molecule from $[M]^{\cdot +}$ is followed by stepwise loss of two carbon monoxide molecules,[24] the resulting [M − 28], [M − 56], and [M − 84] peaks all being relatively unstable odd-electron species. Confirming metastable transitions for the first two steps are found in the spectra of all three compounds. Additional experiments to further elucidate the results of Table V do not seem to be a compelling objective at the present time.

Acknowledgment. The authors express their great appreciation to Professor F. W. McLafferty and Dr. J. W. Serum of Cornell University for furnishing the low-resolution and most of the high-resolution mass spectra. We also thank Mr. G. A. Cockayne, Mr. P. J. Taylor, and Dr. R. B. Webster of Imperial Chemical Industries Limited, Macclesfield, Cheshire, England for exact mass measurements of compounds **3c** and **24b**.

Registry No.—**3a**, 23652-94-0; **3b**, 53432-94-3; **3c**, 23754-49-6; **3d**, 23652-96-2; **3e**, 23112-27-8; **3f**, 23652-95-1; **3g**, 23674-49-9; **12a**, 23652-79-1; **12b**, 53432-95-4; **12c**, 23652-80-4; **24a**, 23674-56-8; **24b**, 23645-83-2; **24c**, 53432-96-5; **24d**, 23674-57-9; **34a**, 77-04-3; **34b**, 1130-18-3; **47a**, 1130-77-4; **47b**, 1216-47-3; **47c**, 1149-82-2.

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(1) Part II, D. L. Ostercamp, *J. Org. Chem.*, **35**, 1632 (1970).

(2) J. J. Jakobsen, S.-O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc. B*, 940 (1966).

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(8) See ref 1 for details concerning stereochemical classification of compounds used in this project. Intramolecular hydrogen bonding (where possible) would be strongly favored within the mass spectrometer vacuum.

(9) Presence of an electron-withdrawing *N*-acyl substituent would destabilize this fragment ion (as compared to **2a**). Apparently contradictory results have been obtained for three *N*-acyl vinylogous urethanes and one vinylogous imide.[5] However, all four are heterocyclic compounds, and alternative fragmentation would disrupt the ring.

(10) Sucn ions would result from direct loss of an acyl group. Cyclic azirinium ions have been postulated as minor fragment ions in the mass spectra of vinylogous amides.[3,4] The present expectation regarding stability is based on the twin factors of favorable ring size and aromatic character.

(11) D. L. Ostercamp, *J. Org. Chem.*, **30**, 1169 (1965).

(12) Representative starting compounds were shown to be thermally stable at 200°, thus precluding any thermal reaction in the inlet system.

(13) Ions analogous to **6** and/or **7** are essentially absent whenever the appropriate carbonyl group is stereochemically barred from participation (see discussion of cyclic compounds). Alternative structures, *i.e.*, acyclic or azirinium cations, would not enjoy aromatic stability. Oxazolium ion structures have been assigned to base peaks in the mass spectra of 5-methyl- and 4,5-dimethyl-2-hexyloxazole and 2,5-dimethyl-4-hexyloxazole: J. H. Bowie, P. F. Donaghue, H. J. Rodda, R. G. Cooks, and D. H. Williams, *Org. Mass Spectrom.*, **1**, 13 (1968).

(14) D. J. Brown and P. B. Ghosh, *J. Chem. Soc. B*, 270 (1969). We refrain from commenting on the relative resonance stabilization of ions **6** and **7**, as we are unable to find a reference to heats of hydrogenation and/or combustion of oxazole and isoxazole.

(15) The results are limited here to ions whose *m/e* is equal to or greater than 69.

(16) The second step, **8** → **9**, is equivalent to a prominent first step, **1a** → **2a**, in the fragmentation of the molecular ion of a vinylogous amide. As **9a** is here, so is **2a** often the base peak.[2-4]

(17) Relative intensities of [M − R^2CO] cations for the following compounds are, for **24c**, 0.4% and, for **24d**, 0.2%.

(18) This would produce a diradical, and so detract from product stability.

(19) Ring closure is accompanied by inversion of configuration at a vinyl carbon atom. The process may be viewed as an SNi reaction, carbon monoxide being the leaving group.

(20) Such fragmentation is also shown by analogous vinylogous esters and amides[3] and 5,5-dialkylbarbituric acids.[21]

(21) H.-F. Grutzmacher and W. Arnold, *Tetrahedron Lett.*, 1365 (1966).

(22) J. T. Watson and F. C. Falkner, *Org. Mass Spectrom.*, **7**, 1231 (1973).

(23) A. J. Bowles, E. F. H. Brittain, and W. O. George, *Org. Mass Spectrom.*, **2**, 809 (1969).

(24) See ion compositions for compound **47a** in Table V.

Site Selectivity on Hydrogenation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one. A Possible Effect of Homoaromatic Delocalization

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The synthesis of bicyclo[4.2.1]nona-2,4-dien-9-one (2) by catalytic and diimide reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1) was investigated. It was found that direct reduction of 1 gave five reduced ketones, whose structures were determined spectroscopically, but none of 2. An authentic sample of 2 was prepared in low yield by further reactions of two of the other reduced ketones. However, conversion of the ketone group of 1 to a dimethyl ketal, an ethylene ketal, or an alcohol prior to reduction, followed by treatment with diimide and then either hydrolysis or oxidation, respectively, gave high yields of 2. The reduction *via* the dimethyl ketal has been developed into a useful preparative procedure for 2. The reluctance of 1 to give 2 on direct reduction is attributed to homoaromatic interaction of the electrons on the isolated double bond at C_7–C_8 with the carbonyl at C_9 leading to sharply reduced electron density at C_7–C_8 compared to the diene moiety. The electron density in the diene may even be increased by bis(homocyclopentadienyl) interaction with the carbonyl. These effects are removed by conversion of C_9 to a tetrahedral configuration from the trigonal configuration in 1. Steric effects in this system are analyzed and are concluded to be of less significance than the electronic effects.

We had need of bicyclo[4.2.1]nona-2,4-dien-9-one (2) for photochemical studies described elsewhere[2] and sought to prepare 2 by reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1). Compound 1 was recently synthesized through different routes by three groups.[3,4] We naively assumed that catalytic or diimide hydrogenation of 1 would preferentially reduce the isolated double bond (C_7–C_8) as opposed to the diene moiety.

Results

The synthesis of 1 utilized was essentially that of Antkowiak and Shechter.[3] The synthesis of 2 from 1 would seem to be simply accomplished by reduction of the C_7–C_8 double bond, since isolated double bonds are reduced preferentially to a conjugated diene grouping. However, 2 was not present in the complex product mixture derived from

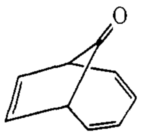
Table I
Product Distributions on Reduction of 1 and Derivatives

			Products, % yield[b]						
Reactant	Reducing agent	Mole ratio[a]	1	2	3	4	5	6	7
1	H_2[c]	0.5	50	0	40	2	4	4	Tr
1	H_2[c]	1.2	0	0	70	10	7	10	3
1	H_2[c]	1.6	0	0	41	17	16	18	8
1	H_2[c]	2.5	0	0	3	25	26	12	34
1	H_2[c]	2.0	0	0	15	35	20	20	10
1	Diimide[d]	1.5	70	0	20	5	0	5	Tr
1	Diimide[d,e]	2.0	45	0	35	10	0	10	Tr
1	Diimide[d]	2.0	33	0	42	10	0	13	3
1	Diimide[d]	2.0	40	0	40	10	0	5	5
1	Diimide[d]	4.0	Tr	0	Tr	40	0	Tr	60
9	Diimide[d]	1.0	0	67	2	0	0	30	1
10	Diimide[d]	1.0	0	62	15	0	0	19	3
11	Diimide[d]	2.0	0	39	25	1	0	30	5

[a] Ratio of reducing agent to reactant. [b] Products were analyzed by glpc on a 5-ft column of 30% Carbowax 20M on 80–100 Chromosorb W at 190°. Ketones 1 and 2, which are not separated on this column, were separated on a 6-ft column of 10% UCON 50 LB 550 X on Chromosorb P at 160°. Yields given are based on glpc peak areas measured by disk integration assuming equal response factors for all ketones and are percentages of the total measured area. Tr = trace peak in chromatogram. [c] Catalytic hydrogenation carried out in dioxane using a 10% Pd/C catalyst. [d] Diimide was generated from potassium azodicarboxylate *in situ*. Mole ratio based on quantity of PADA used. [e] Carried out in very dilute solution.

catalytic hydrogenation or from diimide reduction of **1**, which included virtually all of the other possible ketonic reduction products **3–8**.

Reduction of trienone **1** with up to 2 mol of hydrogen or potassium azodicarboxylate per mole of **1** using standard procedures led to a complex product mixture, from which ketones **3**, **4**, **5**, **6**, and **7** could be isolated using preparative glpc. Dienone **2** was not present in detectable amount in any of the hydrogenation product mixtures. The distribution of products is given in Table I.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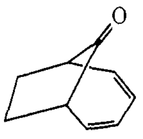
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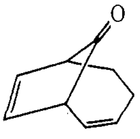
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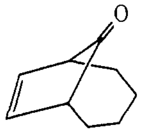
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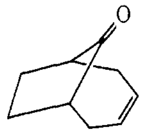
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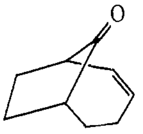
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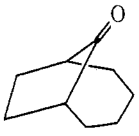
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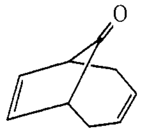
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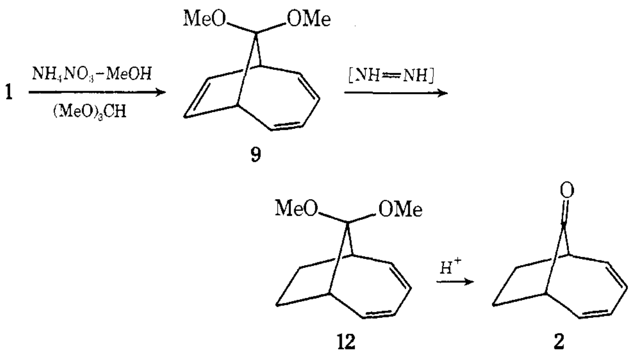
It should also be noted that the total yields of the possible products of further hydrogenation of **2**, namely, ketones **5**, **6**, and **7**, always comprised a minor fraction of the total reaction mixture in the runs starting with trienone **1**. A synthesis of **2** was devised as follows. The catalytic hydrogenation of **1** was controlled to maximize the yield (39%) of **5** and **6**. The hydrogenated mixture without prior purification was brominated with a large excess of *N*-bromosuccinimide and then treated with zinc in acetic acid. The other three hydrogenated ketones **3**, **4**, and **7** present in the original hydrogenation mixture do not interfere with the subsequent reactions. Either these ketones do not possess allylic positions which can be brominated or the brominated products give the starting material after treatment with zinc and acetic acid. Dienone **2** in 19% yield was isolated from the final mixture by preparative glpc (gas–liquid partition chromatography).

Mass spectroscopy distinguished between dihydro (**2**, **3**, and **8**), tetrahydro (**4–6**), and hexahydro (**7**) reduction products of **1**. Dienone **3** was distinguished from **2** on the basis of nmr spectroscopy. In **3**, there are two different bridgehead protons at 2.92 and 3.19 ppm. Dienone **3** had two isolated olefinic protons at 5.76 and 6.16 ppm, whereas **2** had four protons of a butadiene group at 5.44 ppm, which collapsed on irradiation of the bridgehead protons (160 Hz) in a decoupling experiment. The decoupling of **3** was consistent with the structure and is described in the Experimental Section. Dienone **8** should have two different olefinic protons, probably different from those of **2** and **3**. Enone **4** showed two bridgehead protons (2.92 ppm), which are allylic and in the position α to the carbonyl. However, the bridgehead protons in enone **5** were not as deshielded as in **4** and, hence, did not appear as a separate peak. Enone **5** was detected only in the catalytic hydrogenation mixture, which is reasonable since the diimide molecule supplies two hydrogen atoms to the double bond through a six-membered cyclic transition state, and is thus unable to achieve 1,4 reduction. Enone **6** had an unsymmetrical pattern in its nmr spectrum, which could be distinguished from the symmetric spectrum of **4**.

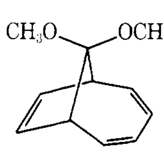
After preliminary rationalization of the lack of formation of **2** from the reduction of **1** (as discussed below), a new approach to **2** *via* ketal **9** was designed as shown in Scheme I.

Scheme I



Since trienone **1** isomerizes to indanone in the presence of Lewis acids (discussed below), a mild catalyst[5] and longer reaction time (5 days) were necessary for ketal formation in this case.

Reduction of **9** by diimide produced in about 70% yield the dimethyl ketal of **2** (see Table I), which was hydrolyzed to **2** without difficulty. The synthesis of **2** *via* **9** occurs in good overall yields and has been worked up into a useful preparative procedure for this elusive material. The synthesis of **2** could also be accomplished *via* the ethylene ketal **10**, which gave 62–67% yields of **2** on diimide reduction and acid hydrolysis. This route was much less useful preparatively because of difficulty in formation of ketal **10**.



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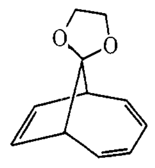

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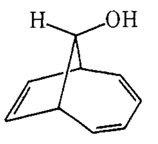


11

Alternatively, the carbonyl group of **1** could be reduced with sodium borohydride to alcohol **11**, reported previously,[6–8] which was then reduced with diimide. The crude reaction mixture was oxidized directly with magnesium dioxide to a mixture of ketones, which was analyzed by glpc by coinjection with the previously isolated ketones **2–7**. The major product produced in this way, as shown in Table I, was indeed **2**. A large decrease in the yields of **3** and **4** was also observed, further indicating that the primary site of reduction had shifted (relative to **1**) to C_7–C_8.

Discussion

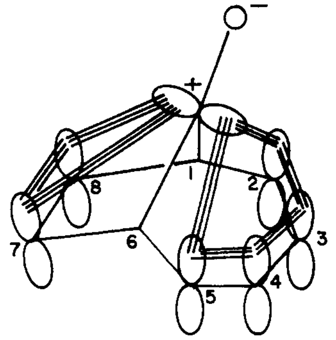
Earlier studies have established that the rates of reduction of olefins by diimide are sensitive to a variety of structural parameters, including torsional strain, bond angle bending strain, and substituent effects.[9] Electronic rather than steric effects of substituents appear to dominate in most systems,[9] although other workers[10] find that diimide reductions are sensitive to steric approach control. For example, only exo–cis addition to 2-norbornene-2,3-dicarboxylic acid is observed, and trans-substituted double bonds are reduced by diimide more rapidly than corresponding cis bonds in acyclic olefins. Special electronic effects can operate in certain systems, as demonstrated by the predominant reduction by diimide of the syn rather than the anti double bond in 7-hydroxy-, 7-acetoxy-, and 7-*tert*-butoxynorbornadiene.[11] The fact that the more sterically hindered (to exo–cis attack) double bond is the preferred site of reaction is rationalized by coordination of diimide with the oxygen atom attached to C_7, followed by delivery of hydrogen to the proximate double bond.

Thus, a variety of factors may be involved in catalytic and diimide reduction of the bicyclo[4.2.1]nonatrienes **1**, **9**, **10**, and **11** described in this paper. Models suggest that the diene moiety in **1** is highly strained, with the angle between the C_2–C_3 and C_4–C_5 double bonds perhaps as high as 135°. This would suggest that diimide reduction at the diene site in **1** ought to be particularly favored over reduction of the isolated double bond at C_7–C_8 because of greater relief of steric strain.[9] While this steric strain is undoubtedly relieved to some extent on conversion of the trigonal center at C_9 in **1** to a tetrahedral configuration at C_9 in **9**, **10**, and **11**, the residual strain would appear from models to be sufficient to expect preferential attack by diimide or hydrogen on the diene in **9**, **10**, and **11** on the basis of strain considerations alone. Furthermore, the orientation of the hydroxyl group in **11** should promote diimide attack on the diene moiety, by extrapolation of the earlier study[11] of substituted norbornadienes. This proximity effect[11] should be largely equalized in the ketals **9** and **10**.

Models also suggest that the five-membered ring in the bicyclo[4.2.1]nonatrienes is quite flat, although attempts at deuterium exchange of the bridgehead protons in **1** and **2** by extended treatment with D_2O and KOH in acetonitrile were unsuccessful. The reaction was monitored by nmr for a period of 2 months.[12] In any event, saturation of the carbonyl group of **1** should result in increased steric hindrance to exo–cis attack at the diene moiety relative to attack at the isolated double bond at C_7–C_8. On this basis, some decrease in the amount of products arising from initial attack on the diene in **9**, **10**, and **11** is anticipated purely on steric grounds. However, the extent of steric shielding of the diene in ketals **9** and **10** ought to be different, because of the freely rotating methyl in **9** which can assume conformations severely shielding the diene, while in **10** the methylene groups are rigidly held back from the reaction site. It is therefore striking that the course of hydrogenation of these two ketals is in fact very similar, suggesting that steric factors are probably not important in these systems.

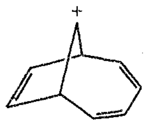
The hydrogenation data demonstrate that none of **2** is formed on either direct hydrogenation or diimide treatment of trienone **1**, although **2** is the major product of the three-step sequence involving protection of the carbonyl at C_9, hydrogenation, and regeneration of the carbonyl. Thus, the isolated double bond which is totally unreactive relative to the diene **1** is the most reactive hydrogenation site in **9**, **10**, and **11**. This striking change in site reactivities is not readily rationalized on the basis of the various effects cited above. It seems that some special factors(s) are involved which operate so as to selectively reduce the reactivity of the isolated double bond in trienone **1**.

The results seem to us to be best understood on the basis of the operation of homoaromatic (and perhaps also antihomoaromatic) delocalization of π electrons in **1**.[13] Interaction of the C_7–C_8 π bond with the carbonyl p orbital at C_9 should remove electron density from C_7–C_8, by analogy with bis(homocyclopropenyl) interaction in the 7-norbornadienyl cation.[13,14] However, overlap in a similar manner of the p orbital at C_9 with the C_2–C_5 diene moiety on the other side of the molecule should be energetically unfavorable, since it would create an antiaromatic bis(homocyclopentadienyl) cation,[15] as shown in structure I. It is even possible that electron density at the diene moiety may be increased in **1** if the (empty) p orbital at C_9 acts as a conductor of electron density from the potentially aromatic bis(homocyclopropenyl) cation on one side of the molecule to a potentially antiaromatic bis(homocyclopentadienyl) anion on the other side. On this basis, exclusive hydrogenation of **1** at the diene moiety is understandable. Reduction at C_9 would cancel these electronic effects and restore the "normal" reactivity pattern of a bicyclo[4.2.1]nonatriene, *i.e.*, preferred reduction at C_7–C_8.[16]



I

These considerations have obvious relevance to the discussion in recent literature of bicycloaromaticity[17] in the bicyclo[4.2.1]nonatrienyl cation **13** and related molecules. The first report relating to **13** showed that solvolysis of tosylate **14** is accompanied by deep-seated rearrangement.[7] Thus, reaction of **14** in tetrahydrofuran in the presence of lithium aluminum hydride gives *cis*-8,9-dihydroindene (**15**). This is consistent with results of later studies,[18,19] *e.g.*, the formation of acetate **16** on acetolysis of **14**. The rate of acetolysis of **14** is enhanced by a factor of 10^4 over that of the more saturated analogs **17** and **18**, despite the rate-retarding inductive effect of the butadiene moiety in **14**. This suggests that there is a stabilizing interaction of the bis(homocyclopropenyl) type between the C_7–C_8 π electrons and the developing p orbital at C_9 in **13**. There seems to be agreement that the observation of rearrangement coupled with rate acceleration on solvolysis of **14** seems best understood in terms of initial formation of a bicycloaromatic ion **19** in which stabilization by homoaromatic [*i.e.*, bis(homocyclopropenyl)] interaction[20] provides only a small portion (estimated as 20%)[19b] of the total stabilization. The interaction of the butadiene and homocyclopropenyl moieties is not sufficient, however, to prevent rearrangement of **19** to the bis(homotropylium) ion **20** which is the source of the observed products.[18,19]



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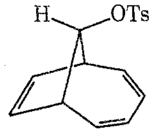

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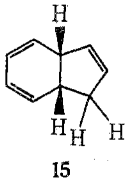

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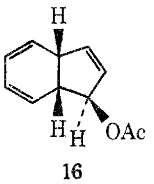

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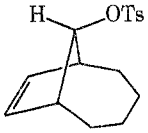

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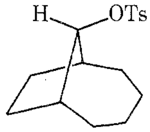

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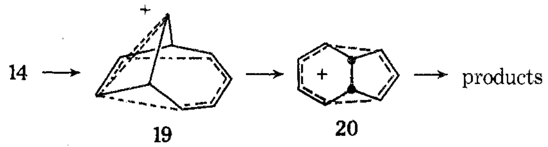
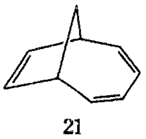


19 20

Photoelectron spectroscopy provides some additional information about π-electron interaction in these systems. Data for the triene **21** indicate no appreciable interaction of this type,[21] although extensive π interaction is indicated for tetraene **22**.[22] Nonetheless, the authors in the latter study[22] do not feel that the evidence at present *demands* the operation of bicycloaromatic delocalization in **22**. Similarly, we do not claim that our results *prove* that π delocalization of either the homoaromatic[20] or bicycloaromatic[17] variety is occurring to a significant extent in **1** and/or the hydrogenation transition states and that the data can be rationalized *only* on the basis of such effects. However, we do believe that such interactions and their mechanistic implications provide a consistent as well as compelling explanation of the experimental observations.[24]



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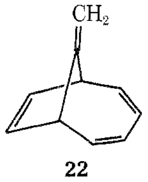


22

Experimental Section

All melting points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer. Abbreviations used in reporting data are s = singlet, d = doublet, q = quartet, m = multiplet, br = broad, and sh = sharp. Mass spectra were obtained with a Varian M-66 double focusing cycloidal path mass spectrometer. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord spectrophotometer and ultraviolet spectra on a Cary Model 15 spectrophotometer.

Gas–Liquid Partition Chromatography. Analytical studies were carried out on a Hewlett-Packard Model 5750 research chromatograph using flame ionization detection. Preparative separations were made on an Aerograph preparative gas chromatograph, Model A-90-P. The column used for most of the ketone analyses was a 6 ft × ⅛ in. stainless steel column containing 20% Carbowax 20M on 80–100 mesh Chromosorb W, operating at a column temperature of 160° and the injection port set at 280°. The flow rates were helium 40–60 ml/min, hydrogen 40–60 ml/min, and air 300–400 ml/min. Under these conditions the retention times (min) of the ketones were as follows: **1** and **2** (not separated), 13.2; **3**, 8.6; **4**, 6.2; **5**, 10.4; **6**, 11.2; and **7**, 8.4. Where other columns and conditions are used, they are specifically indicated.

Bicyclo[4.2.1]nona-2,4,7-trien-9-one. The synthesis of **1** was essentially the same as that of Antowiak and Shechter[2] except that hydroquinone was added to the reaction mixture to lessen tar formation. After the reported work-up procedure, the crude reaction product was distilled quickly at 0.5 mm and was then redistilled through a short Vigreux column to give **1**, bp 80–90° (0.9 mm), as a colorless liquid: ν_{max}^{neat} 3025, 2945, 1760, 1580, 1260, 1150, 920, and 865 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 267 nm (ϵ 3000), 276 (2800), and 320 (630); $\delta_{TMS}^{CDCl_3}$ 5.46 (m, 6 H, olefinic) and 2.73 (br s, 2 H, bridgehead); *m/e* 132, 131, 116, 104, 103, 91, 78, and 72.

A by-product from the above reaction is the assumed dimer of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**): ν_{max}^{KBr} 3000, 2950, 1675 (split), 1205, 880, 865, 695, and 660 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 2.2 (br s, 4 H), 3.2 (br s, 1 H), 3.6 (d, 1 H), 4.0 (br s, 1 H), and 5.9 (m, 8 H).

Bicyclo[4.2.1]nona-2,4-dien-9-one (2). Bromination–Debromination Route. Trienone **1** (2.11 g, 0.016 mol) in 40 ml of dioxane was catalytically hydrogenated over 10% Pd/C. A total reaction time of 13 hr was required to consume 920 ml of hydrogen at room temperature. The relative yields of the five reduced products at this point (glpc) were as follows: **1** (none), **2** (none), **3** (3.0%), **4** (24.7%), **5** (26.4%), **6** (12.4%), and **7** (33.7%).

To the above crude mixture in 30 ml of carbon tetrachloride were added 5.70 g (0.032 mol) of *N*-bromosuccinimide and 0.03 g of benzoyl peroxide. The mixture was heated at reflux for 50 min under a nitrogen atmosphere. The solid was removed by filtration, and the solvent was removed. The crude product was dissolved in 100 ml of ethyl ether and to it were added 1.64 g (0.025 g-atom) of zinc dust and 1.1 g (0.018 mol) of acetic acid. The mixture was stirred for 1.5 hr at room temperature and then heated at reflux for 30 min. After the mixture was cooled, 4.0 ml of pyridine was added. The salt formed was filtered off, and the ether layer was washed, dried, and concentrated. Dienone **2** was collected (18.8% overall yield) by preparative glpc using an 8-ft 10% Carbowax 20M column: ν_{max}^{neat} 3025, 2950, 2865, 1750, 1450, 1180, 865, 745, 700, and 650 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 264 nm (ϵ 3300) and 313 (500); $\delta_{TMS}^{CDCl_3}$ 5.44 (m, 4 H, butadienyl), 2.42 (br s, 2 H, bridgehead), and 2.00 (m, 4 H, ethanyl); *m/e* 134, 119, 106, 91, 85, 83, and 78.

Bicyclo[4.2.1]nona-2,4-dien-9-one (2). Dimethyl Ketal Route. In a typical run, ammonium nitrate (0.6 g) dissolved in 20 ml of methyl alcohol was added to a mixture of 2.11 g (0.016 mol) of trienone (**1**) and 2.12 g (0.020 mol) of trimethyl orthoformate.[5] The reaction mixture was stirred at room temperature for 5 days. Sodium carbonate (1.0 g) followed by 200 ml of ethyl ether was added. The ether layer was filtered and concentrated and the crude mixture was separated by column chromatography on silica gel, eluting with ether–hexane mixtures. Pure 9,9-dimethoxybicyclo[4.2.1]nona-2,4,7-triene (**9**, 400 mg) was obtained from the fourth, fifth, and sixth fractions (700 ml each), eluted with 20% ether–80% hexane: ν_{max}^{neat} 3025, 2930, 2825, 1450, 1295, 1205, 1130, 1055, and 710 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.86 (m, 4 H), 5.19 (d, J = 1.5 Hz, 2 H), 3.10 (sh s), 3.05 (sh s), and 3.10 (br) (total 8 H); *m/e* 178, 177, 147, 131, 121, 105, and 91.

Into a slurry of 194 mg (1.0 mmol) of potassium azodicarboxylate in 10 ml of dioxane under a nitrogen atmosphere was introduced 178 mg (1.0 mmol) of dimethyl ketal **9**. To this was added half of a solution of 120 mg (2.0 mmol) of glacial acetic acid in 3 ml of dioxane at the start of the reaction and the other half after 20 hr. After a total reaction time of 44 hr, the yellow color of the mixture was totally bleached. The solid was separated by filtration, and 100 ml of ethyl ether was added to the filtrate. The ether layer was washed with 5% carbonate solution and then with saturated sodium chloride solutions. The ethereal solution was dried over anhydrous magnesium sulfate and then concentrated. Analysis of the crude product by glpc and nmr indicated 67% conversion to ketal **12.** The mixture was chromatographed on a column of aluminum oxide of pH 7.8 (J. T. Baker) which was eluted with ether–hexane mixtures. In addition to ketal **12,** some dienone **2** was eluted directly from the column. However, the overall material balance was very poor. Attempts at separation of **12** from the crude mixture by fractional distillation and liquid–liquid partition chromatography were also unsuccessful. The ketal **12** was eventually separated in a pure state most efficiently by preparative glpc using a 15-ft column of 30% Carbowax 20M on Chromosorb W at 215° with the injection port set at 310°. The ketal **12** was identified primarily by its nmr spectrum: $\delta_{TMS}^{CDCl_3}$ 6.87 (m, 4 H), 3.34 (s, 6 H), 2.70 (br s, 2 H), and 2.08 ppm (m, 4 H).

In a typical run, 17.0 g of a sample which was about 70% of the ketal **12** was hydrolyzed by stirring with 3 *N* HCl for 15 min at room temperature. After the conventional work-up, a total of 2.09 g of bicyclo[4.2.1]nona-2,4-dien-9-one **2** was collected by preparative glpc on the 15-ft 30% Carbowax 20M column.

The material obtained was identical with that obtained earlier according to glpc analysis on two different columns: 6 ft × ⅛ in. column of 15% Carbowax 20M on 80–100 mesh Chromosorb W at 175° with the injection port at 265° (retention time 5.8 min); 15 ft × 0.25 in. column of 15% Carbowax 20M on 80–100 mesh Chromosorb W at 190° with injection port at 275° (retention time 20.2 min).

Bicyclo[4.2.1]nona-2,4-dien-9-one. Ethylene Ketal Route. Trienone **1** (1.4 g, 0.01 mol), 25 ml of ethylene glycol, a small amount of ammonium nitrate, and a trace of hydroquinone were mixed and stirred for 15 days at room temperature. Analysis by glpc indicated approximately 70% conversion to ketal **13.** The reaction was stopped after 17 days, 100 ml of water was added, and the mixture was extracted with 500 ml of pentane. The pentane layer was washed once with carbonate solution and three times with saturated salt solutions. The aqueous layer was extracted once with 300 ml of ether, and then the ether layer was washed as above with carbonate and saturated salt solutions. The pentane and ether layers were combined, dried over anhydrous sodium sulfate, and concentrated. The ketal **10** was obtained by preparative glpc on a 6 ft × ⅛ in. column of 25% Carbowax 20M on 80–100 mesh Chromosorb W. Spectral data for ethylene ketal **10** are as follows: ν_{max}^{neat} 3020, 2950, 2900, 1600, 1480, 1350, and 1275 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.83 (m, 4 H), 5.28 (d, 2 H), 3.81 (s, 4 H), and 2.82 ppm (m, 2 H); *m/e* 176, 175, 104, 86, and 84 (base peak).

The ketal **10** (80 mg, 0.46 mmol), 88 mg (0.46 mmol) of potassium azodicarboxylate, and 60 mg (1.0 mmol) of glacial acetic acid in 10 ml of dioxane were allowed to react as described for ketal **9.** The reduction was stopped after 9 hr of stirring at room temperature. After work-up, as above, the crude product was hydrolyzed with 3 *N* HCl for 15 min at room temperature. The ketonic mixture was analyzed by glpc as previously described and showed 62.0% **2,** 14.5% **3,** 19.4% **6,** and 2.6% **7.**

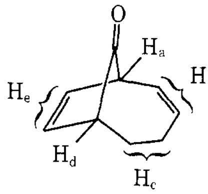
Bicyclo[4.2.1]nona-2,4-dien-9-one. Route *via* 9-Hydroxybicyclo[4.2.1]nona-2,4,7-triene. A solution of 1.06 g (0.008 mol) of trienone **1** and a trace of hydroquinone in 10 ml of methyl alcohol was slowly added to a stirred solution of 0.296 g (0.008 mol) of sodium borohydride and a drop of 50% aqueous KOH in 5 ml of water. The mixture was stirred for 20 hr, keeping the temperature below 25°. Hydrochloric acid (20 ml of a 2% solution) was added to destroy excess hydride, and the organic material was extracted with 300 ml of ether. The ether layer was washed with saturated salt solution, dried, and concentrated. A white solid was obtained with mp 47–51° (lit.[6] mp 52.0–52.5°; lit.[7] mp 51.0–52.5°) which showed only one peak by glpc analysis. The spectral data, in substantial agreement with previous reports,[6,7] are consistent with the assignment of structure **11,** 9-hydroxybicyclo[4.2.1]nona-2,4,7-triene, to this material: ν_{max}^{neat} 3560, 3020, 2950, 1405, 1220, 1105, 1060, 980, 910, and 690 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.85 (m, 4 H), 5.08 (d, J = 1.5 Hz, 2 H), 4.20 (br s, 1 H), 2.89 (m, 2 H), and 2.03 ppm (br s, 1 H); *m/e* 134, 133, 115, 105, 92, 91, and 78. The nmr spectrum agrees well with that reported by Shechter, *et al.*,[7] under somewhat better resolution: δ 5.89 (m, 4 H, diene), 5.03 (m, 2 H, olefinic), 4.26 (triplet of doublets, 1 H, C_9), 2.92 (br tr, J = 6 Hz, 2 H, bridgehead), and 1.64 (d, J = 12 Hz, OH).

Into a magnetically stirred slurry of 1.83 g (9.4 mmol) of potassium azodicarboxylate in 20 ml of dioxane under a nitrogen atmosphere was dissolved 630 mg (4.7 mmol) of alcohol **11,** above. A solution of 0.6 g (9.4 mmol) of glacial acetic acid in 2.5 ml of dioxane was added dropwise. After 12 hr of stirring at room temperature, a second portion of 0.6 g of acetic acid in 2.5 ml of dioxane was added. The yellow color of the mixture was completely bleached after a total reaction time of 24 hr. After 100 ml of ether was added, the mixture was filtered and the solvent was then removed on a Rotovap. The crude product (120 mg) was chromatographed on an aluminum oxide column. A liquid product, 94 mg, was isolated from a 300-ml fraction eluted with 15% ethyl acetate–85% ethyl ether. This material was dissolved in 20 ml of distilled hexane and activated manganese dioxide (1.0 g) was added. The reaction mixture was stirred for 2 days at room temperature. The solid was removed on a Rotovap. The crude mixture was analyzed by glpc on a 6-ft column of 10% UCON 50 LB 550 X on Chromosorb P by coinjection with authentic samples of ketones **2–7.** The relative amounts of products were 38.7% **2,** 24.9% **3,** 0.8% **4,** 30.2% **6,** and 5.4% **7.**

Diimide Reduction of Trienone 1. Into a magnetically stirred slurry of potassium azodicarboxylate (76.5 g, 0.394 mol) in 2.5 l. of distilled dioxane under a nitrogen atmosphere was added trienone **1** (26.0 g, 0.197 mol). A solution of distilled acetic acid (23.8 g) in 50 ml of dioxane was added dropwise into the reactor at room temperature over a period of 1 hr. After 10 hr of stirring, a second portion of acetic acid (23.8 g, total 0.788 mol) in 50 ml of dioxane was added. The reaction mixture was stirred for a total of 36 hr until the yellow color had almost disappeared. The remaining solid was removed by filtration, and the dioxane was removed. The residue was dissolved in 500 ml of ethyl ether. The ether solution was washed, dried, and concentrated. The crude product was distilled through a short Vigreux column. A portion boiling between 46 and 49° (0.1–0.06 mm) was collected, weighing 10.5 g. The glpc analysis of the distillate showed four components in addition to the starting material. The first three compounds were separated by preparative glpc on a 3-ft 20% Carbowax 20M column. The fourth peak overlapped with other components and was separated by a 15-ft 30% Carbowax 20M column. These four compounds were spectroscopically identified as **3, 4, 6,** and **7.**

Bicyclo[4.2.1]nona-2,7-dien-9-one (3): ν_{max}^{neat} 3030, 2950, 1765, 1430, 1155, and 745 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 255 nm (ε 330) and 295 (160); $\delta_{TMS}^{CDCl_3}$ 6.16 (doublet of quartets, J = 4, 7 Hz, 2 H), 5.76 (m, 2 H), 3.19 (m, 1 H), 2.92 (m, 1 H), and 2.12 (m, 4 H); *m/e* 134, 106, 91, 78 (base peak), and 28.

An nmr decoupling experiment on dienone **3** was carried out. On irradiation at H_a (196 Hz), the resonances of H_b and H_e were broadened, whereas only H_e peaks were broadened on irradiation at H_d (172 Hz). On irradiation at H_c (146 Hz), the H_b peaks were again broadened.



Bicyclo[4.2.1]nonan-7-en-9-one (4): ν_{max}^{neat} 2925, 2850, 1750, 1440, 1175, 850, 790, and 730 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 270 and shoulder extending to 310 nm; $\delta_{TMS}^{CDCl_3}$ 6.06 (d, 2 H), 2.92 (br s, 2 H), and 1.52 (br s, 8 H).

Bicyclo[4.2.1]nonan-2-en-9-one (6): ν_{max}^{neat} 3025, 2950, 1745, 1640, 1450, 1150, 715, and 660 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 295 and shoulder extending to 310 nm; $\delta_{TMS}^{CDCl_3}$ 5.77 (m, 2 H), 1.5–2.8 (10 H).

Bicyclo[4.2.1]nonan-9-one (7): ν_{max}^{neat} 3000, 2930, 2850, 1725, 1450, 1220, 1190, 1105, and 740 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 1.1–2.5 (14 H).

Catalytic Hydrogenation of 1. Trienone **1** (0.264 g, 2 × 10^{-3} mol) was hydrogenated in 10 ml of dioxane using 10% Pd/C as catalyst. During 3 hr of reaction at room temperature, 65 ml of hydrogen gas (118% based on one double bond) was absorbed. After removal of the catalyst and the solvent, a glpc analysis of the crude reaction mixture indicated none of the starting material and five reduced products: **3** (70%), **4** (3%), **5** (7%), **6** (10%), and **7** (3%). The new component (**5**) was isolated by preparative glpc and identified as bicyclo[4.2.1]nonan-3-en-9-one (**5**): ν_{max}^{neat} 3010, 2950, 2880, 1740, 1425, 1175, and 650 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.86 (br s, 2 H) and 2.9–1.2 (10 H).

Modified Synthesis of Potassium Azodicarboxylate. The procedure described below is a modification of the reaction originally reported by Thiele.[23] Azodicarbonamide, 20 g (Aldrich Chemical Co.), was dumped into a 2-l. beaker at 0° containing 50 ml of 50% potassium hydroxide solution. The mixture was vigorously agitated while the ammonia evolved caused foam. The yellow paste was then agitated for 10 min, filtered quickly, and dissolved in 100 g of ice–water maintained at 1–2°. If the water temperature rises to about 5°, the compound decomposes rapidly. The aqueous solution was filtered very quickly into 500 ml of 95% ethyl alcohol at −20°. The yellow crystals precipitated in the alcohol were again filtered quickly. The recrystallization process was repeated once more with 100 g of ice–water and 500 ml of 95% ethyl alcohol. The potassium azodicarboxylate was washed with methanol by swirling for a few minutes. The material was dried overnight at high vacuum at room temperature and kept under vacuum in the refrigerator.

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Registry No.—**1**, 34733-74-9; **1** dimer, 53535-25-4; **2**, 52902-51-9; **3**, 42948-89-0; **4**, 42948-91-4; **5**, 40863-57-8; **6**, 52089-56-2; **7**, 14252-11-0; **9**, 53555-53-6; **10**, 53555-54-7; **11**, 34712-67-9; **12**, 53555-55-8; trimethyl orthoformate, 149-73-5; potassium azodicarboxylate, 4910-62-7; azodicarbonamide, 123-77-3; potassium hydroxide, 1310-58-3.

References and Notes

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(6) Compound **11** was cited in a communication by M. Sakai, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4452 (1970), but no properties of the material were reported. Subsequently, data for **11** were obtained in 1972 privately from Dr. M. Sakai, University of Alberta, which agree in general with those obtained in this work and also by Shechter, *et al.*,[7] and Diaz and Fulcher.[19b]
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(8) The nmr spectrum of the crude reduction product indicated that only one epimer of **11** was formed, as also found in the parallel studies cited above.[6,7] The epimer with the hydroxyl syn to the diene moiety would be the expected product, on the basis of attack by hydride on the less hindered face of the carbonyl group.
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(24) Note Added in Proof. Photoelectron spectroscopic data for trienone **1** have now been reported.[25] These are interpreted as showing the *absence* of homoconjugation and bicycloconjugation among the π systems of **1**, although interaction of the nonbonding orbital on oxygen and the HOMO of the butadiene moiety is indicated. These results argue against the interpretation presented above. However, it must be kept in mind that the PE data reflect interaction in the ground state of **1** while our discussion pertains to possible transition states for reaction of **1**.
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