12}^{\Delta 1,3,7}$ (5)	$C_4H_6^{\Delta 1,3}$ (20)	230	4	25	32	n-$C_{12}H_{18}^{\Delta 1,3,6,10}$[a]	n-$C_{12}H_{26}$	95
							n-$C_{16}H_{24}$ (5)[b]	n-$C_{16}H_{34}$	~5
b	n-$C_8H_{12}^{\Delta 1,3,7}$ (2)	n-$C_7H_{10}^{\Delta 1,3,6}$ (4)	123	2	25	49	n-$C_{15}H_{22}$ (5)	n-$C_{15}H_{32}$	44
							n-$C_{16}H_{24}$ (5)	n-$C_{16}H_{34}$	37
							n-$C_{14}H_{20}$ (5)	n-$C_{14}H_{30}$	19
c	n-$C_8H_{12}^{\Delta 1,3,7}$ (5)	n-$C_{12}H_{18}^{\Delta 1,3,7,11}$ (5)	110	2	25	24	n-$C_{20}H_{30}$ (6)	n-$C_{20}H_{42}$	44
							n-$C_{16}H_{24}$ (5)	n-$C_{16}H_{34}$	56
							n-$C_{24}H_{36}$ (7)	n-$C_{24}H_{50}$	Trace
d	n-$C_8H_{12}^{\Delta 1,3,7}$ (5)	n-$C_{16}H_{24}^{\Delta 1,5,2,10,15}$ (5)	50	1	25	15	n-$C_{24}H_{36}$ (7)	n-$C_{24}H_{50}$	30
							n-$C_{16}H_{24}$ (5)	n-$C_{16}H_{34}$	60
e	n-$C_8H_{12}^{\Delta 1,3,7}$ (5)	n-$C_8H_{12}^{\Delta 1,3,6}$ (5)	100	2	25	45	n-$C_{16}H_{24}$ (5)	n-$C_{16}H_{34}$	97
f	n-$C_{12}H_{18}^{\Delta 1,3,7,11}$ (5)		60	2	25	~10	n-$C_{24}H_{36}$ (7)[c]	n-$C_{24}H_{50}$	85
g	n-$C_7H_{10}^{\Delta 1,3,6}$ (10)		103	2	25	6	n-$C_{14}H_{20}$ (5)	n-$C_{14}H_{30}$	95

[a] 90% selectivity. [b] Number of double bonds in parentheses. [c] Two isomers.

the results obtained. Principally, it is possible to linearly codimerize 1,3,7-octatriene with dienes (reaction a), trienes (reactions b, e), tetraenes (reaction c), and pentaenes (reaction d). However, besides codimerization, normal dimerization of the 1,3,7-octatriene and the coolefin takes place. For instance, the codimerization of 1,3,7-octatriene with 1,3,7,11-dodecatetraene (Table I, reaction c) yields, in addition to n-eicosane, n-hexadecane and n-tetracosane. The ratio of these three products can be influenced by altering the concentration of 1,3,7-octatriene to 1,3,7,11-dodecatetraene.

The results of Table I also show that the linear dimerization is not unique to 1,3,7-octatriene and linear dimerization can be carried out with other triene or polyenes as shown in reactions f and g.

In our experiments, no emphasis has been placed on yield and selectivity since the detection of catalytic activity and proof of feasibility of codimerization have been the primary design.

Generalizing, it can be stated that bis-π-allylpalladium is an excellent catalyst for the linear oligomerization of trienes or polyenes containing a 1,3-diene unit. Disappointingly, however, all attempts to codimerize 1,3,7-octatriene with compounds of the general type $CH_2{=}CHCH{=}CHY$ (Y = functional group such as OH, CN, Cl) or $CH_2{=}CHCHX$ (X = O, CN) have been unsuccessful so far.

Experimental Section

Oligomerization Procedure.—All reactions were carried out under the exclusion of oxygen and water. In general, the reactants and the palladium catalyst were charged into a glass ampoule and stirred magnetically. Reaction temperatures above 25° were maintained with a preheated silicone oil bath. The progress of the reaction was monitored by glc analysis. The products were isolated by glc trapping or distillation in the conventional manner. To avoid possible product isomerization during work-up, the active palladium catalyst was reduced to the metal by reduction with gaseous carbon monoxide at atmospheric pressure and removed by filtration. Product identification rests on nmr, ir, uv, and mass spectral analyses before and after hydrogenation. Whenever possible, glc emergence times of the hydrogenated products were compared with those of authentic samples.

1,5,7,10,15-Hexadecapentaenes (1).—A mixture of 53.7 g of 1,3,7-octatriene and 693 mg of bis-π-allylpalladium was charged into a two-neck round-bottom flask and stoppered. After a reaction period of 3 days at ambient temperature, glc analysis of the product mixture showed a 54% octatriene conversion to 97% n-hexadecapentaenes (70% selectivity to n-$C_{16}H_{24}^{\Delta 1,5,7,10,15}$) and 3% yield of butenyldodecatetraenes. Distillation at reduced pressure gave 26.9 g of hexadecapentaenes [bp 93° (2 mm)]. Linearity of the dimer mixture rested on comparison of the hydrogenated dimer product with an authentic sample of n-hexadecane by mass spectral analyses and glc emergence times. Mass spectral analysis of **1** confirmed the empirical formula, 216. Nmr spectrum[15] of **1** ($CDCl_3$): 4.8–6.6 (m, 12, vinyl plus terminal vinyl), 2.85 (t, 2, J = 6 Hz, double allylic), 1.9–2.3 (m, 8, allylic), 1.5 ppm (g, 2, J = 7 Hz, aliphatic methylene). The ir spectrum exhibited strong bands indicative of terminal and internal cis and trans double bonds (1005, 996, 910, 778 cm^{-1}). The ultraviolet spectrum had a λ_{max} 232 (ϵ 31,000).

Anal. Calcd for $C_{16}H_{24}$: C, 88.9; H, 11.1. Found: C, 88.7; H, 11.1.

The unreacted 1,3,7-octatriene consisted of the cis isomer.

Hexadecapentaene–Maleic Anhydride Adduct 2.—A reaction mixture of 1.58 g (7.32 mmol) of 1,5,7,10,15-hexadecapentaene and 0.72 g (7.34 mmol) of maleic anhydride was heated under reflux of benzene (20 ml) for 4 hr. Glc analysis showed that reaction with maleic anhydride to give predominantly (90%) one isomer had taken place. The product was isolated by glc trapping using a 6 ft × 0.25 in. o.d. SE-30 chromatographic column. Mass spectral analyses confirmed the empirical formulas, 314 and 322 [bp 180° (1 mm)], for the product before and after hydrogenation. Nmr spectrum of **2** ($CDCl_3$): 4.9–6.0 (m, 10, vinyl plus terminal vinyl), 2.9–3.1 (m, 2, substitute succinic anhydride), 1.3–2.6 ppm (m, 14, allylic plus substituted allylic plus aliphatic methylene). Mass spectral analysis of the hydrogenated **2** confirmed the location of the anhydride adduct on the linear carbon skeletal chain.

4-(Butenyl-3)-dodecatetraene-1,6,8,11 (3).—A reaction mixture of 10 ml of 1,3,7-octatriene, 67 mg of bis-π-allylpalladium, and 94 mg of triphenylphosphine was charged into a glass ampoule. After a reaction period of 2 days at 65° glc analysis showed a 70% octatriene conversion to give 51% yield of n-hexadecapentaenes and 49% yield of butenyldodecatetraenes [95% selectivity to 4-(butenyl-3)dodecatetraene-1,6,8,11]. Mass spectral analyses confirmed the empirical formulas, 216 and 226, of the branched C_{16} product before and after hydrogenation. Nmr spectrum of **3** ($CDCl_3$): 4.8–6.5 (m, 13, vinyl plus terminal vinyl), 2.95 (m, 2, double allylic), 1.3–2.5 ppm (m, 9, allylic plus aliphatic methylene).

Linear Codimerization of 1,3,7-Octatriene with Polyolefins Containing a 1,3-Diene Unit.—The general procedure followed for the codimerization reaction was to charge the appropriate olefin reactants and the bis-π-allylpalladium catalyst into a glass ampoule and seal in the normal manner. After a reaction period of 1–2 days at 25°, the per cent conversion to products was determined by glc analysis. The codimer products were isolated by glc trapping, and their empirical formulas were obtained by mass spectral analyses. Linearity proof rested on mass spectral analysis, nmr analysis, and glc emergence times of the hydrogenated codimers with authentic samples. The data obtained are summarized in Table I.

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(15) Nmr spectra of compounds **1–3** will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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.

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Oligomerization and Co-oligomerizations of Allene

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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.

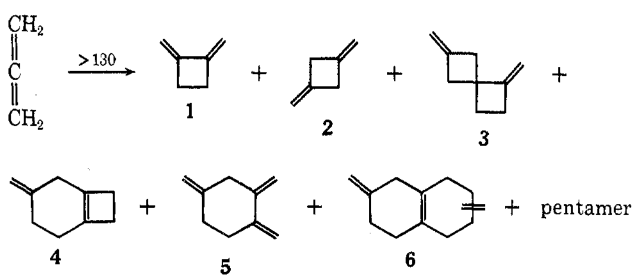
In spite of the amount of recent work which has been devoted to the dimerization and further oligomerization reactions of allene,[2] there has been little or no discussion of the detailed *pathways* to the various oligomers which are formed. Nor has any attempt been made to regulate this process so as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