with a 50-mL syringe for GLC analysis on the 20-ft SE-52 column at room temperature for the low-boiling fraction (butenes and methyl bromide) and at 108 °C for chloroform. A small amount (<1%) of the low-boiling fraction and chloroform were also detected in the reaction solution. All compounds except **2** were identified by retention-time comparison and coinjection with known samples. Response factors for all compounds except the butenes were determined by injection of standard solutions containing *tert*-butylbenzene. Following detection of **2** by GLC and NMR, it was isolated by preparative GLC on a $^3/_8$-in. × 10-ft Pyrex column with 15% SE-52 on acid-washed and DMCS-treated 60/80 Chromosorb P at 135 °C with a Pyrex insert in the injection port. ^{1}H NMR (CH_2Cl_2) δ 0.13, -0.12, 0.14, 0.40, 0.41 (9 H, s and tin-coupled side bands, Me_3Sn), 0.9-1.06 (3 H, t, C-4 Me), 1.59, 1.60, 1.84, 2.09, 2.10 (3 H, s and tin-coupled side bands, C-1 Me), 1.87-2.10 (2 H, q, CH_2). Anal. Calcd for $C_7H_{17}SnBr$: C, 28.04; H, 5.72; Br, 26.65. Found: C, 28.1; H, 6.1; Br, 26.5. The results of the GLC and NMR analyses of this reaction are in Table IV.

Attempted Thermal Decomposition of 2 in $BrCCl_3$. A sample of **2** (0.339 g, 0.001 13 mol) was dissolved in 4 mL of $BrCCl_3$, and *tert*-butylbenzene (0.0472 g, 0.000 351 mol) was added. This solution was placed in the apparatus used for the total product analysis for the decomposition of **1** and heated to 95 °C (540 mmHg) for 3 h during which time approximately 1 mL of $BrCCl_3$ distilled into the gas trap. Analysis of the volatile fraction by GLC indicated no butenes were present. Comparison of **2** to *tert*-butylbenzene by NMR integration before and after the heating period showed a 15% decrease in **2**, but no trimethyltin bromide was detected.

In an independent experiment 1.5 mL of the pot fraction from the total analysis reaction containing approximately 0.000 71 mol of **2** was placed with 1 mL of $BrCCl_3$ in the reaction apparatus. The solution was heated to 95 °C (520 mmHg) for 3 h during which time approximately 1 mL of $BrCCl_3$ distilled into the gas trap. Comparison of **2** to *tert*-butylbenzene by NMR integration before and after the heating period showed a 4% loss of **2** and a corresponding increase in trimethyltin bromide.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. GP-33669 and by the National Institutes of Health under Grant No. GM-15373.

Registry No. **1**, 15095-79-1; *erythro*-**1**-*d*, 71195-42-1; *threo*-**1**-*d*, 71195-43-2; **2**, 71195-44-3; $(Me)_3SnNa$, 16643-09-7; $(Me)_3SnK$, 38423-82-4; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; methyl bromide, 74-83-9; chloroform, 67-66-3; benzene, 71-43-2; trimethyltin bromide, 1066-44-0; bromobenzene, 108-86-1; hexachloroethane, 67-72-1; *p*-toluenesulfonyl chloride, 98-59-9; *threo*-3-deuterio-2-butanol, 10277-60-8; *erythro*-3-deuterio-2-butanol, 10277-59-5; trimethyltin chloride, 1066-45-1; (-)-*sec*-butyl tosylate, 61530-30-1; hexamethylditin, 661-69-8; (*S*)-(+)-*sec*-butyl mesylate, 50599-13-8; $BrCCl_3$, 75-62-7.

Thermal Rearrangement of Alkynyl Three-Membered Rings. Evidence for an Oxacycloheptatriene Intermediate[1]

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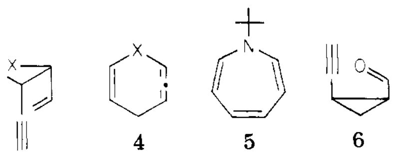
The substituted ethynylvinyloxiranes **9a–e** were obtained by condensation of vinylsulfonium ylides with acetylenic carbonyl compounds. Thermolysis of the cis isomers of **9** was investigated in both the gas phase and the liquid phase. The first procedure afforded only cyclopropanecarboxaldehydes **17a–e**, the stereochemistry of which depended on the nature and position of the substituents and on the experimental conditions. In the liquid phase **9a–e** rearranged to yield, besides **17a–e**, dihydrooxepins **20** and **21c–e** or phenol **19a**, these products also being obtained from **17a–e**. Moreover, thermolysis of **21c,d** led to the corresponding phenols **19c,d**. Compounds **19** are believed to arise from arene oxides in equilibrium with substituted oxepin intermediates. All these findings are consistent with the initial formation of an oxacycloheptatriene (**22**) by a Cope reaction from **9** or a retro-Claisen reaction from **17**. The observed stereoselectivity of the reaction is explicable in terms of conformational preferences.

During the last few years, several authors have reported the thermal isomerization of ethynyl vinyl three-membered rings. In every case the isolated products strongly suggested the intermediacy of the highly reactive heptacyclic compound **4** (Scheme I). Thus, Dolbier and co-workers[2] obtained a dimer arising from cycloheptatriene **4** (X = CH_2). Manisse and Chuche[3] prepared *N*-*tert*-butylazepine (**5**) by thermal isomerization of *N*-*tert*-butylaziridine (**2**) and also *cis*-2-ethynyl-1-formylcyclopropane (**6**) from *cis*-2-ethynyl-3-vinyloxirane (**3**).

Scheme I



1, X = CH_2
2, X = N+
3, X = O

4 5 6

This last molecular rearrangement (**3** → **6**) seemed of interest to us, from both mechanistic and synthetic viewpoints: (i) the formation of a heptacyclic intermediate (X = O) has not heretofore been experimentally proved; (ii) a [1,3] hydrogen shift similar to that affording **5** (X = *N*-*t*-Bu), not yet observed from **4** (X = O), should give oxepins which are valence isomers of arene oxides; (iii) compounds **6**, which can be used as starting material in natural product synthesis,[4] are not readily available by other methods.

A general study of the thermal isomerization of variously substituted epoxides **3** was undertaken to obtain further information about the proposed mechanism and to test the

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[1] Preliminary accounts of this work may be found in *Tetrahedron Lett.*, 283 (1978), and *J. Chem. Soc., Chem. Commun.*, 584 (1979).

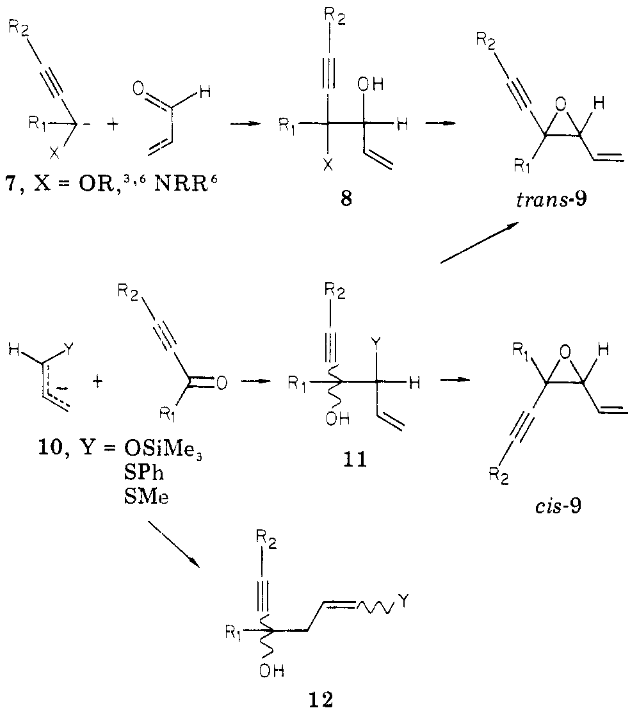
[2] W. R. Dolbier, O. T. Garza, and B. H. Al Sader, *J. Am. Chem. Soc.*, **97**, 5038 (1975).

[3] N. Manisse and J. Chuche, *Tetrahedron*, **33**, 2399 (1977); *J. Am. Chem. Soc.*, **99**, 1272 (1977).

[4] Experiments in progress.

0022-3263/80/1945-0428$01.00/0

Scheme II



synthetic applications of this reaction.

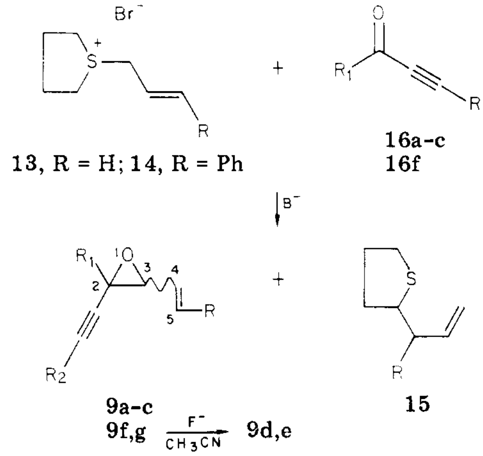
Results

Preparation of Substituted 2-Alkynyl-3-vinyloxiranes (9). To our knowledge, only *cis-* and *trans-*2-ethynyl-3-vinyloxiranes (**3**) and *trans-*2-propynyl-3-vinyloxirane have been prepared in the laboratory[3] by dehydration of glycols[5] obtained (in the first case) by reductive dimerization[6] of propynal or (in the second case) by condensation of the anion from tetrahydropyranyl ether[7] with acrolein. The first method is not suitable for the preparation of substituted oxiranes **9** (Scheme II). On the other hand, propargylic anions which have a good α leaving group give adducts with various carbonyl compounds;[7] when the substrate is an aldehyde, there is almost exclusive formation of a single diastereoisomer of the compound **8** which leads to the trans oxirane[3] by intramolecular elimination.

Using the opposite approach, i.e., addition of an allylic carbanion (**10**) bearing a protected alcohol function (Y = OSiMe$_3$) or a good leaving group (Y = SPh, SMe) in the α position to an acetylenic ketone or aldehyde, we obtained a mixture of adducts **11** and **12**, with the latter predominating. The use of different chelating agents (HMPT, Dabco)[8b] or the addition of zinc iodide[7b,8c] allowed considerable but not satisfactory regioselective control of addition—the was never more than 1/1.5.

Moreover, the synthesis of oxiranes **9** appeared possible by sulfonium ylide condensation[9] with appropriately chosen carbonyl compounds. Propargylsulfonium ylides could not be used since they undergo [2,3] sigmatropic rearrangement, producing allenic thioethers,[10] and give complex reactions with carbonyl compounds.[11] On the other hand, vinylsulfonium ylides have been successfully condensed with ketones[12a] or aldehydes.[12b,c] When vinyldimethylsulfonium ylide is prepared in anhydrous medium,[12a] a [2,3] sigmatropic rearrangement of the isomeric ylide leads to the predominant formation of an allylic thioether, whereas in aqueous medium this side reaction is not encountered.[12b] It can also be avoided by the use of diphenylallylsulfonium tetrafluoroborate as the ylide precursor (Scheme III).[12a]

Scheme III



a, R$_1$ = H; R$_2$ = Ph; R = H
b, R$_1$ = H; R$_2$ = n-Bu; R = H
c, R$_1$ = n-Bu; R$_2$ = Ph; R = H
d, R$_1$ = n-Bu; R$_2$ = H; R = H
e, R$_1$ = n-Bu; R$_2$ = H; R = Ph
f, R$_1$ = n-Bu; R$_2$ = SiMe$_3$; R = H
g, R$_1$ = n-Bu; R$_2$ = SiMe$_3$; R = Ph

Table I. Epoxides Yields Obtained by Condensation of Ylides from 13 or 14 with Carbonyl Compounds 16a-c,f

		isomers, %[c]	
method[a]	epoxides, %[b]	cis	trans
A	9a, 72	42	58
A	9b, 40	45	55
B	9c, 45	55	45
B	9f, 40	56	44
B	9g, 34	46	54

[a] A: 50% NaOH, CH$_2$Cl$_2$; B: THF, NaH. [b] Yields of isolated products. [c] Determined by ^{1}H NMR. Cis and trans isomers were not separated. Some column chromatography fractions had only better percentage in one or the other isomer.

For the above reasons, sulfonium salts **13** or **14** obtained from tetrahydrothiophene[13] and allyl or cinnamyl bromide were used. The ylides were prepared in two ways, depending on the substrate. The action of aqueous sodium hydroxide on sulfonium bromide **13** in the presence of aldehydes **16a,b** in dichloromethane (method A) produced mixtures of the cis and trans isomers of oxiranes **9a,b**; under these conditions, rearrangement into allyl thioether

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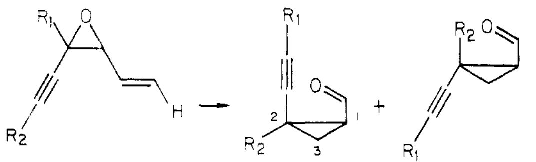
Scheme IV



cis-9a–d *cis*-17a–d *trans*-17a,c

a, R_1 = H; R_2 = Ph
b, R_1 = H; R_2 = *n*-Bu
c, R_1 = *n*-Bu; R_2 = Ph
d, R_1 = *n*-Bu; R_2 = H

15 was not observed. This first method could not be used with ketones which undergo aldol condensation in basic aqueous medium.[12b] In these cases, ylides were generated by addition of sodium hydride to **13** or **14** in tetrahydrofuran (method B). Mixtures of cis and trans isomers of the trisubstituted oxiranes **9c,f,g** were obtained in this way. When used with aldehydes the method B yields predominantly the trans isomer.[12c] Results are given in Table I.

Diastereoisomeric mixtures of oxiranes **9** were purified by column chromatography or by distillation, after first eliminating thioether **15**, if present, by formation of methylsulfonium iodide.

Protection of the acetylenic hydrogen of ketone **16f** was necessary to reduce the proportion of polymers formed during the condensation. Deprotection of **9f,g** to give oxiranes **9d,e** was achieved by treatment with tetraalkylammonium fluoride in acetonitrile followed by hydrolysis.[14]

Configurations of the oxirane rings were assigned on the basis of their NMR spectra. In the case of **9a** and **9b** disubstituted in positions 2 and 3, the coupling constants $J_{2,3}$ are about 4 and 2 Hz for the cis and trans isomers, respectively; these values correspond to those previously reported.[3,15] For trisubstituted cis oxiranes **9c–e** (cis ethynyl and vinyl groups), the signal due to H_3 appears further upfield than in trans isomers; this difference is attributed to the shielding effect of the triple bond on H_3 of *cis*-**9c–e**. In addition, the coupling constant between H_3 and vinylic H is always higher for cis oxiranes (~6.5 Hz) than for trans isomers (~5 Hz). The configurations thus assigned were confirmed by the difference in the isomerization temperatures of cis and trans isomers.

Gas-Phase Thermolysis of Oxiranes 9a–d and 9e. Rearrangements were effected either at high temperatures under dynamic conditions in a flow system described earlier[16] or at lower temperatures under static conditions in sealed tubes (Scheme IV).

At temperatures in the range 300–350 °C, cis oxiranes **9a–d** were converted to the corresponding cyclopropanecarboxaldehydes **17a–d**, whereas trans isomers remained unchanged (Table II). At these temperatures, the formylcyclopropanes **17a** and **17c** substituted by a phenyl group at C-3 underwent a cis → trans isomerization.

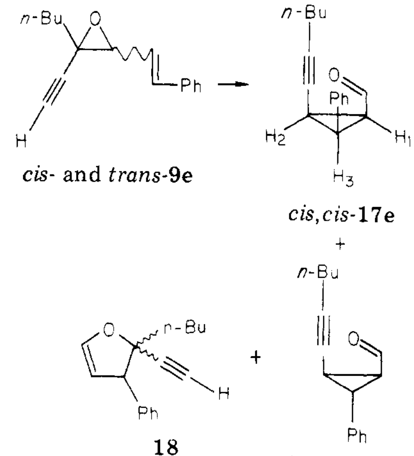
The structures of aldehydes **17a–d** were established by spectroscopic analysis. The signals of the aldehydic protons of the cis isomers of **17a** and **17c** (cis alkynyl and formyl groups) appear at lower field (δ 9.32 and 9.36) than in the trans isomers (δ 8.57 and 8.50), this difference being due to the anisotropic effect of the phenyl group.[17] Cis configurations of the isolated compounds **17b** and **17d** were assigned by comparison with the spectra of the *cis*- and *trans*-2-ethynyl-1-formylcyclopropanes.[3] Further confirmation of these assignments followed from the chemical behavior of the products (see next section).

Table II. Thermal Rearrangement of *cis*-9a–d in the Gas Phase[a]

epoxides	temp,[b] °C	rearranged 9[c]	product	cis isomer, %	trans isomer,[c] %
9a	300	35	17a	61	39
	350	>90		62	38
9b	335	83	17b	100	
9c	310	40	17c	75	25
	345	>90		66	34
9d	300	76	17d	100	
	330	88		100	

[a] Unchanged trans isomers were isolated after reaction by column chromatography. [b] Flow pyrolysis. [c] Determined by ^1H NMR of crude products; aldehydes were then isolated (yields >70%).

Scheme V



cis- and *trans*-9e

cis,cis-17e

18

cis,trans-17e

Unlike the case with **9a–d**, selective rearrangement of *cis*-**9e** was not possible under dynamic conditions; both isomers led to *r*-1-formyl-*c*-2-hexynyl-*c*-3-phenylcyclopropane (*cis,cis*-**17e**) and *r*-1-formyl-*c*-2-hexynyl-*t*-3-phenylcyclopropane (*cis,trans*-**17e**), with trace amounts of 2-butyl-2-ethynyl-3-phenyl-2,3-dihydrofuran (**18**) (Scheme V). The two isomers of **17e** were separated by column chromatography and thermolyzed independently; both were recovered unchanged after heating at 330 °C (Table III).

At lower temperatures and under static conditions (without solvent), differences in the thermolytic behavior of the two stereoisomers of **9e** were observed, and *cis,cis*-**17e** was selectively formed. Careful examination of the relative amounts of unrearranged *cis*- and *trans*-oxiranes **9e** with those of the starting mixtures (Table III) reveals a cis → trans isomerization with an activation energy very close to that of the *cis*-**9e** rearrangement. A similar observation had already been made[18] during the study of the thermolysis products of *cis*- and *trans*-2-(phenylethynyl)-3-styryloxiranes; in both these experiments, the starting products were substituted by a phenyl group on the vinylic carbon.

A study of the coupling constants of the cyclopropane hydrogens allowed a choice to be made among the four

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[14] E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972); T. H. Chan, P. W. K. Lau, and M. P. Li, *Tetrahedron Lett.*, 2667 (1976).

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Table III. Thermolytic Behavior of *cis*- and *trans*-9e, *cis,cis*-17e, and *cis,trans*-17e in the Gas Phase

	experimental conditions		distribution of reaction products,[a,b] %				
			9e		17e		18
starting product[a]	temp, °C	time, h	cis	trans	*c,c*	*c,t*	
9e, cis 46, trans 54	148[c]	3	18	46	36		
cis 13, trans 87[d]	148[c]	3	18	54	24		
cis 35, trans 65[d]	320[e]		10	10	45	35	
cis 46, trans 54	330[e]				55	45	trace
cis 13, trans 87[d]	330[e]				54	46	trace
17e, c,c trans 100	330[e]				100		
c,t trans 100	330[e]					100	

[a] Isomer distribution determined by ^{1}H NMR. [b] Yields of crude reaction products. [c] Sealed tubes. [d] Isolated compound from thermal rearrangement of *cis*- and *trans*-9e in the liquid phase. [e] Flow pyrolysis.

Table IV. Thermal Rearrangement of *cis*-9a–e, *cis*-17a–d, and *cis,cis*-17e in the Liquid Phase

starting product	experimental conditions			rearranged product, %[b]	reaction products[a,b]
	concn, mol/L	temp, °C	time, h		
9a	1	123	1	0	
	1	141	1	21	**19a**
	1	160	1	83	**19a**
17a	0.10	105	1	16	**19a**
	0.10	130	1	90	**19a**
9b	0.36	142	1	57	**17b**[c] 36, **20** 64 ($Z \simeq E$)[d]
	0.36	151	1	71	**17b**[c] trace, **20** 98 ($Z \simeq E$)[d]
17b	0.12	131	1	40	**20** ($Z \simeq E$)
	0.14	151	1	90	**20** ($Z \simeq E$)
9c	0.53	142	1	18	**21c** (Z)
	0.50	142	4	80	**21c** (Z)
17c	0.10	100	1	70	**21c** (Z)
	0.10	140	0.16	>90	**19c** trace **21c** (Z)
9d[e]	0.17	128	1	72	**17d**[c] 20, **21d** 80 ($Z > E$)[d]
	0.17	133	1	78	**17d** 28, **21d** 72 ($Z > E$)
17d[e]	0.17	128	1	13	**21d** ($Z > E$)
	0.17	133	1	19	**21d** ($Z > E$)
9e	0.44	147	3	59	**17e**[f] 30, **21e** 70 (Z)
17e[f]	0.58	147	3	40	**21e** (Z)
	0.58	159	1	>90	**21e** (Z)

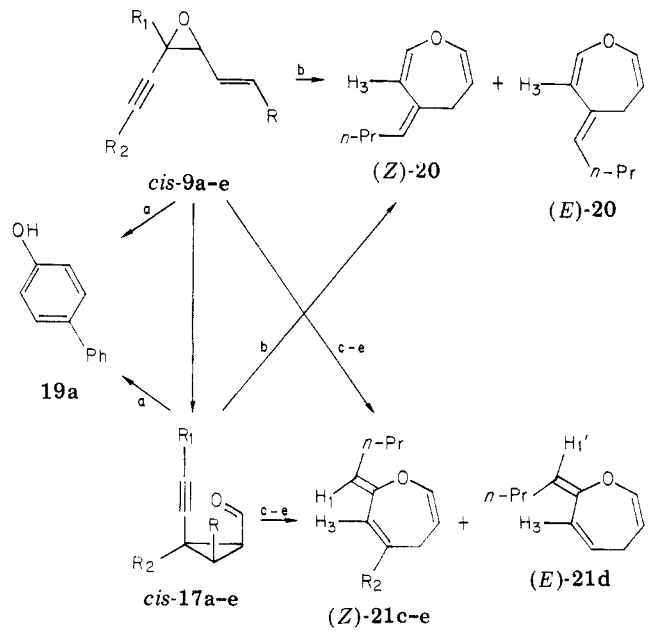
[a] Relative distribution. [b] Determined by ^{1}H NMR except for reactions from 9d or 17d. [c] Configuration cis. [d] Cis and trans isomers were separated by column chromatography. [e] Yields of reaction products determined by VPC. [f] Configuration cis,cis.

possible structures for **17e**. NMR spectra were recorded from solutions containing various amounts of europium complex, Eu(DPM)$_3$. This technique allowed observation of the signals of each of these protons and determination of coupling constants by double irradiation. For one isolated isomer, $J_{1,3}$, $J_{1,2}$, and $J_{2,3}$ were all equal to 9 Hz, corresponding to three cis protons;[19] only the cis,cis configuration can account for this result. The assignment of cis,trans configuration for the second isomer followed from the $J_{1,2}$ value of 8 Hz (cis H$_1$ and H$_2$), whereas $J_{1,3}$ and $J_{2,3}$ were found to be 6 Hz, indicating trans stereochemistry[19] for H$_1$/H$_3$ and H$_2$/H$_3$.

Liquid-Phase Thermolysis of Oxiranes 9a–e and Aldehydes 17a–e. Reactions were conducted in Pyrex sealed tubes at different concentrations and usually in carbon tetrachloride as solvent. Oxiranes **9a–e** and aldehydes **17a–e** were thermolyzed at temperatures inducing rearrangement of cis isomers only. Mixtures were then analyzed by ^{1}H NMR and/or VPC. Results are given in Table IV.

Compounds **9a** and **17a** gave *p*-phenylphenol (**19a**)[20] as the only product, whereas the oxiranes **9b–e** and aldehydes **17b–e** afforded either 4-butylidene-4,5-dihydrooxepin (**20**) or 2-butylidene-2,5-dihydrooxepins **21c–e**, depending on the initial position of the butyl substituent (Scheme VI).

Scheme VI



a, R$_1$ = H; R$_2$ = Ph; R = H
b, R$_1$ = H; R$_2$ = *n*-Bu; R = H
c, R$_1$ = *n*-Bu; R$_2$ = Ph; R = H
d, R$_1$ = *n*-Bu; R$_2$ = H; R = H
e, R$_1$ = *n*-Bu; R$_2$ = H; R = Ph

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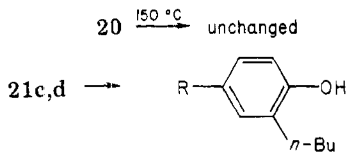
(19) H. Booth, *Prog. Nucl. Magn. Reson. Spectrosc.*, **5**, 167 (1969).

(20) The Aldrich Library of NMR Spectra, Vol. 4, No. 144 A.

Scheme VII



19c, R = Ph; 150 °C, 1 h
d, R = H, 160 °C, 2 h

Compounds **21c** and **21e** possessed *Z* stereochemistry, and **20** and **21d** were mixtures of *Z* and *E* isomers, which were separated by chromatography. In addition, the rearranged mixture from oxiranes **9b,d,e** contained aldehydes **17b,d,e**, respectively, in amounts depending on the experimental conditions. Further experiments were done with compound **9d**. Addition of water (1–7% by volume) to the solvent greatly enhanced the yield of (*Z*)- and (*E*)-oxepin **21d**. On the other hand, introduction of catalytic amounts of potassium carbonate led to the almost exclusive formation of formylcyclopropane **17d**.

The structures of the different oxepins were assigned on the basis of their spectroscopic data. Double irradiation experiments enabled the determination of the chemical shifts and coupling constants for each isomer. The spectra of 2,5-dihydrooxepin[21] and 4,5-dihydrooxepin[22] were useful for comparison. In addition, the signals due to H_3 in (*E*)-**21d** and (*Z*)-**20** (C_3 cis to propyl group) are deshielded and appear further upfield[23] than in the (*E*)-**20** and (*Z*)-**21d** isomers. Similarly, the $H_{1'}$ chemical shift is higher[24] in (*E*)-**21d** ($H_{1'}$ cis to oxygen) than in (*Z*)-**21d**. *Z* configurations of **21c** and **21e** were assigned by comparison.

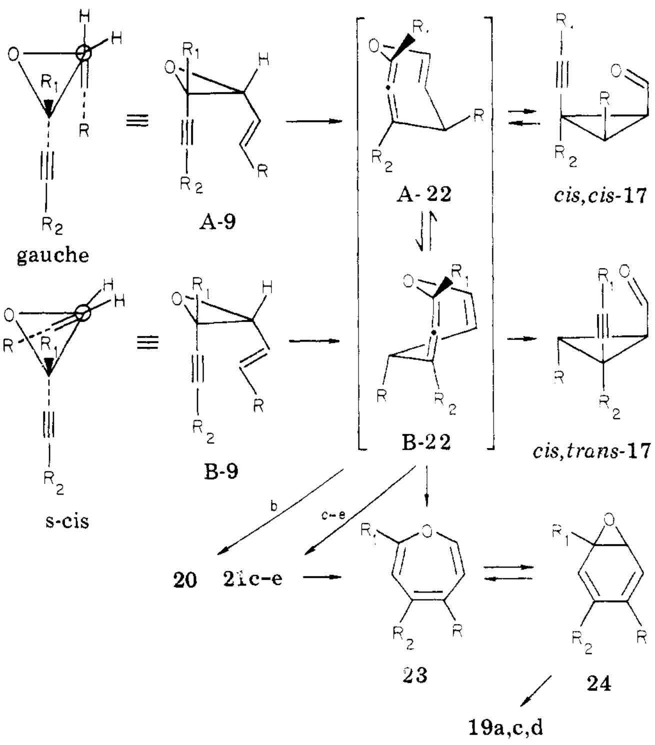
We also studied the thermal behavior of oxepins **20**, **21c**, and **21d**. Whereas 4-butylidene-4,5-dihydrooxepin (**20**) remained unchanged at 150 °C, the 2-butylidene-2,5-dihydrooxepins **21c** and **21d** afforded phenols **19c** and **19d**,[25] respectively (Scheme VII). The higher temperatures required for these conversions also increased polymerization, and yields of phenol were reduced to about 50%.

Discussion

Isolation of dihydrooxepins **20** and **21** and phenol **19** from the liquid-phase thermal rearrangement of both 2-alkynyl-3-vinyloxiranes and 2-alkynyl-1-formylcyclopropanes supports the intermediacy of an oxacycloheptatriene (**22**) in these reactions (Scheme VIII).

Cope transposition of compounds **9** into **22** is quite general and appears to be independent of the substitution; following this, a Claisen-type reaction converts **22** into cyclopropanes **17**. Since standard enthalpy for 2-ethynyl-1-formylcyclopropane formation has been shown to be about 15 kcal mol^{-1} lower than for 2-ethynyl-3-vinyloxirane,[3] a complete conversion of **9** to **17** seems reasonable. Furthermore, the **22** → **17** rearrangement is reversible since the products resulting from a retro-Claisen reaction of aldehyde **17** were observed during the liquid-phase thermolysis.

Scheme VIII



Dihydrooxepins **20** and **21** and phenol **19a** were produced from **22** by a formal [1,3] hydrogen shift, an unfavorable isomerization according to the Woodward–Hoffmann rules. In view of the experimental results obtained in the presence of potassium carbonate on one hand and of water on the other, we believe that this [1,3] prototropy is actually a catalyzed reaction.

With **9a** (R_2 = Ph) only one endocyclic proton shift can take place, and it gives oxepin **23a**. When R_1 or R_2 is an alkyl group, formation of an exocyclic double bond seems more favored since only compounds **20** and **21** are obtained. At higher temperatures, 2,5-dihydrooxepins **21c,d** probably undergo a thermally permitted [1,5] sigmatropic rearrangement, giving oxepins **23c,d**. Such a transposition would be impossible from 4,5-dihydrooxepin **20**. Oxepins are known to be in valence[26] equilibrium with arene oxides **24** and to give phenols under the influence of acid or high temperatures. A cationic or zwitterionic intermediate is believed to intervene since the phenol obtained comes from the most stable carbocation.[27] The substitution of the unique phenol formed is indeed the expected one.

Finally, the fact that the stereochemistry of the isolated compound **17e** depends on the experimental process provides additional information about the highly strained seven-membered intermediate **22**. Theoretical calculations performed on the 1,2-cycloheptadiene[28] suggest a distortion of the allenic system in two directions. The C_2–C_3–C_4 angle θ is likely less than 180°, and the dihedral angle ϕ formed by the C_3–C_2–H and C_3–C_4–H planes is apparently less than 90°. Molecular models constructed with $\theta = 120°$ indicate a twisted double bond and two possible conformations for the oxacyclohepta-2,3,6-triene **22**.

Only two conformations (A and B) of the vinyl group of oxirane **9** present a maximum overlap of π vinyl and ethynyl orbitals which favors the [3,3] sigmatropic process. The gauche form A leads to the chair conformation A-**22**, whereas the s-cis form B gives the boat conformation B-**22**.

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Taking into account the findings[29] concerning the respective populations of vinyloxirane conformers (51% gauche, 0%, s-cis), it is conceivable that the first pathway is highly favored. This rationalizes our observations, especially the exclusive *cis,cis*-**17e** isomer formation at low temperatures, starting from the A conformation. At higher temperatures, the two *cis,cis*- and *cis,trans*-**17e** stereoisomers (whose direct interconversion does not occur) appear to arise from the A- and B-**22** conformations, respectively, B-**22** being formed either directly from the epoxide or from A-**22**. The experimental results now in hand do not allow a choice between these two processes to be made.

Experimental Section

Column chromatography was performed on Kieselgel 60, 70–230 mesh (with few indicated exceptions). Solutions were dried over $MgSO_4$. Melting points were determined on a Büchi apparatus and are uncorrected. GLC analysis was performed on a Girdel Model 300 gas chromatograph; the column was silicon OV-1 (1%) on Chromosorb WHP 100–120 mesh. Microanalysis was performed by the Microanalytical Laboratory, Université de Reims. Mass spectra were obtained on a Bell and Howell 21-490 instrument. IR spectra were recorded on a Perkin-Elmer 521 spectrometer. NMR spectra were determined on a Varian A-60 or Brucker W.P.60 spectrometer with Me_4Si as an internal standard. Coupling constants are expressed in hertz; s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, pt = perturbed triplet, q = quadruplet, m = multiplet.

2-Heptynal (16b). This compound was obtained by the known procedure[30] from 1-hexyne (17.2 g, 0.21 mol) and DMF (0.63 mol). Distillation of the crude product afforded 11.7 g of 2-heptynal (**16b**) (50% yield): bp 61 °C (18 mmHg); IR (CCl_4) 2738, 2200, 1670 cm^{-1}; NMR (CCl_4) δ 0.95 (CH_3, pt, J = 6.5), 1.56 (CH_2CH_2, m), 2.43 ($CH_2C{\equiv}$, pt, J = 6.5), 9.2 (CHO, s).

1-Phenyl-1-heptyn-3-one (16c). Phenylacetylene (51 g, 0.5 mol) in THF (150 mL) was added dropwise to an ethylmagnesium bromide solution in THF (200 mL) prepared from ethyl bromide (0.55 mol) and magnesium (0.55 mol). The mixture was refluxed for 1 h and then cooled to 0 °C. Valeraldehyde (43 g, 0.5 mol) in THF (50 mL) was added dropwise at this temperature and the mixture allowed to stand overnight. Hydrolysis was carried out with saturated NH_4Cl solution. After separation, the aqueous layer was extracted with ether. The combined organic layers were washed with brine and dried. The solvent was removed under vacuum and the crude product distilled to yield 59 g of 1-phenyl-1-heptyn-3-ol (63% yield): bp 116 °C (0.2 mmHg); IR (CCl_4) 3620, 3380, 2210, 1600, 1490 cm^{-1}; NMR (CCl_4) δ 0.89 (CH_3, pt, J = 6.5), 1.1–1.93 ($CH_2CH_2CH_2$, m), 3.83 (OH), 4.53 (CH, pt, J = 6.5), 7.25 (Ph, m).

A three-neck vessel equipped with a mechanical stirrer, a thermometer, and a dropping funnel was filled with this alcohol (56 g, 0.3 mol) in acetone (180 mL). Jones reagent[31] (120 mL) was added dropwise to the stirred, cooled solution at a rate that maintained the temperature below 20 °C. The mixture was stirred at room temperature for 3 h and then diluted with water (100 mL). The aqueous layer was extracted with several portions of ether. The combined organic layers were washed successively with 5% $NaHCO_3$ solution and with water. After the solvent was dried and evaporated the crude product was distilled to afford 26.5 g of 1-phenyl-1-heptyn-3-one (**16c**) (48% yield): bp 118–119 °C (0.7 mmHg); IR (CCl_4) 2210, 1665, 1490 cm^{-1}; NMR (CCl_4) δ 0.93 (CH_3, pt, J = 7), 1.2–1.9 (CH_2CH_2, m), 2.58 (CH_2CO, pt, J = 7), 7.36 (Ph, m).

1-(Trimethylsilyl)-1-heptyn-3-one (16f). To a cooled suspension (0 °C) of aluminum chloride (26 g, 0.2 mol) in carbon disulfide (50 mL) were added dropwise valeroyl chloride (24 g, 0.2 mol) and bis(trimethylsilyl)acetylene (31.5 g, 0.2 mol) successively.[32] The mixture was stirred at 0 °C for 30 min and then allowed to warm to room temperature. The hydrolysis was carried out by slow addition of a 5% HCl solution (70 mL). After separation the aqueous layer was extracted with ether, and the combined organic layers were washed with a 5% $NaHCO_3$ solution and with water and then dried. After evaporation the crude product was distilled to yield 28 g of the ketone **16f** (77% yield): bp 97–99 °C (21 mmHg); IR (CCl_4) 2140, 1672 cm^{-1}; NMR (CCl_4) δ 0.22 ($3CH_3Si$, s), 0.89 (CH_3, pt, J = 7), 1.1–1.8 (CH_2CH_2, m), 2.47 (CH_2CO, pt, J = 7).

Synthesis of Disubstituted Oxiranes 9a,b. To a stirred mixture of allyltetramethylenesulfonium bromide (**13**) (0.1 mol), water (35 mL), aldehyde **16** (0.1 mol), and dichloromethane (140 mL) was added a 50% NaOH solution (20 mL). After an additional stirring at room temperature for 1 h, the mixture was diluted with 50 mL of water, and ether (200 mL) was added. The aqueous layer was separated and extracted with additional portions of ether. The combined organic layers were washed with water up to neutral and dried. The solvent was removed under vacuum, the crude product was analyzed by GLC, and the oxiranes were isolated by column chromatography (pentane/$CHCl_3$ 80:20).

The reaction of **16a** with **13** afforded by this procedure 12.2 g of the mixture of ***cis*- and *trans*-2-(phenylethynyl)-3-vinyloxiranes 9a** (72% yield): bp 97–100 °C (0.3 mmHg); mass spectrum, *m/e* 170 (M^+, 4%), 114 (100); IR (CCl_4) 2260, 1640, 1600, 1490 cm^{-1}; NMR (CCl_4) δ 3.33 and 3.68 (H_2 trans isomer and H_2 cis isomer, 2 d, J_t = 2 and J_c = 4), 3.41–3.56 (H_3, m), 5.14–5.76, $CH{=}CH_2$, m), 7.3 (Ph, m). Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.59; H, 6.00.

From the reaction of **16b** with **13**, the mixture of ***cis*- and *trans*-(1-hexynyl)-3-vinyloxiranes 9b** (6 g) was obtained (40% yield): IR (CCl_4) 2240, 2220, 1638 cm^{-1}; NMR (CCl_4) δ 0.93 (CH_3, pt, J = 7), 1.25–1.61 (CH_2CH_2, m), 2.18 ($CH{\equiv}$, m), 3.06 (H_2 trans isomer, q, J = 1.6), 3.23–3.48 (H_3 and H_2 cis isomer, m), 5.11–5.63 ($CH{=}CH_2$, m). Anal. Calcd for $C_{10}H_{14}O$:C, 79.95; H, 9.39. Found: C, 79.86; H, 9.37.

Synthesis of Trisubstituted Oxiranes 9c,f,g. To a stirred mixture of ketone **16c,f** (0.1 mol), K_2CO_3 (0.008 mol), and sulfonium bromide **13** or **14** (0.2 mol) in THF (500 mL) was added NaH powder (0.2 mol) under N_2 while the temperature was maintained at -10 °C. After an additional stirring for 30 min at this temperature, the mixture was allowed to warm at room temperature and then was filtered and evaporated under a slight vacuum. The residue was treated with ether (150 mL). The ethereal layers were washed with brine and dried. The solvent was removed under vacuum, the crude product was analyzed by GLC, and the oxiranes were isolated by column chromatography (pentane/$CHCl_3$ 80:20).

The reaction of **16c** with **13** afforded 10.2 g of **2-butyl-*r*-2-(phenylethynyl)-*c*-3-vinyl- and -*t*-3-vinyloxiranes 9c** (45% yield): mass spectrum, *m/e* 226 (M^+, 28%), 141 (100); IR (CCl_4) 2230, 2202, 1640, 1595, 1490 cm^{-1}; NMR (CCl_4) δ 0.94 (CH_3, pt, J = 7), 1.21–1.75 ($CH_2CH_2CH_2$, m), 3.22 and 3.59 (H_3 cis isomer and H_3 trans isomer, 2 d, J_c = 6.5 and J_t = 5), 5.1–5.92 ($CH{=}CH_2$, m), 7.26 (Ph, m). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.03; H, 8.09.

The condensation of **16f** with **13** afforded 8.9 g of **2-butyl-*r*-2-[(trimethylsilyl)ethynyl]-*c*-3-vinyl- and -*t*-3-vinyloxiranes 9f** (40% yield): NMR (CCl_4) δ 0.18 (3 CH_3, s), 0.93 (CH_3, pt, J = 6.5), 1.1–1.76 ($CH_2CH_2CH_2$, m), 3.07 and 3.43 (H_3 cis isomer and H_3 trans isomer, 2d, J_c = 6.5 and J_t = 5), 5.1–5.8 ($CH{=}CH_2$, m).

The reaction between **16f** and **14** was conducted by the same procedure but began only at 23 °C. Stirring was maintained for 1 h at 39 °C. Usual workup afforded 10.1 g of **2-butyl-*r*-2-[2-(trimethylsilyl)ethynyl]-*c*-3-styryl- and -*t*-3-styryloxiranes 9g** (34% yield):NMR ($CDCl_3$) δ 0.18 (3 CH_3, s), 0.91 (CH_3, pt, J = 7), 1.26–1.76 ($CH_2CH_2CH_2$, m), 3.42 and 3.79 (H_3 cis isomer and H_3 trans isomer, 2 d, J_c = 8 and J_t = 7), 6.01 and 6.2 (H_4 trans isomer and H_4 cis isomer, 2 dd, J_t = 7 and 16, J_c = 8 and 16), 6.83 and 6.86 (H_5 trans isomer and H_5 cis isomer, 2 d, J = 16), 7.33 (Ph, m).

Desilylation of Oxiranes 9f,g. A solution of oxiranes **9** (0.12

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mol) in acetonitrile (35 mL) was stirred at room temperature for 2 h with tetrabutyl- or tetraethylammonium fluoride.[14] Water (50 mL) was then added and the oxirane extracted with three portions of ether. The combined organic layers were washed with brine, dried, and evaporated.

The crude reaction product from **9f** afforded by distillation 11 g of **2-butyl-*r*-2-ethynyl-*c*-3-vinyl- and -*t*-3-vinyloxiranes 9d** (61% yield): bp 50–55 °C (0.3 mmHg); mass spectrum, *m/e* 150 (M^+, 5%), 79 (100); IR (CCl_4) 3307, 2217, 1636 cm^{-1}; NMR (CCl_4) δ 0.93 (CH_3, pt, J = 6.5), 1.13–1.75 ($CH_2CH_2CH_2$, m), 2.20 and 2.26 ($HC\equiv$ trans isomer and $HC\equiv$ cis isomer, 2 s), 3.09 and 3.45 (H_3 cis isomer and H_3 trans isomer, 2 d, J_c = 6.5 and J_t = 5), 5.15–5.95 ($CH{=}CH_2$, m). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.93; H, 9.39.

From **9f**, 16.5 g of **2-butyl-*r*-2-ethynyl-*c*-3-styryl- and -*t*-3-styryloxiranes 9e** (61% yield) were isolated by column chromatography (pentane/$CHCl_3$ 80:20): mass spectrum *m/e* 226 (18%), 115 (100); IR (CCl_4) 3320, 1600, 1495 cm^{-1}; NMR (CCl_4) δ 0.92 (CH_3, pt), 1.2–1.75 ($CH_2CH_2CH_2$, m), 2.23 and 2.30 ($HC\equiv$ trans isomer and $HC\equiv$ cis isomer, 2 s), 3.32 and 3.69 (H_3 cis isomer and H_3 trans isomer, 2 d, J_c = 8 and J_t = 7), 5.97 and 6.11 (H_4 trans isomer and H_4 cis isomer, 2 dd, J_t = 7 and 16, J_c = 8 and 16), 6.77 and 6.81 (H_5 trans isomer and H_5 cis isomer, 2 d, J = 16), 7.26 (Ph, m). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.77; H, 8.17.

Thermal Rearrangement of Oxiranes 9a–e in the Gas Phase. In the flow system, compounds **9a–e** ((1–6) × 10^{-3} mol) in tetrachloride solution (~10%) were dropped through a hot vertical Pyrex tube (60 cm in length, 1 cm in diameter) filled with Pyrex balls, under an 18-torr pressure. Reaction products were collected in a cooled trap (liquid N_2) and then evaporated. Static condition reactions were realized in tubes sealed under vacuum (10^{-2} torr) without solvent. After ^1H NMR analysis of the crude products the aldehydes **17a–e** were separated from the trans isomers **9a–e** by column chromatography. Yields were calculated on the basis of introduced cis isomer.

***c*-2-Ethynyl- and *t*-2-Ethynyl-*r*-1-formyl-2-phenylcyclopropanes 17a.** Separation of the pyrolysis mixture (350 °C) from **9a** (1.07 g, 6.10^{-3} mol, cis/trans 63:37) afforded 473 mg of cis- and trans-**17a** (eluent: pentane/$CHCl_3$ 30:70) (70% yield): IR (CCl_4) 3310, 2118, 1720, 1600, 1498 cm^{-1}; NMR (CCl_4) δ 1.65–2.53 (H_2, 2 H_3 and $HC\equiv$, m), 7.25 (Ph, m), 8.57 and 9.32 (CHO trans isomer and CHO cis isomer, d and m, J_t = 5.5). Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.38; H, 5.93.

***cis*-2-Butyl-2-ethynyl-1-formylcyclopropane (17b).** The thermal rearrangement at 335 °C of **9b** (572 mg, 3.8 × 10^{-3} mol, cis/trans 70:30) afforded a mixture from which 330 mg of *cis*-**17b** were separated (eluent: pentane/$CHCl_3$ 20:80) (81% yield): IR (CCl_4) 3316, 2764, 2112, 1730 cm^{-1}; NMR (CCl_4) δ 0.93 (CH_3, pt, J = 6), 1.2–1.86 (H_2, 2H_3 and $(CH_2)_3$, m), 2.06 ($HC\equiv$, s), 8.98 (CHO, m). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.81; H, 9.58.

***r*-1-Formyl-2-phenyl-*c*-2-(1-hexynyl)- and *t*-2-(1-hexynyl)cyclopropane (17c).** Separation of the pyrolysis mixture (345 °C) of **9c** (1 g, 4.4 × 10^{-3} mol, cis/trans = 56:44) afforded 400 mg of *cis*- and *trans*-**17c** (pentane/$CHCl_3$ 80:20) (70% yield): IR (CCl_4) 2760, 1710, 1600, 1490 cm^{-1}; NMR (CCl_4) δ 0.91 (CH_3, m), 1.23–2.23 (H_2, 2 H_3 and $(CH_2)_3$, m), 7.26 (Ph, m), 8.50 and 9.36 (CHO trans isomer and CHO cis isomer, d and m, J_t = 5.5). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.66; H, 8.05.

***cis*-1-Formyl-2-(1-hexynyl)cyclopropane (17d).** The thermal rearrangement (330 °C) of **9d** (900 mg, 6 × 10^{-3} mol, cis/trans 56:44) afforded a mixture from which 381 mg of *cis*-**17d** were separated (pentane/$CHCl_3$ 70:30) (74% yield): IR ($CHCl_3$) 2760, 1703 cm^{-1}; NMR (CCl_4) δ 0.9 (CH_3, m), 1.13–1.6 (CH_2CH_2 and 2 H_3, m), 1.62–2.23 ($CH_2C\equiv$, H_1 and H_2, m), 9.15 (CHO, d, J = 6). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.66; H, 9.40.

***r*-1-Formyl-*c*-2-(1-hexynyl)-*c*-3-phenyl- and -*c*-2-(1-hexynyl)-*t*-3-phenylcyclopropane (17e).** Epoxide **9e** (1 g, 4.4 × 10^{-3} mol, cis/trans 48:52) was thermolyzed at 330 °C. Column chromatography afforded successively 2-butyl-2-ethynyl-3-phenyl-2,3-dihydrofuran (**18**) (pentane/$CHCl_3$ 80:20, 50 mg, 6% yield): NMR (CCl_4) δ 0.75–1.38 (*n*-Bu, m), 2.38 ($HC\equiv$, s), 4.31 (H_3, pt, J = 2.5), 5.05 (H_4, t), 6.48 (H_5, pt, $J_{4,5}$ = 2.5), 7.21 (Ph, m), **17e** (pentane/$CHCl_3$ 50:50, 670 mg, 67% yield). Coupling constants were determined by double irradiation experiments on solutions of *cis,cis*- or *cis,trans*-**17e** and $Eu(DPM)_3$ (1:1). The cis,trans isomer was eluted first: IR (CCl_4) 2750, 1735, 1600, 1500 cm^{-1}; NMR (CCl_4) δ 0.95 (CH_3, pt, J = 7), 1.16–1.63 (CH_2CH_2, m), 2.1–2.25 (H_1, H_2 and $CH_2C\equiv$, m, $J_{1,2}$ = 8, $J_{1,3}$ = $J_{2,3}$ = 6), 2.88 (H_3, t, J = 6), 7.25 (Ph, m), 9.33 (CHO, m). Cis,cis isomer: IR (CCl_4) 1719, 1603, 1500 cm^{-1}; NMR (CCl_4) δ 0.82 (CH_3, pt, J = 7), 0.96–1.5 (CH_2CH_2, m), 1.86–2.20 ($CH_2C\equiv$, and H_2, m), 2.36 (H_1, tt, $J_{1,2}$ = 9 and J = 2), 2.81 (H_3, t, $J_{2,3}$ = $J_{1,3}$ = 9), 7.25 (Ph, m), 9.06 (H_5, d, J = 7). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.53; H, 8.20.

General Procedure for Thermal Rearrangement of Epoxides 9a–e, Aldehydes 17a-e, and Oxepins 20, 21c–d in the Liquid Phase. Reactions were carried out on tetrachloride solutions of products (0.1–1.0 mol/L) in Pyrex tubes sealed under vacuum (10^{-2} torr). These tubes were immersed in a hot thermostatic bath for a known time and then cooled. The crude solutions were analyzed by ^1H NMR or GLC. Solvent was evaporated and column chromatography afforded the following compounds.

(*Z*)- and (*E*)-4-Butylidene-4,5-dihydrooxepin (20). Thermolysis of *cis*-**17b** (110 mg in 5 mL of CCl_4) at 151 °C for 1 h (>90% rearranged product) afforded (*Z*)- and (*E*)-**20** (80% yield). The *E* isomer was eluted first (pentane/$CHCl_3$ 98:2): NMR ($CDCl_3$) δ 0.9 (CH_3, pt), 1.13–1.6 (CH_2, m), 2.03 (exo $CH_2C{=}$, q, J = 7.2), 3.03 (2 H_5, dm), 4.87 (H_6, dt, $J_{6,5}$ = 5.6), 4.93 ($H_{1'}$, t, J = 7.2), 5.27 (H_3, d), 6.03 (H_2, d, $J_{2,3}$ = 8), 6.31 (H_7, dt, $J_{7,6}$ = 7.2 and $J_{7,5}$ = 1.2). *Z* isomer: NMR ($CDCl_3$) δ 0.9 (CH_3, pt), 1.13–1.6 (CH_2, m), 2.08 (exo $CH_2C{=}$, q, J = 7.2), 3.0 (2 H_5, dm), 5.0 (H_6, dt, $J_{6,5}$ = 6.4), 5.07 ($H_{1'}$, t, J = 7.2), 5.47 (H_3, d), 6.17 (H_2, d, $J_{2,3}$ = 8), 6.23 (H_7, dt, $J_{7,6}$ = 7.2 and $J_{7,5}$ = 1.2). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.64; H, 9.43.

(*Z*)-2-Butylidene-4-phenyl-2,5-dihydrooxepin (21c). Thermolysis of **17c** (100 mg in 5 mL of CCl_4, cis/trans 75:25) at 100 °C for 1 h (70% rearranged cis product) afforded (*Z*)-**21c** (79% yield), which was purified by column chromatography (pentane/$CHCl_3$ 90:10): NMR ($CDCl_3$) δ 0.92 (CH_3, pt), 1.17–1.7 (CH_2, m), 2.2 (exo $CH_2C{=}$, q, J = 7.2), 3.25 (2 H_5, dm), 4.92 ($H_{1'}$, t, J = 7.2), 5.08 (H_6, dt, $J_{6,5}$ = 5.6), 6.18 (H_3, t, $J_{3,5}$ = 0.5), 6.37 (H_7, dt, $J_{7,6}$ = 6.4 and $J_{7,5}$ = 1.4), 7.3 (Ph, m). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.67; H, 7.95.

(*Z*)- and (*E*)-2-Butylidene-2,5-dihydrooxepin (21d). Thermolysis of *cis*-**17d** (145 mg in 5 mL of CCl_4) at 133 °C for 1 h (19% rearranged product) afforded (*Z*)- and (*E*)-**21d** (>90% yield). The *Z* isomer was eluted first (pentane): NMR ($CDCl_3$) δ 0.9 (CH_3, pt), 1.13–1.6 (CH_2, m), 2.16 (exo $CH_2C{=}$, q, J = 7.2), 2.86 (2 H_5, m), 4.8 ($H_{1'}$, pt, J = 7.2), 4.83 (H_6, dt, $J_{6,5}$ = 5), 5.45 (H_4, pdt, $J_{4,5}$ = 5), 5.9 (H_3, dt, $J_{3,4}$ = 12 and $J_{3,5}$ = 1.6), 6.29 (H_7, dt, $J_{7,6}$ = 7 and $J_{7,5}$ = 1.7). *E* isomer: NMR ($CDCl_3$) δ 0.9 (CH_3, pt), 1.13–1.6 (CH_2, m), 2.04 (exo $CH_2C{=}$, q, J = 7.4), 2.9 (2 H_5, m), 4.85 (H_6, dt, $J_{6,5}$ = 5), 5.16 ($H_{1'}$, t, J = 7.4), 5.6 (H_4, dt, $J_{4,5}$ = 5), 6.25 (H_3, dt, $J_{3,5}$ = 1.7 and $J_{3,4}$ = 12), 6.27 (H_7, dt, $J_{7,5}$ = 1.6 and $J_{7,6}$ = 7). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.90; H, 9.46.

(*Z*)-2-Butylidene-5-phenyl-2,5-dihydrooxepin (21e). Thermolysis of **17e** (87 mg in 4 mL of CCl_4, *c,c*/*c,t* 61:49) at 149 °C for 3 h (>90% rearranged product) afforded (*Z*)-**21e** (40% yield) which was purified by column chromatography (pentane): NMR (CCl_4) δ 0.96 (CH_3, pt), 1.2–1.7 (CH_2, m), 2.24 (exo $CH_2C{=}$, q, J = 7), 4.19 (H_5, m), 4.7–5.03 ($H_{1'}$ and H_6, m), 5.51 (H_4, pdd), 5.98 (H_3, dd, $J_{3,4}$ = 12 and $J_{3,5}$ = 2), 6.34 (H_7, dd, $J_{7,6}$ = 7.5 and $J_{7,5}$ = 2), 7.32 (Ph, m). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.87; H, 8.00.

4-Phenylphenol (19a). The thermolysis of **9a** (110 mg in 0.64 mL of CCl_4, cis/trans 42:58) at 160 °C for 1 h or of **17a** (97 mg in 5 mL of CCl_4, cis/trans 62:38) at 130 °C for 1 h afforded quantitatively **19a** insoluble in CCl_4 and isolated by filtration: mp 165 °C; spectral data identical with those published.[20]

2-Butyl-4-phenylphenol (19c). The thermolysis of **21c** (70 mg in 5 mL of CCl_4) at 150 °C for 1 h afforded **19c**, which was purified by column chromatography on Florisil 100–200 (pentane/$CHCl_3$ 50:50) and then crystallized (H_2O/C_2H_5OH 80:20) (86% yield): mp 57 °C; mass spectrum, *m/e* 226 (M^+, 90%), 183 (100); IR (CCl_4) 3615, 3550, 3460, 1618 cm^{-1}; NMR ($CDCl_3$) δ 0.96 (CH_3, pt, J = 7), 1.26–1.9 (CH_2CH_2, m), 2.68 (CH_2Ph, t, J = 7),

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4,68 (OH, s), 6,80 (H_6, dd, J = 9 and 1.5), 7.4 (Ph, H_3 and H_5, m). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.48; H, 8.15.

2-Butylphenol (19d). The thermolysis of a mixture of **17d** and **21d** (*Z*- and *E*-) at 150 °C for 1 h quantitatively afforded **19d**[25] which was purified by column chromatography on Florisil 100–200 (pentane/$CHCl_3$ 50:50): IR (CCl_4) 3618, 3440, 1620, 1590 cm^{-1}; NMR ($CDCl_3$) δ 0.91 (CH_3, pt, J = 7), 1.13–1.55 (CH_2CH_2, m), 2.61 (CH_2Ph, t, J = 7), 4.9 (OH, m), 6.63–7.18 (H_3, H_4, H_5, H_6, m).

Registry No. *cis*-**9a**, 72206-14-5; *trans*-**9a**, 72206-15-6; *cis*-**9b**, 72206-16-7; *trans*-**9b**, 72206-17-8; *cis*-**9c**, 72206-18-9; *trans*-**9c**, 72206-19-0; *cis*-**9d**, 66713-41-5; *trans*-**9d**, 66713-46-0; *cis*-**9e**, 72206-20-3; *trans*-**9e**, 72206-21-4; *cis*-**9f**, 66713-39-1; *trans*-**9f**, 66713-44-8; *cis*-**9g**, 72206-22-5; *trans*-**9g**, 72206-23-6; **13**, 66713-38-0; **14**, 72206-24-7; **16a**, 2579-22-8; **16b**, 1846-67-9; **16c**, 72206-25-8; **16f**, 66713-37-9; *cis*-**17a**, 72206-26-9; *trans*-**17a**, 72206-27-0; *cis*-**17b**, 72206-28-1; *trans*-**17b**, 72206-29-2; *cis*-**17c**, 72206-30-5; *trans*-**17c**, 72206-31-6; *cis*-**17d**, 66713-53-9; *cis,cis*-**17e**, 72206-32-7; *cis,trans*-**17e**, 72244-27-0; **18**, 72206-33-8; **19a**, 92-69-3; **19c**, 72206-34-9; **19d**, 3180-09-4; *E*-**20**, 72206-35-0; *Z*-**20**, 72206-36-1; *Z*-**21c**, 72206-37-2; *E*-**21d**, 72206-38-3; *Z*-**21d**, 72206-39-4; 1-hexyne, 693-02-7; phenylacetylene, 536-74-3; ethylmagnesium bromide, 925-90-6; valeraldehyde, 110-62-3; 1-phenyl-1-heptyn-3-ol, 72206-40-7; valeroyl chloride, 638-29-9; bis(trimethylsilyl)acetylene, 14630-40-1.

Unreactive 1-Azadiene and Reactive 2-Azadiene in Diels–Alder Reaction of Pentachloroazacyclopentadienes

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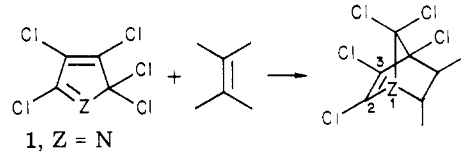
The pentachloroazacyclopentadiene, previously assigned the 1-azadiene structure, a 2*H*-pyrrole, has been used as a Diels–Alder diene addend. Its structure is now validated by IR and ^{13}C NMR studies, particularly diagnostic are the lanthanide-shifted ^{13}C NMR spectra recorded with $Eu(fod)_3$ and $Yb(fod)_3$, thus eliminating both the 2-azadiene structure of a 3*H*-pyrrole and the 1*H* isomer. Also, the nearly superimposable variable-temperature ^{13}C NMR spectra from −30 °C to 130 °C denote the predominance of the 1-azadiene form in the temperature range where it is found reactive. However, its reaction with styrene under various conditions does not yield the expected 1-azanorbornene but yields exclusively the 2-azabicyclo[2.2.1]hept-2-ene as shown by X-ray diffraction. Although the adduct shows $\nu_{C=N}$ 1568 cm^{-1} and resistance to hydrolysis uncommon for an imidoyl chloride, the latter's presence is indicated by the chlorinated carbon resonances of the adduct. It appears that the 1-azadiene has undergone a chlorine [1,5]-sigmatropic shift to form the 2-azadiene prior to cycloaddition with styrene. The exclusivity of the 2-aza adduct shows that 1-azadiene is not a viable diene addend, but the utility of 2-azadienes in a Diels–Alder reaction as a one-step approach to prepare heterocycles containing an imino group is illustrated. The styrene adduct crystallizes in the monoclinic space group $P2_1/n$ with cell constants a = 7.001 (4) Å, b = 16.184 (6) Å, c = 12.667 (6) Å, β = 101.79 (3)°, and ρ_{calcd} = 1.62 g cm^{-3} for Z = 4. The structure was refined to a conventional R value of 0.053 for 1749 observed reflections.

We have reported[1a] that 2,3,4,5,5-pentachloro-1-azacyclopentadiene (**1**) undergoes typical Diels–Alder reaction to produce polycyclic amines. They were assigned the 1-azanorbornene structure wherein a nitrogen replaces the bridgehead C–Cl group of the corresponding chlorinated hydrocarbon derived from hexachlorocyclopentadiene (**2**) (cf. Scheme I). However, as the chlorinated carbon resonances of these two series of adducts are compared, it becomes apparent that the aza adducts exhibit unusual shielding at C-2 and deshielding at C-3 of the 1-azanorbornene structures relative to those of the carbon analogues. Either this presages a reversal of normal enamine polarity at the unsaturated carbons of the 1-azanorbornene or it indicates that cycloaddition of **1** involves a deep-seated rearrangement, yielding a 2-azanorbornene exclusively. Several fundamental questions pertaining to the structure and cycloaddition reactivity of pentachloroazacyclopentadiene are raised: (1) how rigorous is the 2*H*-pyrrole structure established, (2) does a dynamic equilibrium exist among the three pentachloropyrrole forms, and (3) which of the three forms is the most reactive diene addend? In regard to the azadiene adduct, its structure needs to be unequivocally determined so that apparently conflicting spectroscopic properties and hydrolytic behavior of the adduct can be explained. We have chosen the reaction of the azadiene **1** with styrene to elucidate these points. In this paper, we report (1) the IR and ^{13}C NMR studies which validate the structure of the azadiene **1**, (2) an X-ray diffraction study of the azadiene–styrene adduct, (3) IR, ^1H NMR, and ^{13}C NMR data as well as hydrolysis of the above adduct, and (4) the unique rearrangement of a 2*H*- to a 3*H*-pyrrole as manifested by the azadiene **1** and the contrast of Diels–Alder reactivity of the two forms.

Scheme I



1, Z = N
2, Z = C-Cl

Results and Discussion

Validation of the 1-Azadiene Structure. Preparation of the title azadiene was first reported in 1897 and accomplished by the action of phosphorus pentachloride on

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(1) (a) C. M. Gladstone, P. H. Daniels, and J. L. Wong, *J. Org. Chem.*, **42**, 1375 (1977). (b) References 2–6 cited in ref 1a.

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