

The optimized C₂-O₈ bond length is almost as short as that in **3a** (and hence in methyl formate) indicating that there is a partial carbonyl bond in the transition state. Experiments²⁵ with phenyl-2-propanone, again, yield β isotope effects, which are best interpreted in terms of partial re-formation in the rearrangement transition state of the carbonyl character, lost in the addition step (*cf.* Scheme I).

Conclusion

A theoretical treatment of the reaction in Scheme II has yielded results which are in consistent agreement with experiment: the electronic nature of the leaving group affects the energy of the transition state; there is little reorganization in the migrating group; and the lone pair electrons on the hydroxylic oxygen of the

tetrahedral species (**1**) play a part in its rearrangement. These theoretical calculations have the additional advantage of providing information that would be difficult to obtain experimentally. On the basis of the model chosen, the rearrangement in the Baeyer-Villiger reaction is a concerted step, with the transition state occurring before a position 75% along the reaction coordinate. An ion pair intermediate has been excluded.

Acknowledgment. We thank the National Research Council of Canada for financial support and Ms. A. S. Denes for helpful discussions. Mr. Martin Clenman deserves special thanks for his trigonometric analysis of the methyl group coordinates. V. S. expresses her appreciation of a fellowship from the P.E.O. Sisterhood.

Thermal Isomerizations of 7-Alkoxy- and 7-Phenylbicyclo[2.2.1]heptadienes to Cycloheptatrienes¹

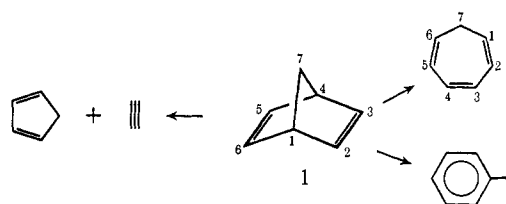
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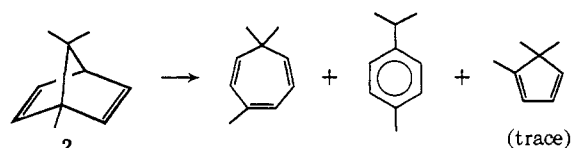
Abstract: 7-Alkoxy- and 7-phenylbicyclo[2.2.1]heptadienes rearrange nearly quantitatively to isomeric cycloheptatrienes. The isomerizations are kinetically first order with rates at 170° that are *ca.* 10⁶ times that of the rearrangement of unsubstituted bicyclo[2.2.1]heptadiene to cycloheptatriene; the isomerization of 7-*tert*-butoxybicyclo[2.2.1]heptadiene has $E_a = 35.5$ kcal/mol, 15 kcal/mol lower than that of unsubstituted bicyclo[2.2.1]heptadiene. The rate of isomerization of 7-*tert*-butoxybicyclo[2.2.1]heptadiene is not affected significantly by the polarity of the solvent, although isomerization in 2-ethoxyethanol furnishes 2-ethoxyethoxy- rather than *tert*-butoxycycloheptatrienes. The significance of these findings is discussed.

This paper describes the effects exerted by 7-alkoxy and 7-phenyl substituents upon the thermal reactions of norbornadiene (bicyclo[2.2.1]heptadiene, **1**). Heating norbornadiene at 320–475° furnishes cycloheptatriene, toluene, cyclopentadiene, and acetylene (Scheme I).^{5–9} Although toluene also is obtained upon heating cycloheptatriene,^{5,10} kinetic evidence suggests that it also can be formed directly from norbornadiene.^{9,10} Not only is the rearrangement to cycloheptatriene greatly accelerated by 7-alkoxy or 7-phenyl substituents, but it becomes the only reaction observed, facilitating its study.

Scheme I



The thermal chemistry of other substituted norbornadienes has been investigated recently. Bornadiene (**2**) furnishes a mixture of products similar to that ob-



tained from the parent system (**1**).^{11,12} However, the methyl substitution does lead to more rapid isomeriza-

(11) M. R. Willcott, III, and C. J. Boriack, *J. Amer. Chem. Soc.*, **90**, 3287 (1968).

(12) M. R. Willcott, III, and C. J. Boriack, *J. Amer. Chem. Soc.*, **93**, 2354 (1971).

(1) This paper is mostly abstracted from ref 2, which contains some additional experimental details. Some of this work was described in a preliminary communication.³

(2) R. K. Lustgarten, Ph.D. Dissertation, The Pennsylvania State University, 1966.

(3) R. K. Lustgarten and H. G. Richey, Jr., *Tetrahedron Lett.*, 4655 (1966).

(4) Author to whom correspondence should be addressed.

(5) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(6) W. M. Halper, G. W. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958).

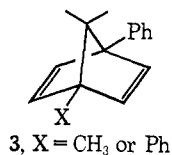
(7) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962).

(8) B. C. Roquette, *Can. J. Chem.*, **42**, 2134 (1964).

(9) W. C. Herndon and L. L. Lowry, *J. Amer. Chem. Soc.*, **86**, 1922 (1964).

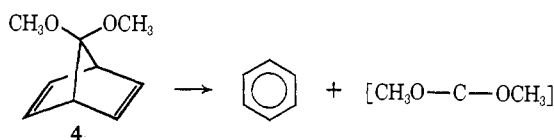
(10) K. N. Klump and J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 130 (1963).

tion. Qualitative observations indicate that the rearrangements to cycloheptatrienes of compounds of structure **3** also are faster than the rearrangement of

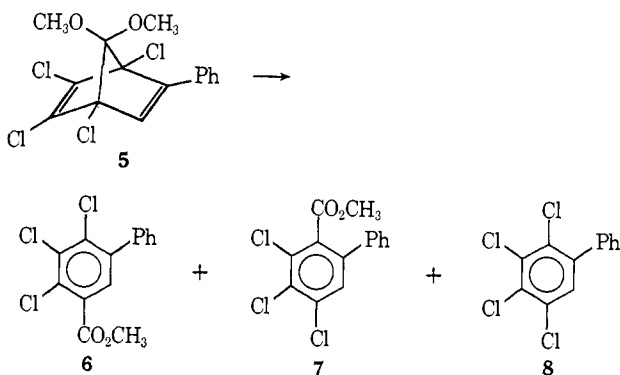


1.¹³ The rapid, base-catalyzed rearrangement of 7-hydroxynorbornadiene to bis(1,3,5-cycloheptatrien-7-yl) ether is almost certainly related to the reactions of **1-3**.¹⁴

Thermal reactions of 7,7-dialkoxy norbornadienes¹⁵⁻²⁰ are even more rapid than those of the monosubstituted norbornadienes investigated in this study. However, the 7,7-dialkoxy compounds characteristically furnish aromatic rather than cycloheptatriene products. The aromatic products are of two types, formed in a ratio that depends on the structure of the reactant and the reaction conditions. Formation of an aromatic product with concomitant loss of the bridge carbon is exemplified by the reaction of **4** which furnishes benzene and



products derived from dimethoxycarbene.¹⁶ Loss of the bridge is analogous to the loss of carbon monoxide from 7-norbornadienones.²³ Other 7,7-dialkoxy norbornadienes yield products which retain the bridge carbon. Esters **6** and **7** are such products, although **5** also furnishes a product (**8**) of bridge loss.¹⁷



(13) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **93**, 5128 (1971).

(14) B. Franzus, W. C. Baird, Jr., R. E. Felty, J. C. Smith, and M. L. Scheinbaum, *Tetrahedron Lett.*, 295 (1971); see also B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **85**, 3902 (1963); **87**, 3423 (1965).

(15) R. W. Hoffmann and H. Häuser, *Tetrahedron*, **21**, 891 (1965).

(16) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Lett.*, 2779 (1965).

(17) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 582 (1966).

(18) R. W. Hoffmann and C. Wünsche, *Chem. Ber.*, **100**, 943 (1967).

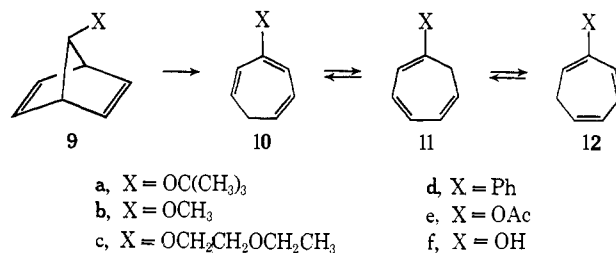
(19) R. W. Hoffmann and R. Hirsch, *Tetrahedron Lett.*, 4819 (1970).

(20) Some of this work has been reviewed briefly.^{21,22} Some earlier studies are cited in ref 15 and 17.

Results

Thermal reactions of solutions of three 7-alkoxy-norbornadienes (**9a-c**) and of 7-phenylnorbornadiene (**9d**) were studied. Product formation usually was monitored by glpc analysis, though in some instances by nmr analysis of reaction mixtures contained in sealed nmr tubes.

Compounds **9b-d** when heated in solution were converted almost quantitatively to isomers **10-12**. The



mixtures, isolated by glpc, were readily identified by their spectral and analytical properties. Compound **9a** also yielded a cycloheptatriene mixture, but its yield (based on disappearance of reactant) decreased slowly during the course of the isomerization. This decrease seemed to be due to a secondary reaction which furnished mainly isobutene and cycloheptadienones (some *tert*-butyl alcohol also was detected); a separate experiment showed that a mixture of **10a-12a** slowly formed the same fragmentation products under the reaction conditions. A particularly careful search for benzene in the products of vapor-phase isomerization of **9a** showed the absence of more than 0.05%.

The compositions of the cycloheptatriene mixtures were observed to change during the course of the reactions. This alteration could be followed particularly readily for the methoxy and phenyl compounds, since absorptions characteristic of each isomer are easily recognized in the nmr spectra of mixtures of **10-12**. Although equilibrium mixtures of the cycloheptatrienes ultimately resulted, it was apparent from the spectra that **10** appeared first, followed by **11**, and finally by **12**.²⁴ The rates of these interconversions (**10** ⇌ **11** ⇌ **12**) were comparable to rates reported for interconversions, by 1,5-hydrogen migrations, of the 3-, 1-, and 2-methoxy-^{25,26} and 3-, 1-, and 2-phenylcycloheptatrienes.^{27,28} Moreover, the sequence of appearance of isomers was that observed when the corresponding 7-substituted cycloheptatrienes (**13**) are isomerized thermally.

(21) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).

(22) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, Chapter 2.

(23) C. F. H. Allen, *Chem. Rev.*, **37**, 209 (1945); J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **93**, 972 (1971).

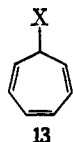
(24) Although **12d** was observed, **12b**, known to be present only in low concentration at equilibrium,^{25,26} was not detected.

(25) (a) E. Weth and A. S. Dreiding, *Proc. Chem. Soc., London*, 59 (1964); (b) T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Jap.*, **38**, 665 (1965).

(26) A. P. ter Borg, E. Razenberg, and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **84**, 1230 (1965).

(27) A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **84**, 245 (1965).

(28) A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 741 (1963).



When **9a** was heated in 2-ethoxyethanol, a mixture of 2-ethoxyethoxycycloheptatrienes (**10c–12c**) rather than of *tert*-butoxycycloheptatrienes (**10a–12a**) was obtained.²⁹ In a control experiment, a mixture of **10a–12a** did not furnish **10c–12c** when heated in 2-ethoxyethanol under the same conditions. Moreover, no **9c** was detected after partial isomerization of **9a** in 2-ethoxyethanol, although the rearrangement rates (Table I) of **9a** and **9c** are such that significant amounts

Table I. Rates of Isomerization of 7-Substituted Norbornadienes^a

Reactant	Temp, °C ^b	Solvent	10 ⁶ k, sec ⁻¹
9a	139.76	Decane	0.728
9a	154.75	Decane	3.37
9a	170.28	Decane	14.3
9a	170.29	Diethylene glycol	
		Dimethyl ether	21.7
9a	170.27	2-Ethoxyethanol	22.83 ± 0.15 ^d
9a	170.6 ± 0.2	Neat	~17 ^e
9a	170.3 ± 0.2	Vapor phase (~60 Torr)	~5 ^e
9b	170.27	Decane	1.83
9c	170.24	2-Ethoxyethanol	2.63
9d	170.28	Decane	2.373 ± 0.002 ^d
9d	170.28	Neat	~2.8 ^f
9e	175 ± 5	Decane ^c	<0.03

^a Unless noted otherwise, concentrations were determined by glpc analysis of 0.3–0.5 *M* solutions. ^b Unless noted otherwise, temperature was controlled to ±0.04° and probably known absolutely to ±0.05°. ^c 5.7 *M* solution. ^d Average of two runs. ^e Slight revision of previously published value.³ ^f Concentration determined by nmr analysis.

of **9c** would accumulate if it was the precursor of the observed product mixture. Therefore, a species that can rapidly exchange alkoxy groups must intervene between **9a** and **10c**. 7-*tert*-Butoxycycloheptatriene (**13**, X = OC(CH₃)₃), a likely candidate, was shown in an independent experiment to rapidly form **10c–12c** under the same reaction conditions.

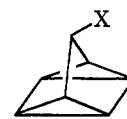
The isomerizations of **9a–d** were studied kinetically. Good first-order kinetic plots were obtained for disappearance of the reactants and were reproducible when duplicate runs were made. The rate constants are listed in Table I. A sample of **9a** to which some quinoline had been added rearranged at about the same rate as a neat sample. Rates for rearrangement of **9a** determined at three temperatures lead to values of $E_a = 35.5$ kcal/mol and $A = 13.6$ ($\Delta H^\ddagger = 34.6$ kcal/mol and $\Delta S^\ddagger = 1.2$ eu).

7-Acetoxy-norbornadiene (**9e**) decomposed slowly to give an intractable tar when heated at 170°. Its rate of rearrangement to cycloheptatrienes could not exceed

(29) The ratio **10c–12c**:**10a–12a** greatly exceeded that expected for a statistical distribution of alkoxy groups between the solvent and cycloheptatrienes. Preponderance of the 2-ethoxyethyl ethers might be favored by a ratio of the rate of 1,5-H migration to that of nucleophilic substitution that is greater for **13c** than for **13a** and by **13c** being favored over **13a** in an equilibrating mixture.

the upper limit given in Table I for its rate of disappearance.³²

The 7-substituted quadricyclic (tetracyclo[2.2.1.0^{2,6}.0^{3,5}]heptyl) ethers **14a** and **14b** also furnished mixtures



14a, X = OC(CH₃)₃
b, X = OCH₃
e, X = OAc
f, X = OH

of cycloheptatrienes when heated at *ca.* 170°. However, the rates of isomerization to their norbornadiene isomers (**9**) were shown by nmr analysis to be faster than the rates of cycloheptatriene formation. For example, the rate of isomerization of a neat sample of **14b** to **9b** was observed to be *ca.* 3.4×10^{-4} sec⁻¹ at 170.6°, and the rates of isomerization of solutions of **14a** were somewhat greater.³³ The failure to observe quadricyclic compounds during isomerization of **9a–d** to the cycloheptatrienes (amounts in excess of 1% would have been detected) has no significance, since the position of equilibrium between norbornadiene and quadricyclane lies far toward norbornadiene.^{34,36}

7-Hydroxynorbornadiene (**9f**) and 7-hydroxyquadricyclane (**14f**) also underwent thermal reactions at *ca.* 170°. Cycloheptatriene and benzaldehyde, in approximately equal amounts, were isolated as products. However, the reaction rates were not reproducible, and the reaction mixtures contained varying, but sometimes significant, amounts of unidentified higher boiling materials. It has recently been reported that, upon treatment with base, 7-hydroxynorbornadiene is rapidly isomerized to bis(1,3,5-cycloheptatrien-7-yl) ether.¹⁴ Moreover, we observed ring cleavage of 7-hydroxynorbornadiene during an attempted alkylation with sodium amide and methyl iodide.² Therefore, it is possible that catalysis by adventitious base intruded into the studies of **9f** and **14f**.

Discussion

The thermal chemistry of 7-substituted norbornadienes **9a–d** differs strikingly from that of the parent

(30) This compound is reported to furnish benzyl acetate on pyrolysis at 375° in a column packed with glass helices or at 225° in the injection inlet of a gas chromatograph.³¹

(31) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(32) Norbornenes substituted at C-7 would not be expected to emulate norbornadienes in so readily forming products containing seven-membered rings. However, an initial step common to that for norbornadienes (for example, cleavage of the C-1–C-7 bond) could lead to new products (for example, due to syn–anti isomerization at C-7). From the failure of a neat sample of *anti*-7-methoxynorbornene to rearrange detectably (>3%) in an experiment at 170°, an upper limit of 1×10^{-7} sec⁻¹ can be set to the rate of any nondegenerate rearrangement.

(33) No effort was made to avoid contamination by transition metals now known to catalyze this transformation: H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967). However, the observed rates are similar to that for the thermal isomerization of quadricyclane to norbornadiene: H. M. Frey, *J. Chem. Soc.*, 365 (1964); see also J. R. Edman, *J. Org. Chem.*, **32**, 2920 (1967).

(34) The heat of formation of quadricyclane has recently been reported to be 10.0 kcal/mol more than that of norbornadiene.³⁵

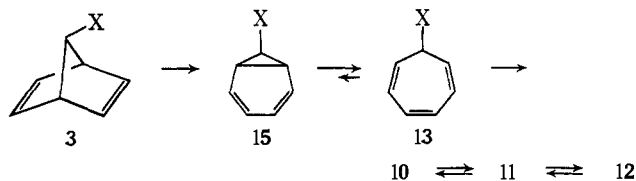
(35) H. K. Hall, Jr., C. D. Smith, and J. H. Baldt, *J. Amer. Chem. Soc.*, **95**, 3197 (1973).

(36) An effort to detect the formation of quadricyclane from refluxing norbornadiene failed: P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958).

hydrocarbon (1). Rearrangement to a cycloheptatriene is accelerated enormously by a 7-alkoxy or 7-phenyl substituent. Comparison of the activation parameters for **9a** ($E_a = 35.5$ kcal/mol, $A = 13.6$ in decane) with those for **1** ($E_a = 50.6$, $A = 14.7$ in the vapor phase)⁹ indicate that introduction of 7-*tert*-butoxy lowers E_a by 15 kcal/mol but effects only a relatively small change in the A factor. Activation parameters were determined only for **9a**. However, the similar rates of isomerization of **9a-d** indicate that E_a values for these compounds also are similar if the reasonable assumption is made that A does not vary significantly. The 7-substituted compounds furnish only cycloheptatrienes, whereas **1** leads to a mixture of products due to similar activation parameters for formation of cycloheptatriene, toluene, and the products of a retrograde Diels-Alder reaction.⁹

Although 7-substituted cycloheptatrienes (**13**) were neither isolated nor detected by spectral observations, there is strong evidence for their intermediacy. The formation of **10c-12c** as the products of rearrangement of **9a** dissolved in 2-ethoxyethanol indicates that some species undergoes alkoxy exchange with the solvent. Independent experiments demonstrated that neither the *tert*-butoxy reactant (**9a**) nor the potential (but unobserved) *tert*-butoxycycloheptatriene products (**10a-12a**) exchange *tert*-butoxy for 2-ethoxyethoxy under the reaction conditions. Therefore, a species that rapidly exchanges its alkoxy group with the solvent must intervene between the reactant (**9a**) and the observed products (**10c-12c**). 7-*tert*-Butoxycycloheptatriene (**13a**) is a likely candidate; a rapid exchange of *tert*-butoxy for other nucleophilic groups is expected because of the large aromatic stabilization of the intermediate cycloheptatrienylium (tropylium) cation. In fact, **13a** was found to rapidly furnish **10c-12c** when solvolyzed in 2-ethoxyethanol at 170°. It is not surprising that 7-substituted cycloheptatrienes (**13**) were not isolated, since isomerizations of **13b** to **10b**^{25,26} and of **13d** to **10d**^{27,28} are so rapid that the concentration of **13** (**b** or **d**) in the reaction solutions never would be sufficiently large to be readily detected by the procedures used in this study. The observation of the sequential formation of **10b(d)**, **11b(d)**, and **12b(d)** from **9b(d)** is consistent with the assumption that **13b(d)** is an initial rearrangement product, since this is the order of formation observed when **13b(d)** is isomerized at lower temperatures.^{24-26,28}

In the most reasonable mechanistic possibilities (discussed below) for these rearrangements, 7-substituted norcaradienes (bicyclo[4.1.0]heptadienes, **15**) are intermediates. However, the norcaradienes (**15**, X = alkoxy



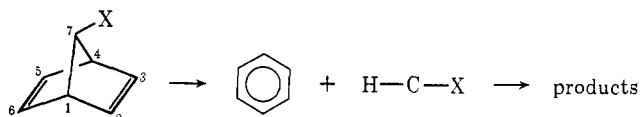
or phenyl) probably are in rapid equilibrium with cycloheptatrienes (**13**),³⁷ which are expected to be consider-

(37) Interconversions of norcaradienes and cycloheptatrienes apparently proceed with only small activation energies. For examples, see the following reports and references cited therein: G. E. Hall and

ably more stable³⁸ (and in turn removed rapidly by rearrangement to **10-12**). Therefore the norcaradienes never should be present in amounts large enough to permit their detection.

The large rate-accelerating effects of 7-alkoxy and 7-phenyl substituents exclude mechanisms for the rearrangements of **9a-d** that do not involve making or breaking a bond at the substituted carbon (C-7).⁴⁴ Although it is conceivable that the 7-substituted norbornadienes rearrange to cycloheptatrienes by a different pathway than that trodden by unsubstituted norbornadiene, this would require the effect of the C-7 substituents to be *even greater than 15 kcal/mol*.

One mechanistic possibility involves simultaneous or stepwise cleavage of the C-1-C-7 and C-4-C-7 bonds to form a carbene and benzene, followed by recombination



to form a norcaradiene. Alkoxy and phenyl substituents could lower ΔH^\ddagger for a symmetry-allowed, concerted (linear cheletropic) process⁴⁵ by stabilizing the carbene or, as discussed below, for the initial cleavage in a stepwise process. However, benzene was not found in the products obtained from **9a-d** in solution or from **9a** in the gas phase, and products derived from alkoxy-carbenes or phe-

J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 2203 (1971); E. Ciganek, *ibid.*, **93**, 2207 (1971); H. Günther, B. D. Tunggal, M. Regitz, H. Scherer, and T. Keller, *Angew. Chem., Int. Ed. Engl.*, **10**, 563 (1971).

(38) Unsubstituted norcaradiene has never been detected in equilibrium with cycloheptatriene. The ΔH_f^\ddagger of unsubstituted norcaradiene has been estimated³⁹ to be ca. 11 kcal/mol more than that⁴⁰ of unsubstituted cycloheptatriene, and it is probable that any difference in ΔS_f^\ddagger is relatively much smaller. The alkoxy or phenyl substituents should not significantly decrease the difference in ΔH_f^\ddagger ; the cyclopropyl ring of **15** is not expected to be stabilized by conjugation with an alkoxy substituent,⁴¹ and conjugation of phenyl (or vinyl) with cyclopropane rings in simpler systems furnishes only negligible stabilization.^{42,43}

(39) W. v. E. Doering and M. R. Willcott, III, unpublished work; M. R. Willcott, III, Ph.D. Dissertation, Yale University, 1963 [referred to in footnote 9 of J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966)].

(40) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, *J. Amer. Chem. Soc.*, **78**, 5469 (1956).

(41) Destabilization of cyclopropyl by oxygen substituents has been predicted: R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); R. Hoffmann and W.-D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971); H. Günther, *Tetrahedron Lett.*, 5173 (1970).

(42) S. W. Staley, *J. Amer. Chem. Soc.*, **89**, 1532 (1967), and references cited therein.

(43) The failure to observe 7-phenylnorcaradiene in equilibrium with 7-phenylcycloheptatriene, even at -100° [H. Günther, M. Görlitz, and H.-H. Hinrichs, *Tetrahedron*, **24**, 5665 (1968)], suggests that the substituted cycloheptatriene is more stable than its norcaradiene isomer by $>3-4$ kcal/mol.

(44) Examples of such mechanisms are (a) rate-determining rupture of the C-1-C-2 bond of norbornadiene⁷ and (b) isomerization (predicted to be orbital-symmetry "forbidden" if concerted)⁴⁵ to a quadricyclane which in turn rearranges to a cycloheptatriene.^{46,47}

(45) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

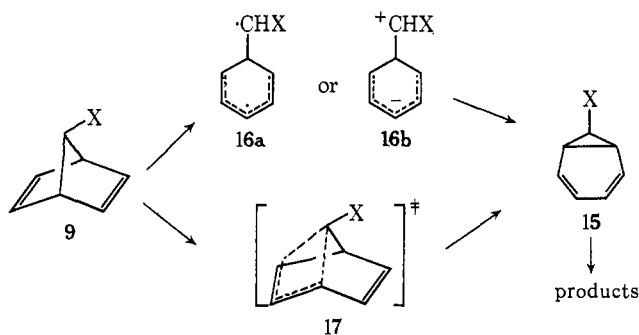
(46) The ready isomerizations of 7-oxa- [H. Prinzbach, P. Vogel, and W. Auge, *Chimia*, **21**, 469 (1967)] and 7-azaquadricyclanes [H. Prinzbach, R. Füchs, and R. Kitzing, *Angew. Chem., Int. Ed. Engl.*, **7**, 67 (1968)] to the corresponding oxepines and azepines, without the intervention of the corresponding norbornadienes, are thought to proceed with conservation of orbital symmetry.⁴⁵

(47) A mechanism for the rearrangement of **9a-d** proceeding through the quadricyclanes can also be eliminated on energetic grounds. The values of $\Delta H^\ddagger = 33$ kcal/mol³³ and $\Delta H_0 = -10$ kcal/mol³⁵ for the transformation of quadricyclane to norbornadiene indicate that ΔH^\ddagger for the reverse process (ca. 43 kcal/mol) is larger than the ΔH^\ddagger observed for the thermal rearrangement of the substituted norbornadienes to cycloheptatrienes.

nylcarbene also were not detected.⁴⁸ Therefore, such a mechanism seems unlikely and would be a possibility only if the association between the carbene and benzene could be so intimate as to preclude any fate other than their recombination.

The thermal rearrangements of **9a-d** can best be rationalized by a pathway which involves cleavage of only one of the bonds to C-7. The remaining discussion will consider such pathways. As an extreme, rate-determining bond cleavage could lead to intermediates resembling **16a** or **16b** (Scheme II). Products would

Scheme II



result from closure of the intermediate to a norcaradiene (**15**), followed by isomerization to cycloheptatrienes. Alternatively, rate-determining bond cleavage could be concerted with formation of the new bond, leading to a transition state represented by **17**. However, except for the extreme where the extent of bond making is comparable to the extent of bond breaking, such a transition state should possess some of the character of **16**.

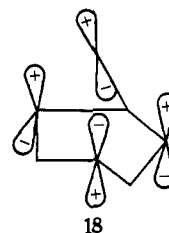
Where do the reactions of **9a-d** (and **1**) belong on the continuum that extends between stepwise pathways in which rate-determining bond cleavage unaccompanied by bond formation leads to formation of an intermediate (**16**) and concerted pathways in which the sum of bonding to C-7 remains so large that the transition state has little of the character of **16**? A demonstration that ΔH for formation of any likely intermediate exceeds ΔH^\ddagger for rearrangement has been used as one means of identifying rearrangements that must proceed with some degree of concertedness. However, reasonable estimates of ΔH_0 for bond cleavages of **1** and **9a-d** give values lower than ΔH^\ddagger for rearrangement to cycloheptatrienes and therefore do not require that the rearrangements have any degree of concertedness.⁴⁹

(48) For example, phenylcarbene might have been expected to react with *n*-decane since this carbene, when generated by photolysis of phenyldiazomethane, inserts into aliphatic methylene groups about as readily as it adds to benzene [C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962)]. This expectation might not be valid if, at the time of product formation, phenylcarbene produced from thermolysis of **9d** did not have the same multiplicity as that produced from photolysis of phenyldiazomethane.

(49) For example, for the cleavage of **9a** to **16a**, the normal dissociation energy (ca. 80 kcal/mol for a primary-secondary carbon-carbon single bond)⁵⁰ will be reduced by (1) release of the ring strain of the norbornadiene system (calculated⁵¹ to be ca. 26 kcal/mol; the cyclohexadienyl radical that is formed would have only a small ring strain), (2) gain of the delocalization energy of the cyclohexadienyl radical (ca. 24 kcal/mol),⁵¹ and (3) stabilization of a radical center by the alkoxy group (ca. 10–20 kcal/mol; see the discussion below). Although each of the parameters used in this estimate is subject to uncertainty, ΔH_0 for cleavage almost certainly is less than ΔH^\ddagger for rearrangement to a cycloheptatriene.

(50) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

An observation of a stereochemical outcome that is not orbital symmetry allowed has been used as one means of identifying rearrangements that proceed by stepwise pathways. A concerted 1,3-sigmatropic rearrangement, suprafacial with respect to an allylic system, is orbital symmetry "allowed" if, as indicated in **18**, the



new bond forms with inversion of configuration at the migrating carbon (C-7).^{45,52} An elegant experiment with an isotopically labeled, chiral bornadiene (**2**) has shown that the stereochemistry at C-7 is lost in the isomerization to trimethylcycloheptatriene.¹² This result is consistent with a pathway involving an intermediate (**16**), since such a pathway lacks any necessary stereochemical consequence. However, this stereochemical result cannot be regarded as conclusive evidence for a stepwise pathway, since it has been suggested recently that in some systems concerted 1,3-sigmatropic rearrangements with orbital symmetry forbidden stereochemistries may be of lower energy than stepwise pathways.⁵³ In fact, studies of 1,3-sigmatropic rearrangements in a variety of other systems have found stereochemistries ranging from completely orbital symmetry allowed to almost completely orbital symmetry forbidden.^{54–56} It should be noted that stereochemistry can be controlled by the maintenance of only relatively weak bonding at a center during the course of a reaction. Therefore, even in reactions which are highly stereospecific, the degree of synchrony could be small, cleavage of a bond to the migrating carbon being almost complete before formation of a new bond has progressed very far.

Because of the large substituent effects, we think it likely that **9a-d** rearrange by pathways at or close to the "stepwise" extreme of the stepwise-to-concerted continuum. Large stabilizing effects of alkoxy or phenyl groups at C-7 are reasonable for transition states resembling diradical **16a** or zwitterion **16b**. For sigmatropic rearrangements that follow concerted pathways,

(51) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 241 (1966); R. Shaw, F. R. Cruickshank, and S. W. Benson, *J. Phys. Chem.*, **71**, 4538 (1967).

(52) For steric reasons, the rearrangement of a norbornadiene must be suprafacial with respect to the cyclohexadienyl ring.

(53) For example, see J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972); J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972); N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 1206 (1973).

(54) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5503 (1967); **92**, 1096 (1970); W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969); W. R. Roth and K. Enderer, *Justus Liebigs Ann. Chem.*, **733**, 44 (1970); P. H. Mazzocchi and H. J. Tamburin, *J. Amer. Chem. Soc.*, **92**, 7220 (1970); R. C. Cookson and J. E. Kemp, *J. Chem. Soc., Chem. Commun.*, 385 (1971); W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, **27**, 2005 (1971); R. A. Clark, *Tetrahedron Lett.*, 2279 (1971); J. S. Swenton and A. Wexler, *J. Amer. Chem. Soc.*, **93**, 3066 (1971); F.-G. Klärner, *Tetrahedron Lett.*, 3611 (1971); J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 269 (1973); W. von E. Doering and E. Birladeanu, *Tetrahedron*, **29**, 499 (1973); J. A. Berson and R. W. Holder, *J. Amer. Chem. Soc.*, **95**, 2037 (1973); J. E. Baldwin and R. H. Fleming, *ibid.*, **95**, 5249, 5256, 5261 (1973).

(55) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969).

(56) F. Scheidt and W. Kirmse, *J. Chem. Soc., Chem. Commun.*, 716 (1972).

we guess that effects of the substituents could be large, only if the sum of the bonding to the migrating carbon became sufficiently small that the transition states had much of the character of **16**.^{57,58}

Would the intermediate resemble (singlet) diradical **16a** or zwitterion **16b**? Unless the C-7 and cyclohexadienyl orbitals of **16** were orthogonal, their overlap could permit a singlet intermediate to be a hybrid of **16a** and **16b**.^{59,60} The abilities of phenyl and alkoxy substituents to stabilize cationic centers⁶¹ are sufficient in magnitude to account for the large rate accelerations caused by these substituents if their effects are to stabilize a positive charge developing at C-7 during formation of zwitterionic intermediate **16b**. Nevertheless, because the rates of rearrangement of **9a** in solvents of different polarities are so similar, we prefer at present to assume that there is little separation of charge in the transition state and that the transition state and any intermediate resemble **16a** much more than **16b**.⁶² Of course, evidence for formation of species which behave as expected for zwitterions has been found in cleavages of favorably substituted carbon-carbon bonds.^{63,64} However, in instances where the effect of solvent variation has been studied,^{63,65} the rates of such cleavages increased significantly with increasing solvent polarity. As an incidental observation, it was noted that the rate of rearrangement of **9a**, although similar in several solvents, was slower in the gas phase (see Table I).⁶⁶ This observation is of interest, particularly in relation to recent reports⁶⁷ for another isomerization of differences

between gas phase and solution rates and products, but discussion should await further experiments.

Is the stabilization that phenyl and alkoxy afford to free radicals sufficient to explain the large rate accelerations caused by these substituents if their effects are to utilize a radical center developing at C-7 during a rate-determining formation of diradical **16a**? The stabilization afforded by α -phenyl to alkyl radicals (*ca.* 18⁶⁸ and 19⁷⁰ kcal/mol to the methyl and ethyl radicals, respectively) is sufficient to explain the kinetic observations, even allowing for the probability that stabilization of a transition state will be less than that of a fully formed radical, since neither bond scission nor alignment of the substituent for maximum stabilization would be complete. However, even considering the sometimes sizable errors, most of the values reported for stabilization of radicals by α -oxygen substituents are lower than the stabilization by alkoxy of the transition state for rearrangement. Although the largest reported estimates of the stabilization afforded by α -methoxy to the methyl radical are 22⁷¹ and 23⁷² kcal/mol, other values⁷³ are *ca.* 11 kcal/mol, and stabilization⁷⁴ by alkoxy of a cyclic secondary radical probably is even less. An alkoxy substituent might be expected to have approximately the same ability to stabilize a radical as would a hydroxyl substituent.⁷⁵ Although one value of 20 kcal/mol has been reported⁷² for stabilization by an α -hydroxyl substituent of the methyl radical, other values have been *ca.* 11 kcal/mol for the methyl radical,⁷⁶ *ca.* 7 kcal/mol for the ethyl radical,⁷⁷ and even less⁷⁸ for more stable radicals.

The slow rate of conversion of 7-acetoxynorbornadiene (**9e**) to intractable material indicates that the maximum rate of rearrangement to a cycloheptatriene must be far less than the rates of the 7-alkoxynorbor-

(57) We know of no systematic studies of effects of similarly placed substituents on rearrangements for which concerted sigmatropic pathways can be considered well established to use as guidelines.⁶⁸ Large rate effects of anti 5-substituents have been observed in stereoselective rearrangements of anti 5-substituted bicyclo[2.1.1]hexanes.^{65,66} However, until the syn isomers are studied, the significance of this stereoselectivity is unknown.

(58) Pentacoordinate carbons also are found in other situations, for example, in bridged carbonium ions (and the related intermediates or transition states for 1,2-migration of alkyl groups in carbonium ions) and in the transition states of bimolecular, nucleophilic (S_N2) or electrophilic (S_E2) substitutions. These pentacoordinate carbons must bear some resemblance to those carbons migrating with retention or with inversion of configuration in concerted sigmatropic rearrangements. However, enough other differences exist, that it seems hazardous to assume that substituent effects might be of comparable magnitude.

(59) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(60) E. W. Yankee, F. D. Badaea, N. E. Howe, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 4210 (1973); E. W. Yankee, B. Spencer, N. E. Howe, and D. J. Cram, *ibid.*, **95**, 4220 (1973); N. E. Howe, E. W. Yankee, and D. J. Cram, *ibid.*, **95**, 4230 (1973); A. B. Chmurny and D. J. Cram, *ibid.*, **95**, 4237 (1973).

(61) For example, ref 71 and R. W. Taft, R. H. Martin, and R. W. Lampe, *J. Amer. Chem. Soc.*, **87**, 2490 (1965).

(62) Evidence for radical intermediates during 1,3-sigmatropic rearrangements in other systems includes the observation of enhanced emission and absorption in the pmr spectrum of a product: J. E. Baldwin and J. E. Brown, *J. Amer. Chem. Soc.*, **91**, 3647 (1969).

(63) For example, substituted cyclopropanes⁶⁹ and norbornadienes.¹⁷

(64) Cyclopropanones [S. S. Edelson and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2770 (1970), and references cited therein] and three-membered rings containing heteroatoms [R. Huisgen and H. Mäder, *ibid.*, **93**, 1777 (1971); A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *J. Chem. Soc., Chem. Commun.*, 1192 (1971); and references cited in these papers] are other examples.

(65) Large solvent effects have also been noted on the rates of cycloadditions thought to proceed by formation of dipolar intermediates: R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969); P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

(66) The rate of rearrangement of **9a** in the gas phase has been more exactly measured [D. W. Shull, unpublished work] and found to be $6.2 \times 10^{-5} \text{ sec}^{-1}$ at 169.5°. A simultaneous determination at the same temperature of the rate in decane gave $12.7 \times 10^{-5} \text{ sec}^{-1}$.

(67) J. I. Brauman, W. E. Farneth, and M. B. D'Amore, *J. Amer. Chem. Soc.*, **95**, 5044 (1973); G. D. Andrews, M. Davalt, and J. E. Baldwin, *ibid.*, **95**, 5045 (1973).

(68) From dissociation energies of the bonds of toluene, ethylbenzene, and *n*-propylbenzene whose cleavage leads to the benzyl radical.⁶⁹

(69) The stabilization energies cited are the differences between the bond dissociation energies of compounds producing the phenyl or alkoxy substituted radicals and of related compounds (taken from ref 50) producing the corresponding unsubstituted radicals.

(70) From the bond dissociation energy for cleavage of isopropylbenzene to the α -phenylethyl radical.⁶⁹

(71) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 1353 (1966).

(72) R. H. Shapiro and J. Turk, *Org. Mass Spectrom.*, **2**, 1067 (1969).

(73) Stabilization energies of 11.1 and 12.9 [L. F. Loucks and K. J. Laidler, *Can. J. Chem.*, **45**, 2785 (1967)], 10.7 [F. R. Cruickshank and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 381 (1969)], and *ca.* 8 kcal/mol [M. A. Haney and J. L. Franklin, *Trans. Faraday Soc.*, **65**, 1794 (1969)].⁶⁹

(74) The bond dissociation energy of an α C-H bond of tetrahydrofuran is *ca.* 1.5 kcal/mol less than that of a C-H bond of cyclopentane: F. R. Cruickshank and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 1289 (1969). The stabilization probably would be *ca.* 5 kcal/mol if, as in the other examples, hydrogen and alkoxy (rather than alkyl and alkoxy) substituents could be compared.

(75) In fact, esr spectra of α -alkoxy and α -hydroxy radicals show evidence for considerable and comparable absorption of the spin density by the substituents [for example, R. O. C. Norman and B. C. Gilbert, *Advan. Phys. Org. Chem.*, **5**, 53 (1967); R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966); A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., A*, 124 (1971)].

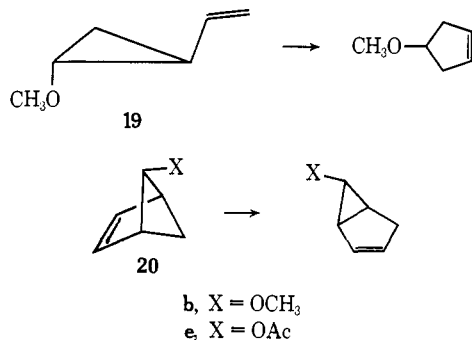
(76) Stabilization energies of *ca.* 12 [E. Buckley and E. Whittle, *Trans. Faraday Soc.*, **58**, 536 (1962)], *ca.* 13.5 [I. P. Fisher and E. Henderson, *Trans. Faraday Soc.*, **63**, 1342 (1967)], and 8.5 kcal/mol [F. R. Cruickshank and S. W. Benson, *J. Phys. Chem.*, **73**, 733 (1969)].⁶⁹

(77) Stabilization energies of *ca.* 8 [A. M. Tarr and E. Whittle, *Trans. Faraday Soc.*, **60**, 2039 (1964)] and 5.0 kcal/mol [Z. B. Alfassi and D. M. Golden, *J. Phys. Chem.*, **76**, 3314 (1972)].⁶⁹

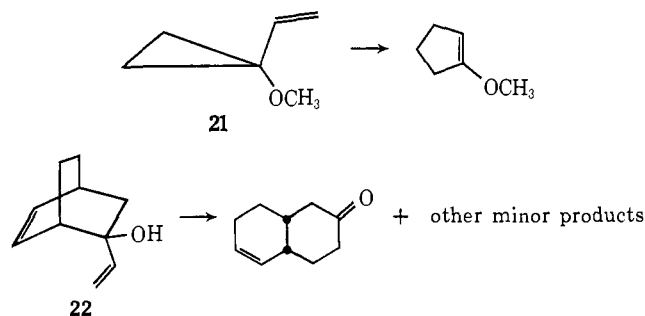
(78) Stabilization energies of 4.2 kcal/mol for the isopropyl radical [R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3480 (1966)], and 3 kcal/mol for the allyl radical [Z. B. Alfassi and D. M. Golden, *Int. J. Chem. Kinet.*, **5**, 295 (1973)].⁶⁹

nadienes.⁷⁹ The smaller effect of acetoxy would be consistent with stabilization by the substituent of the cationic center of **16b**. However, we have not found data that permit comparing the effects of acetoxy and alkoxy on radical centers.

Effects of comparably placed alkoxy or hydroxy substituents on rates of sigmatropic rearrangements in other systems span a wide range. The methoxyl groups at the migrating carbon in **19**^{80,81} and **20b**⁸² lower E_a for the



1,3-sigmatropic rearrangements by *ca.* 11 kcal/mol, a value approaching the magnitude noted for alkoxy in this study. However, the substituents in **21**^{80,81,83} and **22**⁸⁴ lower E_a for thermolysis by only 5 and 2.4 kcal/mol,



respectively. The negligible effect of the substituent on the 3,3-sigmatropic rearrangement of **22** is particularly striking, since the rearrangement of this compound is thought to be stepwise rather than concerted.⁸⁴ The much larger effect of α -oxygen in system **9** than in **21** and **22** could be attributed to a substantially more polar transition state for rearrangement of **9**. However, we think this unlikely since the dependence on solvent polarity is negligible. The different effects of α -oxygen also could be attributed to more concertedness in the rearrangements of systems **21** and **22**, but we see no reason to expect this. Perhaps the smaller magnitudes of the substituent effects in **21** and **22** reside in such factors as a particularly large inhibition to simultaneous conjugation of both the vinyl and oxygen substituents or a larger

(79) It also has been observed that acetoxy is less effective than methoxy in promoting rearrangement of **20**. (ΔH^\ddagger for rearrangement of **20e** in decane⁸⁵ is 3 kcal/mol greater than that for **20b**⁸⁶ in carbon tetrachloride.)

(80) J. M. Simpson and H. G. Richey, Jr., *Tetrahedron Lett.*, 2545 (1973).

(81) Part of the rate-increasing effect of methoxyl in **19** or in **21** could be due to destabilization⁴¹ of these compounds by the oxygen.

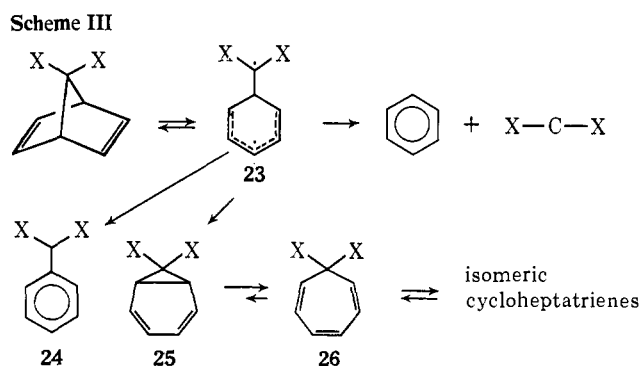
(82) The value⁸⁶ for the substituted system in carbon tetrachloride is compared with that [H. M. Frey and R. H. Hopkins, *J. Chem. Soc. B*, 1410 (1970)] for the parent hydrocarbon in the gas phase.

(83) It is estimated that 1-trimethylsiloxy substituents in several vinylcyclopropanes lower E_a for rearrangement to cyclopentenes by at least 9 kcal/mol: B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 5311 (1973).

(84) J. A. Berson and E. J. Walsh, Jr., *J. Amer. Chem. Soc.*, **90**, 4730 (1968).

fraction of (chemically unproductive) reversion of intermediates⁸⁵ to the reactants.

A rate-determining step involving thermal cleavage of one bond to C-7 also is consistent with most observations that have been made about thermal rearrangements (except retrograde Diels–Alder reactions) of other norbornadienes. Rates depend markedly on C-7 substitution, decreasing in the sequence oxo > dialkoxy > phenyl, alkoxy > dialkyl > hydrogen. Retrograde Diels–Alder reactions should not be sensitive to the nature of the C-7 substitution; the failure to observe this reaction, except in the least reactive (dialkyl and unsubstituted) systems, presumably is due to greatly increased rates of the process that leads ultimately to cycloheptatrienes. Cleavage to intermediates that behave as zwitterions is favored by appropriate (*e.g.*, 7,7-dialkoxy) substitution of the norbornadiene and by polar solvents. However, as is thought to be the case in this work, cleavage probably more commonly results in the formation of diradical species having little polarity. A diradical intermediate (**23**) can (Scheme III) lose a carbene, rearrange to an aromatic system (**24**),



or collapse to a norcaradiene (**25**) followed by isomerization to cycloheptatrienes. Fragmentation is important for those systems (dialkoxy or oxo) that can produce particularly stable carbenes.⁸⁶ The balance between the production of substituted toluenes (**24**) and cycloheptatrienes favors cycloheptatrienes much more in the reactions of 7-alkoxy- and 7-phenylnorbornadiene than of norbornadiene (**1**) or bornadiene (**2**). Apparently with increasing stabilization of **23** by substituents, E_a for the bond formation producing **25** becomes significantly less than E_a for the hydrogen migration producing **24**.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 spectrometer, using tetramethylsilane as an internal standard. Reported splittings are approximate (± 1 Hz), unless noted otherwise. Infrared spectra were recorded on a Beckman IR-5A spectrometer and calibrated with a polystyrene film. Boiling points are uncorrected. Final distillations were performed on a Nester–Faust “semi-micro” (0.25 in. \times 18 in.) stainless steel

(85) It is unlikely that norbornadienes or intermediates of structure **16** (or **23**) are re-formed at a significant rate (compared to the rate of rearrangement to a cycloheptatriene) once a reaction has proceeded to the norcaradiene stage. Even though norcaradienes cannot be much lower in energy than norbornadienes (cycloheptatrienes are only *ca.* 7 kcal/mol more stable than norbornadienes, and norcaradienes generally are significantly less stable^{38,43} than cycloheptatrienes⁴⁰), the activation energies for conversion to the more stable cycloheptatrienes certainly are smaller than for reconversion to the norbornadienes.

(86) See the discussion in ref 21.

spinning-band column unless noted otherwise. Microanalyses were performed by Midwest Microlab, Inc. Melting points were taken in open capillary tubes in a Hershberg apparatus using total immersion thermometers. A single column, thermal conductivity, Nittany Scientific Service, Inc., instrument was used for glpc analyses and preparative separations. The following columns were used: A, 20% Silicone Fluid XF-1150, on Chromosorb P (30–60 mesh), 0.25 in. \times 8 ft; B, 21% Silicone Oil DC-550 on Gas Chrom P (60–60 mesh), 0.25 in. \times 5 ft; C, 20% Apiezon M on Gas Chrom P (60–80 mesh), 0.25 in. \times 8 ft. A description of the conditions used for analytical glpc determinations is given in Table II; preparative glpc's were performed with the same columns, but usually at somewhat higher temperatures.

Materials. 7-*tert*-Butoxynorbornadiene (**9a**) was purchased from Frinton Laboratories, Inc., and redistilled. 7-Phenylnorbornadiene⁸⁷ (**9d**), 7-acetoxynorbornadiene (**9e**),⁸¹ 7-hydroxynorbornadiene (**9f**),⁸¹ and *anti*-7-hydroxynorbornene⁸¹ were prepared as previously reported. Solvents for kinetic measurements were purified as follows. Decane (Eastman "Technical" grade) was distilled, and the center cut, bp 54° (8 Torr), was collected. Diethylene glycol dimethyl ether (Ansol Co.) was stirred with ferrous sulfate, dried over calcium hydride, and distilled from lithium aluminum hydride at reduced pressure. A center cut, bp 50° (7 Torr), was collected. 2-Ethoxyethanol (Eastman "White Label") was stirred with ferrous ammonium sulfate, dried over magnesium sulfate, and distilled. A center cut, bp 83° (119 Torr), was collected.

7-Methoxynorbornadiene (9b). A solution of 22.45 g of **9a** (0.147 mol), 14 ml of concentrated sulfuric acid, and 200 ml of methanol was stirred at 30° for 5 hr. The solution was poured onto 150 g of ice and extracted with four 25-ml portions of methylene chloride. The extract was washed successively with saturated sodium bicarbonate and sodium chloride solutions, filtered through anhydrous magnesium sulfate, and dried (Na₂SO₄). After concentration at reduced pressure, distillation afforded 7.95 g (0.065 mol, 54%, when corrected for 4.30 g (0.028 mol) of recovered **9a**) of **9b**, bp 45° (14 Torr) [lit. 74–75° (56 Torr),⁸⁸ 44 (13)⁸⁹]; ir (CCl₄) 1110 cm⁻¹ (C–O–C); nmr (CCl₄) τ 3.41 (t, 2, $J = 3$ Hz, =CH–), 3.58 (m, 2, =CH–), 6.53 (m, 3, >CHO– and >CH), and 6.90 (s, 3, –CH₃).

7-(2-Ethoxyethoxy)norbornadiene (9c). A solution of 2.55 g (0.017 mol) of **9a**, 5.19 g (0.059 mol) of 2-ethoxyethanol, and 0.25 ml of concentrated sulfuric acid was stirred at 25° for 23 hr. After addition of 10 ml of 10% sodium hydroxide solution, the reaction mixture was extracted with five 15-ml portions of ether. The combined ether layers were washed with three 2-ml portions of water and three 5-ml portions of saturated sodium chloride solution and dried (MgSO₄). After concentration, distillation through a 10-cm Vigreux column gave 1.14 g (0.0063 mol, 37%, when corrected for 0.07 g (0.00046 mol) of recovered **9a**) of **9c**, bp 58° (1.1 Torr): ir (CCl₄) 1115 cm⁻¹ (C–O–C); nmr (CCl₄) τ 3.49 (t, 2, $J = 1$ Hz, =CH–), 3.63 (t, 2, $J = 1$ Hz, =CH–), 6.62 (m, 9, –CH₂–, >CHO–, and >CH), and 8.89 (t, 3, $J = 4$ Hz, –CH₃).

Anal. Calcd for C₁₁H₁₆O₂: C, 73.30; H, 8.95. Found: C, 73.41; H, 9.02.

7-*tert*-Butoxycycloheptatriene (13a). A solution of 6.2 g (0.064 mol) of potassium *tert*-butoxide in 30 ml of *tert*-butyl alcohol was added in one portion to a dispersion of 11.4 g (0.064 mol) of tropylium fluoroborate⁹⁰ in 190 ml of dry *tert*-butyl alcohol. The mixture was stirred at room temperature for 1 hr. Water (500 ml) was added and the mixture was extracted with four 20-ml portions of pentane. The combined organic layers were washed with saturated sodium chloride solution and dried (Na₂SO₄). After concentration, vacuum distillation afforded 0.3 g of material, bp 33° (0.9 Torr): ir (CCl₄) 1080 cm⁻¹ (C–O–C); nmr (neat) τ 3.44 (m, 2, =CH–), 4.00 (m, 2, =CH–), 4.62 (m, 2, =CH–), 6.52 (m, 1, >CHO–), and 8.72 (s, 9, –CH₃). The ir and nmr spectra also showed additional absorptions that corresponded to those expected for contamination by ca. 15% of benzaldehyde. Since attempted purification by glpc (column A, 175°) yielded only *tert*-butyl alcohol and benzaldehyde, the distillate was used without further purification.

***anti*-7-Methoxynorbornene.** A solution of 0.808 g (0.0074 mol) of *anti*-7-hydroxynorbornene⁸¹ was added over a 10-min period to a stirred mixture of 0.77 g (0.032 mol) of sodium hydride in 30 ml of

benzene. The mixture was stirred at 25° for 3 hr. Methyl iodide (3.0 ml, 0.049 mol) was added over a 10-min period and the solution was stirred at ca. 50° for 12 hr. The reaction mixture was poured into an aqueous sodium sulfate solution, the layers were separated, and the aqueous layer was extracted with ether. The extracts were washed with three 7-ml portions of water and one 7-ml portion of saturated sodium chloride solution and dried (MgSO₄). After concentration by distillation at reduced pressure, short-path distillation yielded 0.363 g (0.0029 mol, 39%) of *anti*-7-methoxynorbornene, bp 46° (22 Torr): ir (CCl₄) 1110 cm⁻¹ (C–O–C); nmr (CCl₄) τ 4.05 (t, 2, $J = 2$ Hz, =CH–), 6.80 (s, 3, –CH₃), 7.08 (m, 1, >CHO–), 7.48 (m, 2, >CH), 8.30 (m, 2, >CHH), and 9.10 (m, 2, >CHH).

Anal. Calcd for C₈H₁₂O: C, 77.38; H, 9.74. Found: C, 77.65; H, 9.63.

7-*tert*-Butoxyquadracyclane (14a).⁹¹ The irradiation apparatus used in this preparation consisted of a cylindrical reaction vessel fitted with a small water-cooled condenser at the top and an inner quartz immersion tube containing a Hanovia 83A-1 mercury arc lamp (maximum output, 3.1 W at 2537 Å). The effective volume of the apparatus was about 300 ml. Reaction solutions were stirred magnetically, and the entire apparatus was immersed in a circulating cold-water bath. Prior to each use, the apparatus was washed with an acidic dichromate solution and then thoroughly with water.

A solution of 11.1 g (0.068 mol) of freshly distilled **9a** in 240 ml of spectral-grade isooctane was irradiated for 209 hr.⁹² The solution was filtered to remove the small amount of precipitate which formed during the reaction, washed with five 10-ml portions of saturated silver nitrate solution and three 10-ml portions of water, and dried (MgSO₄). After concentration, distillation afforded 6.7 g (0.041 mol, 60%) of **14a**, bp 59° (2.5 Torr): ir (CCl₄) 1095 cm⁻¹ (C–O–C); nmr (CCl₄) τ 5.36 (t, 1, $J = 1$ Hz, >CHO–), 8.30 (m, 2, >CH), 8.73 (s, 9, –CH₃), and 8.82 (m, 4, >CH).

Anal. Calcd for C₁₁H₁₆O: C, 80.44; H, 9.82. Found: C, 80.50; H, 9.89.

7-Acetoxyquadracyclane (14e).⁹¹ The apparatus and procedure for the preparation of **14e** from **9e** were as described above for the preparation of **14a**. Irradiation of a solution of 12.0 g (0.080 mol) of freshly distilled **9e** in 250 ml of isooctane was essentially complete after 20 hr. After concentration by distillation through a 10-cm Vigreux column, distillation gave 8.4 g (0.056 mol, 70%) of **14e**, bp 45–49° (1 Torr). The product crystallized on standing, mp 33–35°: ir (CCl₄) 1740 cm⁻¹ (C=O); nmr (CS₂) τ 4.58 (t, 1, $J = 2$ Hz, >CHO–), 8.07 (s, 3, –CH₃), 8.39 (m, 2, >CH), and 8.52 (m, 4, >CH). In other experiments, this material could be obtained in sufficiently pure form for further preparative work by crystallization (induced by a seed crystal) from the residue remaining after removal of the isooctane.

Anal. Calcd for C₉H₁₀O₂: C, 71.98; H, 6.71. Found: C, 72.16; H, 6.91.

Addition of a few milligrams of benzophenone to the irradiation solutions did not significantly alter the yield or duration of the reaction.

7-Hydroxyquadracyclane (14f).⁹¹ A mixture of 14.3 g (0.095 mol) of **14e**, 5.0 g (0.13 mol) of sodium hydroxide, and 70 ml of water was stirred for 2 hr at 35°. The reaction mixture was extracted with three 20-ml portions of ether. The combined ether extract was washed with three 5-ml portions of saturated sodium chloride solution and dried (Na₂SO₄). After concentration by distillation through an 8-in. column packed with glass helices, distillation afforded 5.8 g (0.054 mol, 56%) of **14f**, bp 53° (2.8 Torr): ir (CCl₄) 3590, 3400 cm⁻¹ (O–H); nmr (CS₂) τ 5.35 (s, 1, >CHO–), 7.26 (s, 1, –OH), 8.42 (m, 2, >CH), and 8.72 (m, 4, >CH).

Anal. Calcd for C₇H₈O: C, 77.75; H, 7.46. Found: C, 77.56; H, 7.38.

An attempt to convert **14e** to **14f** by reaction with methylmagnesium iodide using the procedure employed by Story⁸¹ to convert **9e** to **9f** furnished **9f** rather than **14f**.

7-Methoxyquadracyclane (14b). A mixture of 8.05 g (0.075 mol) of **14f** and 3.22 g (0.082 mol) of sodium amide in 200 ml of benzene was stirred for 4 hr at ca. 60° under a dry nitrogen atmosphere. After stirring for 2 hr longer at 30°, a solution of 12.5 g (0.088 mol) of methyl iodide in 40 ml of benzene was added over a 15-min period. The mixture was refluxed for 2 hr and allowed to stand over-

(87) P. R. Story and S. R. Fahrenholtz, *J. Org. Chem.*, **28**, 1716 (1963).

(88) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, **84**, 4876 (1962).

(89) G. Wittig and J. Otten, *Tetrahedron Lett.*, 601 (1963).

(90) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(91) This procedure was developed by Buckley [H. G. Richey, Jr., and N. C. Buckley, *J. Amer. Chem. Soc.*, **85**, 3057 (1963)].

(92) Subsequent experimentation showed that the reaction time could be decreased if the quartz immersion tube was cleaned occasionally during the reaction.

Table II. Glpc Conditions for Kinetic Analyses

Substrate	Solvent	Internal standard	Column, T ($^{\circ}\text{C}$) (He flow, ml/min)	Retention times, ^a min		
				Std	Substrate	Products
9a	Decane	Mesitylene	A, 116 (66)	9	13	23, 28, 31
9a	Diethylene glycol Dimethyl ether	Decane	A, 106 (70)	4.5	12	22, 26, 30
9a	2-Ethoxyethanol	Dodecane	B, 126 (70)	16	24	<i>b, c</i>
9b	Decane	Dodecane	A, 118 (70)	6.5	10.5	16.5, 19.5 ^d
9c	2-Ethoxyethanol	Tridecane	B, 172 (56)	11	15	27 ^{e, e}
9d	Decane	Tridecane	C, 190 (128)	10.5	17	30 ^e

^a Except for 2-ethoxyethanol, which eluted between the substrate and products, the solvent was eluted prior to the standard. ^b Not determined. ^c Mixture of 10c–12c. ^d The product isomers appeared in only two peaks. ^e The product isomers appeared in only one peak.

night at room temperature. Water (100 ml) was added, the layers were separated, and the aqueous layer was extracted with four 10-ml portions of ether. The combined organic layers were washed with three 10-ml portions of saturated sodium chloride solution and dried (CaCl_2). After concentration at reduced pressure, distillation afforded 3.75 g (0.031 mol, 56% when corrected for 2.15 g (0.020 mol) of recovered 14f) of 14b, bp 32–35 $^{\circ}$ (2.5 Torr); ir (CCl_4) 1110 cm^{-1} (C–O–C); nmr (neat) τ 5.56 (t, 1, $J = 2$ Hz, $>\text{CHO}-$), 6.60 (s, 3, $-\text{CH}_3$), 8.33 (m, 2, $>\text{CH}$), and 8.58 (m, 4, $>\text{CH}$).

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}$: C, 78.65; H, 8.25. Found: C, 78.80; H, 8.21.

Thermal Isomerizations. Except when noted otherwise, glpc conditions and retention times are given in Table II.

(1) *7-tert-Butoxynorbomadiene* (9a). (a) **Neat or Decane Solution.** Pure 9a was heated at about 170 $^{\circ}$ for 4 hr. Distillation afforded, in addition to starting material, a mixture, bp 77 $^{\circ}$ (8 Torr), of three compounds (see entry 1 of Table II for glpc conditions). The products were collected in one portion by preparative glpc: ir (CCl_4) 1150 cm^{-1} (C–O–C); nmr (CCl_4) τ 3.88 and 4.78 (both m, combined areas = 5, $=\text{CH}-$), 7.65 and 7.80 (d and t, respectively, combined areas = 2, both $J = 7$ Hz, $-\text{CH}_2-$), and 8.65 and 8.95 (both s, combined areas = 9, $-\text{CH}_3$).

Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.82. Found: C, 80.78; H, 10.02

This information, combined with the knowledge that 7-alkoxy-substituted cycloheptatrienes equilibrate rapidly to mixtures of 2-, 3-, and 4-substituted isomers at 170 $^{\circ}$,^{25, 26} leads to assignment of structures 10a–12a to the components of the mixture.

The conversion of a decane solution of 9a at 170 $^{\circ}$ to the mixture of cycloheptatrienes was 93 \pm 5% after 25% disappearance of 9a and 72 \pm 5% after 60% disappearance. The deficiency in mass balance is ascribed to a secondary reaction of 10a–13a, indicated by the experiments in section 2.

(b) **Vapor Phase.** Ether 9a (33 mg) was sealed in an evacuated 100-ml bulb. The bulb was maintained at 170.0 \pm 0.2 $^{\circ}$ for 180 min. The pyrolysate was taken up in CCl_4 and analyzed by glpc (see entry 1 of Table II for glpc conditions). The ratio of 9a to 10a–12a was 56:44. No benzene (>0.05%) was detected.

(c) **2-Ethoxyethanol Solution.** A 0.37 *M* solution of 9a in 2-ethoxyethanol was heated in a sealed tube at 170 $^{\circ}$ for 60 min. Glpc analysis (column B, 175 $^{\circ}$, 50 ml/min) showed one peak (retention time 30 min); the *tert*-butoxycycloheptatriene isomers (>0.1%) were absent.

The product mixture was isolated by glpc from a more concentrated solution: ir (CCl_4) 1160 and 1125 cm^{-1} (C–O–C); nmr (CCl_4) τ 3.90 and 4.73 (both m, combined areas = 5, $=\text{CH}-$), 6.40 (m, 6 $-\text{CH}_2\text{CH}_2\text{OCH}_2-$), 7.52 and 7.73 (d and t, respectively, combined areas = 2, both $J = 7$ Hz, $-\text{CH}_2-$), and 8.82 (t, 3, $J = 8$ Hz, $-\text{CH}_3$).

Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.30; H, 8.95. Found: C, 73.06; H, 8.70.

Two solutions, one having a 6.8 molar ratio of 2-ethoxyethanol to 9a, the other a 0.05 molar ratio, were heated in sealed tubes at 170 $^{\circ}$ for 50 min. Glpc analysis using the conditions specified above indicated that no 9c (>0.1%) was present in the solutions.

(2) **Mixture of 2-, 3-, and 4-Substituted *tert*-Butoxycycloheptatrienes (10a–12a).** (a) **Neat or Tetradecane Solution.** A solution of ca. 60% 10a–12a in tetradecane was heated in a sealed tube at 170 $^{\circ}$ for 2.25 hr. Glpc analysis on column B (conditions not recorded) showed peaks with the same retention times as isobutene and *tert*-butyl alcohol and (153 $^{\circ}$, 50 ml/min) an unsymmetrical peak (15 min) and another peak (24 min). Collection at 25 $^{\circ}$ of the first two peaks gave a material displaying the infrared spectrum of *tert*-butyl alcohol. The 24-min material was identified as the starting

mixture, 10a–12a. The 15-min material displayed strong infrared absorptions (CCl_4) at 1720 and 1665 cm^{-1} . The nmr spectrum (CCl_4) exhibited an unresolved absorption between τ 3.2 and 4.4, a doublet at 6.98 ($J = 6$ Hz), and an unresolved multiplet centered at 7.54. The ratio of areas of downfield to upfield absorptions was 1:1. By comparison of the ir and nmr spectra with published data,⁹³ this material is tentatively identified as a mixture of 2,4- and 3,5-cycloheptadienone.

When a neat sample of 9a was heated in a sealed nmr tube at 170 $^{\circ}$, the nmr spectra showed, in addition to *tert*-butoxycycloheptatriene absorptions, the development of the cycloheptadienone absorptions noted above and at τ 5.51 (septet, $J = 1$ Hz) and 8.31 (t, $J = 1$ Hz) in a 1:2 ratio, absorptions corresponding to those exhibited by isobutene. Some absorption due to *tert*-butyl alcohol may have been present, but this is not certain because of the absorptions of other species at ca. τ 9.

(b) **2-Ethoxyethanol Solution.** A 0.6 *M* solution of 10a–12a (the mixture was obtained as described in part a of section 1) in 2-ethoxyethanol was heated at 170 $^{\circ}$ for 60 min. Glpc analysis indicated the absence (>0.1%) of 10c–12c.

(3) **7-*tert*-Butoxycycloheptatriene (13a).** A 2.3 *M* solution of 13a in 2-ethoxyethanol was heated in a sealed tube at 170 $^{\circ}$ for 28 min and analyzed by glpc (column B). Mixtures of 10c–12c and 10a–12a, in a 15:1 ratio, were the only products detected.

(4) **7-Methoxynorbomadiene (9b).** A 6 *M* solution of 9b in decane was heated in a sealed tube at 170 $^{\circ}$ for 10.2 hr. The product mixture was isolated by preparative glpc (column A): ir (CCl_4) 1160 cm^{-1} (C–O–C); nmr (CCl_4) τ 3.85 and 4.75 (both m, combined area = 5, $=\text{CH}-$), 6.38 and 6.44 (both s, combined area = 3, $-\text{CH}_3$), and 7.55 and 7.75 (d and t, respectively, both $J = 7$ Hz, $-\text{CH}_2-$). Literature^{25b, 24} values for the methylene absorptions of 11b and 10b are τ 7.55 (d, $J = 7.1$ Hz) and 7.77 (t, $J = 6.6$ Hz), respectively.

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}$: C, 78.65; H, 8.25. Found: C, 78.46; H, 8.49.

The conversion of a decane solution of 9b at 170 $^{\circ}$ to a mixture of cycloheptatrienes was 96 \pm 5% after disappearance of ca. two-thirds of 9b.

In another experiment, a sample of 9b was sealed in an nmr tube and heated intermittently at 170 $^{\circ}$ for 10- or 15-min intervals. The nmr spectrum was recorded after each period of heating in order to check for the sequential formation of products. The τ 7.75 triplet appeared initially, followed by the appearance of the 7.55 doublet. This observation was interpreted as an initial formation of 10b, followed by formation of 11b.²⁴ Isomer 12b, known to be present only in low concentration at equilibrium,^{25, 26} was not detected.

(5) **7-(2-Ethoxyethoxy)norbomadiene (9c).** A 4.2 *M* solution of 9c in dodecane was heated in a sealed tube at 170 $^{\circ}$ for 14.5 hr. The only product observed on preparative glpc analysis (column B) exhibited the same ir and nmr spectra and retention time exhibited by the mixture isolated in part 1c above.

(6) **7-Phenylnorbomadiene (9d).** A neat sample of 9d was heated

(93) A. P. ter Borg and H. Kloosterziel [*Recl. Trav. Chim. Pays-Bas*, **82**, 1189 (1963)] report the carbonyl stretching frequency of 3,5-cycloheptadienone to be 1723 cm^{-1} and that of 2,4-cycloheptadienone to be 1668 cm^{-1} . The methylene protons of the former give a doublet at τ 7.00 ($J = 5.7$ Hz) and those of the latter an absorption at τ 7.17–7.83. These authors also report that interconversion of these two ketones is very rapid at 170 $^{\circ}$. Also see ref 25; J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *J. Amer. Chem. Soc.*, **77**, 4401 (1955); O. L. Chapman and P. Fitton, *ibid.*, **83**, 1005 (1961); and W. E. Parham, R. W. Soeder, and R. M. Dodson, *ibid.*, **84**, 1755 (1962).

(94) Also see ref 24 and G. W. Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *J. Amer. Chem. Soc.*, **89**, 2979 (1967).

in a sealed tube at 170° for 600 min. The product mixture was isolated by glpc (column C): ir (CCl₄) 1495 cm⁻¹ (aryl C=C); nmr (CCl₄) τ 2.70 (m, 5, aryl H), 3.66 and 4.56 (both m, combined area = 5, =CH-), and 7.30 and 7.74 (d and t, respectively, combined area = 2, J = 8 and 7 Hz, respectively, -CH₂-). In another experiment, a sample of **9d** containing 5% cyclohexane was sealed in an nmr tube and heated intermittently at 170° for about 25-min periods. The nmr spectrum was recorded after each period of heating in order to check for the sequential formation of products. In the methylene proton region (τ 6.9 to 8.6), the following absorptions appeared sequentially (splittings are accurate to ± 0.4 Hz): τ 7.74 (t, J = 7.0 Hz), 7.30 (d, J = 7.4 Hz), and 7.72 (t, J = ca. 6.5 Hz, shoulders superimposed on the first triplet). No absorption in the τ 7.3 region, other than the doublet noted above, was observed during at least the first half-life of the reaction, indicating the absence of significant amounts (>3%) of **13d**.^{28,95} Literature^{28,95} values for the methylene absorptions of **10d**, **11d**, and **12d** are 7.77 (t, J = 6.8 Hz), 7.34 (d, J = 7.0 Hz), and 7.75 (t, J = 6.9 Hz), respectively.

The conversion of a decane solution of **9d** at 170° to the mixture of cycloheptatrienes was 100 \pm 10% after disappearance of ca. 85% of **9d**.

A solution of **9d** in 2-ethoxyethanol was heated in a sealed tube at 170° for 8.5 hr. Analysis by glpc (column B) showed the absence of detectable (>1%) amounts of **10c-12c**.

(7) **7-Acetoxybornadiene (9e)**. A 5.8 *M* solution of **9e** in decane was heated in a sealed tube at 170–180° for 114 hr. At this time a small amount of intractable material, corresponding to no more than 10% of the original quantity of **9e**, had separated from the solution. Glpc, ir, and nmr analyses of the decane solution showed that at least 99% of dissolved material was unreacted **9e**.

(8) **anti-7-Methoxybornene**. A neat sample was sealed in an nmr tube and heated intermittently at 170 \pm 1°. The spectrum, recorded after each interval, showed that the sample remained unchanged for at least 71 hr.

(9) **7-tert-Butoxyquadricyclane (14a)**. A 3.8 *M* solution of **14a** in bromobenzene was sealed in an nmr tube at reduced pressure and heated at 185–190° for short periods. In the nmr spectra taken after each period of heating, absorptions of **14a** diminished, while absorptions identical with those exhibited by **9a** appeared. The isomerization had $t_{1/2}$ \leq 20 min. Continued heating of the sample resulted in further reaction as described in section 1.

(10) **7-Methoxyquadricyclane (14b)**. A neat sample of **14b** was sealed in an nmr tube at reduced pressure and heated at 170.6 \pm 0.2° for short periods. In the nmr spectra taken after each period of heating, the absorptions of **14b** diminished with time, while absorptions identical with those exhibited by **9b** appeared. A rate constant for the isomerization was obtained by following the integrated areas of the two methoxyl signals (and assuming the sum of their areas to be constant). Continued heating of the sample resulted in further reaction as described in section 4 above.

(95) See also ref 27.

Kinetic Procedure. The temperature of a standard, liquid-filled, constant-temperature bath was controlled to $\pm 0.04^\circ$ and measured absolutely to $\pm 0.05^\circ$ by calibration against a NBS thermometer. A kinetic solution, 0.3 to 0.5 *M* in substrate and 0.04 to 0.2 *M* in inert reference, was divided into ca. 12 1-ml aliquots. The aliquots were degassed and sealed in 0.7 \times 10 cm Pyrex tubes at 77°K. Prior to use, the tubes were washed with dilute ammonium hydroxide and distilled water and dried. The charged tubes were totally immersed in the constant-temperature bath, and one was removed for each kinetic point. Each tube was cooled to 25° immediately after removal from the bath. Times between points were chosen to correspond to the disappearance of ca. 12% of the reactant. All of the reactions were followed for at least 3.5 half-lives, except for the isomerization of **9c** which was followed for 1.7 half-lives. The contents of each tube were analyzed in duplicate by glpc. The concentration of reactant was expressed as its average peak area (measured with a planimeter) divided by the average peak area of the standard. Representative conditions for analyses are given in Table II. First-order rate constants were computed using a standard least-squares computer program; it was assumed that the infinity concentration of substrate was zero.

Determination of Per Cent Conversions of Norbornadienes to Cycloheptatrienes. Conversions were determined using concentrations of norbornadiene reactants and of the mixtures of cycloheptatriene products obtained from aliquots of the kinetic runs by comparing glpc peak areas due to these species with the peak area due to the internal standard. For the *tert*-butoxy system, it was shown that the thermal conductivities of the norbornadiene (**9a**) and of the cycloheptatriene mixture (**10a-12a**) were identical; a similar equality was assumed for the other systems. Since the apparent conversion of reactant to product decreased significantly with time for **9a** (due to the cleavage described above) and perhaps slightly for the other systems, the conversions were calculated using data from the first few half-lives. The error figures are the largest variations noted for duplicate analyses.

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