vestigation before being satisfactorily resolved.[25] Additional ^{18}O-labeling experiments would be desirable, especially with alkenes having medium and large substituents before speculating further on reasons for the differing behavior.

A final point can be noted with regard to the ozonides labeled d in Tables I and II. For these cases, a small loss of [18]O enrichment between added aldehyde and final ozonide is observed which may seem inconsistent with the Criegee[1] and other zwitterion mechanisms.[2-4] This effect appears to be real; it is not due to a propylene impurity in the alkene and it also is not a result of impurities in the aldehyde or solvent. Perhaps this can be accounted for by an isotope effect involving the aldehyde. Considering the low reaction temperatures and the low molecular weight of the aldehydes, the expected magnitude of an oxygen isotope effect is not in-

consistent with the small loss of enrichment observed. Other possible explanations are decompositions of ozonide or other reaction side products such as chain peroxides during the ozonolysis to produce an aldehyde. The latter reaction has already been proposed to account for aldehydes formed during ozonolysis of a number of alkenes.[26,27] Thus, any aldehyde produced from such decompositions will be mostly unenriched, and this will tend to decrease the overall enrichment of the aldehyde in solution.

(25) Another possibility is that exchange of [18]O between labeled aldehyde and "Criegee" zwitterion might occur by a mechanism which becomes more important for alkenes with bulkier electron-donating groups. Such a mechanism has been described by Fliszár and Carles (ref 18).

(26) S. Fliszár, D. Gravel, and E. Cavalieri, Can. J. Chem., 44, 1013 (1966).

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Thermal Isomerization of 1,2-Dialkenylcyclopropanes[1]

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Abstract: The ctc, ctt, and ttt isomers of 1,2-di(prop-1'-enyl)cyclopropane isomerize at 165° at comparable rates to give, respectively, *cis,cis,cis*-di(prop-1'-enyl)cyclopropane, *trans*-6,7-dimethylcyclohepta-1,4-diene, and *cis*-6,7-dimethylcyclohepta-1,4-diene. These highly stereoselective and stereospecific reactions are interpreted in terms of a common mechanism involving a one-center epimerization as the rate-limiting step, followed by rapid Cope rearrangement of the *trans,cis,trans*- and *cis,cis,trans*-dipropenylcyclopropanes.

Among the archetypal thermal isomerizations, the *cis*-divinylcyclopropane (1) to 1,4-cycloheptadiene (2) reaction occupies a prominent interstice between
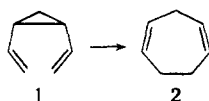
the electrocyclic conversion of 1,3,5-hexatriene to 1,3-cyclohexadiene and the degenerate [3,3] sigmatropic rearrangement of 1,5-hexadiene.

Since the initial demonstration of this process by Vogel in 1960,[2-5] and the first studies exploiting this reaction to demonstrate fluxional isomerism by Doering and Roth,[6,7] numerous examples have been investigated.

One major theme has been development of the fluxional isomerism field for the homotropylidene, semibullvalene, bullvalene, and related systems.[8] A second has been synthesis, detection, and characterization of *cis*-1,2-dialkenylcyclopropane systems unable to rearrange degenerately;[9-20] many cases are now documented, including *cis*-1,2-divinylcyclopropane itself.[16] Some *cis*-1,2-dialkenylcyclopropanes undergo Cope rearrange-

(1) This work was supported by grants from the National Science Foundation, Hoffmann-La Roche, Inc., and the Swedish Natural Science Research Council.

(2) E. Vogel, Angew. Chem., 72, 4 (1960).

(3) E. Vogel in "Festschrift zum 10-jährigen Bestehen des Fonds der Chemischen Industrie," Verband der Chemischen Industrie, Düsseldorf, 1960, p 225.

(4) E. Vogel, K.-H. Ott, and K. Gajek, Justus Liebigs Ann. Chem., 644, 172 (1961).

(5) E. Vogel, Angew. Chem., Int. Ed. Engl., 2, 1 (1963).

(6) W. von E. Doering and W. R. Roth, Tetrahedron, 19, 715 (1963).

(7) W. von E. Doering and W. R. Roth, Angew. Chem., Int. Ed. Engl., 2, 115 (1963).

(8) For a concise review and leading references, see G. Maier, "Valenzisomerisierungen," Verlag Chemie, Weinheim, 1972, p 57–64.

(9) C. Cupas, W. E. Watts, and P. v. R. Schleyer, Tetrahedron Lett., 2503 (1964).

(10) J. M. Brown, Chem. Commun., 226 (1965).

(11) E. Vedejs, R. A. Shepherd, and R. P. Steiner, J. Amer. Chem. Soc., 92, 2158 (1970).

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(14) M. S. Baird and C. B. Reese, Chem. Commun., 1519 (1970).

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(19) G. Ohloff and W. Pickenhagen, Helv. Chim. Acta., 52, 880 (1969).

(20) K. Kajiwara, Y. Inouye, and M. Ohno, Bull. Inst. Chem. Res., Kyoto Univ., 49, 179 (1971).

ment so slowly that another thermal reaction is seen, reversible isomerization to a *trans*-1,2-dialkenylcyclopropane (3 ⇌ 4, 5 ⇌ 6).[15,18-20]


3   4

R = H or CH₃

5   6
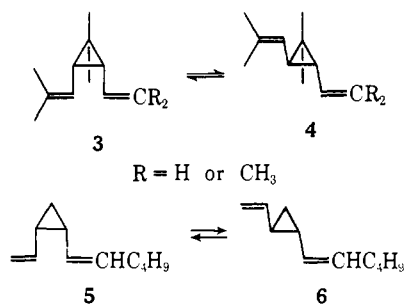
trans-1,2-Divinylcyclopropane is converted to 1,4-cycloheptadiene at 190°,[2,3,5] either through a one-center epimerization followed by Cope rearrangement of *cis*-1,2-divinylcyclopropane, or through formation of an intermediate diradical species.

7   2
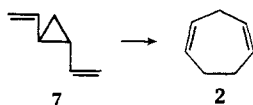
The characterization of *trans*-1-(*trans*-hex-1'-enyl)-2-vinylcyclopropane (**8**) and *trans*-1-(*trans,cis*-hexa-1',3'-dienyl)-2-vinylcyclopropane (**9**) as fragrant odor-of-the-

8   9
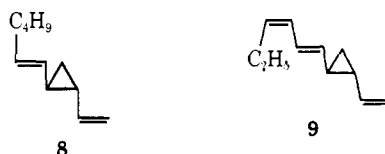
sea constituents, and of the corresponding cyclo-heptadienes (**10, 11**), all derived from the essential oil

10   11
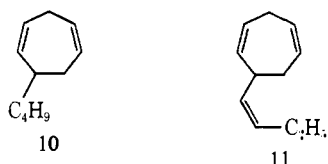
of seaweed of the genus *Dictyopteris*,[21-23] and of 6-(*cis*-but-1'-enyl)cyclohepta-1,4-diene (**11**) as the male-attracting substance excreted by the female gametes of the marine brown alga *Ectocarpus siliculosis*[24] has stimulated work leading to syntheses of all four natural products in racemic form[17-20,25,26] and to reconsiderations of the thermal chemistry of *trans*-1,2-dialkenyl-cyclopropanes.

The present work reports the thermal chemistry of the three geometrical isomers of *trans*-1,2-di(prop-1'-enyl)cyclopropane. The product and rate data have a direct bearing on the mechanistic problem posed by the *trans*-1,2-divinylcyclopropane to cyclohepta-1,4-diene isomerization.

(21) R. E. Moore, J. A. Pettus, Jr., and M. S. Doty, *Tetrahedron Lett.*, 4787 (1968).

(22) J. A. Pettus, Jr., and R. E. Moore, *Chem. Commun.*, 1093 (1970).

(23) J. A. Pettus, Jr., and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

(24) D. G. Müller, L. Jaenicke, M. Donike, and T. Akintori, *Science*, **171**, 817 (1971).
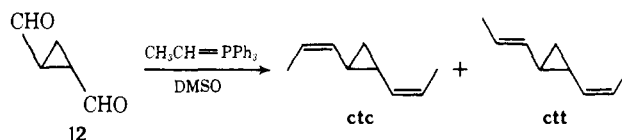
(25) L. Jaenicke, T. Akintori, and D. G. Müller, *Angew. Chem., Int. Ed. Engl.*, **10**, 492 (1971).

(26) A. Ali, D. Sarantakis, and B. Weinstein, *Chem. Commun.*, 940 (1971).

Results[27]

Syntheses of the *trans*-1,2-dipropenylcyclopropanes were accomplished utilizing routes that by now are well explored.

In the first, *trans*-cyclopropanedicarboxaldehyde (**12**)

was condensed with ethylidenetriphenylphosphorane in dimethyl sulfoxide. Under these conditions for the Wittig condensation, the new 1,2-disubstituted double bonds are predominantly cis: the product distribution according to glpc analysis was ctc:ctt:ttt in the proportions 65:33:2.

In the second, sorbaldehyde (**13**) was reduced with lithium aluminum hydride to give a hexadienol (**14**) convertible through a Simmons–Smith reaction to *trans*-2-(*trans*-prop-1'-enyl)cyclopropanemethanol (**15**). Oxidation with activated manganese dioxide gave the corresponding aldehyde (**16**). The Wittig–Schlosser
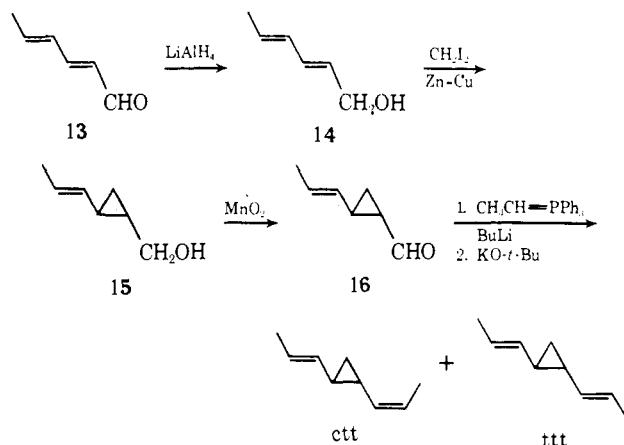
synthesis between the aldehyde and ethylidenetriphenyl-phosphorane[28,29] afforded a product mixture containing ctc:ctt:ttt isomers in 4:17:79 proportions.

The three isomers were well separated on a squalane capillary column and preparatively separable, though not as readily, on larger columns using squalene as the stationary phase.

Structural assignments for the isomers were based on infrared and nmr spectral data. Carbon disulfide solutions of the isomers showed characteristic vinyl hydrogen out-of-plane bending bands for the cis and trans 1,2-disubstituted double bonds,[30] for the ctc 1,2-di-propenylcyclopropane at 713 cm⁻¹, for the ctt isomer at 712 and 955 cm⁻¹, and at 958 cm⁻¹ for the ttt compound.

The nmr spectral parameters for the more symmetric dipropenylcyclopropanes are given in Table I. The C_2 symmetric ctc and ttt isomers were recognized with the aid of double irradiation techniques. Isolation of the ring protons by irradiation of the olefinic region

(27) Preliminary account: C. Ullenius, P. W. Ford, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **94**, 5910 (1972).

(28) M. Schlosser and K. F. Christmann, *Angew. Chem., Int. Ed. Engl.*, **5**, 126 (1966); *Justus Leibigs Ann. Chem.*, 708, 1 (1967).

(29) E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226 (1970).

(30) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 24.
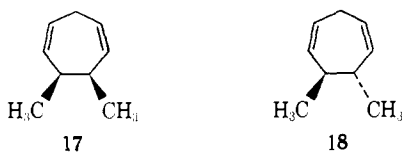
Table I. Proton Magnetic Resonance Chemical Shifts for Symmetric 1,2-Di(prop-1'-enyl)cyclopropanes

		Chemical shifts			
Isomer	C(1,2)-H	C(3)-H	C(1')-H	C(2')-H	C(2')-CH₃
Ctc	1.55	0.77	4.89	5.42	1.74
Ttt	1.30	0.71	5.04	5.51	1.65
Ccc	1.8	0.46, 1.15	5.10	5.53	1.72

Table III. First-Order Rate Constants for Isomerization of 1,2-Di(prop-1'-enyl)cyclopropanes at 165°

Substrate	Product	$k \times 10^4$ sec
Ttt	**17**	2.8 ± 0.1
Ctt	**18**	2.7 ± 0.2
Ctc	Ccc	0.9 ± 0.09^a
Ccc	Ctc	3.8 ± 0.4^a

^{a} Equilibrium ratio 81:19.

provided symmetric AA'MM' patterns of lines. For the C_s symmetric ccc isomer encountered later in this study, the ring protons constituted an A_2BC set, with $J_{gem} = (-)4$, $J_{vic,cis} = 8$, and $J_{vic,trans} = 6$ Hz. The vinyl–vinyl couplings were 15 Hz in the ttt isomer and 10 Hz in the ctc and ccc dienes.

The unsymmetrical ctt compound showed the expected complexity in its nmr spectrum and resistance to immediate simplification through double irradiation techniques.

Thermal isomerization of the ttt isomer at 178° for 4.2 hr produced *cis*-6,7-dimethylcyclohepta-1,4-diene (**17**), while the ctt diene was converted to *trans*-6,7-dimethylcyclohepta-1,4-diene (**18**) under these conditions.

Both the basic structure and the stereochemical disposition of the methyl groups for these rearrangement products were clear from the nmr spectra (Table II).

Table II. Proton Magnetic Resonance Chemical Shifts for 6,7-Dimethylcyclohepta-1,4-dienes

		Chemical shifts (δ)		
Isomer	vinyl H	C(3)H	C(6,7)H	CH₃
cis-**17**	5.58	2.55, 3.07	2.61	0.99
trans-**18**	5.57	2.78	2.37	1.04

The cis isomer, being of C_s symmetry, showed the doubly allylic methylene protons at C(3) as nonequivalent, $J_{gem} = 19$ Hz. In the trans product, these protons appeared as a clean singlet when olefinic protons were irradiated.

The ctc hydrocarbon isomerized to *cis,cis,cis*-di(prop-1'-enyl)cyclopropane much faster than *cis*-dimethylcycloheptadiene was produced. The equilibrium between these isomers was approached from both sides: the ctc:ccc equilibrium ratio was found to be about 76:24 at 178°.

Gas-phase kinetic measurements at 165° were performed. For the ttt and ctt isomers, simple first-order decay of the cyclopropanes and production of the cycloheptadienes were observed. The approach to equilibrium between ctc and ccc isomers was monitored, giving $(k_1 + k_{-1})$ from the least-squares linear plot of ln ([ctc]$_t$ − [ctc]$_e$) vs. time. The rate constants determined are given in Table III.

The kinetic work both verified the high stereoselectivity shown in the isomerizations of each substrate and established that the rearrangements of ttt and ctt dienes to cycloheptadienes occur at rates very similar to

the one-center epimerizations shown by the ctc and ccc isomers.

Discussion

The stereochemical disposition of the methyl groups in the dipropenylcyclopropanes is retained in all conversions observed in this work.

The simplest kinetic scheme accommodating the other experimental findings would involve in the rate-determining step epimerization at C(1) or C(2) of the 1,2-dipropenylcyclopropanes. For the *trans,cis,trans*- and *cis,cis,trans*-1,2-dipropenylcyclopropanes, rapid Cope rearrangement to *cis*- and *trans*-6,7-dimethylcyclohepta-1,4-diene would be expected. For the ccc isomer, however, severe methyl–methyl steric interaction in the required boat-like transition-state geometry should impede the isomerization to *cis*-6,7-dimethylcyclohepta-1,4-diene; the ctc and ccc isomers equilibrate much faster than they are converted to monocyclic diene.
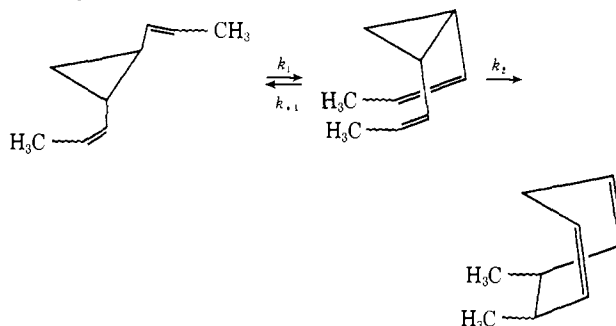
This would rationalize the stereochemistry of the methyl groups in the cycloheptadiene products and the kinetic findings of Table III: if all four reactions there have the same rate-limiting step, the similarity in reaction rates is not merely a coincidence.

Arai and Crawford[31] interpreted their kinetic data for the conversion of *trans*-1,2-divinylcyclopropane to 1,4-cycloheptadiene in these terms; they assumed that *cis*-1,2-divinylcyclopropane was formed in the rate-determining step and that it isomerized rapidly and quantitatively to the monocyclic diene.

From the activation parameters reported by Arai and Crawford, the epimerization step at 165° would have a rate constant equal to 1×10^{-4} sec⁻¹. The preliminary rate data of Pettus and Moore[23] may be interpolated for 165° to yield a rate constant of 2×10^{-4} sec⁻¹ for the isomerization of *trans*-(*trans*-hex-1'-enyl)vinylcyclopropane to 6-butylcyclohepta-1,4-diene. The rate constants for the trans–cis and cis–trans epimerizations shown by the 1,2-diisobutenyl-3,3-dimethylcyclopropanes **3** and **4** (R = CH₃) are about 0.5×10^{-4} and 1.4×10^{-4} sec⁻¹ at 165°.[15] All four rate constants are very close to those listed in Table III.

(31) M. Arai and R. J. Crawford, *Can. J. Chem.*, **50**, 2158 (1972).

Thus, each step in the postulated kinetic scheme has direct precedent and together they rationalize efficiently at least in a phenomenological sense all available information on the thermal chemistry of dl-1,2-dialkenylcyclopropanes.

How does the epimerization take place? Arai and Crawford measured rates for both the structural isomerization and the racemization of (−)-trans-1,2-divinylcyclopropane; they analyzed the raw data in terms of a direct interconversion of antipodes, a measurable epimerization to cis-1,2-divinylcyclopropane, and a very rapid Cope rearrangement step.
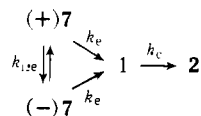
Yet their mechanistic conclusions were founded on the assumption that both observable processes were dependent on the formation of diradical intermediates. If one ignores the complexities inherent in recognition of ten possible O,O-trimethylene diradicals or π-cyclopropanes substituted 1,3 with vinyl groups[31] and considers only the simplest possible sort of kinetic analysis, the assumed scheme would involve one additional chemical entity, the intermediate, and one additional independent rate constant when compared with the simpler scheme utilized for data reduction.
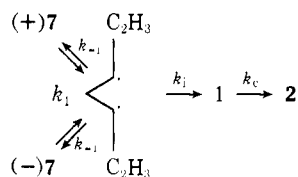
In unsymmetrical cases, such as the racemization and isomerization of dictyopterene A, a kinetic scheme analogous to our proposal for the dipropenylcyclopropanes and including a direct two-center epimerization process relating the antipodal trans substrates[32] would have to include two distinct one-center epimerization processes (Scheme I).
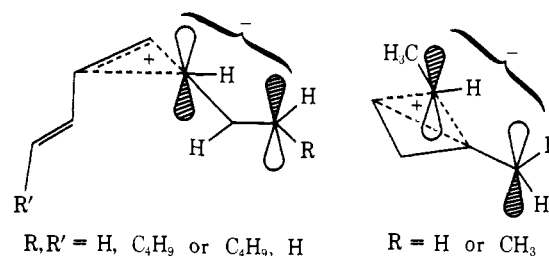
Scheme I
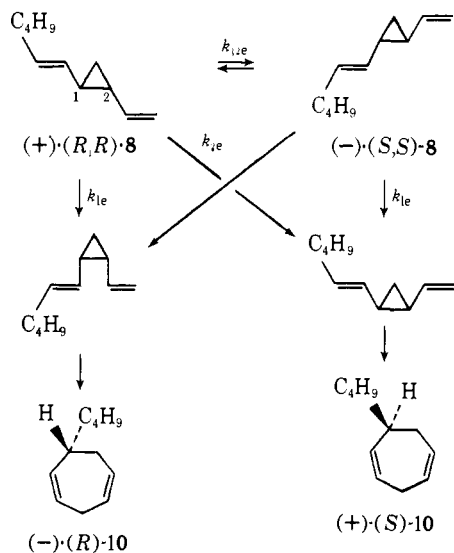
The entire scheme could account for the concentrations of both antipodes of the dialkenylcyclopropane and both antipodes of cycloheptadiene product as a function of time in terms of three experimentally determinable rate constants. An alternative scheme based on postulation of diradical species would involve at least two extra chemical entities (antipodal diradicals) and four independent rate constants.

In terms of the first and simpler mechanism, the optical character of the 6-butylcycloheptadiene would depend upon both the rate of racemization of starting material and the relative rates of k_{1e} and k_{2e}. In terms of the second and more complex mechanism, various partitioning ratios for the intermediate diradicals would determine the stereochemical outcome.
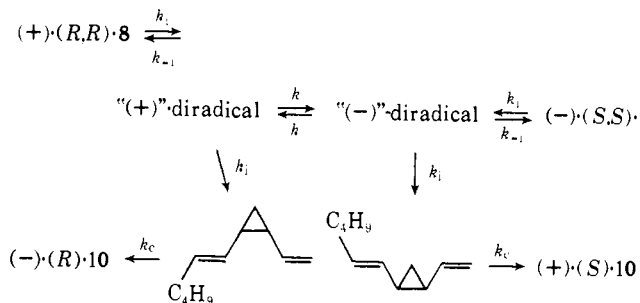
Experimentally, there is some net preference for formation of the (+)-(S)-6-butylcyclohepta-1,4-diene product.

The more rapid epimerization at C(1) in (+)-R,R substrate has an intriguing parallel in the relative rates of thermal epimerization of 1-methylene-2-methylcyclobutane and (Z)-1-ethylidene-2-methylcyclobutane: the former epimerizes faster at 333°.[33] If the epimerizations of both dialkenylcyclopropane and methylenecyclobutane systems proceed through planar methane transition states,[34,35] the observed relative rates could be rationalized: electron density donating alkyl substituents on the allylic anion-like element within these planar methane species would be destabilizing.

R,R′ = H, C_4H_9 or C_4H_9, H   R = H or CH_3

The kinetic and mechanistic scheme proposed here is simpler than diradical alternatives, accounts for the continuity in rates and discontinuity in products observed with various 1,2-dialkenylcyclopropanes in a natural way, and involves no disallowed steps. The scheme may be structured for the thermal chemistry of dl-1,2-dialkenylcyclopropanes or for optically active systems that can suffer racemization as well as one-center epimerizations and Cope rearrangements; in both cases it is simpler than formulations based on hypothetical diradical intermediates. Whether it is

(32) Compare F. S. Collins, J. K. George, and C. Trindle, J. Amer. Chem. Soc., 94, 3732 (1972); J. E. Baldwin and J. Ollerenshaw, submitted for publication.

(33) J. E. Baldwin and R. H. Fleming, J. Amer. Chem. Soc., 95, 5256 (1973).
(34) F. T. Smith, J. Chem. Phys., 29, 235 (1958).
(35) R. Hoffmann, R. W. Alder, and C. F. Wilcox, Jr., J. Amer. Chem. Soc., 92, 4992 (1970).

more likely to be correct than diradical mechanisms remains a moot question. It is not demonstrated to be so. But until and unless data become available it cannot accommodate, it should be preferred over the more complicated diradical-based constructs that are identical in phenomenological kinetic form and explicative power.[36]

Experimental Section

Proton nmr spectra were measured with deuteriochloroform solutions on a Varian Associates XL-100-FT spectrometer in the frequency sweep mode; infrared absorption spectra were obtained with carbon disulfide solutions on a Beckman IR 7 spectrophotometer; mass spectra run on a CEC 110-21B instrument and elemental analyses were secured by Dr. Susan Rottschaefer.

For the C_9H_{14} isomers, preparative glpc separations were done using a Varian Aerograph A-90-P3 and 10% squalene on basewashed 60-80 mesh Chromosorb P columns (6 mm × 3.6 m and 6 mm × 6 m); analytical glpc work was done on a Perkin-Elmer F-11 with either a squalane capillary column (0.5 mm × 15 m) or a 5% β,β'-oxydipropionitrile on 90-100 mesh pH 9 Anakrom (3 mm × 6 m), and using flame ionization detection and disc integration. The six isomers all had very similar mass spectra, with M^+ at m/e 122, and strong fragment ions at 107, 105, 93, 91, 79, and 77.

trans-1,2-Cyclopropanedimethanol. Commercial diethyl 1,2-cyclopropanedicarboxylate (Aldrich) was found by glpc on an XF 1150 column at 140° and by nmr spectroscopic analysis to be predominantly the trans isomer. Reduction with lithium aluminum hydride gave the diol:[37,38] nmr δ 0.4 (2 H, t), 0.9 (2 H, m), 3.4 (4 H, m), and 5.0 (2 H, s).[39]

trans-Cyclopropanedicarboxaldehyde was prepared by oxidation of *trans*-1,2-cyclopropanedimethanol with either manganese dioxide in methylene chloride or ceric ammonium nitrate in water:[40] bp 70-73° (11 mm) (lit.[41] bp 78.1-81° (11 mm)]; nmr δ 1.7 (2 H, t), 2.5 (2, H, m), and 9.25 (2 H, d).

cis,cis,cis- and *cis,cis,trans*-1,2-Di(prop-1'-enyl)cyclopropane.[42] *trans*-1,2-Cyclopropanedicarboxaldehyde (1.5 g, 15.3 mmol) in 25 ml of dry dimethyl sulfoxide was added over a 1-hr period to a stirred room temperature solution of ethylidenetriphenylphosphorane (39 mmol) in 200 ml of DMSO.[43,44] Following the addition, the reaction mixture was brought to 60° for 1 hr, stirred at room temperature overnight, extracted with two 100-ml portions of petroleum ether, bp 30-60°, and then quenched with 750 ml of water. Petroleum ether was used to wash the copious white precipitate thoroughly and for extraction of the aqueous phase (4 × 100 ml). The combined petroleum ether solutions were washed with water (5 × 100 ml), dried (MgSO₄), filtered, and concentrated by distillation at atmospheric pressure. The isomeric products were isolated by preparative glpc and characterized as detailed below.

trans,trans-2,4-Hexadien-1-ol. Freshly distilled sorbic aldehyde (28.7 g, bp 45° (12 mm), Aldrich) in 100 ml of ether was added dropwise over a 2.3-hr period to an ice-bath cooled suspension of lithium aluminum hydride (4.66 g) in 500 ml of ether. The reaction mixture was stirred at room temperature overnight, then quenched in the normal sequential manner with water, 15% sodium hydroxide, and water. The ethereal phase decanted from precipitated material and three 200-ml portions of ether used to wash the inorganic salts

were combined, dried over molecular sieves, filtered, and concentrated to give 28.6 g (96%) of product: nmr δ 1.7 (3 H, d), 4.0 (2 H, d), 4.8 (1 H, broad singlet), and 5.2-6.6 (4 H, m); glpc analysis on an XF 1150 column at 95° showed only one peak. The alcohol crystallized upon storage at 0° [lit.[45] mp 30.5-31.5°].

trans-2-(*trans*-Prop-1'-enyl)cyclopropanemethano¹. Zinc-copper couple was prepared from cupric acetate monohydrate and granular zinc in glacial acetic acid by the procedure of LeGoff.[46] To a magnetically stirred mixture of this couple (17.8 g) and 29 ml of ether was added a few drops of diiodomethane to initiate reaction. Then the balance of 48 g (179 mmol) of diiodomethane and *trans,-trans*-2,4-hexadien-1-ol (12.6 g, 128 mmol) in 18 ml of ether was added dropwise over a 2-hr period as the reaction mixture maintained reflux. It was stirred overnight, then decanted into a separatory funnel containing ice and dilute hydrochloric acid. The ether solutions from this and a parallel reaction were combined, washed with ice-cold 1 N hydrochloric acid and with water (5 × 100 ml), and dried over molecular sieves. Filtration and concentration gave 26 g (90%) of crude product. Analysis by nmr indicated that unreacted starting material was the major contaminant. Simple distillation at atmospheric pressure gave a 10.6-g fraction, bp 74-78° (12 mm), which was sufficiently pure for synthetic purposes. An anaytical sample was obtained by preparative glpc on a Carbowax 20M column: nmr δ 0.58 (2 H, t), 0.9-1.5 (2 H, m), 1.5 (1 H, s), 1.64 (3 H, d), 3.49 (2 H, d), 5.06 (1 H, d of d), and 5.52 (1 H, d of q) [$J_{vicinal,vinyl-vinyl} = 15$ Hz].

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.69; H, 10.88.

trans-2-(*trans*-Prop-1'-enyl)cyclopropanecarboxaldehyde. In each of two parallel runs, 5.2 g of the cyclopropylcarbinol and 53 g of activated manganese dioxide were combined with 300 ml of methylene chloride and stirred at room temperature for 3 days. The oxidant prepared from Norit A and potassium permanganate according to Carpino[47] proved somewhat more effective than a commercial sample (Beacon Chemical Industries), according to glpc monitoring. Filtration and thorough washing of the solid with methylene chloride, followed by concentration of the filtrate, gave 8.25 g (81%) of crude product. Analysis by glpc on Carbowax 20M at 110° showed, in addition to the desired product, minor amounts of 2,4-hexadienal, unreacted starting material, and one unidentified component. A vacuum transferred sample, 4.71 g, bp 22° (0.4 mm), was used in the subsequent synthetic step. The analytic sample was secured by glpc on a Carbowax column: nmr δ 1.12 (1 H, m), 1.46 (1 H, quint), 1.68 (3 H, d), 1.7-2.2 (2 H, m), 5.08 (1 H, d of d), 5.67 (1 H, d of q) [$J_{vicinal,vinyl-vinyl} = 15$ Hz], and 9.15 (1 H, d); m/e 110.072 (calcd for $C_7H_{10}O$, 110.073).

cis,trans,trans- and *trans,trans,trans*-1,2-Di(prop-1'-enyl)cyclopropane. A solution of ethylidenetriphenylphosphorane in tetrahydrofuran (55 ml)-ether (27 ml) was prepared from 11 g (29.7 mmol) of ethyltriphenylphosphonium bromide and butyllithium. The *trans,trans*-propenylcyclopropanecarboxaldehyde described above (3.25 g, 29.5 mmol) dissolved in 15 ml of ether was added to the ylide solution at -70° over a 9-min period. The resulting suspension was stirred another hour, slowly warmed to -55°, and treated dropwise with butyllithium (20 ml of 1.5 M solution in hexane). Following the 20-min addition, and another 20 min of continued stirring, the red homogeneous reaction mixture was brought to -30°. A mixture of potassium *tert*-butoxide in *tert*-butyl alcohol (5 g in 3.4 g) was added. The suspension formed was stirred another hour, allowed to warm to room temperature, and poured onto ice. The hydrolysis mixture was extracted with four 100-ml portions of ether, and the extracts were combined, washed with water (4 × 100 ml. until neutral), dried over molecular sieves, and filtered. Concentration of the filtrate to about 100 ml by rotary evaporation and then by distillaton left a product-containing residue. Extraction of this material with petroleum ether, bp 30-60° (3 × 100 ml), then concentration of the petroleum ether solution and vacuum transfer at 40-70° (12 mm) gave a series of fractions containing 2.72 g (70%) of dipropenylcyclopropanes.

Analytical glpc on a squalane capillary column at 100° revealed the presence of three isomers, subsequently identified as ctc (4%), ctt (17%), and ttt (79%); the relative retention times of these components were 1.00:1.07:1.18.

(36) The dictum now known as Ockham's razor is usually formulated "pluralitas non est ponenda sine necessitate." An alternative statement from William of Ockham's writings, "frustra fit per plura quod potest fieri pauciora," follows closely an earlier version written by the scholastic thinker Odo Rigaldus, "frustra fit per plura quod quod potest fieri per unum."

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(38) Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, 20, 1695 (1964).

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(41) T. Shono, M. Kimura, A. Oku, and R. Oda, *Kogyo Kagaku Zasshi*, 69, 2147 (1966); *Chem. Abstr.*, 66, 94708z (1967).

(42) This reaction was conducted by Dr. P. W. Ford.

(43) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 84, 866 (1962).

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

(45) "Handbook of Tables for Organic Compound Identification," 3rd ed, compiled by Z. Rappoport, The Chemical Rubber Co., Cleveland, Ohio, 1967, p 88.

(46) E. LeGoff, *J. Org. Chem.*, 29, 2048 (1964).

(47) L. A. Carpino, *J. Org. Chem.*, 35, 3971 (1970).

Similar analysis of the isomeric mixture derived from the trans dialdehyde and ethylidenetriphenylphosphorane in DMSO indicated the ctc:ctt:ttt proportions 65:33:2.

Pure samples of these isomers for characterization, preparative scale thermolyses, and kinetic studies were obtained by preparative glpc on squalene columns.

cis,trans,cis-1,2-Di(prop-1'-enyl)cyclopropane had a strong infrared band at 713 cm⁻¹. The nmr spectral parameters are given above.

cis,trans,trans-1,2-Di(prop-1'-enyl)cyclopropane had strong infrared bands at 712 and 955 cm⁻¹; nmr, see above.

trans,trans,trans-1,2-Di(prop-1'-enyl)cyclopropane had a strong infrared band at 958 cm⁻¹. The nmr spectrum is discussed above.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.50; H, 11.52.

cis-6,7-Dimethylcyclohepta-1,4-diene. A 40-μl sample of the *trans,trans,trans*-dipropenylcyclopropane (98.6% pure) was degassed through three or four freeze–pump–thaw cycles at 10^{-4} Torr, then sealed under vacuum in a base-washed and thoroughly dried ampoule and heated in an oil bath at 178° for 4.2 hr. The reaction mixture contained one product (98.8%) and no starting material, according to glpc analyses. By thorough analysis of the nmr spectrum, as given above, the product was identified as *cis*-6,7-dimethylcyclohepta-1,4-diene.

trans-6,7-Dimethylcyclohepta-1,4-diene. An 18-μl sample of the *cis,trans,trans*-dipropenylcyclopropane (94.2%) pure) was sealed in a degassed ampoule and kept 4.2 hr at 179°. The product (95.0%) was identified through its nmr spectral properties (see above). The impurities in the original sample were unchanged by the thermolysis.

cis,cis,cis-1,2-Di(prop-1'-enyl)cyclopropane. A 35-μl sample of

the *cis,trans,cis*-dipropenylcyclopropane was heated in a sealed ampoule at 179° for 4.2 hr. Analysis by glpc using a $\beta\beta'$-ODPN column revealed three components having relative retention times 0.76:1.00:1.21. The first and second proved to be *cis*-6,7-dimethylcyclohepta-1,4-diene and unconverted starting material. The third was identified as *cis,cis,cis*-1,2-di(prop-1'-enyl)cyclopropane; nmr, see text above.

A pure sample of the ctc isomer kept at 178° for 4.2 hr gave rise to a 4:72:24 product distribution. Another sample kept at this temperature for 75 hr gave a 35:50:15.6 product ratio.

Pyrolysis of a mixture containing *cis*-6,7-dimethylcyclohepta-1,4-diene, *cis,trans,cis*-dipropenylcyclopropane, and *cis,cis,cis*-dipropenylcyclopropane in 11:6:84 proportions at 182° for 4.2 hr gave a 12:68:20 mixture of these isomers. Product identifications were confirmed nmr spectroscopically.

Gas-phase isomerization kinetics were obtained using a static reactor, vacuum line, pentane as diluent, and glpc to measure isomeric distributions as a function of time.[48] The isomeric purity of reactants was determined on the squalane capillary column, while product distiributions were measured on $\beta\beta'$-ODPN columns. The impurities in reactants (4% of the ctt isomer in the ttt material, 8% of ctc compound in the ctt, and 3% of ctt in ctc), persisting after two or three consecutive preparative glpc separations on squalene columns, contributed to the observed distributions of C_9H_{14} isomers as functions of time to a minor and easily corrected for extent. The rate constants determined are given in Table III above.

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Transformation of Sulfide Linkages to Carbon–Carbon Double Bonds. Syntheses of *cis*- and *trans*-15,16-Dimethyldihydropyrene and *trans*-15,16-Dihydropyrene[1]

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Abstract: It is shown that the transformation of sulfide linkages to carbon–carbon double bonds in highly strained molecules can be effected conveniently and in high yield by a reaction sequence of a Stevens rearrangement followed by a Hofmann elimination. This route is of particular advantage for preparing cyclophane derivatives since the medium-sized ring sulfides required as starting materials are easy to prepare. When *m*-xylylene dibromide is treated with 1,3-bis(mercaptomethyl)benzene, 2,11-dithia[3.3]metacyclophane (25) is formed in 80% yield. Similarly, 2,6-bis(bromomethyl)toluene (5) can be converted to 2,11-dithia-9,19-dimethyl[3.3]metacyclophane, which exists in both the syn and anti conformations (7 and 8). Subjection of these three 2,11-dithia[3.3]metacyclophane derivatives to the Stevens rearrangement leads in each case to the corresponding ring-contracted bis(methylthio)-[2.2]cyclophane, isolated as a mixture of isomers. When the mixture of isomers 10, resulting from the *anti*-9,18-dimethyl derivative, is subjected to a Hofmann elimination, *trans*-15,16-dimethyldihydropyrene (14) forms in excellent overall yield. Similarly, the mixture of isomers 18 from the *syn*-8,16-dimethyl derivative is converted to *cis*-15,16-dimethyldihydropyrene (21). Surprisingly, the Hofmann elimination reaction with the parent bis(methylthiomethyl)[2.2]metacyclophane (26) gives *anti*-[2.2]metacyclophane-1,9-diene (31), rather than the expected *trans*-15,16-dihydropyrene. Although *anti*-[2.2]metacyclophane-1,9-diene (31) is a stable compound and does not undergo spontaneous valence tautomerization, it is converted on irradiation to *trans*-15,16-dihydropyrene (35). Some of the physical and chemical properties of these bridged [14]annulenes are presented.

Previous syntheses of the interesting *trans*-15,16-dialkyldihydropyrenes have been lengthy and have not provided the possibility of preparing either the cis isomers or the parent substance, *trans*-15,16-dihydro-

pyrene (35).[2-4] Inasmuch as the formation of medium-

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