ferrioxalate solution and one into the sample cell containing HMD and electron acceptor. Both solutions were stirred continuously during irradiation. Laser pulses went into the sample at a frequency of about 1 Hz. The absorbance of both solutions was adjusted so that more than 99% of the laser light was being absorbed. After irradiation the absorption of the ferrioxalate solution was determined, and the amount of HMD converted to HMB was determined by gas chromatograph as described above. All solutions were taken to low conversion to minimize participation from HMB in the chain reaction sequence.

Photosensitization of HMB with PCA. A solution of PCA (0.03 M) and HMB (0.03 M) in acetonitrile was prepared and deoxygenated by purging with N_2. Irradiation at 337 nm with the nitrogen laser, or with 350-nm lamps in a Rayonet photoreactor, gave two major products. The first precipitated from the solution as the reaction progressed and was identified as decamethylbibenzyl:[36] mp 242-244 °C; ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 18 H), 240 (s, 12 H), 2.88 (s, 4 H); mass spectrum (75 eV), *m/e* 322 (M^+), 161. The second product was shown to be the cross coupling product of the PCA ketyl radical and HMB radical by mass spectrometry.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank Mr. James Wehmer for his help with the laser experiments and Mr. John Hurst for the use of his data reduction software.

Registry No. HMD, 7641-77-2; HMD^+, 85293-78-3; HMB^+, 34473-51-3; TCNQ, 1518-16-7; $TCNQCl_2$, 21004-03-5; $TCNQCl_2^+$, 85353-34-0; TMB, 135-77-3; $TCNQBr_2$, 56403-70-4; $TCNQF_4$, 29261-33-4; $TCNQF_4^+$, 85353-35-1; DCN^-, 68331-38-4; CPH^-, 68271-79-4; PCA^-, 59273-30-2; *p*-dinitrobenzene, 100-25-4; *p*-dicyanobenzene, 623-26-7; 1,4-dicyanonaphthalene, 3029-30-9; 1-cyanopyrene, 4107-64-6; 9-cyanophenanthrene, 2510-55-6; tetrachlorophthalic anhydride, 117-08-8; *p*-cyanoacetophenone, 1443-80-7; anthraquinone, 84-65-1.

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[2.1.1]Propellane. Reaction of 1,4-Diiodobicyclo[2.1.1]hexane with *tert*-Butyllithium and with Potassium Atoms

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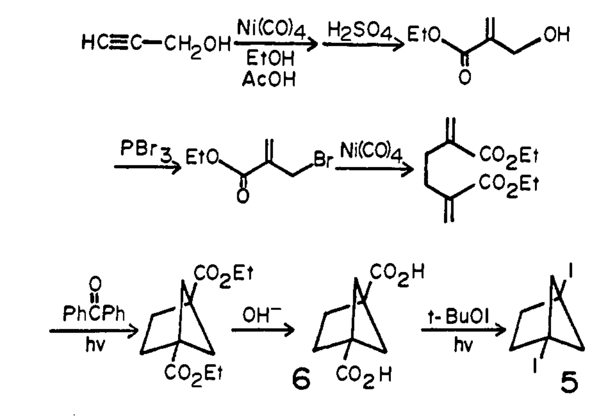
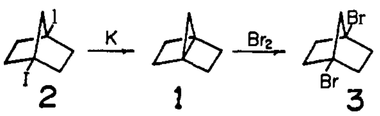
Abstract: The synthesis of 1,4-diiodobicyclo[2.1.1]hexane (**5**) is described. The reaction of **5** with *tert*-butyllithium in hexane gave the same type of products as previously observed in the reaction of 1,4-diiodonorbornane (**2**) with *tert*-butyllithium. Evidence has been presented indicating the latter reaction to proceed via the [2.2.1]propellane as an intermediate, and it appears likely that the [2.1.1]propellane was involved in the former reaction. The reaction of **5** with potassium atoms in the gas phase led to the formation of an unstable compound which has been isolated in a nitrogen matrix and tentatively identified as the [2.1.1]propellane on the basis of its infrared spectrum.

[2.2.1]Propellane (**1**) has received considerable study. Wilcox and Leung[2] examined the reaction of 1,4-dichloronorbornane with lithium and obtained only the dilithio compound, suggesting that the propellane may have been formed and then added lithium across the central C–C bond. We have studied the electrochemical dehalogenation of 1,4-dihalonorbornanes[3] and found norbornane, bisnorbornyl, and higher oligomers to be formed. They could most simply be derived by dehalogenation forming the propellane, followed by its reduction. Subsequently, Peters and Carrol[4] showed that 1-bromonorbornane was not an intermediate in the reduction of the 1,4-dibromide, and that the reaction was a net three-electron reduction. This provides strong evidence for the formation of **1** as the product of a two-electron reduction of the dihalide which then undergoes further reduction at the mercury electrode.

We also have examined the reduction of 1,4-diiodonorbornane (**2**) with *n*-butyl- and *tert*-butyllithium.[5] The major product was the corresponding 1-butyl-4-iodonorbornane. The reduction of 1-bromo-4-iodonorbornane with butyllithium led to the same product. This provided evidence for an intermediate in which both halogens had been lost, presumably the [2.2.1]propellane. Finally, we have studied the reaction of the 1,4-dihalonorbornanes with metal atoms in the gas phase, and have been able to trap the propellane (**1**) in a matrix at low temperature.[6] The infrared spectrum and the reaction with bromine to form 1,4-dibromonorbornane provided evidence for the assigned structure.

Scheme I





2 **1** **3**

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[1] (a) Yale University. (b) Taken in part from the Ph.D. theses of W.E.P., 1980, and F.H.W., 1982. (c) University of Utah.

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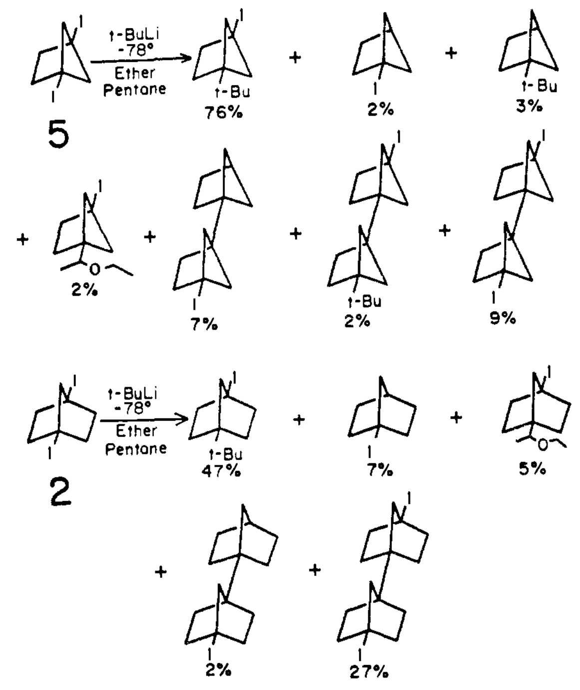
Scheme II



In a continuation of this work, we wish to examine the reactions of the 1,4-dihalobicyclo[2.1.1]hexanes to see if they may form the corresponding [2.1.1]propellane (4). We now report the

4

preparation of 1,4-diiodobicyclo[2.1.1]hexane (5) as well as a study of its reaction with butyllithium and with metal vapor.

Bicyclo[2.1.1]hexane-1,4-dicarboxylic acid (6) is readily prepared as shown in Scheme I. Ethyl α-(bromomethyl)acrylate is coupled with nickel carbonyl[7] to give diethyl hexa-1,5-diene-2,5-dicarboxylate. This is followed by triplet-sensitized photolysis to give diethyl bicyclo[2.1.1]hexane-1,4-dicarboxylate,[8] which can be hydrolyzed to the diacid (6).

The conventional Hunsdiecker reaction, using mercuric oxide,[9] gave the dibromide (7). However, we were unsuccessful in transforming the dibromide into the diiodide using aluminum foil, methyl iodide, and catalytic bromine.[10] Presumably, the reaction must in this case proceed via carbonium ion intermediates which rearrange under the reaction conditions.[11] We were successful in transforming the diacid directly into 1,4-diiodobicyclo-[2.1.1]hexane (5) using potassium *tert*-butoxide and iodine with concomitant irradiation[12] under carefully controlled conditions.

The reaction of 5 with *tert*-butyllithium was carried out under the conditions previously used for the reaction of 2,[5] except that 1.3 equiv of the reagent as employed. The products of the two reactions are compared in Scheme II. In both cases, the major product is the 1-*tert*-butyl-4-iodide. Indeed, the products of both reactions are essentially the same, strongly suggesting that the two reactions proceed via similar intermediates. Since good evidence is now available for the [2.2.1]propeilane as the inte mediate in the reaction of 2, we believe the present results provi evidence for the formation of 4 as an intermediate in this reactio This conclusion is further reinforced by our preparation of tl [1.1.1]propellane (9) by the corresponding reaction of 1,3-d bromobicyclo[1.1.1]pentane.[13]

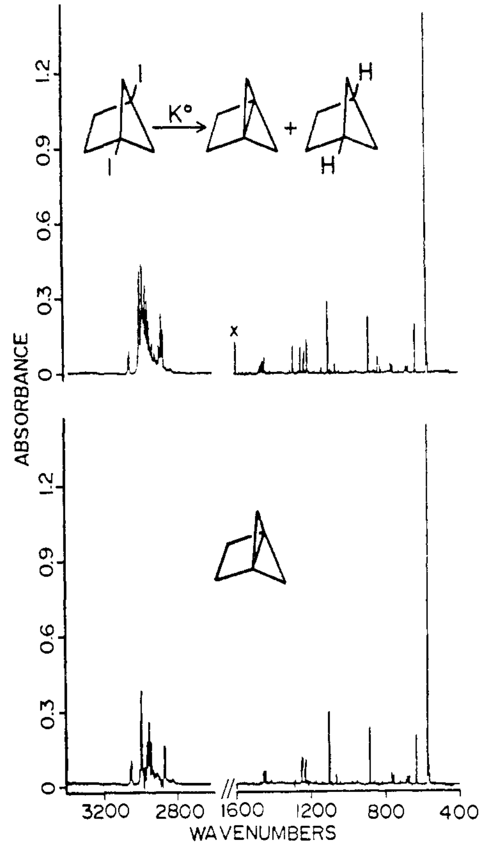
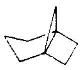
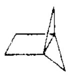


Figure 1. Infrared spectrum of the product of the reaction of the diiodi with potassium (upper), and with the spectrum of bicyclo[2.1.1]hexa subtracted out (lower).

Table I. Infrared Frequencies for Strained Ring Propellanes[a]

							
cm^{-1}	rel abs	cm^{-1}	rel abs	cm^{-1}	rel abs	cm^{-1}	re ab
515	0.32	530	1.00	574	1.00	603	1.
955	0.14	907	0.18	635	0.15		
981	0.10	1043	0.15	885	0.14		
1023	0.11	1069	0.06	1101	0.20	1093	~0.
1034	0.11	1167	0.09				
1232	0.10	1250	0.08	1229	0.06		
1260	0.22	1254	0.06	1247	0.07		
1439	0.10	1431	0.05	1442	0.04		
1453	0.22	1439	0.11	1452	0.04		
		1445	0.04				
2859	0.61	2855	0.25	2871	0.10		
2928	1.00	2933	0.40	2954	0.18		
2961	0.63	2985	0.52	2995	0.27	3006	~0.
3067	0.07	3056	0.06	3050	0.07	3069	~0.

[a] Data are for matrix-isolated compounds[6] except for [1.1.1]-propellane which was studied in carbon disulfide solution.[13]

In the case of the [2.2.1]propellane, the most convincing ev dence for its formation arose from a study of the reaction of with metal atoms in the gas phase.[6] This reaction was shown i yield a mixture of 1 and norbornane as well as traces of 1,1 bisnorbornyl. When 5 was treated with potassium vapor at 1 1

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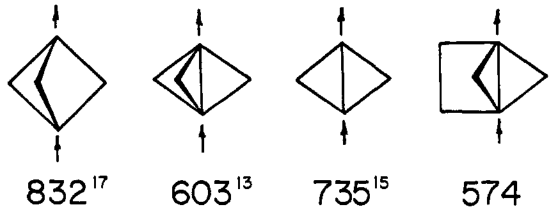
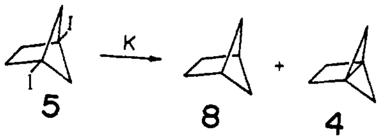


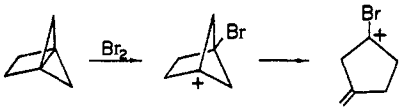
Figure 2. Vibrational modes and frequencies (cm^{-1}) for strong low-frequency infrared bands of propellanes and related compounds.

°C in a sonicated stream of nitrogen, the IR spectrum shown in Figure 1 (top) was obtained. Bicyclo[2.1.1]hexane (**8**) is clearly



identified by bands at 2982, 2980, 2881, 1466, 1422, 1291, 1213, 838, and 824 cm^{-1}. With computer subtraction, the bands due to **8** can be removed (Figure 1, bottom). The resulting spectrum displays remarkable similarity to the IR spectra of [3.2.1]propellane (**11**), **1**, and **9** (Table I). In particular, note the cyclopropyl CH stretch at 3050 cm^{-1} and the very intense band at 574 cm^{-1}. This intense absorption at low frequency seems to be characteristic of highly strained propellanes, and is found in the spectra of **1**, **9**, and **11**. In addition, the latter hydrocarbons have prominent bands at 1044, 1023, and 1093 cm^{-1}, respectively, which are attributable to cyclopropane ring deformations.[14] In the case of [2.1.1]propellane (**4**), this band is shifted to 1101 cm^{-1}, in good agreement with the intense band at 1106 cm^{-1} in the gas-phase spectrum of bicyclo[1.1.0]butane.[15]

In contrast with the behavior of **1**, attempts to trap **4** with bromine did not yield the bridgehead dibromide. Instead, a variety of unidentified products was obtained, some of which were shown by GC/mass spectroscopy to contain three or more bromine atoms. It is known that 1-bromobicyclo[2.1.1]hexane solvolyzes 10^7 times faster than 1-bromonorbornane, and that no 1-bicyclo[2.1.1]-hexanol is obtained from that reaction.[11] Indeed, evidence seems to indicate that 1-bicyclo[2.1.1]hexyl carbonium ion rearranges before it is ever completely formed.[16] Thus, if bromine were to add to **4** by an electrophilic process, it is likely that rearrangement



would occur which could lead to a variety of polybrominated products.

When the contents of a nitrogen matrix formed by the reaction of **5** with potassium vapor are distilled into an NMR tube containing CD_2Cl_2, the only product present in significant amount is **8**. It is not surprising that **4** did not survive such treatment. Most probably, **4** polymerizes when the nitrogen distills upon warming the matrix. Similar results were obtained upon such treatment of **1**. The most important observation in this experiment is the complete absence of any olefinic hydrogens in the NMR spectrum. Since the expected thermolysis products of **4** would certainly have been stable to such treatment, they were not formed. We have also prepared 1-iodobicyclo[2.1.1]hexane from 1-lithiobicyclo[2.1.1]hexane and determined that it is not present in the observed matrix spectrum. Thus, we believe that the only structure that could account for the observed IR spectrum is indeed [2.1.1]propellane (**4**).

Table II. Mulliken Populations at Bridgehead and Methylene Carbons[a]

compound	bridgehead	methylene
bicyclo[1.1.0]butane	6.194	6.350
[1.1.1]propellane	6.017	6.379
[2.1.1]propallane	6.042	6.341, 6.361
[2.2.1]propellane	6.036	6.325, 6.376

[a] Values are derived from calculations using the 6-31G* basis set.[22]

The origin of the intense 500–600-cm^{-1} band in these compounds is of interest. In the cases of bicyclo[1.1.1]pentane[17] and bicyclo[1.1.0]butane,[15] strong infrared bands were found at 831 and 735 cm^{-1}, respectively, which correspond to antisymmetric C–C stretching modes. This results in the bridgehead carbons moving together with respect to the rest of the molecule (Figure 2). An estimate of the vibrational frequencies of **4** made use of the force constants for bicyclobutane for the corresponding portion of **4** and those for cyclobutene[18] for the two-carbon bridge. This predicted a band of the same type of 660 cm^{-1} which is in reasonable agreement with the observed band at 574 cm^{-1}. MNDO calculations for **1**, **4**, and **9** lead to the same type of assignment for this band and correctly predict its very high intensity.[19]

Although it is known that the Mulliken population analysis[20] gives the incorrect sign for the C–H bond dipole in hydrocarbons,[21] it nevertheless is linearly related to the correct populations in most cases. Thus, the relative values are meaningful. The Mulliken populations for the carbons of the compounds shown in Figure 2 are given in Table II.[22] It can be seen there is a marked difference in population between the bridgehead and methylene carbons, and the motion indicated in the figure will lead to a large change in dipole moment during the vibration, and hence a large intensity. This problem will receive a more detailed analysis via calculation of ab initio molecular force fields and via a quantum topological analysis[23] of the charge distributions.

Experimental Section

Bicyclo[2.1.1]hexane-1,4-dicarboxylic Acid (6). A 1-L, three-necked flask was equipped with a magnetic stir bar, a dry-ice condenser, and an addition funnel. Ethyl α-(bromomethyl)acrylate (183 g, 0.95 mol) and 500 mL of dimethylformamide (freshly distilled from barium oxide) were added. The flask was evacuated and filled with nitrogen. Nickel carbonyl (246 g, 1.44 mol; danger!) was placed in the dropping funnel and was added dropwise, keeping the flask at room temperature. The addition was completed in 1.5 h, and then the solution was stirred overnight. Excess nickel carbonyl was removed by adding 200 mL of ether and distilling it from the flask. This was repeated three times. The DMF solution was diluted with an equal portion of water and extracted with three 200-mL portions of pentane. The pentane solution was washed with two 50-mL portions of water and with 50 mL of brine. After drying over sodium sulfate, the solution was concentrated using a rotary evaporator. The light-yellow liquid was placed on 400 g of Florisil and eluted with pentane. Concentration gave 75 g (70%) of diethyl hexa-1,5-diene-2,5-dicarboxylate. Photolysis[8] gave diethyl bicyclo[2.1.1]hexane-1,4-dicarboxylate. The hydrolysis of 4.8 g (10 mmol) of the ester was effected with 6.2 g of sodium hydroxide in 18 mL of water under reflux (12 h). The aqueous solution was extracted with ether, and then acidified and taken to dryness using a rotary evaporator. The acid was extracted from the solid mixture with acetone using a Soxhlet extractor, giving 2.6 g (79%) of the diacid, mp 223–224 °C. The ^1H NMR spectrum (90 MHz, CD_3CN) had bands at δ 10.13 (br s), 1.84–2.14 (6 H, singlet and multiplet), 1.64 (2 H, $J = 4.6$, 2 Hz). Anal. C, H.

1,4-Diiodobicyclo[2.1.1]hexane (5). Potassium *tert*-butoxide (3.09 g, 28 mmol) and a magnetic stir bar were added to a dry 1-L three-necked flask in a drybox. The flask was removed from the drybox and placed

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under an atmosphere of nitrogen from which oxygen had been removed by first passing the gas through an activated copper catalyst. The flask was wrapped with aluminum foil, and 180 mL of azotropically dried benzene was added. An addition funnel containing 10.5 g (41 mmol) of iodine (azeotropically dried with benzene) in 40 mL of dry benzene was attached to the flask, and the solution was rapidly added with stirring. The mixture was stirred an additional 20 min and allowed to sit for 20 min.

Meanwhile, a dry 1-L, three-necked water-jacketed flask with gas inlet and outlet and a mechanical stirrer was up next to the first flask. Dry oxygen-free nitrogen was passed through the flask and then through a trap held in a dry-ice/acetone bath. The gas was then bubbled through an aqueous silver nitrate solution, followed by a silica gel-calcium chloride drying tube, and finally a weighed tube containing Ascarite. The jacketed flask was charged with 0.70 g (4.1 mmol) of bicyclo[2.1.1]hexane-1,4-dicarboxylic acid (**6**). 15 mL of dry sulfolane (distilled from and stored over molecular sieves), and 20 mL of dry benzene. Water from a constant-temperature bath held at 55 °C was circulated through the jacket of the flask by means of an immersion pump.

The *tert*-butyl hypoiodite solution was pumped into the jacketed flask by means of a positive pressure of nitrogen. When the transfer was completed, stirring was begun, and the jacketed flask was irradiated with three 300-W flood lamps. The progress of the reaction could be monitored by periodically stopping irradiation and weighing the Ascarite tube. After 1.7 h there was an 88% CO_2 uptake, which increased to 90% after 2.0 h, and 91% after 2.5 h. Irradiation was discontinued, and the contents of the flask and dry-ice trap were poured into a separatory funnel. Pentane (250 mL) was added, and the solution was washed with two 100-mL portions of saturated sodium bisulfite, 100 mL of water, 100 mL of saturated sodium bicarbonate, two 100-mL portions of water, and 75 mL of brine. After drying over magnesium sulfate, the solvent was removed using a rotary evaporator. To remove the sulfolane still present, the product was redissolved in 60 mL of pentane, washed with three 15-mL portions of water and 10 mL of brine, and dried over magnesium sulfate; the solvent was removed. The product was then passed through a column of 3 g of neutral alumina and eluted with pentane. Removal of solvent gave 1.3 g of crude light-yellow solid contaminated with iodobenzene. Purification was effected by dissolving in pentane at room temperature and recrystallizing at -78 °C, to yield 0.83 g (2.5 mmol, 60%) of a white solid, mp 51.5–53 °C. Analysis by VPC (6 ft 10% SE-30) showed the product to be >99% pure: ^1H NMR ($CDCl_3$, 500 MHz) δ 2.14 (broad apparent s, 4 H), 2.15 (dd, 2 H, $J = 4.5, 1.9$ Hz), 2.42 (broad m, 2 H); mass spectrum, parent at *m/e* 334. A sample for elemental analysis was further purified by sublimation at reduced pressure. Anal. C, H, I.

Reaction of 1,4-Diiodobicyclo[2.1.1]hexane with *tert*-Butyllithium. A magnetically stirred solution of 1.00 g of 1,4-diiodobicyclo[2.1.1]hexane (**5**) in 42 mL of dry ether and 14 mL of dry pentane (both solvents were distilled from $LiAlH_4$) was cooled to −78 °C under an atmosphere of nitrogen. Freshly titrated *tert*-butyllithium (1.7 mL, 2.2 M in pentane) was added via a syringe, and the mixture was stirred for 0.5 h. Water (5 mL) was added, the cooling bath was removed, and the solution was allowed to come to room temperature. After 5 mL of cold brine was added, the organic layer was separated and washed with two 10-mL portions of cold water and 10 mL of cold brine. The solution was then dried over magnesium sulfate, filtered, and concentrated by evaporation of solvent under a stream of nitrogen. This gave 0.66 g of oil, which contained only traces of solvent. The product mixture was analyzed, and the components were separated using a 12-ft 20% DC-710 column at 150 °C for the volatile components and a 5-ft 20% SE-30 column, manually temperature programmed, for the less volatile components. The relative area ratios were determined with a thermal conductivity detector and are not corrected for detector response. The components were (relative area) 1-*tert*-butylbicyclo[2.1.1]hexane (3%), 1-iodobicyclo[2.1.1]hexane (2%), 1-*tert*-butyl-4-iodobicyclo[2.1.1]hexane (76%), and 1-(1′-ethoxyethyl)-4-iodobicyclo[2.1.1]hexane (2%). The less volatile components were 4-iodobi(bicyclo[2.1.1]hexane) (7%), 4-*tert*-butyl-4′-iodobi(bicyclo[2.1.1]hexane) (2%), and 4,4′-diiodobi(bicyclo[2.1.1]hexane) (9%). These compounds were identified by their spectral and other data shown below.

1-*tert*-Butylbicyclo[2.1.1]hexane: ^1H NMR ($CDCl_3$, 500 MHz) δ 0.88 (s, 9 H, C_4H_9), 0.89 (dd, 2 H, H_{endo}, $J = 4.1, 2.0$), 1.40 (broad apparent s, 2 H, H_{exo}), 1.48 (m, 2 H), 1.62 (m, 2 H), 2.32 (7-line m, 1 H); mass spectrum *m/e* (rel intensity) 79 (15), 81 (100, P − *t*-Bu), 95 (54), 123 (18, P − CH_3) (no parent was observed).

1-Iodobicyclo[2.1.1]hexane: The product from the reaction had an NMR spectrum in complete agreement with authentic material prepared by the reaction of 1-lithiobicyclo[2.1.1]hexane with iodine:[15] ^1H NMR ($CDCl_3$, 500 MHz) δ 1.59 (dd, 2 H, H_{endo}, $J = 4.1, 2.1$ Hz), 1.72 (m, 2 H, H_3), 2.07 (m, 4 H, H_{exo} and H_2), 2.51 (7-line m, 1 H, H_4); mass spectrum *m/e* (rel intensity) 79 (48), 81 (100, P − 1), 208 (19. P).

1-*tert*-Butyl-4-iodobicyclo[2.1.1]hexane: ^1H NMR ($CDCl_3$, 270 MHz) δ 0.88 (s, 9 H, C_4H_9), 1.59 (dd, 2 H, H_{endo}, $J = 4.1, 2.1$ Hz), 1.62 (m, 2 H, H_2), 1.95 (broad apparent s, 2 H, H_{exo}), 2.15 (m, 2 H, H_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.3 (q, long-range coupling), 26.6 (s). 28.5 (t), 41.4 (t), 49.4 (t, long-range coupling), 59.5 (s); mass spectrum *m/e*, (rel intensity) 57 (74), 79 (48), 80 (11), 81 (87), 95 (66), 137 (100, P − I), 264 (0.7, P). Anal. C, H, I.

1-(1′-Ethoxyethyl)-4-iodobicyclo[2.1.1]hexane: ^1H NMR ($CDCl_3$, 500 MHz) δ 1.08 (d, 3 H, CH_3CH, $J = 6.7$ Hz), 1.17 (apparent t, 3 H, CH_3CH_2O–. X portion of ABX_3, $J_{AX} = J_{BX} = 7.0$ Hz), 1.65 (m, 3 H), 1.71 (dd, 1 H, $J = 9.4, 6.3$ Hz), 1.98 (br d, 1 H, $J = 6.2$ Hz), 2.03 (br d, 1 H, $J = 6.2$ Hz), 2.16 (m, 2 H), 3.41 (1 H, $CH_3(\mathit{H})CHO$-, B portion of ABX_3, $J_{BX} = 7.0$, $J_{AB} = 9.3$ Hz), 3.50 (q, 1 H, $CH_3C\mathit{H}$, $J = 6.4$ Hz), 3.55 (1 H, $CH_3(\mathit{H})CHO$-, A portion of ABX_3, $J_{AX} = 7.0$ Hz, $J_{AB} = 9.3$ Hz); mass spectrum *m/e* (rel intensity) 43 (100), 45 (69), 73 (67), 77 (32), 79 (58), 80 (11), 81 (56), 107 (37), 153 (62) (no parent was observed).

4-Iodobi(bicyclo[2.1.1]hexane): ^1H NMR ($CDCl_3$, 270 MHz) δ 0.97 (dd, 2 H, H'_{exo}, $J = 4.0, 1.9$ Hz), 1.34 (broad m, 2 H, H'_{endo}), 1.42 (m, 2 H), 1.62 (m, 4 H), 1.63 (dd, 2 H, H_{exo}, $J = 4.1, 1.9$ Hz. superimposed on the multiplet at 1.62), 1.90 (br m, 2 H, H_{endo}), 2.16 (m, 2 H). 2.39 (7-line m, 1 H, $H_{4'}$); mass spectrum *m/e* (rel intensity) 77 (53), 79 (93), 80 (18), 81 (81), 91 (100), 93 (48), 95 (16), 105 (81), 119 (53), 133 (56), 161 (41, P − I), 288 (4.6, P).

4-*tert*-Butyl-4′-iodobi(bicyclo[2.1.1]hexane): ^1H NMR ($CDCl_3$, 500 MHz) δ 0.86 (s, 9 H, C_4H_9), 0.98 (dd, 2 H, H_{exo}, $J = 4.0, 1.9$ Hz), 1.21 (br m, 2 H, H_{endo}), 1.46 (m, 2 H), 1.57 (m, 4 H), 1.63 (dd, 2 H. H'_{exo}, $J = 4.0, 1.9$ Hz), 1.89 (br m, 2 H, H'_{endo}), 2.16 (m, 2 H. $H_{3'}$); mass spectrum *m/e* (rel intensity) 57 (100), 77 (32), 79 (49), 80 (17), 81 (52), 91 (59), 95 (34), 105 (44), 109 (30), 147 (47), 161 (46), 217 (42, P − I), 344 (5, P).

4,4′-Diiodobi(bicyclo[2.1.1]hexane): ^1H NMR ($CDCl_3$, 270 MHz) δ 1.58 (m, 4 H, H_2), 1.65 (dd, 4 H, H_{exo}, $J = 4.1, 1.9$ Hz), 1.88 (br m. 4 H, H_{endo}), 2.17 (m, 4 H, H_3). Irradiation of the broad multiplet at δ 1.88 resulted in collapse of the doublet of doublets δ 1.65 to a singlet, while irradiation of the doublet of doublets led to a still somewhat broadened singlet at δ 1.88. Thus, the methylene bridge protons form a AA′BB′ spin system in which the AB coupling constant is 4.1 Hz and the AB′ coupling constant is 1.9 Hz: mass spectrum *m/e* (rel intensity) 79 (51), 80 (34), 81 (13), 91 (54), 105 (36), 117 (52), 131 (44), 132 (22), 145 (34), 159 (46), 160 (53, P − I_2), 207 (16), 287 (100, P − 1), 288 (13), 414 (0.9, P).

Reaction of 1,4-Diiodobicyclo[2.1.1]hexane with Potassium. The apparatus was a modified version of that shown in ref 24. Its core was the reaction zone, a heated glass tube attached at one end to the shroud of a closed-cycle helium cryostat (Air Products Co.) so as to face a cesium iodide window held at about 30 K. The other end was attached to a nitrogen gas inlet and was provided with a side arm containing potassium metal, which could be heated separately. The nitrogen gas entered the inlet from a leak value through a miniature trap in which it passed over the solid diiodide. The trap was immersed in an ultrasonic bath to ensure optimal vapor mixing. A slow stream of nitrogen was passed through the apparatus at about 1 torr pressure; potassium vapor was passed into the reaction zone by heating the side arm to about 120 °C, and it reacted there with the diiodide vapor. The reaction mixture, including excess metal and a large excess of nitrogen, solidified on the cold plate.[25] When the experiment was completed, the plate containing the matrix was rotated and was placed in the beam of a Nicolet-7000 series FT-IR spectrometer. The resulting spectrum is shown in Figure 1.

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Registry No. 4, 36120-91-9; **5**, 85407-64-3; **6**, 85407-65-4; **8**, 285-86-9; 1-*tert*-butylbicyclo[2.1.1]hexane, 85407-66-5; 1-iodobicyclo[2.1.1]hexane, 74725-75-0; 1-*tert*-butyl-4-iodobicyclo[2.1.1]hexane, 85407-67-6; 1-(1′-ethoxyethyl)-4-iodobicyclo[2.1.1]hexane, 85407-68-7; 4-iodobi(bicyclo-[2.1.1]hexane), 85407-69-8; 4-*tert*-butyl-4′-iodobi(bicyclo[2.1.1]hexane), 85407-70-1; 4,4′-diiodobi(bicyclo[2.1.1]hexane), 85407-71-2; ethyl α-(bromomethyl)acrylate, 17435-72-2; diethyl hexa-1,5-diene-2.5-dicarboxylate, 32670-57-8; diethyl bicyclo[2.1.1]hexane-1,4-dicarboxylate, 85407-72-3.

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(24) Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840.

(25) The full details of the apparatus will be described elsewhere (Otteson, A. D.; Michl, J., to be submitted for publication), and also may be found in the Ph.D. thesis of F.H.W.