Thermolysis of 5,5-Dimethyl-1,3-cyclohexadiene. Evidence for Rearrangement *via* [1,5] Sigmatropic Methyl Migration[1]

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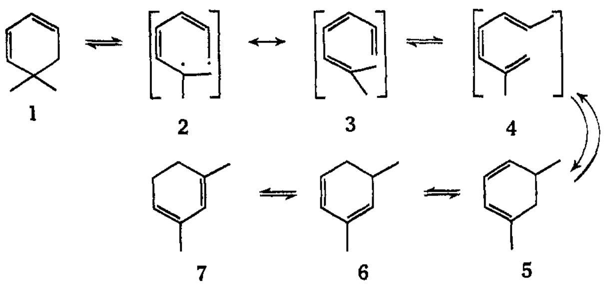
Thermolysis of 5,5-dimethyl-1,3-cyclohexadiene at temperatures ranging from 300 to 475° yields mixtures composed of toluene, 1,5-dimethyl-1,3-cyclohexadiene, 2,6-dimethyl-1,3-cyclohexadiene, 1,3-dimethyl-1,3-cyclohexadiene, and *m*-xylene. The distributions of dienes and their relative rates of appearance are consistent with an initial slow [1,5] sigmatropic migration of a methyl group, followed by rapid [1,5] sigmatropic migration of hydrogen. Toluene and *m*-xylene are formed by elimination of methane or hydrogen from either the starting material or any of the intermediate dienes, respectively.

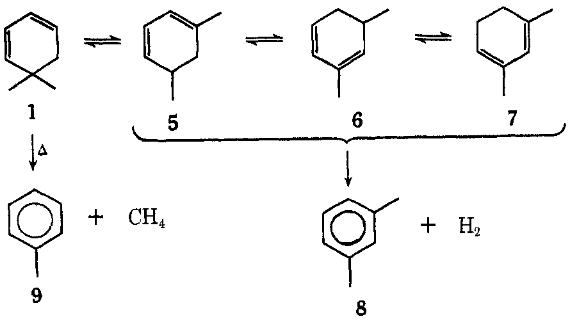
Thermal [1,5] sigmatropic migration of hydrogen in cyclic dienes and trienes is well known and has been studied extensively.[2] However, [1,5] migration of groups of greater complexity than hydrogen or deuterium has not attracted the same attention until recently.[3] De Haan and Kloosterziel[4,5] and Herndon and Manion[6] have interpreted the thermal migration of a methyl group in the thermolysis of 1,5,5-trimethylcyclopentadiene in terms of a rate-determining [1,5] sigmatropic methyl shift. Boekelheide and coworkers[7,8] have observed apparent [1,5] alkyl migration in the *trans*-15,16-dialkyldihydropyrenes for methyl, ethyl, and *n*-propyl substituents. Similarly, Maier and coworkers[9] have interpreted the low-temperature (60°) thermolysis of 1,6-dimethyl-2,5-diphenyl-3,4-diazabicyclo[4.4.0]deca-2,4,7,9-tetraene also as occurring *via* [1,5] methyl migration as the initial step. Finally Millet, *et al.*,[10] have been able to obtain relative migratory aptitudes in substituted indenes by kinetic studies and found that hydrogen migrates faster than phenyl which in turn migrates faster than methyl, a result that is substantiated in part by Shen, *et al.*[11]

Previous to the present study, Pines andKozlowski[12] had reported a 500° thermolysis of 5,5-dimethyl-1,3-cyclohexadiene (**1**) in which there occurred an apparent methyl migration, as well as many other reactions. Their product distributions were interpreted in terms of a biallyl–biradical mechanism proceeding through two intermediate trienes, ring closure, and further isomerization. Toluene and *m*-xylene as well as various methyl-methylenecyclohexenes were also reported products. However, no trienes were detected in the reaction products. Therefore, we were hopeful that by carrying out the thermolysis of **1** at various temperatures and times, followed by rapid quenching, that we could obtain direct experimental evidence for the intermediates actually involved in the apparent rearrangement and thus distinguish between the biallyl–biradical and sigmatropic pathways.



5,5-Dimethyl-1,3-cyclohexadiene (**1**) was thermolyzed over a wide temperature range (167–475°) under both flow and static conditions. Static runs were in sealed tubes in thermostatically controlled baths, while flow experiments were conducted utilizing techniques described previously.[13] In both cases, glpc analyses were performed immediately following low-temperature quenching. Results of the flow experiments are presented in Table I, while those from the static runs are found in Table II.

It can easily be seen from the results in Table I that the first detectable product in the thermolysis at 300° is 1,5-dimethyl-1,3-cyclohexadiene (**5**), the product one would expect from initial [1,5] methyl migration in **1**. At higher temperatures, operating under faster conversion rates,[14] the appearance of **6** and **7** as well as **8** and **9** lead us to postulate the following reaction scheme.



The formation of **8** and **9** complicates the mechanistic interpretations of these thermolyses. Aromatization of cyclic dienes *via* elimination of either methane or hydrogen at high temperatures is well known[12,15] and

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[2] R. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie and Academic Press, Weinheim/Bergstr., Germany, 1970, pp 114–140, and references cited therein.

[3] J. Berson, *Accounts Chem. Res.*, **1**, 152 (1968), and references cited therein.

[4] J. De Haan and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **84**, 1594 (1965).

[5] J. De Haan and H. Kloosterziel, *ibid.*, **87**, 298 (1968).

[6] W. Herndon and J. Manion, *J. Org. Chem.*, **33**, 4504 (1968).

[7] V. Boekelheide and E. Sturm, *J. Amer. Chem. Soc.*, **91**, 902 (1969).

[8] V. Boekelheide and T. Hylton, *ibid.*, **92**, 3669 (1970).

[9] Von G. Maier, I. Fuss, and M. Schneider, *Tetrahedron Lett.*, 1057 (1970).

[10] L. Millet, R. Greisinger, and R. Boyer, *J. Amer. Chem. Soc.*, **91**, 1578 (1969).

[11] K. Shen, W. McEwen, and A. Wolf, *Tetrahedron Lett.* 827 (1969).

[12] H. Pines and R. Kozlowski, *J. Amer. Chem. Soc.*, **78**, 3776 (1956).

[13] C. Spangler and N. Johnson, *J. Org. Chem.*, **34**, 1444 (1969).

[14] At all temperatures flow rates are set such that the residence time in the heated zone is not more than *ca.* 10 sec.

[15] H. Pines and C. Chen, *J. Amer. Chem. Soc.*, **81**, 928 (1959).

TABLE I

THERMOLYSIS OF 5,5-DIMETHYL-1,3-CYCLOHEXADIENE (1) UNDER FLOW CONDITIONS

Temp, °C	% recovery	% of total product[a]					
		1	**5**	**6**	**7**	**8**	**9**
300	95	99.9	0.1	0.0	0.0	0.0	0.0
350	88	99.7	0.3	0.0	0.0	0.0	0.0
400	88	93.7	0.5	0.8	3.7	0.2	1.1
450	75	63.0	4.7	4.6	17.5	6.5	3.7
475	75	39.0	7.7	6.4	26.7	11.5	8.6

[a] Per cent composition of degassed liquid product; methane and hydrogen were not determined quantitatively. Below 300° **1** was recovered unchanged in almost quantitative yield.

essentially irreversible under the conditions of our experiments. This fact is evident when one compares the static *vs.* the flow results. Toluene is the major product in all static results, wherein products have an opportunity to undergo equilibration. Thus it would appear that the methyl migration is reversible, as well as [1,5] hydrogen migration in our system. One can also extrapolate the static results to completetion, and at elevated temperatures it is likely that the final products would consist mainly of toluene and *m*-xylene.

We believe that the above results indicate that sigmatropic migrations account for the thermolytic behavior of **1** as opposed to the biallyl–biradical mechanism proposed several years ago by Pines, *et al.*,[12,15] and which we indicated previously. We can find no evidence for the trienic intermediates **3** and **4** necessary to the latter mechanism. In order to establish that they are indeed not involved in the rearrangement of **1**, the following was carried out: (1) **4** was prepared separately and was shown to be easily detectable under the conditions of our isolation and analysis techniques, and (2) **4** was thermolyzed over the temperature range 375–425° to demonstrate that sufficient quantities survive to be detected in the thermolysis product. When mixed with either **1** or with the thermolysis products, **4** is easily separated and quantitatively detected by glpc. The results of the thermolysis of **4** are shown in Table III.

It can be seen from these results that significant quantities of both geometric isomers of **4** do survive thermolysis. In addition, the product distributions are dissimilar in their relative make-up, particularly in the formation of the exocyclic methylenecyclohexene structures. No evidence could be found for reversible formation of **3** at any of the above temperatures. This observation is important in that our static experiments indicate that all transformations should be reversible. We feel that the above establishes the fact that **4** was not present in any of our thermolysis samples from **1**, both static and flow.

Another aspect of the biallyl–biradical mechanism that we cannot accept without direct evidence is the conversion of **3** to **4**. Presumably, this occurs *via* a thermal [1,7] shift of hydrogen. In order for this shift to be allowed, it must take place antarafacially, presumably *via* a spiral conformation. Such transitions are known,[16–18] but are primarily limited to examples such as the vitamin D_2–precalciferol and similar transformations. We are not aware of any [1,7] shifts occurring in simple acyclic trienic systems. In order to test the ease of such a transformation, we thermolyzed 1,3,5-octatriene (**11**) in a manner similar to that of **1**, in the temperature range 375–425°. In no case did we observe the formation of even trace quantities of 2,4,6-octatriene. The only products from this thermolysis are the various ethyl-1,3-cyclohexadienes. We have previously demonstrated that this transformation is facile if acid catalyzed.[19] We can only conclude from this that a thermal [1,7] sigmatropic hydrogen migration is a highly unlikely process in this temperature range, and that the postulated transformation of **3** to **4** is similarly unlikely.

TABLE II

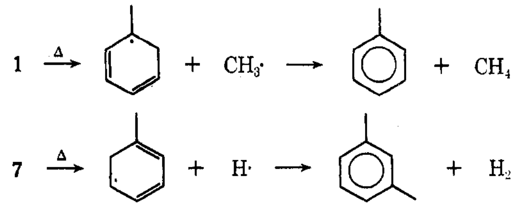
THERMOLYSIS OF 5,5-DIMETHYL-1,3-CYCLOHEXADIENE UNDER STATIC CONDITIONS

Temp, °C[a]	Time, min	% of total products[b,c]					
		1	**5**	**6**	**7**	**8**	**9**
290	30	74.2	2.0	0.1	0.5	0.0	23.2
290	60	60.5	2.8	0.2	0.5	0.5	35.4
320	30	66.3	2.8	0.5	0.1	0.4	29.8
320	60	35.8	4.6	0.6	0.4	2.5	56.2
350	30	18.4	7.2	0.4	0.2	7.5	66.1
350	60	10.1	6.6	0.3	0.6	11.3	71.0

[a] Bath temperatures ±2° over the course of the reaction. [b] Per cent composition of degassed liquid product as in Table I. [c] At 250° for 90 min, there was no apparent reaction.

It can be argued that the absence of trienic products at any stage of these reactions does not prove that a sigmatropic process is therefore operative. We do, however, feel that most of the evidence does point in this direction and our reasoning can be outlined as follows: (1) the first *new*[20] product to appear in the early stages of the reaction is **5**, which would result from a [1,5] sigmatropic methyl migration; (2) at progressively higher temperatures in the flow studies, **6** and **7** appear, which one would predict for an increased rate for the same residence time;[14] (3) **7** eventually becomes the major product at higher temperatures than one would predict on the basis of relative diene stabilities. At first glance it might seem that the static studies do not show the same results; however, we feel that they do provide evidence for the reversibility of all migrations, both methyl and hydrogen. Thus the thermolysis of **1** under conditions approaching equilibrium yields progressingly greater quantities of toluene and *m*-xylene, both with respect to time and temperature.

It can be argued also that some reaction may proceed *via* a free radical pathway. Indeed, this pathway is probably responsible for the aromatization products, as first postulated by Pines.[12,15]



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[16] E. Havinga and J. Schlatmann, *Tetrahedron*, **16**, 146 (1961).

[17] R. Autry, D. Barton, A. Ganguly, and W. Reusch, *J. Chem. Soc.*, 3313 (1961).

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[19] C. Spangler and R. Feldt, *Chem. Commun.*, 709 (1968).

[20] The authors recognize that [1,5] hydrogen migration probably occurs much more rapidly and at a lower temperature, but that this migration is degenerate for **1** and undetectable without some suitable tracer (deuterium substitution).

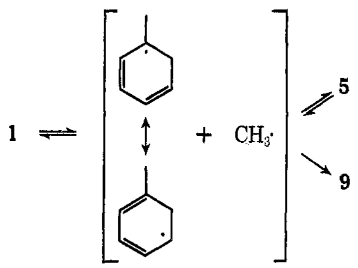
TABLE III

THERMOLYSIS OF 2-METHYL-1,3,5-HEPTATRIENE (4)[a] UNDER FLOW CONDITIONS

Temp, °C	% Recovery	% of total product[b]						
		t,t-4	*c,t*-4	5	6	7	8	10[c]
375	82	66.5	4.1	2.3	Trace	18.7	Trace	6.1
400	82	54.5	3.8	3.2	Trace	28.9	0.6	8.2
425	84	11.7	1.0	13.3	5.7	36.3	10.8	19.2

[a] Initial composition: 84.8% *t,t*; 15.2% *c,t*. [b] Per cent composition of degassed liquid product as in Tables I and II. [c] Compound **10** is a mixture of 5-methyl-3-methylenecyclohexene and 1-methyl-3-methylenecyclohexene, the latter predominating, which could not be totally resolved by glpc.

However, we do not believe that this can explain both the flow and static experiments. If the original methyl migration occurred by a reversible free radical recombination mechanism, then one would expect other alkyl-1,3-cyclohexadiene systems to undergo similar reaction. However, in our previous studies[13,21] on the high-temperature generation and isomerization of methyl-1,3-cyclohexadienes, we found no trace of such contribution.[22] On this basis we conclude that the initial [1,5] methyl migration, commencing at 300°, and subsequent [1,5] hydrogen migrations are sigmatropic in nature and separate from the aromatization reactions.



Experimental Section[23]

5,5-Dimethyl-1,3-cyclohexadiene (1).—4,4-Dimethyl-2-cyclohexenone (12) was prepared by base-catalyzed condensation of methyl vinyl ketone and isobutyraldehyde essentially by the method of Eliel and Lukach.[24]

p-Toluenesulfonylhydrazide[25] (78.6 g, 0.42 mol) and 4,4-dimethyl-2-cyclohexenone (50.0 g, 0.40 mol) were mixed with sufficient THF to yield a homogeneous solution. Two drops of concentrated HCl were added and the resulting yellow solution was refluxed for 6 hr, during which time product began precipitating from solution. Cooling and filtration of the resulting mixture yielded a pale yellow solid. Addition of water to the filtrate yielded additional product (113 g, 97% crude yield, mp 194–198°). Recrystallization of the combined impure product from EtOH–water yielded 4,4-dimethyl-2-cyclohexenone tosylhydrazone (98.0 g, 83%), mp 197–199°.

The tosylhydrazone (131 g, 0.45 mol) in 450 ml of anhydrous ether was treated with 1 mol of methyllithium[26] in ether solution essentially by the method of Dauben, *et al.*,[27] yielding 1: bp 25–26° (20 mm) (20 g, 41%); $n^{26}{}_D$ 1.4550; λ_{max} (isooctane) 257 nm (ϵ 4300); nmr τ 4.1–4.6 (m, 4 H, vinyl), 7.8–8.0 (m, 2 H, allylic), 9.0 (s, 6 H, methyl) [lit.[12] bp 111–114°; $n^{20}{}_D$ 1.4558; λ_{max} (EtOH) 258 nm].

Thermolysis of 5,5-Dimethyl-1,3-cyclohexadiene (1). **A.**—1 (5 g) was added dropwise at a rate of 0.25 ml/min through a 22-mm Pyrex tube packed to a depth of 26 cm with $^1/_{16}$-in. Pyrex helices and externally heated with a Lindberg Hevi-Duty split-tube furnace. A pressure of 20–25 mm was maintained in the system to facilitate rapid removal of the product from the column. The product was trapped in a flask immersed in a Dry Ice–acetone bath and subsequently warmed to room temperature and analyzed immediately by glpc. Gas evolution (a mixture of hydrogen and methane) was complete prior to analysis except for a small quantity of dissolved methane.

B.—Samples of 1 (0.5 ml) were sealed in 8-mm heavy-wall tubes previously washed in distilled water. The samples were degassed and sealed under vacuum in the usual manner. Heating was accomplished by either oil bath (<200°) or air bath (>200°). Temperature control was ±0.1 and ±2°, respectively. Tubes were removed after a specified time interval, quenched rapidly to room temperature, broken, degassed, and analyzed by glpc.

Analysis of Products.—The thermolysis samples both from the flow and static studies were submitted to glpc analysis. Each peak emanating from the chromatograph was trapped in two different ways in V tubes immersed in cooling baths: (1) in isooctane for uv analysis, and (2) in $CDCl_3$ for nmr analysis. Structural assignments were made as follows.

Compound **5**: λ_{max} (isooctane) 260 nm (ϵ *ca.* 4000); nmr τ 4.2 (very broad s, 3 H, vinyl), 7.8–8.3 (m, 3 H, allylic), 8.5 (s, 3 H, $=CCH_3$), 9.0 (d, J = 7 Hz, 3 H, methyl).

Compound **6**: λ_{max} (isooctane) 262 nm (ϵ *ca.* 4000); nmr τ 4.2–4.5 (m, 2 H, vinyl), 4.6 (m, 1 H, vinyl), 7.7–8.5 (m, 3 H, allylic), 8.2 (s, 3 H, $=CCH_3$), 9.0 (d, J = 6 Hz, 3 H, methyl).

Compound **7**: λ_{max} (isooctane) 263 nm (ϵ *ca.* 4000); nmr τ 4.4–4.5 (broad s, 1 H, vinyl), 4.5–4.7 (broad s, 1 H, vinyl), 7.6–8.0 (m, 4 H, allylic), 8.1–8.4 (m, 6 H, 2 $=CCH_3$).

Compounds **8** and **9**: Both **8** and **9** had identical uv and nmr spectra compared to those of authentic *m*-xylene and toluene. Glpc retention times were also identical with those of authentic samples. Although we were unable to totally resolve 5-methyl-3-methylenecyclohexene and 1-methyl-3-methylenecyclohexene, comparison of their crude uv spectra to published[28,29] examples easily identified them (λ_{max} 233 and 235 nm, respectively).

The similar nmr spectra of **5** and **6** were resolved by comparison of the vinyl multiplet splittings with those of authentic 1-methyl-1,3-cyclohexadiene and 2-methyl-1,3-cyclohexadiene. We have found this method to be most reliable in the assignment of positional isomerism in both the 1,3-cyclohexadiene and 1,3,5-hexatriene systems.

1,5-Octadien-4-ol (13).—2-Pentenal (63.0 g, 0.72 mol) dissolved in 200 ml of anhydrous ether was added to an ether solution of allylmagnesium bromide prepared from allyl bromide (145 g, 1.2 mol), magnesium turnings (73 g, 3.0 g-atoms), and 500 ml of ether. Hydrolysis and isolation was carried out in the usual manner, yielding **13** as a colorless liquid (75 g, 83%): bp 66–67° (10 mm); $n^{23}{}_D$ 1.4523; nmr τ 9.0 (t, 3 H, J = 7.5 Hz, methyl), 8.12 (s, 1 H, OH), 7.5–8.2 (m, 4 H, allylic), 5.89 (q, 1 H, J = 6.0 Hz, methine), 3.75–5.15 (broad m, 5 H, vinyl).

Benzyldimethyl-4-(1,5-octadienyl)ammonium Bromide.—1,5-Octadien-4-ol (75 g, 0.69 mol) in 200 ml of anhydrous ether was added dropwise to phosphorus tribromide (81 g, 0.30 mol) over

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[21] C. Spangler and R. Hennis, *J. Org. Chem.*, **36**, 917 (1971).

[22] One of the referees has suggested that Pines and Chen[15] report reversible skeletal isomerization of ethylcyclohexadiene to 1,2- and 1,4-dimethylcyclohexadienes, and that this supports the biallyl-biradical mechanism. On the contrary, we think this supports a reversible free-radical contribution to the mechanism, especially since this occurs *only* at 450° and higher. Our migrations, on the other hand, begin to develop at 300°, a highly significant difference.

[23] Gas–liquid partition chromatography (glpc) was performed with an Aerograph Model 202-1B dual column instrument equipped with a Hewlett-Packard Model 3370A electronic integrator for peak area measurement; dual 15-ft 15% TCEP on 60/80 mesh Chromosorb W columns were utilized for all analyses. Ultraviolet spectra were obtained with a Cary Model 14, nmr spectra with a Varian A60-A using TMS as an internal standard ($CDCl_3$). All spectra were consistent with the assigned structures, and satisfactory C and H analyses were obtained for all compounds.

[24] E. Eliel and C. Lukach, *J. Amer. Chem. Soc.*, **79**, 5986 (1957).

[25] L. Friedman, R. Little, and W. Reichle, *Org. Syn.*, **40**, 93 (1960).

[26] Alfa Inorganics, Inc., Beverly, Mass.

[27] W. Dauben, M. Lorber, N. Vietmeyer, R. Shapiro, J. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, **90**, 4762 (1968).

[28] E. Braude, B. Gofton, G. Lowe, and E. Waight, *J. Chem. Soc.*, 4054 (1956).

[29] A. Thomas and M. Stoll, *Chem. Ind.* (*London*), 1491 (1963).

a 2-hr period with ice-bath cooling. The product mixture was then allowed to stand overnight at room temperature. The mixture was hydrolyzed by adding to a mixture of ice and water, and the resulting mixture was neutralized with saturated sodium carbonate solution. The organic product was extracted with ether, washed with water, and finally dried with anhydrous magnesium sulfate. The ether was removed under reduced pressure, yielding crude 4-bromo-1,5-octadiene (**14**) as a yellow, lachrymatory, unstable liquid (99 g, 87% crude yield).

Crude 4-bromo-1,5-octadiene (99 g, 0.52 mol), *N*,*N*-dimethylbenzylamine (94.5 g, 0.70 mol), and toluene (800 ml) were mixed and allowed to stand overnight at room temperature. The mixture was then heated on a steam cone for 8 hr to complete formation of the quaternary salt, which was then removed by filtration as a crude brown semisolid (126 g, 75%). A small portion was recrystallized from EtOH–EtOAc, mp 141–142°. The remainder of the crude product was dissolved in 600 ml of water, and the aqueous solution was extracted several times with ether to remove suspended organic impurities. The aqueous solution of the salt was then heated to boiling to remove any dissolved ether, yielding a clear yellow solution of benzyldimethyl-4-(1,5-octadienyl)ammonium bromide (**15**).

1,3,5-Octatriene (11).—The above aqueous solution of **15** was added dropwise to a solution of sodium hydroxide (128 g in 800 ml of water) which was undergoing distillation. The organic product was extracted from the distillate with ether, and the ether solution was washed several times with 3 *N* HCl, followed by several water washings. The ether solution was dried with anhydrous magnesium sulfate, filtered, and distilled at reduced pressure, yielding **11** (12 g, 28%): bp 52–53° (23 mm); $n^{23}\mathrm{D}$ 1.5200; $\lambda_{\max}^{\mathrm{iso}}$ 274, 263, 254 nm ($\epsilon \times 10^{-4}$ 3.10, 3.90. 290) [lit.[30] $n^{26}\mathrm{D}$ 1.5170; $\lambda_{\max}$ 274, 264, 254 nm ($\epsilon_{\max} \times 10^{-4}$ 2.72, 3.46, 2.76)]; nmr τ 9.0 (t, 3 H, J = 7 Hz, methyl), 7.6–8.2 (q, 2 H, J = 7 Hz, allylic methylene), 2.8–5.2 (m, 7 H, vinyl). Glpc analysis indicated a mixture of geometric isomers composed of 68% trans,trans- and 32% cis,trans configurations.

2-Methyl-1,3,5-heptatriene (**4**).—*trans*-2-Methyl-1,5-heptadien-4-ol[31] (141 g, 1.12 mol) in 200 ml of anhydrous ether was allowed to react with phosphorus tribromide (120 g, 0.42 mol) in a manner similar to that described above for 4-bromo-1,5-octadiene, yielding 4-bromo-2-methyl-1,5-heptadiene (187 g, 99%) as a crude lachrymatory liquid. The crude bromide (0.99 mol), in 100 ml of DMSO, was added dropwise to a solution of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (1.05 mol) and the reaction mixture was worked up as we have recently described.[32] 2-Methyl-1,3,5-heptatriene (**4**) (32 g, 30%) was obtained as a mixture of geometric isomers composed of 85% *trans,trans*- and 15% *cis,trans*-**4**: bp 68–70° (25 mm); $n^{25}\mathrm{D}$ 1.5263; $\lambda_{\max}$ 272, 262, 252 nm ($\epsilon \times 10^{-4}$ 3.84, 4.68, 3.48); nmr τ 8.0–8.3 (m, 6 H, 2 $CH_3C{=}$), 5.05 (s, 2 H, $CH_2{=}$), 3.6–4.6 (m, 4 H, $CH{=}CH$) (lit.[32] identical with those above).

Thermolysis of 1,3,5-Octatriene, a Typical Run.—1,3,5-Octatriene (2.0 g) was thermolyzed in a manner identical with that described for **1**. At 425° 1.9 g of product was obtained (95% recovery) and submitted to glpc analysis, yielding the following product distribution: 5-ethyl-1,3-cyclohexadiene, 18.6%; 1-ethyl-1,3-cyclohexadiene, 26.2%; *trans,trans*-**11**, 55.0%; *cis,trans*-**11**, 0.2%. No other products were detected. Assignment of structure to the thermolysis products was accomplished by comparison of uv, nmr, and glpc retention times to those of authentic samples.

Thermolysis of 2-Methyl-1,3,5-heptatriene, a Typical Run.—2-Methyl-1,3,5-heptatriene (5.0 g) was thermolyzed in a manner identical to that described for **1**. The results are tabulated in Table III. At 425° 4.2 g of product was obtained (84% recovery) and submitted to glpc analysis.

Registry No.—**1**, 33482-80-3; *trans,trans*-**4**, 17679-94-6; *cis,trans*-**4**, 18304-16-0; **5**, 1453-17-4; **6**, 2050-32-0; **7**, 4573-05-1; *trans,trans*-**11**, 33580-04-0; *cis,trans*-**11**, 33580-05-1; **12**, 1073-13-8; **12** tosylhydrazone, 21195-63-1; **13**, 33580-07-3; **15**, 33580-08-4.

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[30] K. Alder and H. von Brachel, *Justus Liebigs Ann. Chem.*, **608**, 195 (1956).

[31] Chemical Samples Co., Columbus, Ohio.

[32] C. Spangler, R. Eichen, K. Silver, and B. Butzlaff, *J. Org. Chem.*, **36**, 1695 (1971).

Reactions of Dienamines and Dienol Ethers

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The bicyclic morpholine dienamines I and II derived from 4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone and the corresponding 4a-methyl compound reacted on the nitrogen-substituted double bond with a nitrile oxide, an acyl azide, diethyl diazodicarboxylate, and the methylene-donating reagent methylene iodide and diethylzinc. The latter reagent reacted preferentially at the alternative double bond of the corresponding enol ether. Reactions of the dienamines with a sulfonimide occurred at both double bonds while phenylsulfene was regiospecific for the terminal double bond of the activated dienamine systems.

Conjugated dienes, which are substituted by electron-donating or -withdrawing substituents can be expected to react at more than one position. Prediction of a specific preferred reaction site should be governed by considerations of location of maximum charge density in the ground state of the diene, optimum electronic stabilization in the reaction transition state, as well as steric barriers at either reaction stage. Since these factors may or may not act in the same direction and will be differently weighted for different reactions, one would anticipate variations in the preferred position of attack on conjugated dienes. Indeed, lacking suitable analogies, one may find it difficult to predict a preferred reaction site with strong conviction for a given diene and reagent. The present study was undertaken to extend information on such reactions.

It has previously been found that fluorination of dienamine derivatives[1-6] of Δ^4-3-keto steroids leads to 4-fluoro products, whereas the corresponding enol ether[6,7] and enol acetate[8,9] derivatives gave predominantly 6-fluoro products. Halogenation of dienol ethers with *N*-halosuccinimides also led to substitution

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