# BICYCLO[2.2.0]HEX-1(4)-ENE

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Abstract—The preparation of bicyclo[2.2.0]hex-1(4)-ene(1) via ring expansion of a cyclopropylcarbene or the dehalogenation of 1-bromo-4-chlorobicyclo[2.2.0]hexane is described. It is one of the most reactive of the alkenes which may be observed at room temperature. Its reactions, including dimerization and cycloaddition reactions, are described. The latter lead to convenient preparations of [m.2.2] propellanes. The vibrational spectrum was examined via matrix isolation and *ab initio* MO calculations.

It is known that the introduction of a trigonal center into a cyclobutane ring increases its energy by only 1 kcal mol<sup>-1 1</sup> whereas with cyclopropane the increase in energy is 13 kcal mol<sup>-1,2</sup> Our interest in the increase in strain caused by the introduction of a double bond into small ring systems led us to study bicyclo[2.2.0]hex-1(4)-ene(1).<sup>3</sup> Here, the second ring will lead to a very large external angle which could lead to marked destabilization. The geometry and energy of 1 have



recently been estimated via extended basis set *ab initio* calculations<sup>4,5</sup> and may be compared with cyclobutene<sup>6</sup> and cyclopropene<sup>7</sup> which also have large external bond angles. The strain energies were derived from the enthalpies of formation. In order to correct for the strain inherent in the ring systems, it was subtracted giving the  $\Delta SE$  values which represent the increase in strain caused by the introduction of the double bonds. It can be seen that 1 is predicted to be markedly destabilized, suggesting high reactivity and difficulty of preparation.<sup>8</sup>

The first synthesis of 1 was derived from the observation of Kirmse and Pook<sup>9</sup> that the tosylhydrazone anion derived from [2.4]spiroheptan-4-one (2) gave bicyclo[3.2.0]hept-1(5)-ene (3) on photolysis. When the tosylhydrazone anion derived from [2.3]spirohexan-4-one (4) was photolyzed, however, only the azine (5) was obtained.<sup>3</sup> This suggests that the intermediate diazoalkane is relatively unreactive, builds up in concentration, and then reacts with the corresponding carbene to give 5.

It was found that the thermolysis of 2 at 190° under reduced pressure also gave 3 with no other products being formed. The thermolysis of 4 was then examined,



and a mixture of 1 and 1,2-dimethylenecyclobutane (6) was found.<sup>3b</sup> Examination of the <sup>1</sup>H-NMR spectrum of the product showed a singlet at  $\delta$  3.2 in addition to the bands derived from 6. The <sup>13</sup>C-NMR spectrum also was obtained in CDCl<sub>3</sub>. In addition to the signals of the diene at  $\delta$  148.7, 103.2 and 27.2 ppm, there were two signals at  $\delta$  162.8 and 43.4 ppm.<sup>10,11</sup> Although the olefinic signal is at quite low field, it is certainly compatible with the structure 1.<sup>10</sup>



The ratio of 1:6 was dependent on the pressure in the system during the reaction. When it was 1 mmHg, a 1:3 ratio of 1 to 6 was formed, whereas when it was kept below 70  $\mu$ , a 4:1 ratio was obtained. These data show that 6 is formed from 1 during the reaction, and that the reaction proceeds with a short half-life at 190°.

We have not as yet succeeded in determining the kinetics of the conversion of 1 to 6. A rough estimate may be made on the basis of the above data. The half-life of the reaction at 190° should be of the order of 1 ms.† Using this value, the rate constant would be of the order of 700 s<sup>-1</sup>, which may be compared with the rate constant for the conversion of cyclobutene to butadiene at 190° ( $7 \times 10^{-3} \text{ s}^{-1}$ ).<sup>12</sup> It can be seen that the thermolysis of 1 proceeds about 10<sup>5</sup> times faster than that of cyclobutene, in good accord with the greatly increased strain.

The bands assigned to 1 disappeared quickly if the solution from the pyrolysis was warmed to  $-30^{\circ}$ , and were replaced by the spectrum of the Diels-Alder

 $<sup>\</sup>uparrow$  Nitrogen is the other product of the reaction and will sweep the bicyclohexene out of the heated zone. The contact time at a pressure of 70  $\mu$  must be much less than 1 s, and 1 ms appears to be a reasonable estimate. If it were in error by a factor of 10, it would not significantly affect the conclusion about the reactivity compared to cyclobutene.

adduct (7) between 1 and 6. The structure of 7 was determined from its molecular formula, C12H16, and its NMR spectra. The <sup>1</sup>H-NMR spectrum consisted of multiplets at  $\delta$  1.84 (4H), 2.07 (4H), 2.20 (4H) and 2.42 (4H). The <sup>13</sup>C-NMR spectrum had bands at  $\delta$  138.1, 39.4, 34.5, 33.6 and 29.9 ppm. The Raman spectrum had a C=C band at 1680 cm<sup>-1</sup>, and there was no corresponding IR band. The latter suggests a symmetrically substituted cyclobutene, and the <sup>13</sup>C-NMR spectrum suggests a plane of symmetry. The <sup>1</sup>H-NMR band at 2.42 ppm is appropriate for the methylene hydrogens of a cyclobutene.<sup>13</sup> The presence of a bicyclo[2.2.0] hexane unit in 7 was indicated by the AA'BB' pattern at  $\delta$  2.07 and 2.20. Thermolysis at 350° in a flow system gave an isomer (8) having four vinyl protons ( $\delta$  4.55 (2H), 4.83 (2H)), weak IR absorption at 1600 and 1630 cm<sup>-1</sup>, and strong IR absorption at 865  $cm^{-1}$ . Thus, the internal double bond in 7 has been converted to a conjugated diene in 8 as would be expected for the proposed structure.



When an excess of cyclopentadiene was added to the cold reaction mixture before it was allowed to warm to room temperature, no 7 was formed, but rather 6 and a  $C_{11}H_{14}$  hydrocarbon (9) were found. The spectra of 9 were consistent with the Diels-Alder adduct of 1 with cyclopentadiene.

The above method of preparation is inconvenient in that the reactive diene, 6, is formed as an impurity. All attempts to remove 6 from the mixture via a Diels-Alder or other reaction were unsuccessful due to the high reactivity of 1. In a search for another method of preparation, we examined the dehalogenation of 1bromo-4-chlorobicyclo[2.2.0]hexane (10). It was conveniently prepared from the readily accessible 4chlorobicyclo[2.2.0]hexane-1-carboxylic acid<sup>14</sup> by a modified Hunsdiecker reaction.<sup>15</sup> The conventional reagents, Zn, Mg and Li amalgam, failed to react.<sup>16</sup> The use of sodium in liquid ammonia, which frequently is successful in forming cyclobutenes from the corresponding vicinal dihalides,<sup>17</sup> led to reduction, but the main product was bicyclo[2.2.0]hexane(11) along with a  $C_{12}H_{18}$  hydrocarbon (12). The formation of 1 as an intermediate was demonstrated by adding 10 to one equivalent of sodium in ammonia at  $-78^\circ$ , and then quickly adding cyclopentadiene. The Diels-Alder adduct, 9, could then be isolated in small yield. Although not useful for the preparation of 1, this reduction does provide a convenient source of 11 which is relatively difficult to obtain by other methods.<sup>18,19</sup> The C12 compound formed in the reduction had NMR spectra consistent with the structure 12. Other reagents such as sodium on alumina<sup>20</sup> or potassium-graphite<sup>21</sup> failed to give dehalogenation leading to the formation of 1.

Metal-halogen exchange frequently provides a route to dehalogenation.<sup>22</sup> The reaction of **10** with n-



butyllithium in hexane proceeded slowly at room temperature. After quenching with water, cyclopentadiene was added. A small amount (8%) of the Diels-Alder adduct, 9, was obtained, but the major product was 1-bromo-4-n-butylbicyclo[2.2.0]hexane (13). This was probably formed by initial conversion to 1, followed by addition of n-butyllithium and a second metal-halogen exchange. In order to minimize subsequent reaction of 1 with alkyllithium, tbutyllithium was tried. In this case, a larger amount of Diels-Alder adduct was obtained after adding cyclopentadiene (35%), but alkyllithium addition to 1 still predominated.



Electrochemical reduction provides a convenient alternative to conventional reduction methods. Reduction of 10 was effected in dimethylformamide solution using 0.1 M tetraethylammonium bromide as the supporting electrolyte, a Pt gauze electrode, and a potential of -1.95 V vs a mercury pool reference electrode. A two compartment cell was required in order to isolate the alkene from the oxidation products formed at the cathode. The reduction proceeded quantitatively,<sup>23,24</sup> and the solutions could readily be assayed by forming the easily isolated Diels-Alder adduct with cyclopentadiene.



In some cases, it was desirable to examine the course of reactions of 1 in the electrolysis solvent, dimethylformamide. This could easily be done by the use of <sup>2</sup>H-NMR spectroscopy. Deuterium labeled 1 was prepared as shown in Scheme 1. Electrolysis of 10a gave 1a which had the same chemical shift in the <sup>2</sup>H spectrum as 1 had in the <sup>1</sup>H spectrum. The spectrum could readily be observed in 0.02 M solutions.

When the <sup>2</sup>H-NMR spectrum of 1a was examined at  $\sim 30^{\circ}$ , the intensity of the band was found to decrease



with time, and an AB pattern appeared (with proton decoupling) at  $\delta$  2.13 and 2.92 ppm. The product (14a) was isolated by extracting the DMF solution with pentane followed by washing with dilute acid and concentrating in the absence of air. The <sup>1</sup>H-NMR spectrum in CDCl<sub>3</sub> had bands at  $\delta$  2.24 and 2.99 ppm, and the downfield band was broadened by coupling with the cross-ring deuterium.

The reaction was repeated using unlabeled 1, and 14 was isolated, having a <sup>1</sup>H-NMR spectrum similar to that of 14a. In this case, however, bands for both the exo and endo hydrogens appeared as broadened doublets. The <sup>13</sup>C-NMR spectrum had bands at  $\delta$  35.6 and 139.2 ppm. The upfield band resulted from a carbon coupled to two hydrogens ( $J_{13C-H}$  133 Hz), whereas the downfield band was due to a quaternary carbon and had a chemical shift characteristic of olefinic carbons. It will be shown below that 14 is a dimer of 1. These data indicate that 14 is a diene having the structure shown below. In view of the thermal reactivity of the [2.2.2] propellane,<sup>25</sup> it is reasonable to propose that the pentacyclic propellane (15) is an intermediate and undergoes ring opening under the conditions of its formation.



The kinetics of the dimerization of 1 have been reported.<sup>26</sup> The reaction was second order in dilute solution (0.01-0.02 M) and had an activation entropy  $(\Delta S^{\ddagger} = -25 \text{ eu})$  which is characteristic of bimolecular reactions. The activation enthalpy was remarkably low  $(\Delta H^{\ddagger} = 11.5 \text{ kcal mol}^{-1})$ . The dimerization of 1 cannot be concerted, both from orbital symmetry<sup>27</sup> considerations, and because of the steric effect of the methylene hydrogens. The reaction probably occurs via the formation of an intermediate 1,4-diradical species (16) in a fashion similar to the thermal initiation of polymerization and related reactions.<sup>28</sup> Several reaction paths are available to 16. It could react with more 1 ultimately leading to a polymer. This course is observed at higher alkene concentrations. It could also transfer a hydrogen atom to give an ene type product, as is found in the thermal dimerization of cyclopropene.<sup>29</sup> This reaction is less favored in the present case since it will lead to a bicyclo [2.2.0] hex-1-ene which is expected to have considerable strain. Finally, it could couple the radical centers to give 15, which would cleave a different bond to give 14.



The dimerization of 1 always leads to a small amount of another diene, 17, and it was found that 14 was

converted via a Cope rearrangement to 17 on heating. The NMR spectrum of 17 showed two signals for hydrogens on a methylene group at  $\delta$  4.79 and 4.57 ppm. Four allylic hydrogens appeared as a singlet at  $\delta$  2.33, and there was an AA'BB' pattern (J = 3.3, 9.6 Hz) at  $\delta$  2.28 which is characteristic of a bicyclo[2.2.0]hexane unit. This suggested the structure 2,5-dimethylenetricyclo[4.2.2.0]decane. The assignment was strengthened by the observation of an *exo*methylene stretch at 1641 cm<sup>-1</sup> and its wag at 885 cm<sup>-1</sup>. The <sup>13</sup>C-NMR spectrum had bands at  $\delta$  154 and 107 corresponding to an *exo*-methylene unit. The kinetics of the isomerization of 14 to 17 have been examined.<sup>26</sup>

The structure of 17 was proven by reduction with hydrogen over Pt black to *cis*-2,5-dimethyltricyclo-[4.2.2.0]decane (18). The same compound was obtained via the Diels-Alder reaction between 1 and *trans,trans*-hexa-2,4-diene giving 19 which could be reduced to 18 using diimide. The hydrogenation of 19 using Pt or Pd catalysts led to rearranged products. The formation of 17 from 14 provides additional evidence for the structure of 14.



The Diels-Alder reactions of 1 were noted above. With cyclopentadiene, butadiene, 1,2-dimethylenecyclobutane and *trans,trans*-hexa-2,4-diene, the reaction proceeds rapidly well below room temperature (Scheme 2). Not surprisingly, the reaction with *cis,trans*-hexa-2,4-diene is quite slow, and cannot compete with dimerization of 1. The Diels-Alder reaction with 1,3-cyclohexadiene also did not compete effectively with dimerization of 1. However, it is known that this diene reacts slowly in some Diels-Alder reactions.<sup>30</sup> These reactions provide a convenient route to the preparation of a number of [m.2.2] propellanes which have been used to explore the mechanism of the thermal rearrangements of these and related compounds.<sup>31</sup>



Scheme 2.

The Diels-Alder reactions with isobenzofuran and diphenyltetrazine also were examined. Isobenzofuran reacted to give a quantitative yield of the adduct. Diphenyltetrazine reacted rapidly, and the initial adduct readily lost nitrogen to give 20. A similar reaction has been observed with cyclopropene,<sup>32</sup> and here, the product was in equilibrium with its valence isomer. This type of isomerization was examined in the case of 20, but the NMR spectrum was unchanged from  $-50^{\circ}$  to 90°, and corresponded to that expected for 20.



The addition of methylene or one of its derivatives to 1 has not as yet proven successful in forming a [2.2.1] propellane. The reaction of bis(triphenylphosphine) (ethylene) platinum with 1 did occur readily giving the organoplatinum [2.2.1] propellane (21). The structure of 21 was demonstrated by X-ray crystallography, and the structural data have been reported.33 The geometry of 21 is that expected for a propellane: the angle between the two 4-carbon rings is 124° as compared to 114° in bicyclo[2.2.0]hexane.34 A plane passed through the platinum and two methylene carbons attached to the bridgehead carbon intersects the central bond 0.16 Å from the bridgehead carbon. Thus, it does have an "inverted tetrahedral" geometry.35 Its reactions also are those expected for a small ring propellane. Thus, it reacts readily with ethanol to cleave the central C-C bridge giving 22. This is unique among organometallic compounds which normally prefer to undergo metal-carbon bond cleavage. The structure of 22 resembles that of norbornane with an angle between the two 4-carbon units of 112° as compared to 108° in norbornane.36

proceed at 0° and the product was isolated in the normal fashion. Besides the dimer (14) and the Diels-Alder adduct with 1,2-dimethylenecyclobutane (7), there was obtained a small amount of a ketone, 23. having MW 122, IR bands at 1672 and 1625 cm<sup>-1</sup>, and a UV  $\lambda_{max}$  255 nm ( $\varepsilon$  13,400) indicating an unsaturated ketone. The IR spectrum of 6-methylenecyclohex-2ene-1-one<sup>38</sup> was similar to that of 23 (1675 and 1620 cm<sup>-1</sup>) and it had a UV  $\lambda_{max}$  243 nm (e 11,500). These the structure suggest 3-methyl-6data methylenecyclohex-2-ene-1-one. Adding the usual correction of 12 nm per  $\beta$ -alkyl substituent,<sup>39</sup> one would predict  $\lambda_{max}$  255 nm in good agreement with the observed spectrum. It is probably formed as shown below. Confirmation of this structure was obtained by treatment of 23 with palladium on barium sulfate giving 2,5-dimethylphenol (24).



Another possible [2+2] cycloaddition would involve *trans*-cyclooctene which could react in an orbital symmetry allowed process.<sup>27</sup> The reaction, if it does occur, cannot compete with the dimerization of 1. The cycloaddition reactions of 1 are receiving continued attention.

Other reactions of 1 include those with carbon tetrachloride, bromine and *m*-chloroperbenzoic acid. The facile reaction with carbon tetrachloride resembles that of tricyclo[ $4.2.1.0^{2.5}$ ]non-2(5)-ene.<sup>40</sup> However, the less strained bicyclo[3.2.0]hept-1(5)-ene does not react. The reactions with bromine and the peroxy acid presumably involve carbocation intermediates which would be expected to rearrange to give the observed products.



The stability of 21 resembles that of the corresponding adduct of cyclopropene.<sup>37</sup> When the reaction with the Pt-ethylene complex was carried out using bicyclo[3.2.0]hept-1(5)-ene, an adduct appeared to be formed. However, all attempts at bringing the precipitate into solution lead to dissociation back to the bicycloheptene. The alkene, 1, could be recovered from 21, but only by the addition of a good ligand for Pt(0) such as carbon disulfide. Bis(triphenyl-phosphine)(ethylene)iridium chloride reacts with 1 to give a complex with an NMR spectrum very similar to that of 21 and probably has the same type of spectrum.

A [2+2] cycloaddition reaction of I would lead to a [2.2.2] propellane. Since these compounds are not readily prepared,<sup>25</sup> we have examined the addition of ketene to 1. The reaction of 1 formed by the pyrolysis method with a large excess of ketene was allowed to

The preceding has been largely concerned with the formation and reactions of 1. We are also interested in knowing how the bonding in 1 differs from that in related compounds such as cyclobutene. How does the C=C stretching force constant respond to the change in structure, and how are the vibrational modes of the



methylene group effected? This type of information may be derived from an examination of the vibrational spectrum.

The IR and Raman spectra of 1 cannot be determined using conventional techniques because of its rapid dimerization or polymerization. The Raman spectrum in a matrix has been reported by Casanova *et al.*,<sup>11</sup> and they also have reported a matrix IR spectrum.

An analysis of the spectral data is hampered by the inability to determine the symmetries of the transitions using techniques such as rotational band contour analysis. However, it is possible to calculate the spectra of many molecules with satisfactory accuracy via ab inito MO methods.<sup>41,42</sup> Therefore, we have calculated the molecular force field using the 4-31G basis set and the theoretical equilibrium geometry.<sup>4</sup> The vibrational frequencies thus derived are given in Table 1. It is known that the calculated frequencies are invariably somewhat too large. The calculation gives harmonic frequencies whereas the experimental frequencies are anharmonic and therefore lower. It has been found that the C-H vibrational frequencies calculated in this way should be scaled by the factor 0.91 whereas the other vibrational frequencies should be scaled by 0.88.43 The predicted frequencies are given in Table 1. The calculation also leads to the polar tensors from which the intensities of the IR active bands may be estimated.

The calculated frequencies and intensities for the IR active modes do not correspond to those reported by Casanova *et al.*<sup>11</sup> They found only CH stretching bands and bands at ~400 cm<sup>-1</sup> along with one at 288 cm<sup>-1</sup>. The calculations clearly indicate that there should be a relatively strong band at ~1213 cm<sup>-1</sup> as well as a number of other bands with reasonable intensity.

In order to obtain more satisfactory spectra, we have prepared samples of 1 in an argon matrix at 20 K in two ways. First, the pyrolysis of the tosylhydrazone salt, 4, was effected in a slow stream of argon, and the product which consisted of 1 and the diene, 6, was collected at 20 K. The spectrum of 6 was separately recorded, and subtracted giving the spectrum of 1. Second, the dehalogenation of the chlorobromide, 10, was effected with potassium in the gas phase<sup>44</sup> in an argon stream, and the product was again collected at 20 K. Here, 1chlorobicyclo[2.2.0]hexane was found as a second product, and its IR spectrum was again subtracted giving the spectrum of 1. The same set of reasonably strong bands was found in both spectra, and are listed in Table 1. The assignment was based on the agreement with the calculated spectrum.

A sample of bicyclo[2.2.0]hex-1(4)-ene-2,2,3,3- $d_4$ was prepared from 10- $d_4$  by gas phase dehalogenation, and here a remarkably clean IR spectrum was obtained. The D isotope effect may help to minimize hydrogen transfer reactions. The observed spectrum in the 400-1600 cm<sup>-1</sup> range is compared with the calculated spectrum in Fig. 1. There is generally good agreement between the two spectra. The bands, along with those for CH and CD stretching are listed in Table 1.

The calculated spectrum for 1 places the C=C stretching band at 1689 cm<sup>-1</sup> which is in good agreement with the value 1664 cm<sup>-1</sup> observed by Casanova *et al.*<sup>11</sup> in the Raman spectrum. This should be an intense band, and therefore is probably correct. The details of a normal coordinate analysis and a comparison with cyclobutene will be presented at a later time. However, it is interesting to note that the C=C stretching force constant derived from this

Mode		Calc	$d_0^{\bullet}$ Scaled	Obs	Int	Mode		Calc	$d_{4}^{r}$ Scaled	Obs	Int <sup>4</sup>
B <sub>1u</sub>	v <sub>16</sub>	3264	2970	2966	145.9	A <sub>1</sub>	v <sub>1</sub>	3209	2920	2933	74.2
	V17	1219	1073	1061	2.8		v <sub>2</sub>	2335	2125	2163	41.7
	v18	907	798	(790)	0.02		ν4	1653	1455	1437	1.2
	V19	209	184	_	19.5		Vs	1343	1182	1167	4.5
$B_{2u}$	V23	3199	2911	2933	116.5		v7	1209	1064	1067	0.1
	V24	1639	1442	1427	0.01		Vg	876	771	—	0.2
	V25	1378	1213	1226	25.5		V10	771	678	650	1.1
	V26	1036	913	921	0.7	B <sub>1</sub>	V20	3266	2972	2967	72.9
	V27	431	379	_	8.6	-	V <sub>21</sub>	2421	2203	2230	44.3
B <sub>31</sub>	V32	3207	2918	2933	148.9		V22	1193	1050	1044	1.8
	V33	1652	1454	1435	2.4		V23	926	815	815	0.9
	V34	1338	1177	1193	0.02		V24	837	737	733	1.0
	V35	1333	1173	1193	4.9		V25	649	571	577	0.2
	V36	829	730	728	1.3		V26	196	172	-	17.0
						B <sub>2</sub>	V27	3198	2910	2933	58.3
							V28	2324	2115	2119	29.5
							V29	1638	1441	1427	0.01
							V30	1393	1226	1228	10.2
							V31	1273	1120	1154	3.8
							V32	1220	1074	—	0.2
							V33	1084	954	949	2.8
							V34	1010	889	904	1.3
							V35	846	744	_	0.04
							V36	410	361		8.3

Table 1. IR bands of bicyclo[2.2.0]hex-1(4)-ene\*

• The band positions are given in  $cm^{-1}$  and the intensities in km mol<sup>-1</sup>.

"The A and B<sub>g</sub> modes are IR inactive.

Some A1 bands are calculated to have zero intensity and are not listed. The A2 modes are IR inactive.

Calculated intensities.



Fig. 1. Matrix isolated IR spectrum of bicyclo[2.2.0]hex-1(4)ene-2,2,4,4-d<sub>4</sub> (upper) and calculated spectrum (lower).

analysis is 10.0 mdyn Å<sup>-1</sup> which is somewhat larger than that for cyclobutene (9.5 mdyn Å<sup>-1</sup>).<sup>45</sup> The ring bending mode is of some interest in view of the calculations of Wagner *et al.*<sup>46</sup> on the structures of strained alkenes. Although 1 is calculated to be planar, this mode is calculated to be at 184 cm<sup>-1</sup> and to have a force constant of only 0.15 mdyn Å<sup>-1</sup>. Thus, it is a rather "floppy" alkene.

## **EXPERIMENTAL**

Thermolysis of spiro[2.3]hexan-4-one tosylhydrazone. To a soln of 0.48 g (8.9 mmol) of NaOMe in 40 ml of diglyme (distilled from LAH at 25 Torr) in a 100 ml flask contained in a dry box was added 2.0 g (7.6 mmol) of powdered spiro[2.3]hexan-4-one tosylhydrazone.<sup>47</sup> The soln was stirred at room temp for 1-2 h, after which time the mixture solidified. The flask was evacuated with a mechanical pump for 24 h to ensure removal of diglyme. The solid was powdered in a dry box and then placed in a side arm of a flask which was attached to a trap and then to a 2 in diffusion pump through wide bore tubing. The flask was heated to 185–190°. When the pressure in the system reached 1  $\mu$ , a small amount of salt was allowed to drop into the flask. The addition of the salt was under 20  $\mu$ , and required about 3 h.

In one case, after the thermolysis had been completed, 0.75 ml of acetone- $d_6$  and 0.27 g of toluene were distilled into the trap. The trap was warmed to  $-.78^\circ$  and the contents were transferred into an NMR tube. The NMR spectrum was taken at  $-.80^\circ$ , and showed a 4:1 ratio of 1 to 6. Using toluene as the internal standard, the yields were 43 and 10% for 1 and 6, respectively.

The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 100 MHz), of 1 had a band at  $\delta$  3.21. The <sup>13</sup>C-NMR spectrum had bands at 43.4 and 162.8 ppm. The <sup>1</sup>H-NMR spectrum of 6 had bands at  $\delta$  2.50, 4.66 and 5.13.

When the product from a pyrolysis at a higher pressure (1 Torr) which contained an excess of 6 was allowed to warm to room temp and the products separated by GC (12 ft × 3/8 in Dow 710, 110°), after 6 there was found tetracyclo-[6.2.2.0.3.6]dodec-3(6)-ene (50%). <sup>1</sup>H-NMR (CCl<sub>4</sub>, 60 MHz)  $\delta$  1.84 (m, 4H), 2.07 (d, 4H), 2.20 (d, 4H) and 2.42 (m, 4H); <sup>13</sup>C-NMR  $\delta$  29.9, 33.6, 34.5, 39.4 and 138.1. Mass spectrum, parent at *m/e* 160. The IR spectrum showed no C=C band, but it was found in the Raman spectrum at 1680 cm<sup>-1</sup>. Anal. C, H. Thermolysis in a flow system at 350° gave 3,4-dimethylenetricyclo[4.2.2.0]decane which was purified by GC as above. <sup>1</sup>H-NMR (CCl<sub>4</sub>, 60 MHz)  $\delta$  2.08 (bs, 8H), 2.28 (bs, 4H), 4.73 (bs, 2H) and 5.35 (bs, 2H). The IR spectrum had C=C bands at 1600 and 1630 cm<sup>-1</sup> and a strong terminal CH<sub>2</sub> wag at 895 cm<sup>-1</sup>. Mass spectrum, parent ion at m/e 160.

1-Bromo-4-chlorobicyclo[2.2.0] hexane (10). A 1 1 4-necked round-bottomed flask which had been flame dried was fitted with a condenser, additional funnel, stirrer and a thermometer. To the flask was added 19.7 g of red mercuric oxide, 15 g of anhyd MgSO<sub>4</sub> and 160 ml of CH<sub>2</sub>Cl<sub>2</sub>. A soln of 23.1 g (144 mmol) of 4-chlorobicyclo[2.2.0]hexane-1carboxylic acid<sup>14</sup> and 10 ml of Br<sub>2</sub> in 200 ml of CH<sub>2</sub>Cl<sub>2</sub> was added to the stirred slurry over a 1 h period at room temp. The mixture was brought to a gentle reflux and irradiated with a 60 W light bulb for 3 h. The mixture was allowed to cool to room temp, and then 10 ml of sat NaHSO<sub>3</sub> aq followed by enough solid NaHSO<sub>3</sub> to remove the Br color was added.

The CH<sub>2</sub>Cl<sub>2</sub> soln was separated, and the solids were washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined soln was washed with two 150 ml portions of sat NaHSO<sub>3</sub> aq and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure to give a yellow oil which solidified on standing overnight in a freezer ( $-23^{\circ}$ ). The solid was dissolved in a minimum amount of pentane and passed through a short column of basic alumina. It was eluted with 600 ml of pentane. The solvent was removed giving 23.6 g (85%) of 10, m.p. 60–61°. The <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>) had a band at  $\delta$  2.73.

Bicyclo[2.2.0]hex-1(4)-ene (1). The electrolysis cell was a Kimax 14060 dye beaker having an enlarged top and no spout (vol 420 ml). The cell top was a snug fitting machined Teflon stopper fitted with an O-ring and seven ports. The cell was equipped with a large Pt gauze cathode, a Coors porous ceramic cup (76 × 25 mm) fused to a 25 mm Pyrex tube which served as the counter electrode compartment, a mercury pool reference electrode, a gas dispersion tube, a low temp thermometer, and a stirrer. To the cell was added 350 ml of 0.1 N tetraethylammonium bromide in anhyd DMF. Several grams of the electrolyte were added to the ceramic cup (the anode compartment) and it was filled with enough electrolyte soln to match the solvent level in the cell. A graphite felt electrode was placed in the cup. The soin in the cell was purged with N2 which was first passed through reduced BASF R3-11 catalyst to remove traces of  $O_2$ . The soin in the cell was prereduced by setting the working voltage so that the reference potential was between - 1.7 and - 2.0 V. After the current had dropped to  $\sim 50$  mA, the power supply was disconnected and the cell was placed in a cooling soln (1:1 EtOH-water) maintained at -30° by a Forma Scientific model 2026 refrigerated bath. At this point 2.0 g (10 mmol) of 1-bromo-4chlorobicyclo[2.2.0]hexane was added, and the soln was stirred until it dissolved. The working potential was set so that the reference electrode indicated -1.8 to -2.0 V. The initial current was 200-350 mA, and the reaction was considered complete when the current dropped to  $\sim 30$  mA at -2.0 V. The cell temp was maintained between -20 and  $-30^{\circ}$ , and the contents of the anode compartment was replaced regularly. In many of the subsequent experiments, the reagent to be used was added to the electrolyte soln. In other cases, the alkene was first extracted into pentane or butane. The solns must be maintained dilute and cold to avoid dimerization or polymerization of 1.

#### Diels-Alder reactions of bicyclo[2.2.0]hex-1(4)-ene

(a) Butadiene. The electrolysis soln was cooled to  $-60^{\circ}$  under argon and was treated with 8 ml of butadiene. After warming to room temp, the soln was extracted with three 250 ml portions of pentane. The latter was washed with 1 N HCl, dried over MgSO<sub>4</sub> and concentrated to give 1.03 g (62%) of a clear liquid. Analysis by GC (6 ft × 1/8 in SE30 column at 120°) showed 9% of butadiene dimer and 90% of tricyclo[4.2.2.0]dec-3-ene. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 270 MHz)  $\delta$  1.90-2.08 (A part of A<sub>3</sub>B<sub>2</sub> and allylic CH<sub>2</sub>, 8H), 2.08-2.33 (B part, J = 6.6 Hz, 4H), and 5.9 (t, J = 1.5 Hz); <sup>13</sup>C-NMR  $\delta$  32.2 (t), 33.6 (t), 37.9 (s) and 126.9 (d). Anal. C, H.

A similar reaction with *trans,trans*-hexa-2,4-diene gave the Diels-Alder adduct (19). <sup>1</sup>H-NMR  $\delta$  0.83 (d, J = 6.6 Hz, 6H), 1.72 (t, J = 6.6 Hz, 2H), 1.79 (q, J = 6.6 Hz, 2H), 2.04 (q, J = 6.6 Hz, 4H), 2.29 (q, J = 6.6 Hz, 2H) and 5.62 (s, 2H); <sup>13</sup>C-NMR  $\delta$  13.3, 24.8, 32.0, 36.0, 43.1 and 134.9. Anal. C, H. Reduction of 32 mg of 19 with dimide formed from 20 ml of 85% hydrazine hydrate, 20ml of methanol, 0.1 ml of 5% cupric sulfate and 7 ml of 30% H<sub>2</sub>O<sub>2</sub> gave 18 which was purified by GC (10 ft 20% SE30, 140°). NMR (CDCl<sub>3</sub>, 270 MHz)  $\delta$  0.67 (d, J = 6.6 Hz,

6H), 1.31 (m, 2H), 1.52 (m, 2H), 1.68 (q, J = 6.6 Hz, 2H), 1.83 (m, 2H), 1.96 (m, 2H), 2.05 (m, 2H) and 2.15 (m, 2H); <sup>13</sup>C-NMR  $\delta$  14.6, 23.8, 27.5, 31.6, 32.8 and 43.1.

(b) Cyclopentadiene. The electrolysis soln was transferred to a flask and 5.0 g of freahly distilled cyclopentadiene was added. The soln was allowed to warm to room temp over the course of 1 h. Excess cyclopentadiene was removed under reduced pressure. The soln was extracted with three 200 ml portions of pentane, and the pentane extract was washed with two 150 ml portions of 1 N HCl. It was then dried with MgSO<sub>4</sub>, and concentrated to give 1.68 g (94%) of a clear oil which was shown by NMR to be essentially pure tetracyclo-[4.2.2.1<sup>2,5</sup>,0<sup>1,6</sup>]undec-3-ene. Further purification could be effected via preparative GC using a 6 ft × 1/8 in 10% SE30 column, m.p. 74.5-76.5°. Anal C, H.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 270 MHz)  $\delta$  1.48 (d, J = 8.8 Hz, 1H), 1.55–1.67 (m, 2H), 1.78–1.91 (m, 3H), 1.93–2.02 (m, 2H), 2.17– 2.28 (m, 2H), 2.58–2.61 (m, bridgehead, 2H), 6.23 (s, 2H).

(c) Isobenzofuran. The electrolysis soln was extracted at  $-25^{\circ}$  under argon with two 250 ml portions of precooled pentane. To the pentane soln was added dropwise a soln of isobenzofuran in benzene (prepared from 2.98 g of 1,3-dihydro-1-methoxyisobenzofuran<sup>48</sup>) at about  $-60^{\circ}$  over a 10 min period. The soln was allowed to warm to room temp overnight. The soln was washed with four 100 ml portions of sat NaHCO<sub>3</sub> aq, dried over MgSO<sub>4</sub> and concentrated giving 2.01 g (94%) of a clear oil. NMR spectra showed it was mainly 3,4-benzo-11-oxa-tetracyclo[4.2.2.1<sup>2.5</sup>.0<sup>1.6</sup>]undec-3-ene. Purification could be effected by GC using a 2 ft × 1/8 in 20% SE30 column at 130°. Anal. C, H.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 270 MHz)  $\delta$  1.09 (A part of A<sub>2</sub>B<sub>2</sub> system, J = 14.3 Hz, 2H), 1.93 (A' part of A'<sub>2</sub>B'<sub>2</sub> system, J = 12.8 Hz, 2H), 2.23 (m, B and B'<sub>1</sub> parts, 4H), 5.13 (s, bridgehead, 2H), 7.18–7.30(A<sub>2</sub>B<sub>2</sub> multiplet, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 67.9 MHz)  $\delta$  24.15 (t), 26.71 (t), 40.30 (s), 84.22 (d), 120.88 (d), 126.28 (d), 143.44 (s).

(d) 3,6-Diphenyl-s-tetrazine. An electrolysis soln prepared from 1.56 g of 10 was transferred to a cooled separatory funnel  $(-15^\circ)$  and extracted with 200 ml of dry butane. To the butane soln at  $\sim -50^{\circ}$  was added a soln of 1.87 g (8 mmol) of 3,6diphenyl-s-tetrazine in 200 ml of dry ether. The soln was warmed to  $\sim -10^{\circ}$  and loss of color was observed. The soln was allowed to warm to room temp with the butane slowly distilling from the vessel. The products were separated by preparative column chromatography on silica gel using 70% pentane-CHCl<sub>3</sub>. The first fractions contained the tetrazine, the next fraction contained an unidentified compound with <sup>1</sup>H-NMR bands at  $\delta$  8.04 and 7.50, and the later fractions gave 1.06 g(46%) of 20, m.p. 172–173° (dec.). <sup>1</sup>H-NMR  $\delta$  2.93 ( $\overline{A_2B_2}$ m, 8H), 7.45-7.36 (m, 6H) and 7.54 (m, 4H); <sup>13</sup>C-NMR & 34.5, 34.7, 127.5, 128.5, 130.8, 133.0 and 160.9. Mass spectrum, molecular ion at 286.1465 (calc for C20H18N2, 286.1470).

1 - Chloro - 4 - trichloromethylbicyclo[2.2.0]hexane. An electrolysis soln prepared from 1.6 g of  $10 (-30^{\circ})$  was mixed with 75 ml of precooled degassed CCl<sub>4</sub>. The mixture was warmed to 0° and was treated with 175 ml of precooled sat Na<sub>2</sub>SO<sub>4</sub> aq. The CCl<sub>4</sub> layer was separated, washed with two 100 ml portions of 1 N HCl, dried over MgSO<sub>4</sub> and concentrated to give 1.04 g of a low melting solid. NMR spectroscopy showed that it contained 1 - chloro - 4 - trichloromethylbicyclo[2.2.0]hexane along with a small amount of 2,5-dimethylenetricyclo[4.2.2.0]decane.

The crude solid was purified by column chromatography over 15 g of basic alumina using 6 column volumes of pentane. Concentration gave the pure adduct (0.8 g, 42%), m.p. 115– 119°. Anal. C, H, Cl. <sup>1</sup>H-NMR (CDCL<sub>3</sub>, 270 MHz)  $\delta$  2.25 (A part of A<sub>2</sub>B<sub>2</sub> system, 2H), 2.59 (m, B and B' parts, 4H), 2.91 (A' part of A'<sub>2</sub>B'<sub>2</sub> system, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 67.9 MHz)  $\delta$ 29.27 (t), 34.91 (t), 64.90 (s), 65.69 (s), 101.22 (s).

Reaction of 1 with ketene. A pyrolysis was effected using 3.0 g (11.3 mmol) of spiro[2.3]hexan-4-one tosylhydrazone. At the end of the pyrolysis, 50 ml of  $CH_2Cl_2$  was distilled into the trap. The contents were transferred into a 100 ml 3-necked flask and kept at  $-78^{\circ}$  under N<sub>2</sub>. Ketene (100 g) which had

previously been generated from acetone was bubbled through the stirred mixture at  $-78^{\circ}$  over a 30 min period. The soln was allowed to warm to room temp as the excess ketene distilled away. The soln was concentrated and added to 100 g of basic alumina. Elution with 200 ml of pentane gave only the dimer of 1 and its Diels-Alder adduct with 1,2-dimethylenecyclobutane. Elution with 400 ml of ether followed by concentration and purification by gas chromatography gave 3-methyl-6-methylencyclohex-2-en-1-one. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 270 MHz)  $\delta$  2.01 (3H, s), 2.39 (2H, t, J = 6.62 Hz), 2.73 (2H, t, J = 6.62 Hz), 5.58 (1H, s), 5.97 (1H, s), 6.02 (1H, s). UV (EtOH)  $\lambda_{max}$  255 nm ( $\varepsilon$  13,400). Mass spectrum, parent at m/e = 122.

Approximately 5 mg of the enone was dissolved in 1 ml of EtOH, and was treated with  $\sim 1$  mg of Pd on BaSO<sub>4</sub>. Filtration followed by preparative GC using an 18 ft 20% SE30 column at 145° gave a white solid which proved to be identical with authentic 2,5-dimethylphenol by NMR, IR, UV and mass spectroscopy.

Reaction of bicyclo[2.2.0]hex-1(4)-ene with mchloroperbenzoic acid and with bromine. A 2-3 ml aliquot of a soln of 1a in DMF was treated with 0.05 g of mchloroperbenzoic acid in CH<sub>2</sub>Cl<sub>2</sub>. After standing for 1 h at 0°, the NMR spectrum corresponded to that of authentic spiro[2.3]hexan-4-one. In a similar fashion, a 2-3 ml aliquot was treated with 0.4 ml of a soln of 1.15 g of Br<sub>2</sub> in 5 ml of DMF at 0°. An immediate reaction occurred, and the <sup>2</sup>H-NMR spectrum had new bands at  $\delta$  2.91, 2.08 and 1.03 (1:1:2) which are very close to those of the spiroketone ( $\delta$  3.08, 2.15 and 1.1).

Reaction of 1 - bromo - 4 - chlorobicyclo [2.2.0] hexane with sodium in ammonia. A soln of 1.15 g (0.05 mol) of Na in 175 ml of dry ammonia was prepared in a 250 ml 3-necked flask fitted with a mechanical stirrer, stopper and Dewer condenser topped with a KOH drying tube. All at once 1.95 g(0.01 mol) of 10 was added. The reaction was very vigorous. After stirring for 5 min, the reaction was quenched with NH<sub>4</sub>Cl until the blue color was discharged. The ammonia soln was poured gently into 600 ml of water and 200 ml of pentane. The layers were separated and the water tray was washed twice with 150 ml portions of pentane. The pentane soln was washed with 100 ml of 10% HCl, 100 ml of brine. After drying over MgSO<sub>4</sub>, 0.092 g of cycloheptane was added as an internal standard. The mixture was analyzed by GC using a 20 ft  $\times$  1/8 in 30% SE30 column. The ratio of bicyclo[2.2.0]hexane to 1,1'-bis(bicyclo-[2.2.0]hexane) was 17:1. The yield of bicyclo[2.2.0]hexane was 79% and that of 1,1'-bis(bicyclo[2.2.0]hexane) was 6%. Preparative separation was effected using a 10 ft 20% SE30 column at  $130^{\circ}$ . The identity of bicyclo[2.2.0]hexane was established by its NMR and  $^{13}C$  spectra.

Reaction of 1 - bromo - 4 - chlorobicyclo[2.2.0]hexane with butyllithium. To a soln of 1.0 g of 10 in 190 ml of dry ether was added at  $-78^{\circ}$ , 2.4 ml of a 2.4 M soln of n-BuLi in n-heptane. The mixture was warmed to 0°. After 2 h, the soln was treated with 93 µl of water followed by 3.4 g of cyclopentadiene. The mixture was washed with water, dried over MgSO<sub>4</sub> and concentrated. Analysis by GC using a 12 ft × 1/4 in 20% SE30 column at 132° gave 9% (1.3 min) 1-(1'-ethoxyethyl)bicyclo-[2.2.0]hexane, 21% (2.8 min) unreacted 10, 8% (4.0 min) of the Diels-Alder adduct, 42% (6.2 min) 1-bromo-4-nbutylbicyclo[2.2.0]hexane and 4% (11.2 min) of 1-(2'bromoethyl)-2-n-butylcyclobutene. The products were identified by their NMR and mass spectra which are given in detail in the thesis of Matturro (1981).

The reaction of t-BuLi with 10 was carried out in the same fashion and gave 35% of the Diels-Alder adduct.

#### REFERENCES

- <sup>1</sup> K. B. Wiberg and R. A. Fenoglio, J. Am. Chem. Soc. 90, 3395 (1968).
- <sup>2</sup>K. B. Wiberg, W. J. Bartley and F. P. Lossing, *Ibid.* 84, 3980 (1962).
- <sup>34</sup>K. B. Wiberg, J. E. Hiatt and G. Burgmaier, Tetrahedron

Lett. 5855 (1968); <sup>\*</sup>K. B. Wiberg, G. J. Burgmaier and P. Warner, J. Am. Chem. Soc. 93, 246 (1971).

- K. B. Wiberg and J. J. Wendoloski, Ibid. 104, 5679 (1982).
- <sup>5</sup>K. B. Wiberg, J. Comput. Chem. 5, 197 (1984).
- <sup>6</sup>B. Bak, J. J. Lod, L. Nygaard, J. Rastrup-Andersen and G. O. Sorensen, J. Mol. Struct. 3, 369 (1969).
- <sup>7</sup>W. M. Stigliani, V. W. Laurie and J. C. Li, *J. Chem. Phys.* 62, 1890 (1975); P. H. Kasai, R. J. Myers, D. F. Eggers, Jr. and K.B. Wiberg, *Ibid.* 30, 512 (1959).
- <sup>8</sup> Several unsuccessful attempts to prepare 1 have been reported: I. Lantos and D. Ginsburg, *Tetrahedron* 28, 2507 (1972); E. J. Corey and E. Block, *J. Org. Chem.* 34, 1233 (1969); D. H. Aue and R. N. Reynolds, *J. Am. Chem.* Soc. 95, 2027 (1973); J. J. Gajewski and C. N. Shih, *Ibid.* 94, 1675 (1972); B. G. Odell, R. Hoffmann and A. Imamura, *J. Chem.* Soc. B 1675 (1970).
- <sup>9</sup> W. Kirmse and K.-H. Pook, Angew. Chem. Int. Ed. Engl. 5, 594 (1966).
- <sup>10</sup> M. E. Jason, Ph.D. Thesis, Yale (1976). The <sup>13</sup>C spectra of a number of related compounds are given therein. The <sup>13</sup>C-NMR spectrum of bicyclo[3.2.0]hept-1(5)-ene has the olefinic carbon at  $\delta$  149,
- <sup>11</sup> J. Casanova, J. Bragin and F. D. Cottrell, J. Am. Chem. Soc. 100, 2264 (1978).
- <sup>12</sup> W. P. Hauser and W. D. Walters, J. Phys. Chem. 67, 1328 (1963).
- <sup>13</sup>E. A. Hill and J. D. Roberts, J. Am. Chem. Soc. 89, 2047 (1967).
- <sup>14</sup> W. G. Dauben, J. L. Chitwood and K. V. Scherer, Jr., *Ibid.* 90, 1014 (1968).
- <sup>15</sup>S. J. Cristol and W. C. Firth, Jr., J. Org. Chem. 26, 280(1961); A. I. Meyers and M. P. Fleming, *Ibid.* 44, 3405 (1979).
- <sup>16</sup>These reagents normally convert vicinal dihalides to alkenes: cf. J. March, Advanced Organic Chemistry, 2nd Edn., p. 943. McGraw-Hill, New York (1977). One notable exception is 1,2-dibromocyclopropane which is converted to a di-Grignard reagent on treatment with magnesium (K. B. Wiberg and W. J. Bartley, J. Am. Chem. Soc. 82, 6375 (1960)).
- <sup>17</sup> E. L. Allred, B. R. Beck and K. J. Voorhees, J. Org. Chem. 39, 1426 (1974); H. O. House and T. H. Cronin, *Ibid.* 30, 1061 (1965).
- <sup>18</sup> S. Cremer and R. Srinivasan, *Tetrahedron Lett.* No. 21, 24 (1960); C. Steel, R. Zand, P. Hurwitz and S. G. Cohen, J. Am. Chem. Soc. **86**, 679 (1964); R. M. Moriarty, J. Org. Chem. **28**, 2385 (1963); J. J. Tufariello, T. F. Mich and P. S. Miller, *Tetrahedron Lett.* 2293 (1966); C. E. Griffin, N. F. Hepfinger and B. L. Shapiro, J. Am. Chem. Soc. **85**, 2683 (1963).
- <sup>19</sup> R. N. McDonald and C. A. Curi, *Ibid.* 99, 7078 (1977), observed that reduction of 1,4-dichloro-2methoxybicyclo[2.2.0]hexane(either exo or endo) gave only exo-2-methoxybicyclo[2.2.0]hexane, presumably via 2methoxybicyclo[2.2.0]hex-1(4)-ene as an intermediate.
- <sup>20</sup> W. O. Haag and H. Pines, Ibid. 82, 387 (1960).
- <sup>21</sup> D. E. Bergbreiter and J. M. Killough, Ibid. 100, 2126 (1978).

- <sup>22</sup> Cf. K. B. Wiberg and G. Bonneville, *Tetrahedron Lett.* 23, 5385 (1982).
- <sup>23</sup> K. B. Wiberg, W. F. Bailey and M. E. Jason, J. Org. Chem. 39, 3803 (1974).
- <sup>24</sup> J. Casanova and H. R. Rogers, Ibid. 39, 3803 (1974).
- <sup>25</sup> P. E. Eaton and G. H. Temme, III, J. Am. Chem. Soc. 95, 7508 (1973).
- <sup>26</sup> K. B. Wiberg, M. G. Matturro, P. J. Okarma and M. E. Jason, *Ibid.* 106, 2194 (1984).
- <sup>27</sup> R. B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry. Verlag Chemie (1971).
- <sup>28</sup> E. A. Huyser, Free Radical Chain Reactions, p. 338. Wiley, New York (1970).
- 29 P. Dowd and A. Gold, Tetrahedron Lett. 85 (1969).
- <sup>30</sup>G. R. Wenzinger and J. A. Ors, J. Org. Chem. 39, 2060 (1974).
- <sup>31</sup> K. B. Wiberg and M. G. Matturro, *Tetrahedron Lett.* 3481 (1981).
- <sup>32</sup> J. Sauer and G. Heinrichs, Ibid. 4979 (1966).
- <sup>33</sup> M. E. Jason, J. A. McGinnety and K. B. Wiberg, J. Am. Chem. Soc. 96, 6531 (1974).
- <sup>34</sup> B. Andersen and R. Srinivasan, Acta Chem. Scand. 26, 3468 (1972).
- <sup>35</sup> For a review, see K. B. Wiberg, Accts Chem. Res. 17, 379 (1984).
- <sup>36</sup> A. Yokozeki and K. Kuchitsu, Bull. Chem. Soc. Japan 44, 2356 (1971).
- <sup>37</sup> J. P. Visser, A. J. Schipperijn, J. Lucas, D. Bright and J. J. DeBoer, *Chem. Commun.* 1266 (1971); J. P. Visser, A. J. Schipperijn and J. Lukas, J. Organomet. Chem. 47, 433 (1973).
- 38 I. G. Morris and A. R. Pinder, J. Chem. Soc. 1841 (1963).
- <sup>39</sup> R. B. Woodward, J. Am. Chem. Soc. 63, 1123 (1941); 64, 72, 76 (1942).
- <sup>40</sup> R. Reynolds, Ph.D. Thesis (with D. H. Aue), University of California, Santa Barbara (1977).
- <sup>41</sup> J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout and W. J. Hehre, Int. J. Quantum Chem. Quantum Chem. Symp. 15, 269 (1981).
- <sup>42</sup> P. Pulay, The Force Concept in Chemistry (Edited by B. Deb). Van Nostrand, New York (1981).
- <sup>43</sup> K. B. Wiberg and J. J. Wendoloski, J. Phys. Chem. 88, 586 (1984).
- <sup>44</sup> The reaction was carried out essentially as described by D. Otteson and J. Michl, J. Org. Chem. 49, 866 (1984) for other dihalides.
- <sup>45</sup> Unpublished results.
- <sup>46</sup> H.-U. Wagner, G. Szeimies, J. Chandrasekhar, P. V. R. Schleyer, J. A. Pople and J. S. Binkley, J. Am. Chem. Soc. 100, 1210 (1978).
- <sup>47</sup> The spiroketone was prepared as described by K. V. Scherer, Jr. and K. Katsumoto, *Tetrahedron Lett.* 3079 (1967) and converted to the tosylhydrazone in the usual fashion.
- 48 K. Naito and B. Rickborn, J. Org. Chem. 45, 4061 (1980).