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Synthesis and Reactions of Bicyclo[3.1.0]hexatrienes

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Abstract: The feasibility of inducing two HBr eliminations from 4,6-dibromo-2-bicyclo[3.1.0]hexene (**3**) was explored as a route to bicyclo[3.1.0]hexatriene (**1**). Depending on the base employed **3** was converted to bromobenzene or 6-substituted fulvenes. To elucidate the mechanism by which the fulvene arose, **3** was synthesized specifically labeled with deuterium, ^{13}C, and alkyl groups. The labeling results require the formation of triene **1** as a reaction intermediate. A hidden stereospecific reaction revealed by the labeling studies for the transformation of **1** to fulvenoid products is discussed using frontier orbital considerations. Using ab initio calculations **1** is compared to the isomeric dehydrobenzenes.

The central role of benzene with respect to aromaticity has prompted the synthesis of many perturbations of the parent hydrocarbon. Typically, these approaches fall into two major categories: bending of the ring represented by the cyclophanes or bond fixation by fusion to small rings.[1] The consequences of yet a third approach entailing the introduction of further unsaturation have not been extensively investigated since, of the three isomeric dehydrobenzenes, only *o*-benzyne has been well characterized. In each instance the chemistry of the resulting C_6H_4 entity will reflect both the strain and the resonance energy associated with the 6π electrons. The nature of the electronic interactions arising from the introduction of two additional unsaturated centers will determine whether the resulting π system is resonance stabilized or destabilized.

Numerous theoretical endeavors have focused on the dehydrobenzenes. The reliability of the results varies depending on the assumptions entertained. Even simple Hückel calculations, when applied in conjunction with Hess and Schaad's semiempirical approach,[2] reach relatively reliable conclusions concerning the aromaticity of *m*-benzyne and *p*-benzyne represented as bicyclo[3.1.0]hexatriene (**1**) and bicyclo[2.2.0]hexatriene (**2**), respectively. Using the REPE value of 0.065 for benzene as a standard, REPE for **1** is 0.055 but

1

2

−0.06 for **2**.[2,3] Thus, replacement of H_1 and H_3 of benzene with a σ bond is predicted to generate an aromatic hydrocarbon, whereas formation of a 1,4 bond would create an antiaromatic hydrocarbon. In agreement with this analysis, more sophisticated calculations predicted **1** to be more stable than **2** by 45–50 kcal after geometry optimization.[4]

Both *o*- and *p*-dehydrobenzenes have been characterized to varying degrees. The development of a variety of synthetic routes leading to *o*-benzyne has established the chemistry to be that of a strained cyclic acetylene.[5] Moreover, the infrared studies of *o*-benzyne in an argon matrix provided additional confirmation of this bonding arrangement.[6]

The chemistry of *p*-benzyne is not as well established. Two different approaches generated a reactive intermediate possessing quite different properties. Pyrolysis of *cis*-1,2-diethynylethylene produced a symmetrical entity which reacted as a diradical.[7] In contrast, lithium dimethylamide transformed 1-chlorobicyclo[2.2.0]hexadiene into a reactive polyene that was trapped by nucleophiles and dienes.[8] The vigorous conditions required to generate **2** were interpreted to be indicative of a high activation energy associated with formation of an energetically unfavorable species.

Prior to this investigation, *m*-dehydrobenzene had been characterized primarily by computational studies. Early theoretical studies had predicted the singlet–triplet gap of **1** to be small. For example, Hoffmann, using extended Hückel calculations, predicted the ground state to be a singlet.[9] From ab

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initio studies, Whitten predicted **1** to be a triplet.[10] However, both of these studies were hampered owing to consideration of only the benzenoid hexagonal structure for **1**.

We have conducted a geometry optimization study[4b] of **1** using the STO-3G basis set[11] in conjunction with GAUSSIAN 70.[12] Our approach assumed **1** to be planar and to possess C_{2v} symmetry. The bridging C_1C_5 bond was allowed to collapse to an optimum value while holding the peripheral bonds fixed and maintaining similar angles in the developing five-membered ring. The positions of C_6 and C_3 were varied independently to establish an optimum value. In contrast to that observed for *p*-benzyne, no energy barrier was found for the collapse of the hexagonal diradical to **1**. The optimum singlet structure could best be described as a resonance-delocalized bicyclo[3.1.0]hexatriene containing a bridging bond of 1.5 Å. This same conformation was the energy minimum when the 4-31 basis[13] was employed. At the SCF level, using either 4-31 or STO-3G basis sets, the benzenoid hexagonal 1,3-triplet diradical was predicted to be 10 kcal more stable. However, after inclusion of an estimate of configuration interaction, the singlet bicyclo[3.1.0]hexatriene was predicted to be the ground state. In a similar study of the dehydrobenzenes, Dewar, using MINDO/3, concluded that **1** should exist as a singlet species containing a long bridging σ bond between C_1 and C_5.[4a] As might be expected, theoretical treatment of **1** predicts π polarization analogous to that of an azulenoid hydrocarbon.

Despite the unusual geometry of **1**, the total calculated strain is not prohibitive. From Bensen group equivalence tables,[14] the $\Delta H_f°$ is predicted to be +41.5 kcal if strain and resonance contributions are ignored. The latter can be estimated to be +17 kcal by extrapolation of the REPE values based on a resonance energy of benzene of 21 kcal. Using the MINDO/3 prediction of ΔH_f of **1** to be 117.6 kcal the strain would be 93 kcal. Our ab initio calculations predict ΔH_f of **1** to be 145 kcal containing 121 kcal of strain.[15] In comparison, **2** using the MINDO/3 estimate of ΔH_f of 153 kcal and −19 kcal of resonance energy incorporates 93 kcal of strain; our ab initio calculations predict ~140 kcal.[17]

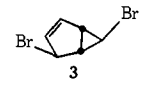
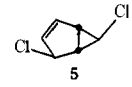
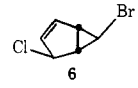
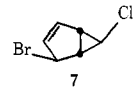
The 90–120 kcal of strain predicted for bicyclo[3.1.0[hexatriene is not excessive when compared with the 101 and 153 kcal of strain measured for benzvalene and prismane, respectively.[20] The reliability of the strain estimate of **1** and **2** can be ascertained by comparing predicted and experimental values for *o*-benzyne. Depending on which experimental value of ΔH_f for *o*-benzyne is employed (100 or 118 kcal),[21] the molecule contains 36–53 kcal of strain as compared to MINDO/3 and ab initio derived estimates of 54 and 55 kcal. Thus in view of the above calculations, the unusual geometry of bicyclo[3.1.0]hexatriene should not induce excessive strain that would preclude its existence.

Synthetic Approaches

With the exception of Berry's flash vacuum pyrolysis of *m*-diazoniumbenzene carboxylate,[22] all approaches to *m*-benzyne have been unsuccessful. Berry was able to observe a C_6H_4 intermediate whose UV spectrum was suggestive of the bicyclohexatriene structure. Attempts to extend this approach to solution chemistry were inconclusive.[23] We believed Rossi's difficulties to be endemic of complications arising in the conversion of a 1,3-difunctionalized benzene to **1** since stepwise loss of the appendant groups would generate a reactive intermediate that could be intercepted prior to the formation of **1**.

One means of circumventing the problem of inducing sufficient distortion in a benzenoid ring to promote formation of a transannular bond would be to begin with the bridging σ bond present. In fact there was one report of an unsuccessful attempt to generate **1** using this approach; i.e., the pyrolysis of 6-*N,N*-dimethyl-2,4-diacetoxybicyclo[3.1.0]hexylamine oxide.[24]

Table I[a]

compd	PhBr	PhCl	4	$PhNMe_2$
 3	100	0.0	8	10
 5	0.0	100	5	2
 6	0.0	100	9	7
 7	100	0.0	9	1

[a] The above are product ratios relative to the aromatic halide.

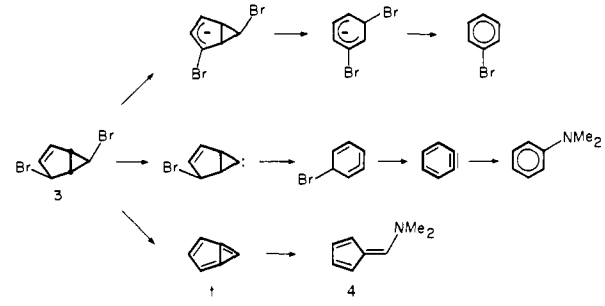
We chose to attempt to induce two successive dehydrohalogenations beginning with an appropriately substituted bicyclo[3.1.0]hexene.[25] The two precursors were 4,6,6-trihalobicyclo[3.1.0]hexene and 4,6-dihalobicyclo[3.1.0]hexene. We hoped that the diene formed by an initial HX elimination would be converted to a resonance-stabilized bicyclo[3.1.0]-hexadienyl anion which would ultimately lose halide ion to generate a 1,3-dehydrobenzene. By this approach, formation of highly reactive intermediates capable of side reactions would be minimized.

The bulk of our investigations utilized the readily available *exo,exo*-4,6-dibromobicyclo[3.1.0]hexene (**3**).[26] $LiNMe_2$/TMEDA in THF at −75 °C converted **3** to bromobenzene, *N,N*-dimethylaniline, 6-dimethylaminofulvene (**4**), and 4-dimethylamino-6-bromobicyclohexene in 50, 5, 4, and 1% yields, respectively. In order to elucidate the mode of reaction of **3** with $LiNMe_2$, the corresponding dichloride (**5**) was prepared from benzvalene by the same procedure used for **3**, except for chlorination at −75 °C. Likewise, *exo,exo*-6-bromo-4-chloro-2-bicyclo[3.1.0]hexene (**6**) and *exo,exo*-4-bromo-6-chloro-2-bicyclo[3.1.0]hexene (**7**) were prepared by hydrolysis of **3** and **5** followed by exposure of the allylic alcohol to anhydrous HCl or HBr in CH_2Cl_2 at 4 °C, respectively.

The products obtained by treatment of **3, 5, 6,** and **7** with $LiNMe_2$/TMEDA in THF at −75 °C are summarized in Table I. In each instance, the halogenated aromatic was the major product (~50%). The aromatic halide formed from the mixed dihalides **6** and **7** entails loss of the C_6 halogen. The simplest mechanism consistent with orbital symmetry constraints is formation of the 2-bicyclo[3.1.0]hexenyl anion followed by an electrocyclic opening to a cyclohexadienyl anion and ultimately expulsion of the C_6 halide (Scheme I). Such base-promoted transformations of bicyclo[3.1.0] hexenes to cyclohexadienes are well documented.[27]

The mechanism by which dimethylaniline was formed was not as apparent, especially since repeated controls established that bromobenzene was not the precursor of the dimethylan-

Scheme I



iline at this temperature. Moreover, a control experiment established that the S_N2' product was not the precursor of $PhNMe_2$, since under the reaction conditions **3** was converted to $PhNMe_2$ 100 times faster than was 4-dimethylamino-6-bromo-2-bicyclo[3.1.0]hexene. If $DNMe_2$ was present during the elimination, the bromobenzene contained no deuterium by mass spectral analysis, whereas the $PhNMe_2$ contained only one deuterium which by ^1H NMR analysis using $Eu(fod)_3$ was in the ortho position. Although prior exchange of **3** was considered as an explanation for deuterium incorporation in $PhNMe_2$, the failure to find any deuterium in the bromobenzene excluded exchange of the hydrogens of **3** which appear in the PhBr. This observation, coupled with the failure of $PhNMe_2$ to undergo exchange, required the intermediacy of some other species capable of incorporating only one deuterium. The labeling pattern strongly suggested *o*-benzyne as the precursor; however, control experiments cited above had established that bromobenzene was not the source of the *o*-benzyne.

The marked decrease in $PhNMe_2$ formation when the 6-bromide was replaced with a chloride suggested that an α-elimination of HX from C_6 was the rate-determining step (Scheme I). The product carbene of such an elimination could open to 6-halocyclohexa-1,2,4-triene, just as bicyclo[3.1.0]-hexaylidene opened to cyclohexa-1,2-diene.[29] Subsequent HBr elimination would generate the prerequisite intermediate *o*-benzyne.

Although the labeling study revealed that dibromide **3** reacted to generate *o*-benzyne, the desired transformation of **3** to *m*-benzyne, trapped as fulvene **4**, remained to be established. Prior to ascertaining the mechanism leading to fulvene **4**, the reaction conditions were modified to maximize the conversion of **3** to **4**.[30]

Presumably, the very strong bases were preferentially abstracting the more acidic C_4 and C_6 hydrogens despite the steric congestion. Substitution of a weaker base favoring less charge development in the transition state would favor attack at the C_1 hydrogen since a concerted elimination of bromide would occur. As predicted, the reaction course varied according to the basicity of the medium. In KO-*t*-Bu/Me_2SO at 25 °C the major product was bromobenzene and its reaction product, *tert*-butoxybenzene. In KO-*t*-Bu/THF at −75 °C dibromide **3** was transformed to a mixture of 6-*tert*-butoxyfulvene (**8**), 6-bromofulvene, and bromobenzene in yields of 90, 0.1, and 0.2%, respectively. If $HNMe_2$ were also present, **3** was converted to **4** in 70% yield.[31] To date, only hindered tertiary alkoxides have promoted this reaction. Less hindered bases such as NaOMe, NaO-*i*-Pr, or DBN gave substitution products in near-quantitative yield.

The reaction course depended not only on the base employed but also on the stereochemistry of the substrate dihalide. For example, when *exo,endo*-4,6-dibromo-2-bicyclo[3.1.0]hexene was treated with KO-*t*-Bu in THF, a 2:1 mixture of 6-*tert*-butoxyfulvene (**8**) and bromobenzene was formed. As expected, the fulvenoid/aromatic halide product ratio decreased since the endo orientation of the C_6 halogen permits a concerted loss of bromide with base abstraction of the C_4 hydrogen, thereby decreasing the activation energy for the formation of bromobenzene.

Numerous mechanisms can be formulated to account for the formation of the 6-substituted fulvenes. If one considers only those possibilities in which no skeletal rearrangement occurs, two general classes exist: an elimination of HBr followed by substitution of a nucleophile for bromide, or two HBr eliminations followed by addition of the conjugate acid of the nucleophile. The mechanistic possibilities are further restricted by the following observations: dibromide **3** was converted to fulvene **8** faster than 4-chloro-6-bromide **6** was converted to **8**; and *exo*-6-bromobicyclo[3.1.0]hexane and *exo,exo*-6-bromo-4-dimethylaminobicyclo[3.1.0]hexene were inert to KO-*t*-Bu at −75 °C. The above data requiring the involvement of the C_4 halogen are consistent with initial formation of 6-bromobicyclo[3.1.0]hexadiene (**9**).

Three potential pathways are illustrated for the conversion of the intermediate diene **9** to **8** (Scheme II). Ionization of **9** forming the resonance-stabilized anion **10** followed by expulsion of bromide would generate triene **1** (path a). Nucleophilic addition of *tert*-butoxide at C_6 of **1** would produce after protonation 6-*tert*-butoxybicyclo[3.1.0]hexadiene, which would be converted to alkoxyfulvene **8** by an allowed disrotatory opening. Nucleophilic attack of KO-*t*-Bu at C_6 of **9** would form a cyclopentadienyl anion which would collapse to generate **8**[32] (path b). Alternatively, **9** could be converted by an electrocyclic reaction to 6-bromofulvene which after addition/elimination would form fulvene **8**[33] (path c).

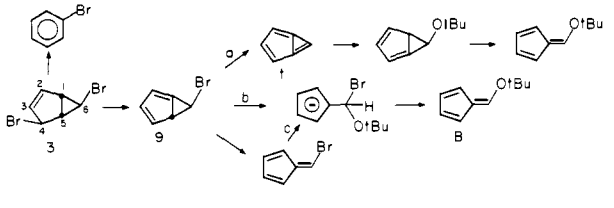
When the reaction of dibromide **3** with KO-*t*-Bu was interrupted at ~50% completion by the addition of acetic acid at −75 °C, only the starting dibromide and the product 6-*tert*-butoxyfulvene were isolated. No evidence of accumulation of **9** or its presumed thermally rearranged product, 6-bromofulvene, was detected. Controls indicated that the latter was stable in the absence of KOtBu. The same results were obtained when 4-bromo-6-chloride **7** was the starting material. Thus, the rate of the second step of the transformations shown in Scheme II must be faster than the initial HBr elimination.

To distinguish among these pathways, we synthesized specifically deuterated, ^{13}C-enriched, and alkylated dibromide **3**. Depending on the location of the label, one of three synthetic routes was employed. **3a** deuterated at C_6 was prepared from benzvalene-*5,6-d*$_2$.[34] The deuterium content of **3a** was 1.5 D as determined by mass spectral analysis of the corresponding 4-dimethylamino-6-bromobicyclo[3.1.0]hexene. By ^1H NMR, the distribution of deuterium was in accordance with that reported by Katz: 0.75 D at C_6, 0.22 D at C_2 and C_4, respectively, and 0.15 D at C_1 and C_5, respectively.

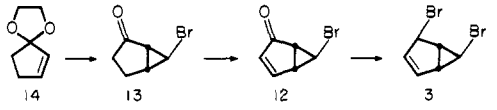
A 50:50 mixture of **3b** and **3c** was prepared by Jones oxidation of 4-hydroxy-6-bromobicyclo[3.1.0]hexene (**11**) to give the corresponding 6-bromo-3-bicyclo[3.1.0]hexen-2-one (**12**) which was reduced with alane-*d*$_3$ to a 4:1 mixture of endo and exo allylic alcohols. The labeled alcohols were converted to **3b** and **3c** upon exposure to anhydrous HBr. Owing to acid-promoted equilibration of the allylic bromide, the label was distributed equally over C_2 and C_4.

Dibromide **3d**, specifically deuterated at C_3, was prepared from 6-bromobicyclo[3.1.0]hexan-2-one (**13**). **13** was prepared in one of two ways: (1) $NaBH_4$ reduction of enone **12** followed by Jones oxidation; (2) Addition of "bromocarbene" to 2,5-dioxa-6-spiro[4.4]nonene (**14**) followed by acid hydrolysis (Scheme III). The product ketone produced by the latter route was a 3:1 mixture of **13** and the C_6 epimer. Catalytic amounts of CF_3CO_2H promoted exchange of the C_3 methylene of both **13** and its epimer in D_2O/dioxane at 60 °C. If the acid con-

Scheme II



Scheme III



centration were too high, both ketones were converted to phenol. **13** was very sensitive to base, since all attempts to generate the enolate, even at −75 °C, resulted in complete decomposition.

Efficient conversion of ketone **13** to enone **12** proved to be difficult. $CuBr_2$ failed to react at temperatures compatible with **13**. Although phenylselenyl chloride would react at 4 °C with **13** in EtOAc, the product enone **12**, formed by ozonolysis followed by pyrolysis in refluxing CCl_4 in the presence of 4 equiv of $HNEt_2$, was contaminated with the starting ketone. This route could be utilized to produce C_3-deuterated enone **12** from dideuterated **13**, provided that $DNEt_2$ was substituted for $HNEt_2$. However, whereas the epimeric bromides at C_6 could be separated on Florisil either as ketones or enones, the separation of enone **12** from ketone **13** was not easily accomplished.

To prepare pure enone **12**, the epimeric ketones were oxidized with SeO_2 at 110 °C in PhCl. PhCl was somewhat superior to dioxane or dioxane/H_2O. The desired enone accompanied by some phenol was formed in yields as high as 50%. Unfortunately, owing to the deuterium isotope effect, the rate of oxidation of **13** dideuterated at C_3 was sufficiently retarded that decomposition of **12** became a major side reaction. However, a catalytic amount of CF_3CO_2H accelerated the oxidation sufficiently that the C_3-labeled enone **12** containing 0.5 D could be prepared in 40% yield. The enone **12**-*3*-d_1 was converted to dibromide **3d** in the previously described manner.

The synthesis of a 1:1 mixture of dibromides **3e** and **3f** deuterated at C_1 and C_5 was the most involved. Bromination in ethylene glycol-d_2 provided a means to convert 2,2,5,5-tetradeuteriocyclopentanone in the standard fashion[35] to ketal **14**-*6,9,9*-d_3 and subsequently to the ketone **13**-*1,3,3*-d_3. However, the deuterium isotope effect on the exchange of C_3 position was sufficiently great that all attempts to completely wash out the deuterium at C_3 failed owing to competitive conversion of **13** to phenol. Ultimately a 50:50 mixture of **3e** and **3f** was prepared from ketal **14**-*6*-d_1 using the procedure outlined in Scheme III. The labeled ketal **14**-*6*-d_1 was prepared by bromination of ketal **14** in CCl_4 followed by successive treatments of NaOEt/Me_2SO and Na/*t*-BuOD. It should be noted that sodium was superior to lithium for the reduction.

3g and **3h** enriched in ^{13}C at C_2 and C_4, respectively, were prepared from [1-^{13}C]cyclopentanone via ketal **14**-*1*-^{13}C using the synthetic sequence outlined in Scheme III. The labeled cyclopentanone was prepared by the reaction of methyl 5-bromopentanoate with $Na^{13}CN$ followed by hydrolysis and pyrolysis.[36] By ^{13}C NMR and mass spectral analysis, the labeled dibromide **3** contained 0.32 ^{13}C equally distributed over C_2 and C_4.

2-Methyl-4,6-dibromo-2-bicyclo[3.1.0]hexene (**15**) was prepared by addition of MeLi at −110 °C to enone **12** followed by exposure of the allylic alcohol to HBr. In a similar fashion, the *tert*-butyl analogue **16** was prepared. However, the reaction of enone **12** and *t*-BuLi was not clean. Conjugate addition and metal halogen exchange of the C_6 bromide were two of the major side reactions. The desired allylic alcohol could be obtained in 15% yield albeit in moderate purity after column chromatography. Both **15** and **16** were more thermally labile than dibromide **3**.

To facilitate the product analysis, the labeled dibromides **3** were reacted with KO-*t*-Bu in the presence of $HNMe_2$ to form the relatively stable aminofulvene **4**. The distribution of the deuterium in **4** was determined using NMR and mass spectroscopy. Although in CCl_4 or $CDCl_3$ the ring hydrogens appear as two sets of triplets, in CH_3CN the four hydrogens are almost resolved.[37] A more reliable measure utilized the chemical reactivity of **4** to group the olefinic hydrogens into three chemical classes: (1) H_1 and H_4, which exchange in MeOH/$CHCl_3$ at 62 °C with a half-life of 3 h; (2) H_2 and H_3, which under the same conditions have a half-life of 100 h; (3) H_6, which does not exchange.[37] If the same medium were made 0.5% in CF_3CO_2H, H_1, H_2, H_3, and H_4 are completely exchanged after 16 h at 60 °C.

By selective exchange of deuterated **4** obtained from labeled dibromide **3**, we could establish the amount of deuterium at the three sets of positions: H_1 and H_4; H_2 and H_3; and H_6. However, several problems were encountered. Control experiments revealed that exchange of H_1 and H_4 of **4** occurred even on activity 5 neutral alumina, thus precluding purification of the reaction product. Furthermore, **4** would undergo exchange in the mass spectrometer.

In order to circumvent these problems, **4** was converted to 6-phenylfulvene **17** by treatment with an excess of freshly prepared phenyllithium in THF at 25 °C, and then acetic acid. Careful but rapid chromatography on neutral alumina activity 1 separated **17** from biphenyl. Control experiments with trideuterated **4** established that no deuterium was lost during the elimination, the workup, the conversion of **4** to **17**, or mass spectral analysis of **17**. Similarly, undeuterated **4** failed to incorporate deuterium when carried through the same sequence using deuterated reagents.

Typically, the product **4** was split into two portions of which one was exchanged prior to the conversion of both to **17**. **17** was analyzed by mass spectrometry for deuterium content. From the differences in deuterium content in the exchanged and unexchanged sample, the amount of deuterium at each set of positions could be determined.

Labeling Results

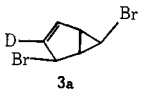
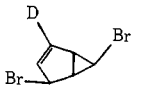
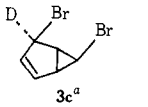
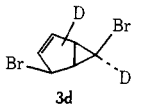
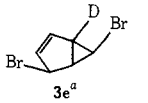
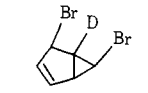
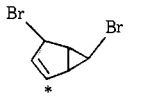
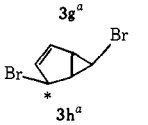
The results from the labeled dibromides are presented in Table II. Examination of the label distribution in the aminofulvene **4** obtained from dibromides **3a** and **3d** indicates that no carbon scrambling occurs during the transformation. The majority of the deuterium appears in the product where a pathway entailing cleavage of the C_1C_6 or C_5C_6 bond would predict. Moreover, beginning with the ^{13}C-enriched dibromides **3g** and **3h**, the product fulvene **4** contained equal ^{13}C enrichment at C_1, C_2, C_3, and C_4; there was no enrichment at C_5 or C_6. Thus, these results reinforce the conclusions reached from the deuterium labeling.

Since the fulvene **4** obtained from the C_3-deuterated dibromide **3d** contains only 65–85% of the original label, it is apparent that in the course of the reaction an intermediate must be formed which can undergo exchange. A priori from Scheme II, either 6-bromobicyclo[3.1.0]hexadiene (**9**) or 6-dimethylaminobicyclo[3.1.0]hexadiene could have undergone the exchange. Further discussion will be deferred for the moment.

With respect to formation of diene **9**, molecular models suggested that a cis 1,4 elimination would be preferred. Consequently, if the hydrogen at C_1 of dibromide **3** were replaced with a deuterium, one would expect that the yield of bromobenzene would increase relative to 6-*tert*-butoxyfulvene, since, owing to a primary isotope effect, the initial elimination to give diene **9** would be less favored than in the undeuterated case. If the C_5 hydrogen of **3** were a deuterium, the partitioning of **3** between bromobenzene and diene **9** would be unaffected, but the partitioning of **9** between 6-bromofulvene and 6-*tert*-butoxyfulvene could be altered. This primary isotope effect could be observed only if fulvene **8** arose via path a of Scheme II under special circumstances. An isotope effect would be observed provided that diene **9** did not exchange with solvent or be converted to **1** via an ElcB reaction.

In reality, the 1:1 mixture of the monodeuterated dibromides **3e** and **3f** was converted to fulvene **4** in approximately the same yield as was the undeuterated dibromide **3**.[38] However, **4** contained only 0.07 D distributed roughly equally between C_1,

Table II

compd	label distribution within dibromide **3**							label distribution within fulvene **4**			
	H_1	H_2	H_3	H_4	H_5	H_6	total	$H_1 + H_4$	$H_2 + H_3$	H_6	total
 **3a**			0.73				0.73	0.09	0.52		0.61
			0.68				0.68		0.4		
			0.51				0.51	0.05	0.28		0.33
 **3b**[a]		1.00					1.00	0.22	0.00		0.22
								0.36	0.02		0.38
								0.42	0.03		0.45
 **3c**[a]				1.00			1.00	0.76	0.12		0.88
								0.80	0.10		0.90
 **3d**	0.17	0.23		0.23	0.17	0.8	1.6	0.26		0.73	0.99
	0.15	0.23		0.23	0.15	0.76	1.52	0.56		0.71	1.27
	0.15	0.23		0.23	0.15	0.75	1.51	0.50		0.69	1.19
 **3e**[a]	0.84						0.84				
								0.03	0.04		0.07
 **3f**[a]								0.08	0.04		0.12
					0.84		0.84				
 **3g**[a]		0.32					0.32				
								0.16[b]	0.16[b]		0.32
 **3h**[a]				0.32			0.32				

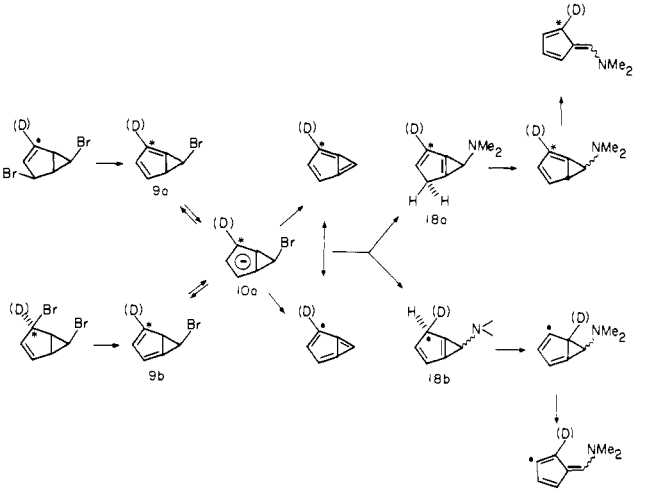
[a] Conversion to **4** run with a 1:1 mixture of **3b** and **3c**, **3e** and **3f**, **3g** and **3h**. [b] By ^{13}C NMR the ^{13}C label was equally distributed over C_1, C_2, C_3, and C_4.

C_2, C_3, and C_4, indicating that both bridgehead protons are lost during the transformation. As predicted, the yield of bromobenzene increased to 2%. Although these results do not rule out paths b and c, for these mechanisms to be valid, the lifetime of **9** must be sufficiently long that virtually all the bridgehead deuterium can be washed out.

A labeling study which does rule out paths b and c of Scheme II involved the 1:1 mixture of monodeuterated dibromides **3b** and **3c**. Depending on the reaction conditions, the isolated aminofulvene **4** contained 30–90% of the original deuterium, of which 85–100% was attached to C_1 and C_4 of **4**. This unusual labeling result was not dependent on the halide at C_6 since the corresponding mixture of monodeuterated **7** was transformed to **4**, containing 0.53 D of which 86% was distributed over C_1 and C_4. As shown in Scheme IV this result is in marked contrast to that obtained with the corresponding ^{13}C-labeled dibromide **3g** and **3h** indicating that this deuterium label must be mobile. The initial elimination would generate two isomeric deuterated 6-bromobicyclo[3.1.0]hexadienes **9a** and **9b** in equal amounts. If the reaction proceeded by either path b or c of Scheme II, **9b** should have been transformed to fulvene **4**, deuterated at C_2 and C_3. Since this prediction was not realized, paths b and c are not viable.

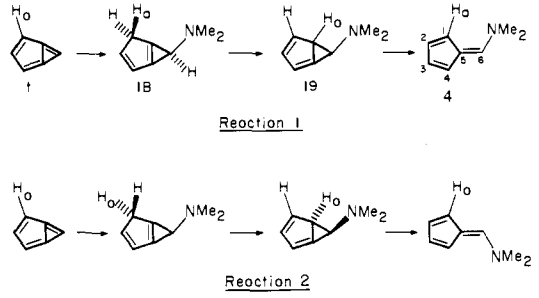
These labeling results are consistent with the intermediacy of bicyclohexatriene; however, the situation is more complex than represented in path a of Scheme II. Clearly, 2-deuterio-6-dimethylaminobicyclohexadienyl anion cannot be formed as an intermediate during the addition of $HNMe_2$ to triene **1**-*2-d*, since this anion would be protonated equally at C_1 and C_5. Protonation at C_1 would result in the deuterium appearing at C_2 and C_3 of fulvene **4**. As outlined in Scheme IV, synchronous nucleophilic attack and proton delivery would convert triene **1** to 6-dimethylamino-$1^{1,5}$,2-bicyclo[3.1.0]hexadiene (**18**), since from frontier orbital considerations C_6 and C_2 would be the site of nucleophilic and electrophilic attack, respectively. A [1,5]-sigmatropic hydrogen migration providing partial relief of the strain would convert **18** to the isomeric 6-dimethylaminobicyclo[3.1.0]hexa-1,3-diene whereupon an electrocyclic opening would complete the transformation of **1** to **4**.

Scheme IV



To be consistent with the labeling results, there is one unusual feature contained in Scheme IV. When the proton is

Scheme V



delivered to C_2 of **1** deuterated at C_2, the deuterium preferentially undergoes a [1,5]-sigmatropic shift, despite a normal primary isotope effect.[39] Assuming for the moment that the deuterium did migrate, the following two mechanisms contained in Scheme V would account for the final labeling pattern. The addition of $HNMe_2$ at C_6 occurs trans to the synchronous delivery of a proton from *tert*-butyl alcohol at C_2 followed by a [1,5] migration of the hydrogen cis to the dimethylamino group and subsequent electrocyclic opening to give **4** (reaction 1). Alternatively, the concerted addition of dimethylamine is cis followed by a [1,5] migration of the hydrogen trans to the dimethylamino group (reaction 2). In each instance, the migratory hydrogen is the original proton attached to C_2 of the triene **1**. For this to be valid a stabilizing factor leading to the migration of only one of the two diastereotopic hydrogens of diene **18** must more than offset the unfavorable isotope effect when a deuterium replaced that hydrogen.

We attempted to evaluate the assumption that the two pathways were different in energy using GAUSSIAN 70 with the STO-3G basis set. With respect to the addition of the dimethylamine to **1**, we found that, depending on whether or not the carbon–nitrogen bond was more developed than the carbon–hydrogen bond, either the cis or trans addition would be more favored. However, the net difference was always less than 2 kcal. With respect to the [1,5] migration, when the migratory hydrogen lay midway between the two carbon atoms and perpendicular to the carbon–carbon bond, the transition state for migration of the hydrogen cis to the dimethylamino group of **18** was favored by less than 1 kcal. Thus ab initio calculations failed to distinguish between reactions 1 and 2.

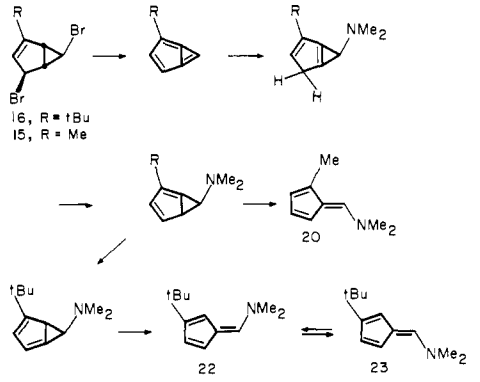
Since computations failed to distinguish between these two possibilities, an experimental means was sought. Depending on which mechanism was correct, a different labeling pattern would be obtained in the products resulting from **1** containing a nonmobile label at C_2. For example, if **1** were enriched in ^{13}C at C_2, by reaction 1 the label would appear at C_2 and C_4 of fulvene **4**, whereas by reaction 2, the ^{13}C label should only be at C_1 and C_3. In reality, as shown in Table II, dibromides **3g** and **3h** were converted to **4** containing ^{13}C equally distributed over C_1, C_2, C_3, and C_4. As will be discussed later the nucleophilic $HNMe_2$ destroyed the stereochemical integrity of the initial product by addition–elimination at C_6 of **4**, thus interchanging C_1 with C_4 and C_2 with C_3.

Despite the failure to distinguish between the two reaction pathways, these results reinforce either mechanism since only these two pathways correctly predict that fulvene **4** arising from an allylicly deuterated and ^{13}C-enriched dibromide would contain the deuterium and ^{13}C label at different carbons. Moreover, the failure to find any ^{13}C enrichment at C_5 or C_6 of **4** confirmed that skeletal rearrangements did not occur during the transformation of **3** to **4**.

Alkylbicyclohexatrienes

The introduction of an alkyl group should retard the nucleophilic attack on **4** since the intermediate cyclopentadienyl

Scheme VI



anion would be destabilized. In support of this hypothesis, *tert*-butylcyclopentadiene is slightly more acidic than indene in THF. Using pK_a values referenced to water for cyclopentadiene and indene, i.e., 16 and 20, the pK_a of *tert*-butylcyclopentadiene would be ~19. Thus, the activation energy for nucleophilic promoted interchange of C_1 with C_4 of an alkylated aminofulvene **4** should increase by ~4 kcal provided that the transition state corresponded to a fully developed cyclopentadienyl anion.

Two potential problems existed with respect to alkyl labels: (1) the enhanced ionic character favoring nucleophilic substitution of the starting dibromides and (2) the site of protonation of the transient 2-alkylbicyclohexatriene during the concerted addition of $HNMe_2$. As a model for the latter, we examined the product from kinetic protonation of methylcyclopentadienyl anion. Addition of the anion to a THF solution of acetic acid at −75 °C followed by excess *N*-phenylmaleimide with warming to −10 °C generated the Diels–Alder adduct of 1-methylcyclopentadiene. Separate control experiments using 5-, 1-, and 2-methylcyclopentadiene excluded the possibility of prior equilibration under these conditions. Thus, in contrast to frontier orbital considerations, protonation occurs at C_2, not C_1, of methylcyclopentadienyl anion. By analogy, the C_2-alkyl substituted triene **1** should protonate at C_4.

Treatment of 2-methyl-4,6-dibromobicyclo[3.1.0]hexene (**15**) under the standard conditions led to two products in a ratio of 4:1. The major product was 4-methylene-6-bromobicyclo[3.1.0]hexene; the minor one was a methyl-6-dimethylaminofulvene (A). By ^{13}C NMR, A was a single compound. The apparent stereospecificity is misleading since neither nucleophilic nor weakly acidic conditions could isomerize A to a second compound indicating that the geometrical isomer of A was of much higher energy than A. Since space-filling models revealed severe steric interaction between a methyl at C_1 and the C_6 dimethylamino group, A was tentatively assigned to be 4-methyl-6-dimethylaminofulvene (**20**). To confirm this assignment, sodium methylcyclopentadienide was reacted with $DMF/(CH_3O)_2SO_2$. Three methyl-6-dimethylaminofulvenes were isolated in a ratio of 2:1:1. ^{13}C and ^1H NMR spectra of the major isomer corresponded to that of A. As expected, equal amounts of the 2-methyl- and 3-methyldimethylaminofulvenes were obtained since the steric environments of the methyl groups are equivalent.

Both reactions 1 and 2 of Scheme V are compatible with formation of **20** (Scheme VI). Reaction 1 would generate **20** directly whereas reaction 2 would generate the isomeric 1-methyl-6-dimethylaminofulvene (**21**) followed by isomerization to **20**. Since we were unable to independently prepare **21** and thereby measure the rate of isomerization, we could not rule out this possibility. The only point about which one could be confident was that the 2-methylbicyclo[3.1.0]hexatriene was protonated at C_4 as predicted. If the proton had been de-

livered to C_2, the product would have been either the 2- or 3-methyl-6-dimethylaminofulvene.

In contrast, the 2-*tert*-butyl-4,6-dibromobicyclohexene **16** was converted slowly under the same conditions to a mixture of two *tert*-butyl-6-dimethylaminofulvenes (B and C). The product ratio varied with reaction time. After a contact time of 24 h, a 3:1 mixture favoring B was obtained, but after 1 week at −70 °C, equal amounts of B and C were obtained. In contrast to fulvene **20,** B and C were completely equilibrated on a neutral alumina column. Furthermore, if **16** were treated with KO-*t*-Bu alone, only one *tert*-butyl substituted 6-*tert*-butoxyfulvene was detected by ^1H and ^{13}C NMR. These results indicate that the transformation of **16** to fulvene B is stereospecific and that the nucleophilic dimethylamine is responsible for the slower equilibration of B with C. Furthermore, this finding substantiates the earlier contention that a similar equilibration of the unsubstituted fulvene **4** was fast.

The substitution pattern of B and C was established by conversion of the mixture to the corresponding phenylfulvenes and then by formation of Diels–Alder adducts with dimethyl acetylenedicarboxylate. From the ^1H NMR spectrum of the adducts, the *tert*-butyl group was bound to an olefinic carbon. Since the above derivatives were formed in 70% overall yield and the ^1H and ^{13}C NMR of the original aminofulvenes and indicated that only two isomers were present in equal amounts, then the only *tert*-butyl 6-aminofulvenes formed from **16** were *syn*-**22** and *anti*-**23**.

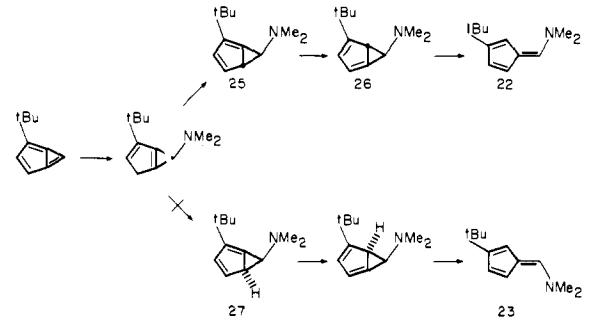
After examination of models, the unique fate of the *tert*-butyl label can be rationalized (Scheme VI). When the substituent at C_2 is small, the diene formed from nucleophilic addition of dimethylamine undergoes a rapid [1,5] hydrogen shift followed by an electrocyclic ring opening resulting in the label appearing at C_1 or C_4. However, if the group is large, the product aminofulvene would be disfavored since the severe steric crowding of the alkyl substituent at C_1 or C_4 with the C_6 hydrogen or C_6 dimethylamino group would necessitate a nonplanar conformation thereby attenuating the resonance stabilization. Presumably, this interaction raises the transition state energy sufficiently that a second [1,5] hydrogen shift occurs to generate an isomeric bicyclohexadiene which can open to give a fulvene with the bulky group attached at C_2 or C_3.

Supporting evidence for the postulated steric congestion experienced by a *tert*-butyl group at C_1 or C_4 was provided by the failure of fulvene **4** to react with *t*-BuCl/$AlCl_3$ to form 1- or 4-*tert*-butyldimethylaminofulvene. Instead, the electrophilic attack occurred at C_2 and C_3 to provide a 50:50 mixture of *syn*-**22** and *anti*-**23**. No other isomer was detected by ^1H or ^{13}C NMR. In contrast, protonation occurs preferentially at C_1 or C_4 of **4**. Similarly, exposure of **4** to DMF/$POCl_3$ yields, after hydrolysis, only the 4-formyl-6-dimethylaminofulvene.[37]

Although we easily established that the *tert*-butyl group of B and C was attached at C_2 and C_3, determination of which isomer was which was more difficult. However, the olefinic absorptions associated with B and those associated with C were known. The actual structural assignments were based on the assumption that the perturbation induced by a *tert*-butyl group at C_2 on chemical shift of the hydrogen at C_3 would be the same as that felt by a hydrogen at C_2 if the *tert*-butyl group were at C_3. From CNDO/2 calculations, the change in electron density of the appropriate carbons and hydrogens of *syn*-**22** and *anti*-**23** from the parent **4** was in agreement with this hypothesis.

To facilitate assignment of H_3 of *syn*-**22** and H_2 of *anti*-**23,** the hydrogens at C_1 and C_4 were replaced with deuterium. Just as had been observed for fulvene **4**, *syn*-**22** and *anti*-**23** underwent selective exchange of the hydrogens at C_1 and C_4 when heated in a 3:1 mixture of methanol-d_1/$CHCl_3$. After exchange, two singlets remained: one at δ 6.39 corresponded to B; the other at δ 6.62 corresponded to C. The difference in chemical shift (0.23 δ) between the two signals was the same as that (0.20 δ) separating H_2 and H_3 of 6-dimethylaminofulvene. Thus, B correspond to *syn*-**22** and C to *anti*-**23**.

Scheme VII



Only reaction 1 of Scheme VII can account for the stereospecific conversion of dibromide **16** and *syn*-**22**. Proton delivery to 2-*tert*-butylbicyclohexatriene at C_4 followed by migration of the syn hydrogen would generate diene **25** just as occurred for the methyl analogue. In contrast to the methyl or deuterio substituted dienes **24** or **19** an electrocyclic opening does not occur since the highly congested 4-*tert*-butyl-6-dimethylaminofulvene would be formed. Instead, a second [1.5] migration transforms **25** to **26** which can open to *syn*-**22**. In contrast reaction 2 would require the migration of an anti hydrogen to generate diene **27** which clearly would not open to form the impossibly congested 1-*tert*-butyl-6-dimethylaminofulvene. Instead, a second [1.5] migration followed by an electrocyclic reaction would generate 3-*tert*-butyl-6-dimethylaminofulvene (*anti*-**23**). By reaction 2 the actual product *syn*-**22** would not be formed.

The results obtained with the *tert*-butyl substituted dibromide **16** not only distinguish between the two reactions of Scheme V but also provided additional support that bicyclohexatriene **1** is generated and converted to fulvene products via a stereospecific reaction sequence. Despite the equal thermodynamic stability of fulvenes *syn*-**22** and *anti*-**23,** only *syn*-**22** was formed. Alternative pathways such as b or c of Scheme II would have generated both isomers.

The exclusive transformation of triene **1** to fulvene **4** via reaction 1 can be rationalized in terms of frontier orbital theory.[40] Since the symmetry of the LUMO of an isolated double bond and a hexatriene is the same, the concerted addition of "$HNMe_2$" across triene **1** should be trans.

In a similar vein, orbital mixing can be applied to predict which hydrogen would preferentially migrate[41] (Figure 1). In the transition state, the hydrogen atom would be moving across the surface of a hybrid heptatrienyl radical created by mixing of the five cyclopentadienyl π orbitals with the highest lying σ bond at C_6. For diene **18,** the C–H bond would be more heavily weighted in the hybrid orbital than would be the C–N bond. As a consequence, the π electron density would no longer be symmetrically distributed at each molecular face but would distort to minimize unfavorable electronic interactions. For the HOMO of this hybrid orbital, C_4 and C_5 of **18** are the same sign but C_2 and the C_6 hydrogen are of the opposite sign. An asymmetrical distribution of the π electrons would result in high electron density at C_4 and C_5 (the origin and terminus of the [1,5] migration) on the molecular face anti to the C_6 hydrogen. The migrating hydrogen would be the one which could maintain the greater bonding in the transition state. H_a of **18,** the hydrogen syn to the dimethylamino groups, should move.

Hydrogen Exchange. Examination of Table II reveals appreciable yet variable loss of deuterium originally present at C_2, C_3, or C_4 of the starting dibromides **3a–d**. A priori, ex-

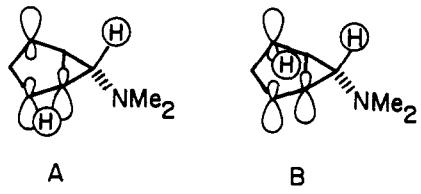
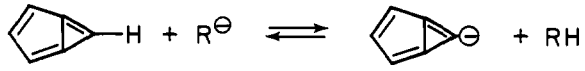


Figure 1.

change could occur by reversible deprotonation/protonation of **9, 18,** or **19.** As previously discussed, the failure for **3b** and **3c** to be converted to fulvene **4** deuterated at C_2 or C_3 indicated that electrocyclic reactions postulated for **18** or **19** must be fast relative to exchange. However, reversible formation of the 6-bromobicyclohexadienyl anion **10** followed by protonation at C_1, C_2, or C_3 would provide a mechanism for deuterium loss from these carbons yet still permit the observed specificity to occur.

Presumably the rate of electrocyclic ring opening is dependent upon the substituent at C_6.[42] An electron-donating group such as dimethylamino lowers the activation energy much more than does a halogen. Consequently 6-bromodiene **9** reacts primarily with base in lieu of undergoing an electrocyclic reaction whereas dienes **18** and **19** undergo rapid electrocyclic reactions.

GAUSSIAN 70 calculations employing minimal basis set for the following isodesmic reaction suggested that the C_6 hydrogen of **1** might be an unusually acidic sp^2 hydridized carbon.



Using the same geometry for the hydrocarbon and corresponding anion, triene **1** was predicted to be more acidic than ethylene, benzene, and cyclopropene. The pK_a of **1** was estimated to be between 40 and 41 by correlating E_{calcd} with the experimental pK_a obtained from kinetic acidities of the above hydrocarbons.

Apparent confirmation of this enhanced acidity was obtained by treating dibromide **3** with 6 equiv of KO-*t*-Bu in the presence of 16 equiv of $DNMe_2$. The product fulvene **4** was found to contain 0.2 D at C_6 and 0.03 D on the ring. The amount of exchange at C_6 could be enhanced by increasing the base strength. For example, after the addition of 1.0 equiv of 18-crown-6 ether, **3** under the above conditions was converted to **4** containing 0.6 D at C_6. The amount of exchange at C_6 was also increased by the presence of a *tert*-butyl group at C_2. Under conditions which promoted 0.2 D incorporation during the transformation of **3** to **4, 16** was converted to *syn*-**22** containing 0.6 D at C_6.

Since control experiments confirmed that neither the starting dibromide **3** nor the product **4** incorporated deuterium, the exchange involved either diene **9** or triene **1.** It was important to ascertain whether triene **1** actually did undergo the exchange because of implications concerning the lifetime of **1** in a nucleophilic media. A means to differentiate between these two possibilities was suggested by the report that bromoform exchanges 100 times faster than chloroform.[44] If the C_6 hydrogen of bromodiene **9** were exchanging, then 6-chlorobicyclohexadiene formed from 4-bromo-6-chloride **7** under the same conditions would incorporate less deuterium. Indeed, in parallel experiments, deuterium was found at C_6 of fulvene **4** obtained from dibromide **3** but not from **7,** thus ruling out the possibility of exchange of triene **1.** Both **7** and **4** reacted by the same pathway since similar results were obtained from all other labeling studies.

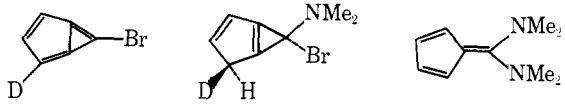
To date, the only chemistry of **1** that we have detected has been the addition of nucleophiles. Presumably, this is a rapid reaction, occurring immediately upon generation of **1.** If so, then the observation that the elimination of dibromide **3** in the presence of 16 equiv of $DNMe_2$ generated **4,** essentially undeuterated at C_1, C_2, C_3, or C_4, can be explained. Triene **1** is formed in the presence of an undeuterated *tert*-butyl alcohol molecule since the proton came from C_5 of dibromide **3.** If the concerted addition of $DNMe_2$ at C_6 and protonation by the *tert*-butyl alcohol were faster than exchange of the hydroxyl proton with dimethylamine-d_1 very little deuterium would be incorporated in the final product.

The failure of reversible protonation of anion **10** to incorporate deuterium at C_2, C_3, or C_4 from a deuterated solvent pool is consistent with the previously postulated mechanism whereby deuterium is lost from C_2, C_3, and C_4 to a protio solvent. Cram has previously reported several examples in which the ratio for the rate of exchange with the solvent pool to the rate of internal racemization is much larger for deuterium loss than for deuterium incorporation.[45]

Halobicyclohexatrienes. In an attempt to further substantiate the existence of triene **1,** we prepared the suitable precursors for the 6-bromo- and 6-chlorobicyclo[3.1.0]hexatrienes. The thermally labile 6,6-dichlorobicyclo[3.1.0]-hexene[46] was chlorinated using *t*-BuOCl at 0 °C in near-quantitative yield to form *exo*-4,6,6-trichlorobicyclo[3.1.0]-hexene (**28**). Addition of **28** to KO-*t*-Bu/THF at −75 °C generated a 1:2 mixture of *m*-dichlorobenzene and 6-chloro-6-*tert*-butoxyfulvene in 80% yield.

The corresponding tribromide **29** was prepared beginning with the addition of dibromocarbene to benzyl 2-cyclopentenyl ether. Subsequent ether cleavage with anhydrous HBr and a Jones oxidation generated 6,6-dibromobicyclo[3.1.0]hex-2-one, which was converted to 4,6,6-tribromo-2-bicyclo[3.1.0]-hexene via the method outlined in Scheme III. KO-*t*-Bu/THF converted **29** to a 1:1 mixture of *m*-dibromobenzene and bis-6,6-*tert*-butyoxyfulvene. In the presence of KO-*t*-Bu/$HNMe_2$, under the standard reaction conditions, **29** was mainly converted to bis-6,6-dimethylaminofulvene (**30**). Thus, the chemistry of the C_6 halogenated trienes paralleled that observed for bicyclohexatriene. The tacit assumption is that the presence of an endo oriented halogen at C_6 does not affect the reaction pathway since *endo,exo*-4,6-dibromo-2-bicyclo[3.1.0]hexene was converted to 6-substituted fulvenes in the same fashion as was the exo,exo dibromide **3,** albeit in poorer yield.

The synthetic route leading to **29** permitted the incorporation of one deuterium distributed over C_2 and C_4. The ultimate fate of the deuterium label of the intermediate 6-bromo-2-deuteriobicyclo[3.1.0]hexatriene (**31**) provided an interesting test for the previously presented rationale derived from frontier orbital considerations. Concerted trans addition of "$HNMe_2$" across C_2 and C_6 of **31** would generate diene **32.** Since the



31 32 30

overlap of the C–N bond with the cyclopentadienyl radical would be greater than that for the C–Br bond, the electron density should be higher at C_4 and C_5 on the molecular face anti to the dimethylamino group. As a consequence the hydrogen should preferentially migrate, resulting in the appearance of the deuterium at C_2 of fulvene **30** in contrast to the conversion of triene **1-2-*d*** to fulvene **4** deuterated only at C_1 and C_4. If protonation occurred at C_4, migration of either hydrogen will result in the deuterium appearing at C_1 of **30.** Thus by this analysis the deuterium should be equally distributed over C_1 and C_2 of **30.** ^1H NMR analysis of the deuterated product confirmed that the deuterium was equally

distributed over C_1 and C_2 of fulvene **30**.[47] Thus the finding that substitution of a bromine for hydrogen at C_6 of triene **1** dramatically changes the fate of a deuterium label at C_2 as predicted provides additional confirmation of the importance of σ/π orbital interaction.

Conclusion

The labeling studies require the intermediacy of bicyclo[3.1.0]hexatriene. The chemistry of triene **1** is that expected of an azulenoid hydrocarbon. Owing to the highly nucleophilic media employed to generate **1**, only nucleophilic addition products have been observed thus far, despite the presence of diphenylisobenzofuran, furan, tetracyclone, and 5,5-dimethoxycyclopentadiene. This current situation is reminiscent of the inability to trap *o*-benzyne by reagents other than nucleophiles when generated from bromobenzene. The labeling studies revealed a hidden stereospecific rearrangement during the transformation of triene **1** to the fulvene products. Despite the strain associated with triene **1**, the final elimination competes favorably with an alternative pathway of low activation energy. This fact would suggest that resonance stabilization offsets the unfavorable ring strain of bicyclo[3.1.0]hexatriene.

Experimental Section

^{1}H NMR were recorded using a Varian T-60 or HA-100 spectrometer. ^{13}C NMR were recorded on a Nicolet TT-23 spectrometer. Low-resolution mass spectra were obtained using an Associated Electrical Industries Ltd. M.S. 12 in conjunction with an INCOs 2000 M.S. Data System. High-resolution mass spectra were obtained using a Consolidated Electronics Corp. 21-110 mass spectrometer. A Perkin-Elmer Model 3920 equipped with temperature programming analysis and a flame ionization detector was employed for GLC analyses. Thin layer chromatograms (TLC) were run on E. Merck plates precoated with silica gel 60-F254.

Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen. Potassium *tert*-butoxide (KO-*t*-Bu), prepared from dry *tert*-butyl alcohol and potassium, after sublimation at 170 °C at 50 μm Hg° was then stored and handled in a glove box under nitrogen atmosphere. Dimethylamine was dried by distillation from calcium hydride.

***exo,exo*-4,6-Dichloro-2-bicyclo[3.1.0]hexene (5).** *syn,anti*-5,6-Dichlorobicyclo[2.1.1]hexene (15 mmol), prepared by treatment of benzvalene with Cl_2, was dissolved in 15 mL of CCl_4 and warmed to 54 °C for 8 h. At 54 °C the isomerization of *anti,syn*-5,6-dichlorobicyclo[2.1.1]hexene was two times slower than that of the corresponding dibromide. The CCl_4 was removed, yielding pure **5** as a colorless liquid in 95% yield: ^{1}H NMR (CCl_4, δ) 6.09 (br d, 1 H, $J_{2,3}$ = 6 Hz), 5.62 (br d, 1 H), 4.74 (br s, 1 H), 2.64–2.17 (m, 3 H).

***exo,exo*-6-Bromo-3-bicyclo[3.1.0]hexen-2-ol (11).** Dibromide **3**[26] (3.0 g, 12.6 mmol) in 5 mL of dioxane was added dropwise with rapid stirring to 50 mL of 1:1 H_2O/dioxane containing 1.4 g of $NaHCO_3$ (19.5 mmol). After 1 h at 25 °C, the solution was poured into water and extracted three times with ether. The combined organic extracts were washed three times with water, dried over Na_2SO_4, and evaporated to yield 2 g (90%) of a colorless oil. The crude product was essentially pure; however, complete purification was effected by chromatography on Florisil using 10% ether/petroleum ether as the eluent. TLC (10% $Et_2O/CHCl_3$, R_f 0.25). ^{1}H NMR (CCl_4, δ): 6.19 (br d, 1 H, $J_{2,3}$ = 6 Hz), 5.71 (br d, 1 H), 4.49 (br s, 1 H), 4.15 (br s, -OH), 2.42 (m, 1 H), 2.12 (m, 2 H). *m/e* (rel intensity): 174, 176 (0.7, 0.5), 157, 159 (54, 51).

Preparation of Dibromide 3 from Alcohol 11. Anhydrous hydrogen bromide was rapidly bubbled through 10 mL of CH_2Cl_2 containing 528 mg (3 mmol) of alcohol **11** and 3 g of Na_2SO_4 at 4 °C until saturation was obtained. Subsequently, the solution was removed from the ice bath and allowed to stand for 10 min at 25 °C, and the solvent was pipetted from the Na_2SO_4. After evaporation, the residue was taken up in benzene, dried over Na_2SO_4 if necessary, and reevaporated to give 640 mg (90%) of the product dibromide **3**.

***exo,exo*-4-Chloro-6-bromobicyclo[3.1.0]hex-2-ene (6) and *exo,exo*-4-Bromo-6-chlorobicyclo[3.1.0]hex-2-ene (7).** Dihalides **6** and **7** were prepared from **3** and **5** by hydrolysis and subsequent treatment with anhydrous HCl and HBr, respectively, as described above.

^{1}H NMR (CCl_4, δ): **7**, 6.03 (br d, 1 H, $J_{2,3}$ = 6 Hz), 5.68 (br d, 1 H), 4.86 (br s, 1 H), 2.55 (br s, 2 H), 2.30 (t, 1 H, J = 2 Hz). **6**, 6.17 (br d, 1 H, $J_{2,3}$ = 5 Hz), 5.67 (br d, 1 H), 4.77 (br s, 1 H), 2.52 (m, 2 H), 2.17 (t, 1 H, J = 2 Hz).

***exo*-6-Bromo-3-bicyclo[3.1.0]hexen-2-one (12).** A slight excess of Jones reagent (2.0 M) was added dropwise with stirring to 5 mL of reagent acetone containing 158 mg (1 mmol) of crude alcohol **11** at 4 °C. The solution was poured into brine and extracted three times with ether. The combined extracts were washed once with brine, dried over Na_2SO_4, and evaporated. The residue was purified by chromatography on Florisil using 1% ether/petroleum ether to elute enone **12** (125 mg, 80%) as a colorless oil. TLC ($CHCl_3$, R_f 0.45).

Alternatively, the oxidation could be easily accomplished in 90% yield using Collins reagent provided that 3 g of Celite for each gram of oxidant was added to the CH_2Cl_2 solution of the Collins reagent prior to the alcohol.

^{1}H NMR (CCl_4, δ): 7.66 (d of d, 1 H $J_{3,4}$ = 6, $J_{4,5}$ = 3 Hz), 5.79 (d, 1 H), 3.10 (t, 1 H, J = 2 Hz), 2.86 (m, 1 H], 2.45 (m, 1 H). *m/e* (rel intensity): 172, 174 (2.3, 2.2), 144, 146 (14.1, 13.6). IR (CCl_4): 5.92 μ. Exact mass: 171.9528, 173.9503 (calcd, 171.9524, 173.9504).

Reduction of *exo*-6-Bromo-3-bicyclo[3.1.0]hexen-2-one (12) with Alane-d_3. To 3 mL of dry ether containing 53 mg (1.26 mmol) of lithium aluminum deuteride cooled to 4 °C was added 56 mg (0.42 mmol) of aluminum chloride. After 5 min of stirring at 4 °C, 173 mg (1 mmol) of enone **12** in 1 mL of ether was added in one portion. After an additional 10 min, the solution was poured over ice and brine and extracted three times with ethyl acetate. The combined extracts were dried over Na_2SO_4 and evaporated to give an oil mainly comprised of a 4:1 mixture of endo/exo epimeric monodeuterated alcohols. After chromatography on Florisil 144 mg (82%) was obtained. The endo alcohol was eluted with 3% ether/petroleum ether. The exo alcohol **11**-*2*-d_1 required 10% ether/petroleum ether as the eluent.

^{1}H NMR (CCl_4, δ): *exo,endo*-6-bromo-3-bicyclo[3.1.0]hexen-2-ol, 5.94 (br d, 1 H, $J_{2,3}$ = 6, $J_{2,1}$ = 2 Hz), 5.40 (br d, 1 H), 5.23 (br d, 1 H, $J_{4,5}$ = 6 Hz), 3.89 (br s, 1 H, -OH), 2.81 (t, 1 H, J = 1.5 Hz), 2.16 (m, 2 H).

6-Bromo-2-bicyclo[3.1.0]hexanone (13). Method A. To enone **12** (100 mg, 0.58 mmol) in 3 mL of ethanol was added 38 mg (1 mmol) of sodium borohydride at 25 °C. After 45 min, the solution was poured into water, made acidic with dilute HCl, and extracted three times with ether. The combined ether extracts were washed twice with water, dried over Na_2SO_4, and evaporated to give 54 mg (90%) of relatively pure *exo*-6-bromo-2-bicyclo[3.1.0]hexanol. ^{1}H NMR (CCl_4, δ): 3.53 (m, 2 H, H_4 and -OH), 2.97 (br s, 1 H), 2.30–1.40 (m, 6 H).

The crude alcohol was oxidized in 15 mL of acetone at 4 ° by the dropwise addition of a slight excess of Jones reagent. The reaction mixture was poured into water, extracted three times with ether, dried over Na_2SO_4, and evaporated. The crude product was quickly passed through a Florisil column to give 48 mg (87%) of the desired ketone **13** as a colorless oil. TLC ($CHCl_3$, R_f 0.45). ^{1}H NMR (CCl_4, δ): 2.98 (t, 1 H, J = 1.5 Hz), 2.53–1.84 (m, 6 H). *m/e* (rel intensity): 174, 176 (7.0, 6.6), 132, 134 (72.8, 70.3). Exact mass: 173.9682, 175.9667 (calcd, 173.9683, 175.9661). IR (CCl_4): 5.8 μ.

Method B. To 11.8 mL of 1.7 M methyllithium at 4 °C under nitrogen was added dropwise 5.9 mL (52 mmol) of hexamethyldisilazane (dried over calcium hydride). The solution was heated to reflux for 30 min and cooled to 4 °C and the solvent was removed under vacuum. The residual solid was heated to ~120 °C at ~3 mm until sublimation began, whereupon the heat source was removed and the nitrogen atmosphere restored. After cooling to 25 °C, 1,4-dioxa-6-spiro[4.4]nonene (**14**, 1.26 g, 10 mmol) in 12 mL of petroleum ether was added and the solid lithium hexamethyldisilazide was broken up (under N_2 positive pressure) with a spatula to permit mechanical stirring. Using a Sage syringe drive, 2.9 mL (42 mmol) of dibromomethane was added dropwise over 1 h to the stirred suspension at 25 °C. After 4 h, the reaction mixture was poured into water and extracted three times with ether. The solvent was evaporated and the bulk of the hexamethyldisilazane removed at 10 mm. By ^{1}H NMR the endo/exo ratio was 1:3.

^{1}H NMR (CCl_4, δ): endo bromide, 3.82 (s, 4 H), 3.29 (t, J = 8 Hz, 1 H), 2.09–1.29 (m, 6 H); exo bromide, 3.82 (s, 4 H), 2.69 (t, J = 1.5 Hz, 1 H), 2.09–1.25 (m, 6 H).

The crude ketals were dissolved in 30 mL of ether at 4 °C and 30 mL of cold 10% H_2SO_4 was added. After stirring for 15 h at 4 °C, the

solution was poured into H_2O and extracted three times with ether. The extracts were washed twice with water and dried over Na_2SO_4 and the solvent was evaporated. After passage through a Florisil column, 1.5 g (86%) of epimeric ketones was obtained (exo/endo = 3).

^1H NMR (CCl_4, δ): endo bromide, 3.54 (br t, 1 H, J = 7 Hz), 2.30–1.42 (m, 6 H).

Conversion of Ketone 13 to Enone 12. Four 177-mg portions of selenium dioxide (708 mg, 6.4 mmol) were added once every 2 h to a stirred solution comprised of 1.01 g of ketones **13** and its C_6 epimer (5.8 mmol, 3:1) and 9 mL of chlorobenzene at 110 °C. After 10 h, the reaction was 95% complete by GLC analysis (6 ft 5% SE-30 on Chromosorb G at 120 °C). The solution was poured into saturated aqueous sodium bicarbonate and extracted three times with ether. After drying over Na_2SO_4 the organic solvents were removed under vacuum at 25 °C. Separation of the isomeric enones was accomplished on Florisil. TLC ($CHCl_3$, R_f 0.40 and 0.45). Ether/petroleum ether (7%) eluted 330 mg (33%) of exo enone **12**, and 10% ether/petroleum ether eluted 160 mg (13%) of the *endo*-6-bromobicyclohex-3-en-2-one.

^1H NMR (CCl_4, δ): endo enone, 7.40 (d of d, 1 H, $J_{3,4}$ = 6, $J_{4,5}$ = 3 Hz), 5.94 (d, 1 H), 4.02 (t, 1 H, J = 7 Hz), 2.82 (m, 1 H), 2.41 (m, 1 H).

***exo*-6-Bromo-3,3-dideuteriobicyclo[3.1.0]hexan-2-one(13-3,3-d_2).** Ketone **13** (2.50 mg, 1.4 mmol) was heated to 65 °C for 15 h in a solution containing 1.2 mL of D_2O, 0.2 mL of trifluoracetic acid, and 2 mL of dioxone. The crude product was isolated after removal of the solvent and was used without further purification. ^1H NMR of **13** indicated that approximately two deuteriums were incorporated.

6-Bromo-1,4-dioxa-6-spiro[4.4]nonene. To a stirred 4 °C solution of 4.6 g of 2,5-dioxa-6-spiro[4.4]nonene (**14**, 26 mmol) in 20 mL of carbon tetrachloride was added 6 g of bromine (37.5 mmol) in 10 mL of carbon tetrachloride over a period of 10 min. After removal of the solvent without delay, the dark residue was dissolved in 10 mL of tetrahydrofuran and subsequently added to 20 mL of Me_2SO containing 6 g of sodium ethoxide (92 mmol) at 4 °C. After being stirred for 8 h at 25 °C, the solution was poured into water, filtered through Celite, and extracted four times with petroleum ether. This product, isolated after removal of the pentane, was purified by passage through a Florisil column using petroleum ether as a eluent to give 5 g (65%) of a colorless oil.

^1H NMR (CCl_4, δ): 5.98 (t, 1 H, J = 2 Hz), 4.30–3.60 (m, 4 H), 2.50–1.80 (m, 4 H).

6-Deuterio-1,4-dioxa-6-spiro[4.4]nonene (14-6-d_1). To 3.4 g of 6-bromo-1,4-dioxa-6-spiro[4.4]nonene (17 mmol) in 25 mL of THF containing 1.8 mL of *tert*-butyl alcohol-d_1 (20 mmol) under argon was added 1.2 g (52 mmol) of sodium foil. The suspension was stirred for 7 h at 25 °C, at which time GLC analysis indicated that the reaction was complete. The product was filtered, added to water, and extracted three times with ether. After drying over Na_2SO_4, the solvent was removed and the product passed through a short Florisil column using petroleum ether to elute 1.8 g of labeled ketal (83%).

***exo,exo*-6-Bromo-2-*tert*-butyl-3-bicyclo[3.1.0]hexen-2-ol.** To a stirred solution comprised of 1.8 g (10.4 mmol) of enone **12** and 30 mL of tetrahydrofuran at −110 °C under nitrogen was added 5 mL of 2.3 M *tert*-butyllithium dropwise over 15 min. After 10 min, the reaction mixture was poured into aqueous NaH_2PO_4 and extracted three times with ether. After drying over Na_2SO_4, the solvent was removed and the residue chromatographed on activity 3 neutral Woelm alumina. The partially purified alcohol was eluted with 10% ether/petroleum ether. Further purification from more volatile components could be achieved by evacuating the product at 15 μm Hg. This procedure yielded 360 mg (15%) of relatively pure alcohol. TLC ($CHCl_3$ major spot R_f 0.3). ^1H NMR (CCl_4, δ): 5.92 (d of d, 1 H, $J_{3,4}$ = 5.5, $J_{4,5}$ = 2 Hz), 5.33 (d, 1 H), 2.69 (t, 1 H, J = 1.5 Hz), 1.94–1.74 (m, 3 H), 0.94 (s, 9 H).

***exo,exo*-4,6-Dibromo-2-*tert*-butylbicyclo[3.1.0]hex-2-ene (16).** Anhydrous hydrogen bromide was vigorously passed through 6 mL of methylene chloride containing 387 mg (1.4 mmol) of *exo,exo*-6-bromo-2-*tert*-butyl-3-bicyclo[3.1.0]hexen-2-ol and 1.0 g of sodium sulfate at 23 °C for 1 min. The volatiles were removed on an aspirator, the residue was taken up in benzene, and the benzene was removed. The resulting thermally labile dibromide **16** was stored at −75 °C until utilized. ^1H NMR (CCl_4, δ): 5.35 (br s, 1 H), 4.93 (br s, 1 H), 2.65 (br s, 2 H), 2.22 (t, 1 H, J = 2 Hz), 1.20 (s, 9 H).

***exo,exo*-6-Bromo-2-methyl-3-bicyclo[3.1.0]hexen-2-ol.** Using the procedure described for the preparation of *exo,exo*-6-bromo-2-*tert*-butyl-3-bicyclo[3.1.0]hexen-2-ol, 542 mg (3.13 mmol) of enone **12** in 10 mL of tetrahydrofuran was reacted with 1.5 mL of 2 M MeLi at −110 °C. After aqueous workup, the product alcohol was isolated as a colorless oil (530 mg, 90%) requiring no further purification. TLC ($CHCl_3$, R_f 0.23). ^1H NMR (CCl_4, δ): 5.86 (d of d, 1 H, $J_{3,4}$ = 5.5, $J_{4,5}$ = 2 Hz), 5.38 (d, 1 H), 3.30 (br s, -OH), 2.75 (t, 1 H, J = 2 Hz), 2.24 (m, 1 H), 1.87 (m, 1 H), 1.44 (s, 3 H). *m/e* (rel intensity): 173, 175 (1.2, 1.2) parent − CH_3), 109 (18.3) (parent − Br).

***exo,exo*-4,6-Dibromo-2-methyl-2-bicyclo[3.1.0]hexene (15).** Using the procedure employed for the *tert*-butyl dibromide **16**, 530 mg of 6-bromo-2-methyl-3-bicyclo[3.1.0]hexen-2-ol in 7 mL of methylene chloride containing Na_2SO_4 was treated with anhydrous hydrogen bromide. The thermally labile product was stored at −75 °C.

^1H NMR (CCl_4, δ): 5.40 (br s, 1 H), 4.96 (br s, 1 H), 2.56 (m, 2 H), 2.35 (t, 1 H, J = 2 Hz), 1.95 (s, 3 H).

Treatment of 4,6-Dibromo-2-bicyclo[3.1.0]hexene with Lithium Dimethylamide. The following procedure was employed not only for dibromide **3** but also dihalides **5**, **6**, and **7**. A solution of 0.4 mL (6 mmol) of dry dimethylamine and 0.4 mL of tetramethylethylenediamine in 12 mL of tetrahydrofuran at 0 °C under argon was treated with 2 mL of 1.8 M methyllithium, stirred for 30 min, and then cooled to −75 °C. Subsequently, 238 mg (1 mmol) of dibromide **3** in 1 mL of tetrahydrofuran was added dropwise. After 30 min the solution was poured into water and extracted three times with petroleum ether. The combined organic layers were washed twice with water and dried over Na_2SO_4, and the solvent was removed. The residue was analyzed by ^1H NMR and GLC (6 ft × ⅛ in., 5% SE-30 on Chromosorb G). Structural assignments of bromobenzene, chlorobenzene, $PhNMe_2$, and fulvene **4**[48] were made by comparison to authentic samples. The absolute yields were determined after correction for response factors using diethylaniline as an internal standard.

Treatment of 4,6-Dibromo-2-bicyclo[3.1.0]hexene (3) with Potassium *tert*-Butoxide. To a stirred solution of 280 mg (2.5 mmol) of sublimed potassium *tert*-butoxide in 3 mL of tetrahydrofuran at −75 °C under nitrogen was added dropwise 120 mg (0.5 mmol) of **3** in 0.75 mL of tetrahydrofuran. After 3 h at −75 °C, the cold solution was poured into water and extracted three times with ether. The ether fractions were washed three times with water and dried over Na_2SO_4, and the solvent was evaporated. By NMR the crude heat- and air-sensitive product was almost pure 6-*tert*-butoxyfulvene **8**. The yield by GLC using cymene as an internal standard and correcting for response factors was 90% prior to isolation. The product assignment was confirmed by comparison to authentic 6-*tert*-butoxyfulvene.[49] Trace amounts of bromobenzene and 6-bromofulvene were also formed. Further purification could be achieved by rapid chromatography on neutral Woelm alumina activity 3 using petroleum ether as the eluent.

Conversion of Dibromide 3 to 6-Dimethylaminofulvene 4. The above precedure was employed except that 0.5 mL of dry dimethylamine was added to the base solution prior to addition of the dibromide **3**. The GLC yield using cymene as an internal standard and correcting for response factors was ~70% (after workup but prior to isolation). The propensity for the fulvene **4** to tail and decompose precluded accurate values. The crude product could be purified by chromatography on neutral Woelm alumina activity 3 using 5% ether/petroleum ether as the eluent. Chromatography on other supports such as Florisil, silica gel, or acidic or basic alumina led to extensive decomposition. All physical and spectral properties of **4** were identical with those reported by Hafner.[48]

Conversion of 3 to 4-6-d_1. the elimination was performed as above except in the presence of 0.5 mL of deuteriodimethylamine. When crown ether was used, the elimination was run at −40 °C in the presence of 660 mg (2.5 mmol) of 18-crown-6-ether.

Exchange of 6-Dimethylaminofulvene (4). Prior to the exchange of the hydrogen at C_1 or C_4, the crude aminofulvene product formed from the dibromide **3** was chromatographed on activity 3 neutral Woelm alumina using 5–10% ether/petroleum ether to elute aminofulvene **4**. The purified aminofulvene (30 mg) dissolved in 4 mL of 3:1 $MeOH/CHCl_3$ was heated to 62 °C for 20 h. The solvent was evaporated, benzene added to the residue, and the flask evaporated to dryness once again. The residue was dissolved in 1 mL of THF and treated with freshly prepared phenyllithium at 25 °C under nitrogen using silica gel TLC ($CHCl_3$) to follow the reaction. After 5 min, 0.2 mL of HOAC was added, followed by H_2O. The solution was extracted twice with petroleum ether and the combined petroleum ether

fractions were washed twice with H_2O, dried over Na_2SO_4, and evaporated. The crude product was chromatographed rapidly on activity 1 neutral Woelm alumina. The yellow phenylfulvene band, eluted with 1% ether/petroleum ether, was fractionated to minimize the possibility of contamination by the slightly faster moving biphenyl. Prior to mass spectral analysis, the purified material was analyzed by GLC (6-ft 5% SE-30 on Chromosorb G, 120 °C for 2 min followed by an 8 °C/min increase) to determine the extent, if any, of biphenyl contaminant.

The unexchanged aminofulvenes were not normally purified prior to conversion to 6-phenylfulvene **17**. The only purification which did not induce exchange at the labile 1,4 position was recrystallization from petroleum ether/ether at −75 °C.

To exchange the hydrogens at C_2 and C_3 ~120 mg of purified aminofulvene **4** was reacted as above in $MeOH/CHCl_3$ except that 20 μL of trifluoracetic acid was added. The substantial decomposition which occurred during the exchange necessitated repurification of the product prior to conversion to **17**.

All mass spectral analyses were performed in conjunction with a d_0 standard.

2-*tert*-Butyl-6-*tert*-butoxyfulvene. Using the procedure described for dibromide **3**, 206 mg (0.7 mmol) of dibromide **16** was added to 600 mg (5.4 mmol) of potassium *tert*-butoxide for 15 h at −75 °C. After workup and extraction, the crude product was chromatographed on neutral alumina activity 3 eluting with petroleum ether.

^1H NMR ($CDCl_3$, δ): 1.21 (s, 9 H), 1.41 (s, 9 H), 6.01–6.58 (m, 3 H), 7.11 (s, 1 H). ^{13}C NMR ($CDCl_3$, proton decoupled) from Me_4Si 28.08 (CMe_3), 30.06 ($OCMe_3$ methyl), 107.85, 123.86, 126.54 (tertiary ring carbon), 114.15, 116.97 (quaternary ring carbon), 147.51 ppm (C_6). *m/e* (rel intensity): 206 (6.6), 150 (25.3), 135 (100). Exact mass: 206.1677 (calcd, 206.1670).

Conversion of Dibromide 16 to Aminofulvenes *syn*-22 and *anti*-23. Using the same procedure as devised for dibromide **3**, 294 mg (1.0 mmol) of dibromide **16** was reacted with 670 mg (6 mmol) of potassium *tert*-butoxide and 1.0 mL of dimethylamine at −75 °C for 15 h. After isolation, the crude product (177 mg) was a 3:1 mixture of two aminofulvenes. Chromatography on neutral alumina activity 3 using 2% ether/petroleum ether not only purified but also epimerized the product to give a 1:1 mixture.

^1H NMR ($CDCl_3$, δ): *syn*-**22**: 1.28 (s, 9 H), 3.24 (s, 6 H), 6.39 (m, 3 H), 7.00 (s, 1 H). *anti*-**23**: 1.28 (s, 9 H), 3.24 (s, 6 H), 6.15 (m, 1 H), 6.62 (m, 2 H), 7.05 (s, 1 H). ^{13}C NMR ($CDCl_3$, proton decoupled) from Me_4Si 1:1 **22** and **23**: 31.20 (CMe_3), 43.11 (NMe_2), 107.00, 114.73, 117.14, 119.28, 125.04, 125.32 (tertiary ring carbons), 147.00, 147.17 ppm (C_6). *m/e* (rel intensity): 177 (29), 162 (100). Exact mass: 177.1523 (calcd, 177.1517).

Confirmation of the structure was obtained by the following independent synthesis. To 3 mL of methylene chloride containing 121 mg (1 mmol) of 6-dimethylaminofulvene (**4**), 130 mg (1.1 mmol) of γ-collidine, and 0.11 mL (1 mmol) of *tert*-butyl chloride at 0 °C was added 60-mg portions of aluminum chloride every 10 min until TLC indicated that all the starting fulvene had been consumed. The reaction product was poured into brine and extracted three times with ether. The organic layers were washed three times with water and dried over Na_2SO_4 and the solvent was evaporated. The crude product was chromatographed on neutral alumina activity 3 using 2% ether/petroleum ether to elute the product (30 mg, 15%) of a 1:1 mixture of fulvenes **22** and **23**.

Diels–Alder Adduct of Fulvenes 22 and 23. To 37 mg (0.21 mmol) of 1:1 fulvenes **22** and **23** in 1 mL of ether at 0 °C under nitrogen was added 0.55 mmol of freshly prepared phenyllithium. After 30 min at 0 °C, the reaction mixture was quenched with ice water and extracted twice with a minimal amount of ether. To the cold ether extract (10 mL) was added 1 mL of methyl iodide and sodium sulfate. After warming slowly to 23 °C, the solvent was removed to yield 44 mg (100%) of a 1:1 mixture of 2- and 3-*tert*-butyl-6-phenylfulvenes by GLC (6-ft 5% FFAP on Chromosorb W at 185 °C). The crude product was dissolved in 1 mL of ether, 46 mg (0.5 mmol) of dicarbomethoxyacetylene added, and the solution refluxed for 24 h under nitrogen. Subsequent chromatography on neutral alumina activity 3 using 10% methylene chloride/petroleum ether as the eluent yielded 53 mg (70%) of a 1:1 mixture of the desired adducts. TLC ($CHCl_3$) showed one spot (R_f 0.25).

^1H NMR ($CDCl_3$, δ): mixture of two isomers, 1.10 (s, 9 H), 3.84 (s, 6 H), 4.27 (m, 1 H), 4.77 (m, 1 H), 5.38 (m, 1 H), 6.50 (m, 1 H), 7.27 (m, 5 H). *m/e* (rel intensity): 352 (86), 292 (100). Exact mass: 352.1680 (calcd, 352.1674).

4-Methyl-6-dimethylaminofulvene (20). Using the procedure developed for the elimination of dibromide **3**, 252 mg (2 mmol) of *exo,exo*-4,6-dibromo-2-methyl-2-bicyclo[3.1.0]hexene (**15**) was treated with potassium *tert*-butoxide/dimethylamine in THF at −75 °C for 15 h. After aqueous workup, the crude products were purified by chromatography on neutral alumina activity 3. Petroleum ether eluted 132 mg (40%) of 6-bromo-4-methylene-2-bicyclo[3.1.0]hexene (**33**) and 3% ether/petroleum ether eluted 19 mg (7%) of **20** as a yellow oil.

33: ^1H NMR (CCl_4) δ 6.23 (br d, 1 H, $J_{2,3}$ = 5 Hz), 5.91 (br d, 1 H), 5.17 (s, 1 H), 5.01 (s, 1 H), 2.53 (s, 3 H); *m/e* (rel intensity) 170, 172 (2.0, 2.0), 91 (100). Exact mass 169.9732, 171.9715 (calcd, 169.9732, 171.9712).

20: ^1H NMR (CCl_4) δ 6.61 (s, 1 H), 6.37–5.70 (m, 3 H), 3.02 (s, 6 H), 2.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, proton decoupled) from Me_4Si 15.16 (CH_3), 45.54 (NMe_2), 111.04, 121.57, 124.93 (tertiary ring carbon), 146.18 ppm (C_6); *m/e* (rel intensity) 135 (98), 120 (53), 91 (72). Exact mass 135.1050 (calcd, 135.1048).

Conformation of the structure assignment of fulvene **20** was obtained by reacting sodium methylcyclopentadienide with dimethylaminomethoxycarbenium methylsulfate following the procedure developed by Hafner for the preparation of 6-dimethylaminofulvene.[48] The crude product was purified by chromatography on neutral alumina activity 3 using 4% ether/petroleum ether to elute a 1:1:2 mixture of the 2, 3 and 4-methyl-6-dimethylaminofulvenes (18%), respectively, as indicated by ^1H and ^{13}C NMR.

^1H NMR (CCl_4, δ): 6.75 (s, 0.25 H), 6.61 (s, 0.75 H), 6.34–5.67 (m, 3 H), 3.05 (m, 6 H), 2.08 (m, 3 H). The peak at δ 6.61 assigned to H_6 was resolved at 100 MHz in acetonitrile by 0.04 ppm to give two signals in a ratio of 1:2. ^{13}C NMR ($CDCl_3$, proton decoupled) from Me_4Si 12.53, 14.42, 15.16 (CH_3), 42.52 (NMe_3), 111.04, 113.28, 114.40, 118.50, 120.56, 121.57, 122.75, 124.93, 127.35 (tertiary ring carbon), 145.02, 146.18 ppm (C_6). The peak heights indicated the ratio to be 1:1:2.

6-Bromofulvene. In a procedure analogous to that developed by Bergman for 6-chlorofulvene,[50] 7.0 g (28 mmol) of bromoform was added over 1 h to 1.0 g (16 mmol) of cyclopentadiene and 3.0 g (27 mmol) of potassium *tert*-butoxide in 30 mL of petroleum ether at −20 °C under nitrogen. After 2 h at −10 °C, the suspension was poured into water, extracted twice with petroleum ether, and dried over Na_2SO_4. The thermally labile crude product was contaminated with bromoform and bromobenzene but could be partially purified by careful vacuum distillation (pot temperature less than 25 °C). Pure 6-bromofulvene can be obtained in poor yield by chromatography on 5% silver nitrate/silica gel using petroleum ether as the eluent.

^1H NMR (CCl_4, δ): 6.90 (s, 1 H), 6.52–5.77 (m, 4 H).

4,6,6-Trichlorobicyclo[3.1.0]hex-2-ene (28). A solution of 0.89 g (6 mmol) of 6,6-dichlorobicyclo[3.1.0]hex-2-ene[46] and 0.97 g (9 mmol) of *tert*-butyl hypochlorite in 4 mL of CCl_4 at 4 °C was irradiated with a sunlamp for ~40 min or until all of the starting olefin was consumed by ^1H NMR. The solvent was removed using an aspirator and the residue chromatographed on Florisil. Petroleum eluted the trichloride **28** (1.0 g, 95%) as light yellow oil.

GLC (10-ft 10% SF-96 on Chromosorb W at 130 °C). ^1H NMR (CCl_4, δ): 2.7 (m, 1 H), 2.9 (m, 1 H), 4.65 (d, 1 H, J = 3 Hz), 5.85 (m, 2 H). *m/e* 184, 182, 148, 146, 113, 111.

4,6,6-Tribromobicyclo[3.1.0]hex-2-ene (29). Using the same procedure devised for the conversion of enone **12** to dibromide **3**, 6,6-dibromo-3-bicyclo[3.1.0]hexen-2-one (**34**) was converted to tribromide **29** in 90% yield. Enone **34** was prepared from 2-cyclopentenyl benzyl ether (**35**) by addition of bromoform (76 g, 0.27 mol) to 19.4 g (0.11 mol) of ether **35** and 35.4 g (0.3 mol) of KO-*t*-Bu suspended in 100 mL of petroleum ether at 4 °C over 2 h. After aqueous workup and removal of the volatile components, the crude product was cleaved at 4 °C by bubbling HBr through a CH_2Cl_2 solution for 30 min. After removal of the solvent, the residue was dissolved in ether and washed with aqueous sodium bicarbonate. Subsequently the crude product was chromatographed on Florisil using 25% ether/petroleum ether to elute the desired alcohol. The product alcohol was oxidized with Jones reagent to give 2.04 g (11%) of 6,6-dibromobicyclohexan-2-one (**36**). Ketone **36** was oxidized to enone **34** in 55% yield by SeO_2 using the procedure utilized for conversion of **13** to **12**. After chromatography on Florisil (10% ether/petroleum ether), enone **34** was isolated as a solid (mp 61–62 °C from CCl_4).

29: ^1H NMR (CCl_4, δ) 2.95 (m, 2 H), 4.65 (m, 1 H), 6.0 (m, 2

H).

34: ^{1}H NMR ($CDCl_3$, δ) 2.78 (d, 1 H, J = 3 Hz), 3.2 (dd, 1 H, J = 3 Hz), 6.05 (d, 1 H, J = 6 Hz), 7.48 (dd, 1 H, J = 6, 3 Hz).

Conversion of Tribromide 29 to 6,6-Bisdimethylaminofulvene 30. The reaction conditions were identical with that used in the conversion of **3** to fulvene **4** except for a reaction time of 12 h. After aqueous workup, a ^{1}H NMR spectrum of the crude product was identical with that of authentic fulvene **30** prepared using Hafner's procedure.[51] The proton assignments were made by following the rapid uptake (30 min) of deuterium at 35 °C into **30** by ^{1}H NMR using 3:1 MeOD/$CHCl_3$ as solvent. Since the multiplet at δ 6.0 diminished faster than that at δ 6.2, that signal corresponded to H_1 and H_4.

^{1}H NMR (CCl_4, δ): 3.0 (s, 12 H), 5.9 (m, 4 H). (CH_3CN, δ): 3.05 (s, 12 H), 6.0 (m, 2 H), 6.2 (m, 2 H).

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