vacuum. All ampules were simultaneously immersed into a constant temperature bath. After 5 min, one ampule was removed from the rate bath and placed in an ice water mixture. A timer was started upon removal of the first ampule. The remaining ampules were removed and cooled at appropriate intervals covering 2 to 3 half-lives. The final amuple was removed after at least 10 half-lives to give an infinity point. The individual ampules were allowed to warm to room temperature, at which point a standard aliquot was removed, diluted with 1 ml of dioxane, and titrated against 0.0192 M perchloric acid in acetic acid using one drop of bromophenol blue indicator. First-order rate data was determined by measuring consumption of tosylate by acetolysis relative to the experimental infinity point. Duplicate runs agreeing within 3% were made at all temperatures.

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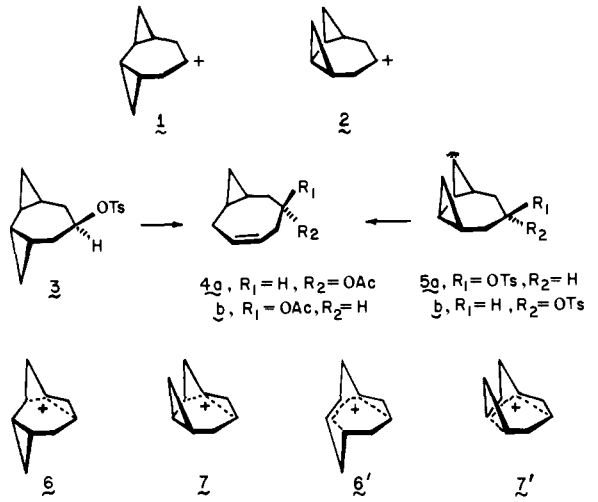
The Fate of Bishomocycloheptadienyl Cations Generated by Deamination

Michael R. Detty[1] and Leo A. Paquette*

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received July 27, 1976*

Abstract: Preparations of *anti*- and *syn*-3,5-bishomocycloheptadienone tosylhydrazones (**10b** and **11b**) together with the anti- and syn-2,5-bishomo isomers (**14b** and **17b**) are described. Photodeamination of **10b** in methanol gave olefin **19** (3%) and ethers **20** (19%) and **21** (78%). Under similar conditions, **11b** was converted to olefin **22** (12%) and a mixture of eight ethers. Seven of these have been identified: **21** (3%), **23** (19%), **24** (11%), **25** (22%), **26** (6%), **27** (22%), and **28** (2%). The ninth component (3%) remains uncharacterized. The anti-2,5-bishomo tosylhydrazone **14b** was more well behaved, giving **12** (11%), **21** (24%), **28** (11%), and **46b** (54%), while **17b** upon comparable deamination returned only ether **25** (99%) and a trace of olefin **15.** The product distributions in aqueous alkaline solution were also examined. The various interconversions, which differ appreciably from those encountered in acetolysis of the corresponding tosylates, are explained in terms of vertical ionization concepts. These arguments are supported by the solvolytic behavior of the tosylates in the common solvent methanol. The varied degrees of complexity arise because of the critical interdependence of the mutual geometry of the cyclopropane rings and the developing cationic center which in turn dictates the level of molecular rearrangement, the extent and stereochemistry of solvent capture, and the possibility of deprotonation. Thermodynamic considerations also gain importance in certain cases, although they never seem to dominate over kinetic control.

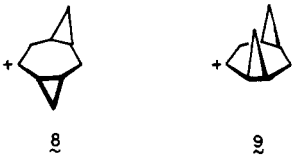
The *anti*- and *syn*-3,5-bishomocycloheptadienyl cations (**1** and **2**) have evoked interest in connection with the questions of the extent and stereochemical dependence of long-range cyclopropane participation. Acetolysis of tosylate **3** resulted in efficient conversion (>98.5%) to **4a** via a deep-seated rearrangement involving rupture of both original cyclopropyl groups and ultimate reconstruction of a third, different three-membered ring.[2] Acetolysis of **5a** revealed the operation of an identical bond reorganization; however, the stereochemical outcome was now diametrically opposite (>98.5%



of **4b**). The solvolysis of **5b** afforded **4b** (55%), **5a**-OAc (9%), *syn*-3,5-bishomocycloheptatriene (25%), and 1,4,7-cyclononatriene (11%). The full range of results eliminates the possibility that **3** and **5a** ionize via cations **1** (C_2 symmetry) and **2** (C_s symmetry). Rather, interaction of one cyclopropyl group with the developing cationic center during ionization, visualized by structures **6** and **7**, does minimally account for the observed formation of **4a** and **4b**.[2] However, that more extended long-range cyclopropyl interaction as represented by **6'** and **7'** may actually operate[3] was not answerable with the data available.

The intervention of **6** and **7** or **6'** and **7'** is seen to involve significant neighboring group participation and consequent distortion of reactant geometry in progressing to products. Alternatively, unperturbed cations such as those represented by **1** and **2** might offer an interesting contrast, since subsequent long-range cyclopropyl interactions would be with a fully developed carbonium ion center. At this point, it appears useful to define "vertical" and "nonvertical" ionization. During vertical ionization, a carbonium ion is formed via the loss of some leaving group free from any intramolecular neighboring group involvement (e.g., **1** and **2**). In contrast, nonvertical processes are characterized by direct neighboring group interactions at the stage of rate-determining ionization (**6**, **7**, **6'**, and **7'**, for example).

Solvolytic studies on β-cyclopropylethyl systems are recognized to proceed by both pathways in many cases, and often the line dividing them is frustratingly obscured. Frequently, widely varying product ratios are found for diazonium ion decompositions when compared with solvolysis mixtures. This has been attributed to much lower activation energies resulting from the excellent leaving group characteristics of the nitrogen molecule. The initial generation of carbonium ions in a vertical ionization manifold is thought to be involved.[4] In order to understand better the relationship between the stereodisposition of cyclopropyl groups and their possible involvement with anchimeric assistance in bishomocycloheptadienyl cations, a study of the fate of **1** and **2** as generated by deamination was

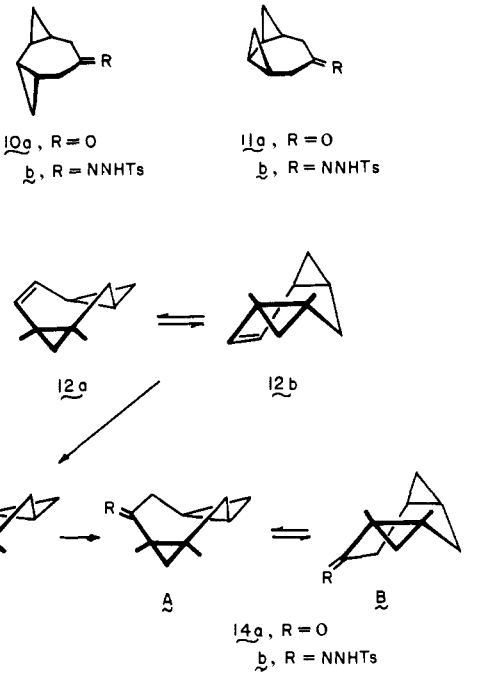


undertaken. Solvolysis of **3** and **5a** in a common solvent (MeOH) was also studied. To complete the mechanistic picture, we have examined as well the behavior of 2,5-bishomocycloheptadienyl cations **8** and **9** (note relationship to **6** and **7**) when generated under comparable conditions.

Results

When tosylhydrazone salts are irradiated in alkaline aqueous or alcoholic solutions,[5] the diazoalkanes which result experience ready in situ protonation,[5f] the procedure virtually ensuring kinetic control by the attacking solvent nucleophile. Such an experimental approach was deemed ideally suited to the stated problem and accordingly was utilized in this study.

The known ketones **10a** and **11a**[2] readily afforded their respective crystalline tosylhydrazones **10b** and **11b**. For the preparation of *anti*-2,5-bishomocycloheptadienone (**14**), olefin

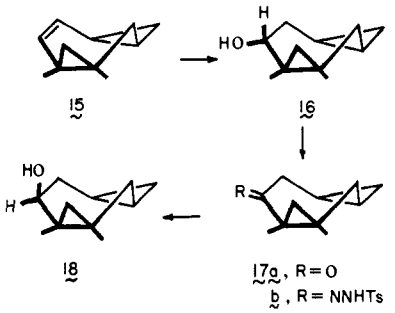


12 was successively hydroborated and oxidized with Collins reagent. The propensity of **12** for rapid conformational ring inversion at room temperature[2] causes both surfaces of the π bond to be equally accessible to the electrophilic reagent. For steric reasons, however, exo attack on **12a** and **12b** is assumedly favored. Conveniently, the inherent C_2 symmetry of this hydrocarbon renders both pathways fully equivalent. Electronic effects, in contrast, contribute substantially to the regioselectivity of addition. Thus, development of positive charge during hydroboration should favor carbon–boron bond formation adjacent to the axially disposed three-membered ring because of more favorable orbital interaction with the internal cyclopropane σ bond in this alignment. That **13** is produced in >95% purity is testimony to the control which conformationally distinguishable cyclopropane rings can exert on such processes.

Ketone **14a** is also conformationally mobile, both faces of its carbonyl group being available for attack by nucleophilic reagents. However, since **13** is formed preferentially (>95%) upon lithium aluminum hydride reduction of **14a**, attack on conformer B from the exo direction is seen to be kinetically favored. This finding agrees with independent assessments of prevailing steric factors made with molecular models.[6]

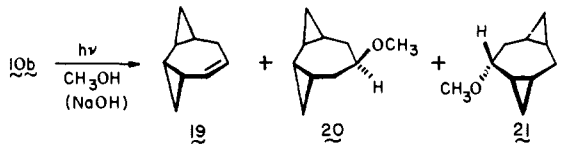
Comparable hydroboration of the more conformationally rigid bishomocycloheptatriene **15** occurred with >95% exo stereoselectivity to provide **16**, oxidation of which gave **17a**. Upon treatment with sodium borohydride, this ketone led expectedly to **16** and **18** in a ratio of 1:4.

When irradiated (450-W Hanovia lamp, Pyrex) in anhydrous methanol 0.2 N in sodium hydroxide, **10b** was converted to a three-component mixture comprised of olefin **19** (3%) and ethers **20** (19%) and **21** (78%). The structural assignments to



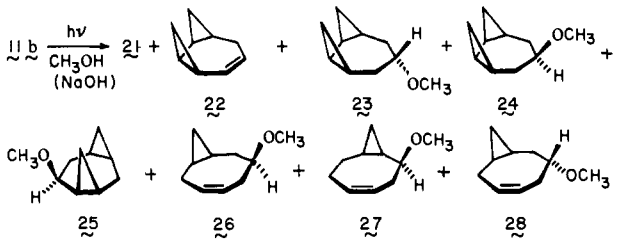
15 16 18 17a, R=O; b, R=NNHTs

20 and **21** follow from their revealing ^{1}H NMR spectra and independent synthesis from the known alcohols. Photodeamination of **10b** in aqueous base gave a reaction mixture containing **3**-OH (16%) and **13** (84%), but no detectable amounts of **19**.



19 20 21

Comparable photolysis of **11b** in methanol was significantly more complex and provided nine detectable products. Preparative VPC separation and detailed spectral analysis revealed several of the constituents to have retained both cyclopropane rings. These were identified as **21** (3%), **22** (12%), **23** (19%), **24** (11%), and **25** (22%). Three of the remaining ethers contained but one three-membered ring and these were characterized as **26** (6%), **27** (22%), and **28** (2%). The ninth

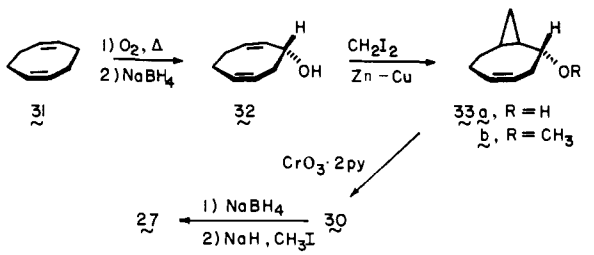


22 23 24 25 26 27 28

component (3%) remains unidentified. Although alternative access to **26** and **28** could readily be gained by suitable chemical modification of **4b** and **4a**, respectively, the isomeric bicyclic ether **27** required more extensive elaboration. For this purpose, **11b** was photodeaminated in aqueous base and the product mixture directly oxidized. Product analysis established that ketones **11a** (17%), **14a** (25%), **17a** (27%), **29** (5%), and **30** (26%) had been formed. The identity of **29** was revealed by

29 30

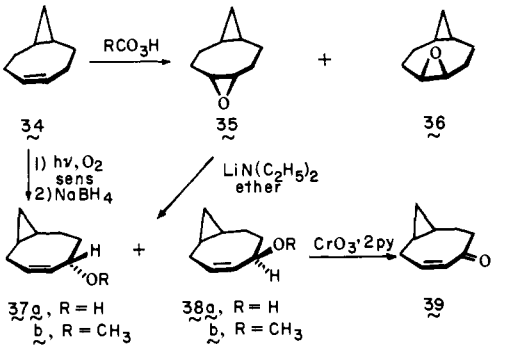
its independent synthesis from **4**.[2] For the unequivocal preparation of **30**, a stream of oxygen was bubbled through a warm sample of 1,5-cyclooctadiene (**31**) and the intermediates directly reduced with sodium borohydride.[7] By preparative VPC methods, pure alcohol **32** was obtained and cyclopropanated



31 32 33a, R=H; b, R=CH$_3$ 27 30

under Simmons-Smith conditions.[8] The major component was separated and assigned the indicated anti stereochemistry (**33a**) in line with existing precedent.[9] Its methyl ether (**33b**) was prepared and found to be different from **27**. Collins oxidation furnished **30**, identical in all respects with the previously isolated ketone. Sodium borohydride reduction and methyl ether formation yielded **27** and **33b** in a 62:38 ratio. The stereochemical disposition of the cyclopropane ring and methoxyl groups in this pair of ethers follows not only from the method of synthesis, but from the relative shielding effects of the neighboring cyclopropane ring on the oxygen substituted methine C–H groups as well.

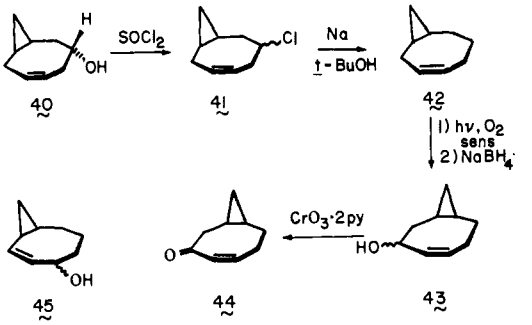
For relevant mechanistic reasons, it was important to eliminate the chance possibility that bicyclo[6.1.0]nonenyl alcohols and ethers structurally related to ketones **39** and **44** had been formed in small amounts but not detected in the product analyses because of peak overlapping, etc. It was instructive, therefore, to effect epoxidation of bicyclo[6.1.0]-non-4-ene (**34**) with *m*-chloroperbenzoic acid. The resulting pair of epoxides were separated under preparative VPC conditions and individually subjected to ring opening with lithium diethylamide in ether. Molecular models show only **35** to have



34 35 36 37a, R=H; b, R=CH$_3$ 38a, R=H; b, R=CH$_3$ 39

a reasonable capacity for conformational folding with resultant trans diaxial orientation of the epoxide ring and a vicinal C–H bond. The epoxide isomer which was returned unchanged under these conditions was accordingly assigned structure **36**. The allylic alcohol to result from **35** is therefore considered to be trans isomer **37a**, a conclusion supported by its isolation as the major photooxygenation product of **34**. Both **37a** and the second photooxygenation alcohol **38a** underwent smooth oxidation to **39** and methylation to give **37b** and **38b**, respectively. Using suitable VPC methods, it could be demonstrated that none of these three compounds had been produced during the deamination of **11b** in either solvent studied.

Treatment of alcohol **40** with thionyl chloride gave chloride **41**, reduction of which with sodium and *tert*-butyl alcohol in tetrahydrofuran gave hydrocarbon **42** in 80% overall yield. Singlet photooxygenation of **42** resulted in 90% conversion

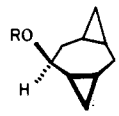


40 41 42 45 44 43

chiefly (>90%) to one allylic alcohol whose ^{1}H NMR spectrum showed a combination of six allylic and cyclopropylcarbinyl protons exclusive of the >C*H*OH signal. These features require the substance to be **43** and rule out alternative formu-

lation **45**. Collins oxidation of **43** led cleanly to ketone **44** which also could be dismissed as a product of photodeamination-oxidation of **11b** in aqueous base.

Light-induced deamination of **14b** in methanolic sodium hydroxide afforded hydrocarbon **12** (11%) in addition to the three ethers **21** (24%), **28** (11%), and **46b** (54%). In aqueous



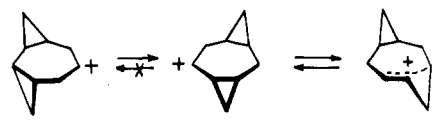
46a, R = H
b, R = CH_3

potassium hydroxide solution, the alcohols **13** (20%), **28**-OH (10%), and **46a** (70%) were formed, but hydrocarbon **12** was not observed. To establish the carbon framework in **46a** and demonstrate its structural relationship to **46b**, the alcohol was both oxidized and methylated. Ketone **14a** and ether **46b** were produced in high yield.

Finally, irradiation of **17b** in alkaline methanol afforded trace quantities of olefin **15** together with ether **25** (99%). In water, **18** proved to be the exclusive product.

Discussion

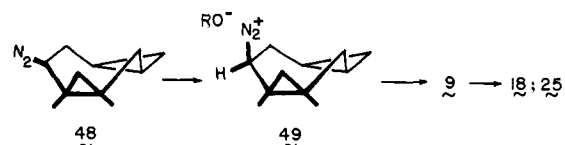
In the case of **14b**, the product distributions which result in methanol and water solution suggest that a mixture of epimeric diazonium ion pair intermediates are formed, with anti protonation of the $>C{=}N_2$ group occurring twice as frequently as the syn alternative. This partitioning, which is likely related directly to the anticipated conformational mobility of this diazo intermediate (see **14**), assumes that tight ion pairs[10] are formed which collapse sufficiently rapidly so that solvent capture occurs with retention of configuration. Were solvent-separated ion pairs involved, a much greater predominance of **21** would be expected as in the case of **10b**. Significantly, the cyclopropylcarbinyl carbonium ion resulting from loss of nitrogen, i.e., **8**, is not particularly prone to structural rearrangement. Although low levels (~10%) of conversion to cation **47** are op-



1 **8** **47**

erative (note stereospecificity in the capture of this ion), no products were detected having structures corresponding to **1**. We view this noninterconvertibility to be a reflection of the enhanced thermodynamic stability of **8** relative to **1**, the energy gap separating them being adequate to insulate **8** from **1** even when vertical stabilization is likely operative. However, **8** is not stable enough to deter measurable rearrangement to its homoallylic isomer **47**. It is of interest that the extent to which **28** (11%) and **28**-OH (10%) are formed falls far short of the true thermodynamic position of equilibrium. Independent treatment of **13** with 10% hydrochloric acid (50 °C, 20 min), for example, resulted in ready conversion to bicyclic alcohol **28**-OH (90%). Thus, the deamination product distribution is kinetically controlled.

Because diazo compound **48** which is formed from **17b** is conformationally rigid (see discussion regarding **15–18** above), highly directed solvent protonation from the anti direction is anticipated. Its decomposition through ion pair intermediate **49** with capture by the geminate methoxide or hydroxide ion



48 **49**

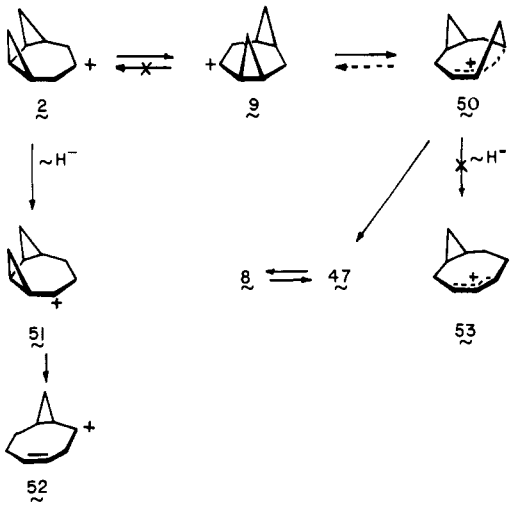
shortly after formation of cation **9** will lead to **25** and **18**, respectively. Since no other products (except for barely detectable levels of deprotonation) are formed, the stability of **9** *at least prior to relaxation* is sufficient to preclude electronic reorganization. This result is once again an obvious frustration of thermodynamics, since alcohol **18** is rapidly isomerized to **4b**-OH (95%) in 10% hydrochloric acid (50 °C, 20 min). The absence of *syn*-3,5-bishomocycloheptadien-1-yl derivatives provides insight into the disinclination of **9** to transform to **2**.

The behavior of **10b** under photochemical deamination conditions is such that solvent capture without skeletal rearrangement was prominent in both media (16–19%) as reflected in the isolation of **20** and **3**-OH. Clearly, the most important process (78–84%) consists of skeletal rearrangement and solvent trapping with full stereoelectronic control. The lack of involvement of the second cyclopropane ring is particularly noteworthy. This behavior is a dramatic departure from that observed during tosylate acetolysis[2] and could speak to the decreased level of molecular distortion required to achieve stabilization of the positive charge under vertical ionization conditions. To conclusively establish this point, however, it becomes imperative to recognize possible differences between tosylate solvolysis in acetic acid and deamination in methanol or water. The far higher nucleophilicity of the latter solvents can conceivably lead to interception of a carbonium ion sequence at an earlier stage. More specifically, reaction of solvent with a carbonium ion intermediate in which delocalization to one cyclopropane ring has occurred can be faster in methanol or water than the conformational changes required for delocalization to the second ring. For these reasons, the solvolysis of **3** in methanol was investigated and observed to give rise to olefin **19** (1%) and ethers **20** (19%), **21** (69%), and **28** (11%). The similarity of this product distribution with that derived from the deamination studies is most striking; the contrast with the acetolysis results is equally so. The behavior of **3** can again be best explained by principal ionization to cation **6** with simultaneous participation by the syn cyclopropyl group.[2] Although there is some apparent leakage to **6'** or **47** (compare the fate of **8**), one can arrive at the plausible conclusion that cyclopropane-cyclopropane interactions do not gain importance in this particular system. Since this behavior is not seen in acetolysis,[2] the increased nucleophilicity of methanol serves to intercept the sequential series of carbonium ion rearrangements after opening of the first cyclopropane ring (rate determining).

Given the reactivity patterns of **11b**, the results of the photodeamination of **10b** can be best rationalized in terms of preliminary conversion to cation **1** and its further reaction along three different pathways as noted above. The cyclopropyl participation (one of these groups only) which occurs subsequently in part leads to a new increase in thermodynamic stabilization (bisected cyclopropylcarbonyl cation generation) and is therefore favored. Should the structural features of **1** not be complicated by ion pairing and the like (rather unlikely—see above),[10] then its axial symmetry would lead to participation by either three-membered ring.[2] A cation of lesser symmetry would favor neighboring group assistance only by the syn cyclopropyl group. However, because the first-formed diazo compound also shares this symmetry property, its protonation by solvent from top and bottom faces then becomes statistically equivalent and redistribution of any label would occur prior to loss of nitrogen. There exists, therefore, no convenient way to address this stereochemical question; fortunately, this point is of low relevance to the present study.

Product mixtures from the photodeamination experiments involving **11b** were substantially more complex. The combined yields of **22–24** (42%) reveal that interconversion of **2** with isomeric cations is less prevalent in methanol than in water

(17% of **11a**). In line with prevailing conformational features, syn protonation of the diazo intermediate dominates by a factor of approximately 2 (assuming negligible incursion of S_N2-type reactions). The formation of **25** (22%) and **17a** (27%) denotes that **2** is capable of β-cyclopropylethyl → cyclopropylcarbinyl interconversion as is **1**. Under normal circumstances, conventional stereocontrol would be expected within both stereoisomeric subsets (**1, 8, 47; 2, 9, 50**) such that leakage from one



series to the other becomes unlikely. This conclusion is generally valid for most acetolysis reactions, but vertical ionization manifolds can sometimes provide surprises as in the present example. Thus, the isolation of **21** (3%) and **14a** (25%) corresponds to leakage to the *anti*-2,5-bishomocycloheptadien-1-yl cation (**8**). From molecular models, it is seen that syn homoallylic cation **50** experiences noteworthy nonbonded interactions not present in its anti conformer **47**. If one makes the reasonable assumption that **50** as generated by twofold rearrangement of **2** is capable of relaxation by ring inversion and generation of **47**, then reclosure of this last intermediate to give **8** becomes a likely event prior to solvent trapping. In fact, the ratio of **21** to **14a** which favors **14a** by a factor of 8 can be accounted for in terms of the enhanced ability of solvent water to permit attainment of more optimal stabilization of positive charge prior to its annihilation by covalent bonding. Additionally, isolation of the epimeric ethers **26** and **28** from the methanol photodeaminations conforms to the presence of both **50** and **47**, respectively, in view of the expectancy that these two cations should react stereospecifically with solvent.

The formation of **27** and **30** denotes that this portion of the product mixtures must arise from a hydride-shift pathway. Since neither **47, 50,** nor **53** can be reasonably implicated, this phenomenon which is unique to **11b** is thought to arise by rearrangement of **2** to **51**, a cation which is geometrically well disposed for ring opening to **52**. This intermediate is both cyclopropylcarbinyl and homoallylic in nature and could thus be thermodynamically attractive. In actuality, the sequence **2** → **51** → **52** has previously been invoked as the primary stages in the transformation of cation **2** to *cis*[3]-1,4,7-cyclononatriene under acetolysis conditions.[2]

The solvolysis of **5a** in methanol led to a markedly different ratio of products: **22** (4.4%), **23** (8.0%), **24** (0.6%), **26** (85.3%), and **28** (1.7%). The high percentage (87%) of compounds resulting from scission of *both* cyclopropane rings contrasts markedly with those results realized upon deamination of **11b** (8% in MeOH; 5% in H_2O). Additionally, there was found no evidence for the formation of **25**, a principal product of diazonium ion decomposition in methanol; nor was hydride shifting operational. Furthermore, the stereoselectivity attending production of the epimeric ethers **26** and **28** (50:1) substantially exceeds that realized from **11b** (3:1). These composite observations provide convincing evidence for the direct generation of **7′** upon solvolysis of **5a**.

One general conclusion to be drawn from the present experiments is that tosylhydrazones can provide ready access to intermediate carbonium ions not accessible by solvolysis. When the relative orientation between the developing cationic center and the proximate cyclopropane rings can be varied substantially as it can in the bishomocycloheptadienyl series, a most critical dependence upon their mutual geometry is clearly evident. In solvolysis,[2] the level of neighboring group participation reaches a maximum, with the result that high stereospecificity during conversion to extensively rearranged products is observed. When an all-cis arrangement is present as in **5a**, ionization by solvolysis results in all-out participation by the pair of three-membered rings. Inversion of stereochemistry of one cyclopropane ring (e.g., as in **3b**) restricts delocalization only to the syn oriented group. In the vertical ionization manifolds reached by deamination, structurally less encumbered cations are first formed. Greater complexity in product formation then develops, but generalizations cannot be transferred from system to system without adequate consideration of geometric considerations. Thus, whether neighboring cyclopropane rings experience direct involvement with a developing cation center or not can be controlled by conformational factors as well as by the method of generation. As shown above, the specific reaction type employed can lead to interception of a series of carbonium ion or ion pair intermediates at different points in the reaction manifold and shed light on the sequential or simultaneous participation of cyclopropyl groups.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The NMR spectra were determined with Varian A-60A and Bruker HX-90 instruments and apparent splittings are given in all cases. Mass spectra were measured with an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative VPC separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***anti*-3,5-Bishomocycloheptadienone Tosylhydrazone (10b).** Into a 15-ml one-necked flask equipped with a drying tube mounted above a reflux condenser and magnetic stirrer was placed a solution of tosylhydrazine (410 mg, 2.2 mmol) and ketone **10a** (200 mg, 1.47 mmol) in 10 ml of absolute ethanol containing one crystal of *p*-toluenesulfonic acid. Heating at the reflux temperature was maintained for 3 h prior to cooling at −20 °C for 12 h. The crystalline solid was separated by filtration and recrystallized from ethanol to give 210 mg (47%) of white solid, mp 163–165 °C.

Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20. Found: C, 63.05; H, 6.65; N, 9.42.

***syn*-3,5-Bishomocycloheptadienone Tosylhydrazone (11b).** A solution containing 200 mg (1.47 mmol) of ketone **11a**, tosylhydrazine (410 mg, 2.2 mmol), and a single crystal of *p*-toluenesulfonic acid in 10 ml of absolute ethanol was heated at reflux for 3 h. The resulting mixture was cooled at −20 °C for 12 h, and the precipitated solid was separated by filtration. Subsequent recrystallization from ethanol afforded 272 mg (61%) of white crystals, mp 145–147 °C.

Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20. Found: C, 62.90; H, 6.65; N, 9.16.

***syn,anti*-2,5-Bishomocycloheptadienol (13).** Into a 250-ml three-necked flask equipped with rubber septa, nitrogen inlet tube, and magnetic stirrer was placed 740 mg (6.16 mmol) of *anti*-1,5-bishomocycloheptatriene (**12**) dissolved in 20 ml of dry tetrahydrofuran. After cooling this solution to 0 °C, 4.20 ml of a 0.95 M solution of diborane in tetrahydrofuran was introduced dropwise via syringe. The reaction mixture was then allowed to warm slowly with stirring to room temperature during 3 h, recooled to 0 °C, and treated sequen-

tially with 15% sodium hydroxide solution (20 ml) and 30% hydrogen peroxide (20 ml). The resulting mixture was stirred overnight, the aqueous phase was saturated with potassium carbonate, the organic layer was separated, and the aqueous phase was extracted with ether (2 × 20 ml). The combined organic extracts were dried and evaporated, and the residue was subjected to molecular distillation at 100 °C and 0.3 Torr. There was obtained 740 mg (87%) of a colorless oil, VPC analysis (0.25 in. × 12 ft 5% DEGS on Chromosorb G, 155 °C) of which denoted the alcohol to be >95% pure: $\delta_{Me_4Si}^{CDCl_3}$ 4.50 (m, 1), 3.50–2.30 (series of m, 4), 3.00 (s, 1), 1.65 (m, 6), and 1.32 (m, 2); *m/e* 138.1047 (138.1045).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.02; H, 10.12.

***anti*-2,5-Bishomocycloheptadienone (14a).** Chromium trioxide (3.0 g, 30 mmol) was added carefully to 4.74 g (60 mmol) of pyridine dissolved in 30 ml of methylene chloride, and the mixture was stirred under nitrogen at room temperature for 0.5 h. A solution of **13** (414 mg, 3.0 mmol) in 5 ml of methylene chloride was introduced by syringe, and after 30 min the organic phase was decanted and concentrated in vacuo. The inorganic solids were washed with ether (50 ml) which was added to the concentrate. A chalky brown precipitate was separated by filtration prior to washing with 10% hydrochloric acid (2 × 50 ml), 5% sodium hydroxide solution (50 ml), and saturated sodium bicarbonate solution (50 ml). After drying, the filtrate was concentrated in vacuo to afford 310 mg (76%) of **14a** as a colorless oil: ν_{max}^{neat} 1680 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 2.75 (m, 2), 1.85 (m, 2), 1.53 (t, J = 6 Hz, 2), 1.20 (m, 2), 0.38 (m, 3), and 0.13 (m, 1); *m/e* 136.0890 (136.0888).

***anti*-2,5-Bishomocycloheptadienone Tosylhydrazone (14b).** Reaction of 150 mg (1.1 mmol) of **14a** with 205 mg (1.10 mmol) of tosylhydrazine in 5 ml of ethanol in the predescribed manner (2 h reflux period) and threefold recrystallization of the product from ethanol gave 210 mg (68%) of white crystals, mp 145–147 °C.

Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20. Found: C, 62.89; H, 6.65; N, 8.98.

Lithium Aluminum Hydride Reduction of 14a. A solution of **14a** (100 mg, 0.74 mmol) in 3 ml of dry ether was added dropwise by syringe to a stirred slurry of lithium aluminum hydride (30 mg, 3.2 molar equiv) in 5 ml of ether. After 1 h at the reflux temperature, the mixture was cooled in ice while 0.05 ml of water, 0.05 ml of 15% sodium hydroxide solution, and 0.05 ml of water were introduced sequentially. The ether layer was decanted, and the white precipitate was washed with 10 ml of ether. The combined organic layers were dried and concentrated to yield 85 mg (84%) of **13** whose purity was >95% (VPC analysis).

***anti,anti*-2,5-Bishomocycloheptadienol (16).** As before, a solution of diborane in tetrahydrofuran (1.68 ml of 0.95 M) was added dropwise to a solution of **15** (215 mg, 1.79 mmol) in 1 ml of the same solvent cooled to 0 °C. Workup and molecular distillation (100 °C, 0.3 Torr) afforded 210 mg (85%) of **16** as a colorless oil (>95% purity). An analytical sample was obtained by preparative VPC purification: ν_{max}^{neat} 3350 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 3.27 (m, 1), 2.73 (s, 1), 1.4–2.9 (m, 4), 0.70 (m, 6), and −0.13 (m, 2); *m/e* 138.1047 (138.1045).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.79; H, 10.32.

***syn*-2,5-Bishomocycloheptadienone (17a).** The oxidation of **16** (200 mg, 1.45 mmol) dissolved in 5 ml of methylene chloride with chromium trioxide (1.45 g, 14 mmol) and pyridine (2.29 g, 29 mmol) in methylene chloride (20 ml) was performed as described previously to give 140 mg (71%) of **17a** as a colorless oil: ν_{max}^{neat} 1680 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 3.80–2.80 (m, 2), 2.70–1.00 (m, 9), and −0.10 (m, 1); *m/e* 136.0890 (136.0888).

***syn*-2,5-Bishomocycloheptadienone Tosylhydrazone (17b).** Reaction of **17** (136 mg, 1.0 mmol) in 5 ml of absolute ethanol with 200 mg (1.1 mmol) of tosylhydrazine as above afforded 188 mg (62%) of white crystals, mp 168–174 °C, after three recrystallizations from ethanol.

Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.20. Found: C, 62.95; H, 6.67; N, 9.10.

***syn,syn*-2,5-Bishomocycloheptadienol (18).** Sodium borohydride (38 mg, 1.0 mmol) was added to 31 mg (0.23 mmol) of **17** dissolved in 2 ml of methanol, and the resulting solution was stirred under nitrogen for 2 h. After dilution with 5 ml of water, the product was extracted with ether (3 × 5 ml). VPC analysis of the dried and concentrated organic phase (the 12 ft DEGS column, 155 °C) showed **18** and **16** to be present in a 4:1 ratio. Product separation gave 16 mg (53%) of **18** and 2 mg (7%) of **16**. For **18:** ν_{max}^{neat} 3330 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 4.28 (m, 1), 2.80–1.55 (m, 3), 1.85 (s, 1), 1.50–0.33 (m, 7), 0.16 (m, 1), and −0.16 (m, 1); *m/e* 138.1047 (138.1045).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.96; H, 10.13.

Photodeamination of 10b in Methanol. A solution of **10b** (170 mg, 0.56 mmol) and sodium hydroxide (160 mg, 4.0 mmol) in 25 ml of absolute methanol contained in a 50-ml Pyrex flask equipped with a magnetic stirring bar and reflux condenser was irradiated for 3.5 h at ambient temperature with a 450-W Hanovia lamp. Water (50 ml) was introduced, and the resulting solution was extracted with pentane (3 × 20 ml). The combined organic phases were dried and carefully concentrated to leave 115 mg of a colorless oil. Preparative scale VPC separation (12 ft × 0.25 in. 10% XF-1150 on Chromosorb P, 120 °C) of this mixture afforded pure samples of the three components. The more rapidly eluted substance (13%) proved to be hydrocarbon **19**;[11] the methyl ether of shorter retention time (19%) displayed spectral properties identical with those of **20**, while the major ether isomer was identical with **21**.

***syn,anti*-3,5-Bishomocycloheptadienyl Methyl Ether (20).** A solution of *syn,anti*-3,5-bishomocycloheptadienol[11] (50 mg, 0.36 mmol) in 5 ml of anhydrous tetrahydrofuran was introduced dropwise via syringe to 48 mg (1.0 mmol) of sodium hydride (50% dispersion in mineral oil) which had previously been washed with the same solvent (2 × 5 ml). The resulting mixture was refluxed for 2 h under nitrogen, cooled, and treated with methyl iodide (142 mg, 1.0 mmol). After 30 min, the unreacted sodium hydride was destroyed by the addition of methanol (2 ml), then water (25 ml). The product was extracted into ether (3 × 15 ml) before washing, drying, and evaporation of the solvent in vacuo. Preparative scale VPC purification (12 ft × 0.25 in. 5% DEGS on Chromosorb W, 130 °C) afforded 27 mg (49%) of **20** as a colorless oil: ν_{max}^{neat} 3020, 2990, 2920, 2850, 2815, 1448, 1090, 1022, and 834 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 3.46 (m, 1), 3.32 (s, 3), 2.25 (m, 2), 1.26–0.60 (series of m, 8), and −0.01 (m, 2); *m/e* 152.1204 (152.1201).

***syn,anti*-2,5-Bishomocycloheptadienyl Methyl Ether (21).** Treatment of **13** (60 mg, 0.44 mmol) with sodium hydride (50 mg, 1.04 mmol) and methyl iodide (142 mg, 1.0 mmol) in the above manner and isolation by preparative VPC methods (the 10% XF-1150 column, 120 °C) afforded 33 mg (50%) of **21** as a colorless oil: ν_{max}^{neat} 3060, 2995, 2910, 2860, 2815, 1452, 1191, 1090, 1022, and 729 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 3.37 (s, 3), 3.00 (m, 1), 2.27 (m, 2), 1.70 (m, 2), 0.67 (m, 6), and 0.28 (m, 2); *m/e* 152.1204 (152.1201).

Photodeamination of 10b in Water. A 1-mmol sample of the tosylhydrazone was added to 50 ml of 0.2 N potassium hydroxide solution contained in a Pyrex flask, and the resulting solution was irradiated for 3 h as before. The products were extracted into ether (3 × 15 ml) and the combined ether extracts dried and concentrated prior to VPC analysis and product separation (6 ft × 0.25 in. 5% SE-30 on Chromosorb G, 115 °C). Only two components were observed and these were identified as **3**-OH (16%)[11] and **13** (84%).

Photodeamination of 11b in Methanol. A solution of **11b** (220 mg, 0.73 mmol) and sodium hydroxide (160 mg, 4.0 mmol) in absolute methanol was irradiated for 3.5 h as predescribed to give 90 mg of a colorless oil. For isolation purposes, the resulting mixture of products was subjected to an initial separation on the 10% XF-1150 column at 120 °C. Under these conditions, hydrocarbon **22** (12%) was readily separated from four ether fractions. The two components of longest retention time were shown (further VPC work and ^1H NMR analysis) to be isomerically pure and subsequently characterized as **24** (11%) and **23** (19%), respectively. Spectral examination of the remaining two fractions showed them to consist of three isomers each. Their successful resolution was achieved on a 12 ft × 0.25 in. 5% Bentone-5% SF-96/Chromosorb G column at 120 °C. Fractionation of the most rapidly moving peak gave pure samples of **21** (3%), **27** (22%), and **28** (2%). The percentage composition was ascertained by peak area measurements and integration of methoxyl signals in expanded NMR spectra. Comparable handling of the remaining fraction furnished **25** (22%), **26** (6%), and a third component (3%) which has eluded characterization.

***anti,anti*-3,5-Bishomocycloheptadienyl Methyl Ether (23).** Methylation of **5b**-OH[2] (50 mg, 0.36 mmol) as before and VPC isolation from the 10% XF-1150 column at 130 °C gave pure **23** as a colorless oil (41 mg, 75%): ν_{max}^{neat} 3030, 2995, 2920, 2855, 2815, 1460, 1360, 1085, and 1018 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 3.27 (s, 3), 3.07 (m, 1), 1.92 (m, 4), 0.52 (m, 2), and 0.00 (m, 2); *m/e* 152.1204 (152.1201).

***syn,syn*-3,5-Bishomocycloheptadienyl Methyl Ether (24).** Meth-

ylation of **5a**-OH[11] (50 mg, 0.36 mmol) in the predescribed manner and purification on the 5% DEGS column at 155 °C gave 31 mg (56%) of **24** as a colorless oil: ν_{max}^{neat} 3062, 2995, 2920, 2818, 1465, 1451, 1090, 1015, 832, and 810 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 3.52 (m, 1), 3.29 (s, 3), 2.29 (d of t, J = 15 and 5 Hz, 2), 1.52 (d of t, J = 15 and 7.5 Hz, 2), 0.8–0.3 (m, 4), and 0.14 (m, 2); *m/e* 152.1204 (152.1201).

***syn,syn*-2,5-Bishomocycloheptadienyl Methyl Ether (25).** From 16 mg (0.12 mmol) of **18** and 24 mg (0.50 mmol) of sodium hydride–mineral oil dispersion (50%) with an excess of methyl iodide, there was isolated (the 10% XF-1150 column, 120 °C) 5.3 mg (29%) of **25** as a colorless oil: ν_{max}^{neat} 3060, 2995, 2920, 2815, 1470, 1155, 1093, 1072, 1020, 915, and 730 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 3.87 (m, 1), 3.43 (s, 3), 2.53 (m, 1), 2.05 (m, 1), 1.17 (m, 2), 1.00–0.33 (m, 6), 0.10 (m, 1), and −0.11 (m, 1); *m/e* 152.1204 (152.1201).

***cis*-Bicyclo[6.1.0]non-3-en-*syn*-6-yl Methyl Ether (26).** Methylation of **4b**-OH (60 mg, 0.43 mmol) in the predescribed manner furnished 33 mg (50%) of **26** as a colorless oil (using the 5% DEGS column at 155°): ν_{max}^{neat} 3060, 2990, 2920, 2860, 1465, 1090, and 700 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 5.67 (m, 2), 3.35 (s, 3), 3.28 (m, 1), 2.28–2.00 (m, 5), 1.58 (m, 1), 0.77 (m, 1), and 0.06 (m, 1); *m/e* 152.1204 (152.1201).

***cis*-Bicyclo[6.1.0]non-3-en-*anti*-6-yl Methyl Ether (28).** Methylation of **4a**-OH[2] (13.8 mg, 0.10 mmol) in the usual manner yielded (VPC on the 10% XF-1150 column, 120 °C) 5 mg (33%) of **28** as a colorless oil: $\delta_{Me_4Si}^{CDCl_3}$ 5.83 (m, 2), 4.67 (m, 1), 3.67 (s, 3), 3.00–2.00 (m, 4), 1.33–0.42 (m, 3), and −0.10 (m, 1); *m/e* 152.1204 (152.1201).

Photodeamination of 11b in Water. The general procedure (1 mmol of **11b**) was followed and the alcohol mixture (no evidence for hydrocarbon formation was seen) was oxidized directly with Collins reagent (prepared from 500 mg of chromium trioxide and 790 mg of pyridine in 15 ml of dichloromethane) for 1 h at room temperature. The dichloromethane solution was decanted and concentrated. The inorganic solids were leached with ether (2 × 20 ml), and these were added to the organic residue prior to washing with 10% hydrochloric acid and saturated sodium bicarbonate solutions. Drying, evaporation, followed by VPC analysis and separation (12 ft × 0.25 in. 15% DEGS on Chromosorb G, 165 °C) gave the following ketones: **11a** (17%), **14a** (25%), **17** (27%), **29** (5%), and **30** (26%).

1,5-Cyclooctadien-4-ol (32). A stream of oxygen was bubbled through 40 g (0.37 mol) of 1,5-cyclooctadiene (**31**) warmed to 60 °C for 10 h. Methanol (30 ml) was added, the solution was cooled to 0 °C, and sodium borohydride (1.20 g, 0.13 eq) slowly added. After 1 h at room temperature, the reaction mixture was diluted with water (150 ml) and extracted with hexane–ether (4:1, 2 × 75 ml). The combined organic phases were washed with water, dried, and concentrated. Unreacted starting material was removed by distillation at 60–70 °C and 40 mm. The oxygenated products were distilled at 48–55 °C and 0.1 mm to give 2.51 g of colorless oil. VPC analysis indicated the presence of four components which were separated on the 15% DEGS column at 165 °C and identified as *cis*-9-oxabicyclo[6.1.0]non-4-ene (40%), 9-oxabicyclo[6.1.0]non-4-en-2-ol (20%), 1,4-cyclooctadien-6-ol (12%), and **32** (28%). For **32**: ν_{max}^{neat} 3340, 3020, 2940, 2890, 2830, 1650, 1428, 1030, 805, and 720 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 5.57 (m, 4), 4.88 (m, 1), 2.9–1.7 (m, 6), and 2.17 (s, 1).[7]

***cis*-Bicyclo[6.1.0]non-4-en-*anti*-2-ol (33a).** Zinc powder (325 mg, 5.0 mg-atoms) was added with stirring to 20 mg of silver acetate dissolved in 10 ml of hot acetic acid. The acetic acid was decanted, and the zinc–silver couple was washed with several portions of ether. The flask was now charged with 10 ml of anhydrous ether and diiodomethane (804 mg, 3.00 mmol) was introduced by syringe. After being heated to gentle reflux, the reaction mixture was treated with 124 mg (1.0 mmol) of **32** in dropwise fashion (syringe) and refluxed for 12 h. The ethereal solution was decanted and the inorganic salts rinsed with ether. The combined organic phases were washed with cold 10% hydrochloric acid (25 ml) and saturated sodium bicarbonate solution (25 ml), dried, and concentrated. VPC analysis showed two monocyclopropanated alcohols to be present in a 4:1 ratio. Preparative VPC collection of the major component (the 15% DEGS column at 165 °C) afforded 43 mg (31%) of **33a** as a colorless oil: ν_{max}^{neat} 3340, 3000, 2920, 1645, 1440, 1020, 780, and 710 cm^{-1}; $\delta_{Me_4Si}^{CCl_4}$ 5.47 (m, 2), 3.40 (m, 1), 2.65 (s, 1), 2.57–1.48 (series of m, 6), 1.48–0.42 (m, 3), and 0.13 (m, 1); *m/e* 138.1047 (138.1045).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.61; H, 9.87.

***cis*-Bicyclo[6.1.0]non-4-en-*anti*-2-yl Methyl Ether (33b).** A 40-mg (0.29 mmol) sample of **33a** was methylated in the predescribed manner and the resulting ether (**33b**) was obtained as a colorless oil (30 mg, 68%) after purification on a 12 ft × 0.25 in. 10% XF-1150 on Chromosorb P column at 125 °C; $\delta_{Me_4Si}^{CDCl_3}$ 5.73 (m, 2), 3.42 (s, 3), 3.02 (m, 1), 2.43 (t, J = 6 Hz, 2), 2.15 (m, 4), 0.95 (m, 3), and 0.17 (m, 1); *m/e* 152.1204 (152.1201).

***cis*-Bicyclo[6.1.0]non-4-en-2-one (30).** A 138-mg (1.0 mmol) sample of **33a** was oxidized with 1.00 g (10 mmol) of chromium trioxide and 1.58 g (20 mmol) of pyridine as described above. Standard workup and isolation (15% DEGS column, 165 °C) afforded 53 mg (39%) of **30**: ν_{max}^{neat} 3010, 2925, 1685, 1365, 1275, 1110, 1035, and 710 cm^{-1}; $\delta_{Me_4Si}^{CCl_4}$ 5.50 (m, 2), 3.40–2.60 (m, 2), and 2.6–0.7 (m, 8); *m/e* 136.0890 (136.0888).

***cis*-Bicyclo[6.1.0]non-4-en-*syn*-2-yl Methyl Ether (27).** Sodium borohydride (100 mg) was added to a solution of **30** (53 mg, 0.39 mmol) in 5 ml of methanol, and the mixture was stirred at room temperature for 2 h before dilution with water (20 ml) and extraction with dichloromethane (3 × 5 ml). The usual workup afforded an oil, ^{1}H NMR analysis of which showed the presence of two alcohols in an approximate ratio of 2:1. The major portion of this material (33 mg) was methylated in the conventional manner, and the resulting ethers were separated by preparative VPC methods (10 ft × 0.25 in. 15% XF-1150 on Chromosorb P, 125 °C). The minor component (38%) was identical with **33b** and the major component (62%) identified as **27** was identical with one of the major deamination products of **11b**: ν_{max}^{neat} 3000, 2940, 2880, 2820, 1484, 1355, and 1090 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 5.58 (m, 2), 3.78 (m, 1), 3.40 (s, 3), 2.50–1.80 (m, 5), 1.80–1.33 (m, 1), 1.12–0.50 (m, 3), and 0.30 (m, 1); *m/e* 152.1204 (152.1201).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.97; H, 10.54.

Epoxidation of *cis*-Bicyclo[6.1.0]non-4-ene (34). *m*-Chloroperbenzoic acid (624 mg, 4.00 mmol) in 20 ml of dichloromethane was added dropwise to a stirred slurry of **34** (431 mg, 3.53 mmol) and sodium carbonate (1.06 g, 10 mmol) in 20 ml of dichloromethane at 0 °C. After 5 h at room temperature, 10% sodium bisulfite solution (2 ml) was added and the reaction mixture poured into water (40 ml). The organic phase was separated, washed with saturated sodium bicarbonate solution (3 × 30 ml), dried, and concentrated. The resulting two epoxides (ratio 2:3) were separated by preparative VPC (10 ft × 0.25 in. 15% QF-1 on Chromosorb G, 150 °C).

The less dominant isomer is considered to be **35**: ν_{max}^{neat} 3060, 2990, 2910, 2860, 1470, 1450, 1430, 1010, 911, 902, and 765 cm^{-1}; $\delta_{Me_4Si}^{CCl_4}$ 2.87 (m, 2), 1.92 (m, 6), 1.5–0.2 (m, 5), and −0.28 (m, 1); *m/e* 138.1047 (138.1045).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.99; H, 10.20.

For **36**: ν_{max}^{neat} 3030, 2980, 2920, 2860, 1469, 1443, 1005, 983, 870, and 770 cm^{-1}; $\delta_{Me_4Si}^{CCl_4}$ 2.72 (m, 2), 2.07 (m, 4), 1.5–0.2 (m, 7), and −0.17 (m, 1); *m/e* 138.1047 (138.1045).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.98; H, 10.18.

***cis*-Bicyclo[6.1.0]non-3-en-*anti*-5-ol (37a). A. Lithium Dimethylamide Promoted Ring Opening of 35.** A solution of epoxide **35** (90 mg, 0.65 mmol) in 2 ml of ether was added dropwise at room temperature to lithium diethylamide [prepared from 730 mg (10 mmol) of diethylamine dissolved in ether (2 ml) to which was added 2.15 ml (5 mmol) of 2.5 M *n*-butyllithium at 0 °C]. After 72 h, the reaction mixture was poured into 25 ml of cold 10% hydrochloric acid, the organic phase was separated, and the aqueous layer was extracted with ether. The combined extracts were washed with 10% hydrochloric acid and saturated sodium bicarbonate solutions, dried, and concentrated to leave an oily alcohol spectroscopically identical with the major photooxygenation product (**37a**) synthesized in part B.

B. Photooxygenation of 34. To a solution of Rose Bengal (100 mg) in methanol (20 ml) was added 488 mg (4.0 mmol) of **34** in 130 ml of dichloromethane. A slow stream of oxygen was bubbled through this solution for 5 h with concomitant irradiation from a 600-W DYV tungsten lamp. Sodium borohydride (380 mg, 10 mmol) was added with stirring and after 1 h the reaction mixture was washed with water (3 × 100 ml), allowed to stand over magnesium sulfate and charcoal, filtered, and evaporated. Preparative VPC isolation (the 15% QF-1 column at 130 °C) was employed to separate the two resulting alcohols (ratio 43:57).

The minor component was isolated as a colorless crystalline solid, mp 65–67.5 °C, and identified as **38a**: $\delta_{Me_4Si}^{CDCl_3}$ 5.83–5.35 (m, 2), 5.30 (m, 1), 2.18 (s, 1), 2.50–0.40 (series of m, 9), and 0.02 (m, 1);

m/e 138.1047 (138.1045).

Alcohol **37a** was obtained as a colorless oil: ν_{max}^{neat} 3340, 3060, 2990, 2925, 1655, 1453, 1427, 1040, 1021, 1010, and 841 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 5.42 (m, 2), 5.18 (m, 1), 2.60–2.10 (m, 1), 2.22 (s, 1), 2.3–1.1 (series of m, 5), 0.83 (m, 3), and −0.10 (m, 1); *m/e* 138.1047 (138.1045).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.09; H, 10.26.

***cis*-Bicyclo[6.1.0]non-3-en-*anti*-5-yl Methyl Ether (37b).** Methylation of **37a** (42 mg, 0.30 mmol) as before provided 38 mg (83%) of **37b** as a colorless oil after preparative VPC purification on a 3 ft × 0.25 in. 5% QF-1/Chromosorb G column at 85 °C: ν_{max}^{neat} 3060, 2990, 2925, 2815, 1655, 1452, 1120, 1105, 1083, 1013, 840, and 704 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 6.0–5.4 (m, 2), 3.77 (m, 1), 3.28 (s, 3), 2.70–0.50 (series of m, 9), and 0.00 (m, 1); *m/e* 152.1204 (152.1201).

***cis*-Bicyclo[6.1.0]non-3-en-5-one (39).** A mixture of **37a** and **38a** as obtained from the photooxygenation (330 mg, 2.4 mmol) was oxidized in the customary fashion with 1.00 g (10 mmol) of chromium trioxide and 1.58 g (20 mmol) of pyridine in 30 ml of ether. Preparative VPC isolation (the 15% DEGS column at 165 °C) afforded 225 mg (70%) of **39:** ν_{max}^{neat} 1680 cm^{-1}; $\delta_{Me_4Si}^{CCl_4}$ 5.58 (m, 2), 2.8–2.0 (m, 3), 2.0–1.0 (m, 3), 0.8–0.2 (m, 3), and −0.1 (m, 1); *m/e* 136.0890 (136.0888).

6-Chloro-*cis*-bicyclo[6.1.0]non-3-ene (41). Thionyl chloride (5 ml) was added to alcohol **40**[2] (305 mg, 2.22 mmol) under a nitrogen atmosphere, and the resulting solution was warmed at 40 °C for 3 h. The reaction mixture was concentrated in vacuo to yield 325 mg (94%) of the chloride as a pale-yellow oil which because it darkened rapidly upon exposure to air was reduced without further purification.

***cis*-Bicyclo[6.1.0]non-5-ene (42).** Sodium sand was prepared from molten sodium (920 mg, 40 mg-atoms) in hot xylene (25 ml) under a nitrogen atmosphere. The sand was washed several times with anhydrous tetrahydrofuran and added to a solution of **41** (325 mg, 2.08 mmol) and *tert*-butyl alcohol (300 mg, 4 mmol) in 15 ml of tetrahydrofuran under nitrogen. After an initial exothermic reaction, the mixture was stirred overnight at room temperature. The solution was decanted from the unreacted sodium which was washed with ether (4 × 10 ml). The combined organic layers were concentrated in vacuo, and the residual oil was taken up in hexane (50 ml). The hexane solution was washed with water (3 × 30 ml), dried and concentrated. Molecular distillation afforded 216 mg (85%) of **42** as a colorless oil: bp 100 °C (bath temperature) at 40 mm; ν_{max}^{neat} 3060, 2990, 2915, 2850, 1650, 1460, 1010, 840, 780, and 700 cm^{-1}; $\delta_{Me_4Si}^{CCl_4}$ 6.0–5.2 (m, 2), 3.8–0.4 (series of m, 11), and 0.1 to −0.2 (m, 1); *m/e* 122.1097 (122.1095).

Anal. Calcd for C_9H_{11}: C, 88.45; H, 11.55. Found: C, 88.52; H, 11.47.

Photooxygenation of 42. To a solution of Rose Bengal (100 mg) in methanol (20 ml) was added a solution of **42** (122 mg, 1.0 mmol) in dichloromethane (130 ml). A slow stream of oxygen was bubbled through this solution with concomitant irradiation for 13 h as described for **34.** VPC analysis (the 15% DEGS column, 165 °C) showed greater than 90% conversion to a mixture of alcohols with one isomer predominating (>90%). Chromatography on Florisil (elution first with hexane, then with ether) afforded 63 mg (46%) of a colorless oil: ν_{max}^{neat} 3550, 3000, 2930, 1455, 1042, and 845 cm^{-1}; $\delta_{Me_4Si}^{CCl_4}$ 5.53 (m, 2), 3.33 (m, 1), 2.80 (s, 1), 2.43–0.33 (series of m, 9), and −0.13 (m, 1); *m/e* 138.1047 (138.1044).

***cis*-Bicyclo[6.1.0]non-4-en-3-one (44).** A 50-mg (0.36 mmol) sample of **44** was oxidized with 200 mg (2.0 mmol) of chromium trioxide and 316 mg (4.0 mmol) of pyridine as described earlier. Standard workup and VPC purification (the 15% DEGS column, 165 °C) gave 35 mg (70%) of the pure ketone **44:** ν_{max}^{neat} 3060, 3000, 2920, 1655, 1460, 1320, 1170, and 1025 cm^{-1}; $\delta_{Me_4Si}^{CCl_4}$ 6.2–5.4 (m, 2), 3.0–0.5 (series of m, 9), and −0.15 (m, 1); *m/e* 136.0890 (136.0888).

Photodeamination of 14b in Methanol. The general procedure described earlier was followed (304 mg, 1.00 mmol of **14b**). VPC analysis and separation (the 5% Bentone/5% SF-96 column, 120 °C) gave a single hydrocarbon identified as **12** (11%) and three methyl ethers which were subsequently characterized as **21** (24%), **28** (11%), and **46b** (54%). Because **28** and **46b** proved difficult to separate under these conditions, they were collected together and the percentage composition determined by integration of ^1H NMR spectra.

Photodeamination of 14b in Water. A 1.0-mmol sample of **14b** was irradiated according to the general procedure. VPC analysis and separation (6 ft × 0.25 in. 5% SE- on Chromosorb G, 120 °C) revealed the formation of three alcohols but no hydrocarbon. By suitable spectral comparisons, the three purified products were identified as **13** (20%), **28**-OH (10%), and **46a** (70%).

For **46a:** ν_{max}^{neat} 3370, 3060, 2995, 2805, 1458, 1050, 980, 938, and 846 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 4.35 (m, 1), 2.70–1.60 (series of m, 3), 1.92 (m, 1), 1.60–0.20 (series of m, 8), and 0.10 (m, 1); *m/e* 138.1047 (138.1044).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.09; H, 10.19.

Collins Oxidation of 46a. A 28-mg (0.20 mmol) sample of **46a** was oxidized with chromium trioxide (200 mg, 2.0 mmol) and pyridine (316 mg, 4.0 mmol) in 10 ml of dichloromethane as described earlier (30 min). Standard workup and preparative VPC purification (the 5% SE-30 column, 120 °C) yielded 20 mg (74%) of ketone identical in all respects with **14a.**

***anti,syn*-2,5-Bishomocycloheptadienyl Methyl Ether (46b).** Methylation of 10 mg of **46a** and isolation of the resulting ether by preparative VPC (the 5% SE-30 column, 120 °C) furnished 6 mg (54%) of **46b** whose spectral properties were identical with those of the sample isolated from the photodeamination of **14b:** ν_{max}^{neat} 3060, 2990, 2905, 2850, 2810, 1460, 1095, 1085, 1035, and 1018 cm^{-1}; $\delta_{Me_4Si}^{CDCl_3}$ 3.85 (m, 1), 3.28 (s, 3), 2.68–2.05 (m, 3), 1.88 (m, 1), 1.33–0.4 (series of m, 7), and 0.03 (m, 1); *m/e* 152.1204 (152.1201).

Photodeamination of 17b in Methanol and Water. The generalized procedure was utilized in both experiments. VPC analysis (the 10% XF-1150 column, 120 °C) of the methanolic reaction mixture revealed the formation of >99% of a single methyl ether and <1% of a single hydrocarbon whose retention time proved identical with that of **15** under these conditions. The isolated ether had spectral properties identical with those of **25.**

From the aqueous photodeamination, a single product was detected. VPC isolation (5 ft × 0.25 in. 5% QF-1 on Chromosorb G, 145 °C) afforded crystalline **18**, mp 72–74 °C, whose spectra were superimposable upon those of the authentic sample.

Methanolysis of 5a. A 200-mg (0.69 mmol) sample of **5a** and 121 mg (1.06 mmol) of 2,4,6-collidine were dissolved in 10 ml of dry methanol (distilled from magnesium methoxide) and sealed under reduced pressure in a thick-walled glass ampule. The ampule was immersed in a 145 °C bath for 2.0 h. The contents of the ampule were diluted with 20 ml of cold water. The products were extracted with hexane (3 × 10 ml), and the combined extracts were washed with 10% hydrochloric acid (2 × 20 ml), saturated sodium bicarbonate (20 ml), dried, and concentrated in vacuo. VPC analysis and separation (10 ft × 0.25 in. 15% XF-1150, 135 °C) established the formation of **22** (4.4%), **26** (85.3%), **23** (8.0%), **28** (1.7%), and **24** (0.6%). The spectra of the major products were identical with those of authentic samples. The minor products (**28** and **24**) were identified by their retention time behavior.

Methanolysis of 3. A 200-mg (0.69 mmol) sample of **3** and 121 mg (1.00 mmol) of 2,4,6-collidine were dissolved in 10 ml of dry methanol and sealed under reduced pressure in a thick-walled glass ampule. The ampule was immersed in a 145 °C oil bath for 2.0 h. Workup in the predescribed manner revealed the formation of **19** (1%), **20** (19%), **21** (69%), and **28** (11%). All but **19** were characterized by direct spectral comparisons.

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A Theory of Free Radical Reactions

Vlasta Bonačić-Koutecký,*[1a] Jaroslav Koutecký,[1a] and Lionel Salem*[1b]

Contribution from the Institut für Physikalische Chemie, Freie Universität, 1000 Berlin 33, West Germany, and The Laboratoire de Chimie Théorique, Université de Paris-Sud, Centre d'Orsay, 91405 Orsay, France. *Received April 30, 1976*

Abstract: The simple three-center three-electron model introduced by Yamaguchi is used to describe the elementary abstraction–addition step in the approach of a free radical to a bonded pair of atoms. Consideration of all *covalent* resonance structures shows the colinear approach to be "exchange allowed" and the equilateral triangular approach to be "exchange forbidden". Inclusion of all *polar* resonance structures, as a perturbation to the previous situation, shows that addition of a free radical to a double bond tends to occur at that position for which the incipient bond has maximum partial ionic character. If the position of attack is also that favored from thermodynamic considerations, ionic effects will simply reinforce the thermodynamic control. If the position of attack is opposite to that for the more stable product, ionic and thermochemical controls will compete, with the possibility of contrathermodynamic orientation of addition. These two cases are illustrated by ab initio calculations on simple $Cl\cdot + XHC{=}CH_2$ addition reactions.

Introduction

Free-radical reactions are extremely versatile.[2] The great variety of reactions seem to occur, however, through a limited number of *elementary steps*. For reaction with closed-shell molecules, the two most common elementary steps are *abstraction* of hydrogen atoms from RH bonds[3a] and *addition* to saturated centers.[3b,c] A third, less common elementary step is S_H2 type substitution.[4] The other substitution reactions involve either an abstraction step as in allylic substitution, or an addition step, as in aromatic substitution. Carbenes, of course, will insert into bonds, but generally as singlets with two paired electrons; as such the insertion reaction is not a free-radical reaction proper. Triplets may also insert, but again via multiple steps. With other radicals, reactions such as dimerization and disproportionation may take place. In analogy with photochemical reactions, free-radical reactions can be tailored to yield products which would be difficult to obtain by thermal reactions involving intangible electron pairs.[5] A long-standing topic of interest has been the role of "polar effects" in determining the structure and energy of free-radical reaction transition states.[6] A particularly important question is the extent to which these polar effects may eventually be involved in the *orientation* of free-radical additions, in competition with the relative thermodynamic stabilities of possible primary products.[3b,c,7]

Theoretical attempts at describing free-radical reactions can be traced back to the early days of quantum chemistry. The three-center three-electron system H_3 was one of the first systems to be studied by the traditional valence-bond method.[8] At that time the aim was a quantitative description of the potential energy surface for a chemical reaction. More recently three-electron systems have been considered by Matsen, using a spin-free approach which is closely related to the valence-bond method.[9] Various calculations have recently been performed on specific radical reactions.[10] These theoretical studies have been carried out in the same context as studies of the reactions of closed-shell systems; similar orbital interactions are invoked. Recently, Yamaguchi has made the first attempt to rationalize the behavior of free-radical reagents on the basis of a model which incorporates explicitly the essential characteristic property of these reagents—an unpaired spin.[11] He considered a set of three-electron spins, two of which are initially paired, while the third one seeks out a partner spin from this initial pair. Using a phenomenological Heisenberg Hamiltonian, equivalent to a simplified valence-bond approach in which electron exchange alone is included, Yamaguchi obtained correlation diagrams for the doublet states and the quartet state. These correlation diagrams show qualitatively different behavior for the linear configuration (which was identified with the abstraction process) and for the triangular configuration.[12] In analogy to the Woodward–Hoffmann rules, Yamaguchi concluded that the linear approach is "spin-symmetry allowed" with no crossing between the two doublets, while the triangular approach is "spin-symmetry forbidden" with crossing doublets (compare also ref 8a). This last result is particularly surprising, in view of the extremely facile addition of halogen atoms to double bonds.[12]

In the present work we reconsider the three-center three-electron model for the elementary abstraction–addition reaction step. The energies of the different states for a purely covalent model are then obtained in a straightforward manner from the exact three-particle Hamiltonian. We draw out correlation diagrams for different orientations of approach of the free-radical reagent to the bond. We next extend the simple model, based on covalent structures, to include ionic structures. It is possible to discuss the effect of ionic character in the incipient bond in a qualitative manner. Our main results are: (1) For purely covalent interactions the colinear end-on approach has a small activation barrier ("exchange allowed"), while the triangular approach is favorable only if the free radical can maintain zero overlap with one of the centers of the initial bond. Otherwise the triangular approach is "exchange forbidden". These results are specific to the three-electron model and do not appear in the one-electron approach commonly used for even-electron systems. (2) When ionic interactions are