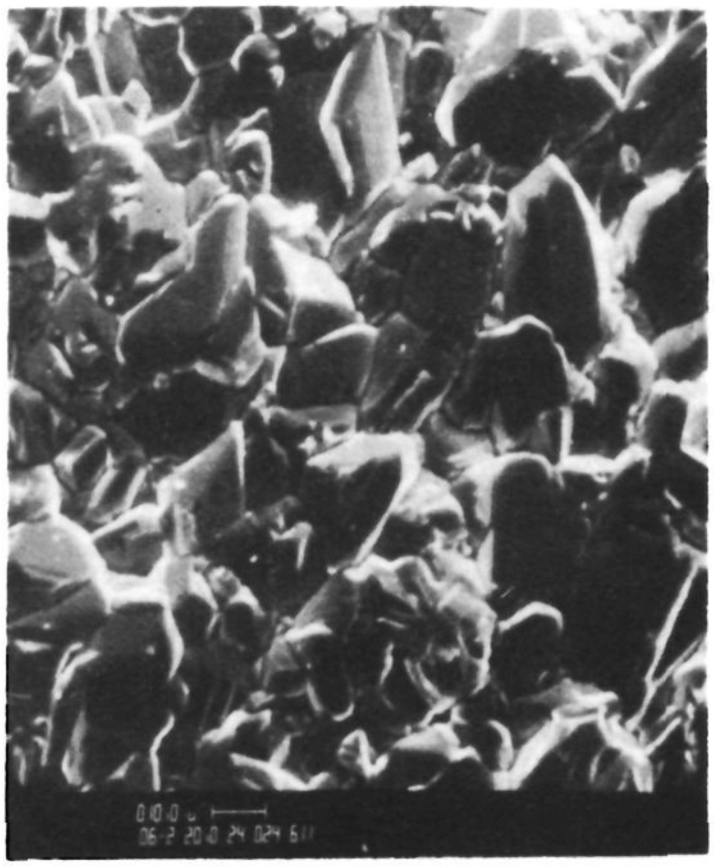

Figure 1. Scanning electron micrograph of the chemically vapor deposited n-GaAs film on tungsten coated graphite.

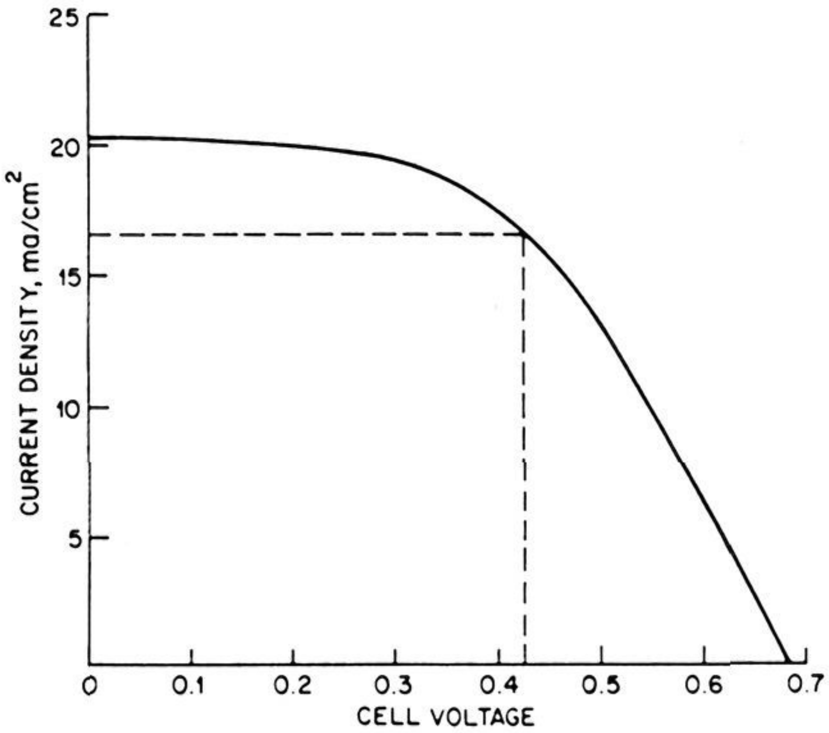

Figure 2. Current voltage characteristics of the thin-film n-GaAs|0.8 M K_2Se-0.1 M K_2Se_2-1 M KOH|C cell at 96.4 mW/cm^2 insolation. The maximum power point is marked with dashed lines.

earlier described[8] using a silver-filled epoxy to attach a copper wire to the graphite. A 3 M Scotchcast XR5241 resin was used to electrically insulate the back of the photoanodes from the solution. The areas of the encapsulated electrodes were measured to within ±2%.

The photoanodes were treated somewhat differently than previously.[2-5] First, they were run as part of the n-GaAs|0.8 M K_2Se-0.1 M K_2Se_2-1 M KOH|C cell until their output no longer increased. The electrodes were then rinsed for 20 s in flowing deionized water, etched in bromine-methanol solution at room temperature for 30 s, rinsed for 20 s in deionized water, and then dipped into 0.01 M $RuCl_3$ in 0.2 M HCl at 60 °C for 2 min to allow diffusion of the ruthenium ions into the grain boundaries. After being rinsed in deionized water for 20 s, the photoanodes were remounted in the cell. An improvement in performance was observed in the current-voltage cycles during the first 15 min, as is also common to single-crystal n-GaAs electrodes[5] and presumably chiefly due to slow chemical surface reequilibration after immersion in the selenide electrolyde.[7] The cell characteristics were determined after the output stabilized.

The measurements were done under 96.4-mW/cm^2 incident sunlight. The insolation was determined by an Eppley Model PSP radiometer, which measures the direct and scattered insolation from the entire sky. The cell was magnetically stirred. The current-voltage characteristics are shown in Figure 2.

The open circuit voltage is 0.67 V, the short circuit current density 20.3 mA/cm^2, and the fill factor 0.51. The maximum power output at 0.425 V and at 16.5 mA/cm^2 is 7.0 mW/cm^2, corresponding to a solar to electrical conversion efficiency of 7.3%. This represents 60% of the efficiency of the single-crystal n-GaAs counterpart. The cell is the most efficient thin-film GaAs cell to date, and one of the most efficient solar cells made with semiconductors of similarly small average grain size.

The importance of these and of earlier results is in the demonstration that grain-boundary diffusion of a strongly bound impurity can reduce the grain-boundary-related losses in solar cells made with thin-film polycrystalline semiconductors. This work and the effect of hydrogenation of grain boundaries of silicon[9] suggest that it is possible to approach more closely single-crystal efficiencies in thin-film polycrystalline solar cells than originally thought.

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Tricyclo[4.3.1.1^{3,8}]undec-3-ene (Homoadamant-3-ene). Stability of Bridgehead Olefins[1]

Sir:

The gas-phase carbene route provides access to the "anti-Bredt" bridgehead olefins, bicyclo[2.2.2]oct-1-ene (**1**),[2] tricyclo[4.3.1.1^{3,8}]undec-3-ene (homoadamant-3-ene) (**2**),[3] and adamantene (**3**).[4] However, **1**, **2**, and **3** were detected only as transient intermediates, as they suffered a retro-Diels-Alder reaction,[2] dimerizations,[2-4] and other trapping reactions[4] under the conditions employed. Modification of our method allows rapid capture at low temperature; we now report the isolation and spectroscopic characterization of homoada-

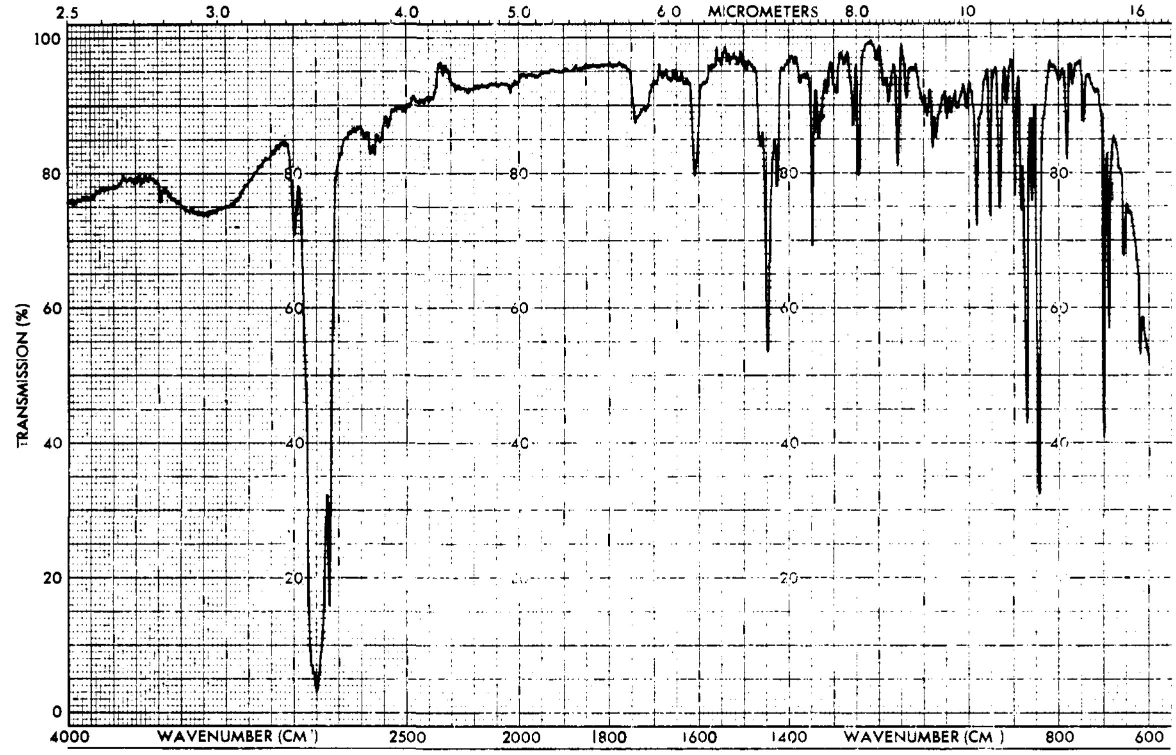
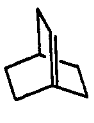


Figure 1. IR spectrum of homoadamant-3-ene (**2**).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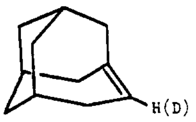

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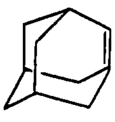
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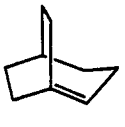
mant-3-ene (**2**). Although a mixture of bicyclo[3.2.2]non-1- and -1(8)-enes (**4** and **5**) has been observed at −80 °C and chemical shifts for the vinyl hydrogens have been reported,[5] this communication represents the first description of a vibrational spectrum for a bridged *trans*-cycloheptene.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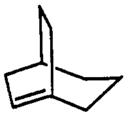
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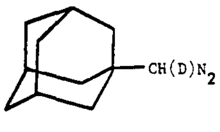

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1-Adamantyldiazomethane (**6**)[6,7] was passed at 10^{-3} Torr through a portion of Pyrex tubing wrapped with Nichrome wire and condensed onto a sodium chloride plate cooled by conduction to −196 °C. After deposition, the plate was rotated 90° and the infrared spectrum recorded using a Perkin-Elmer Model 283 infrared spectrometer. With an unheated tube the spectrum of 1-adamantyldiazomethane (**6**) was observed (3060 cm^{-1}, olefin C—H stretch; 2040 cm^{-1}, C=N=N stretch).

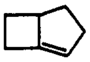
When **6** was passed through a hot zone maintained at 375 °C, the spectrum of the collected product (Figure 1) shows bands at 3000 (olefinic C—H stretch),[8] 1610 (C=C stretch),[8] and 848 cm^{-1} (C—H out of plane deformation for a trisubstituted olefin).[8] When the sodium chloride plate was allowed to warm to room temperature and recooled to −196 °C, a spectrum appeared similar to that of the dimers of homoadamant-3-ene.[3,9] Gas chromatography of the material on the plate confirmed this identification.

Vacuum pyrolysis of **6**-d_1[10] (ν_{C-D} 2240 cm^{-1}) produced 4-deuterio-3-homoadamantene (**2**-d_1). The C—H stretch band shifts from 3000 to 2218 cm^{-1} for C—D. One would anticipate a band at approximately [3000 cm^{-1} $(\nu_{C-D}\,\nu_{C-H})^{1/2}$] = 2206 cm^{-1}. The $\nu_{C=C}$ frequency shifts 15 cm^{-1} from its position in **2** to 1595 cm^{-1}. Shifts of 10–20 cm^{-1} are expected upon deuterium substitution.[11] Finally, the band at 848 cm^{-1} has vanished.

On warming, a weak band at 2155 cm^{-1} appears at the expense of the C—D stretch of **2**-d_1 (these spectra are available as supplementary material). If this band corresponds to a tertiary C—D stretch in the cyclobutane dimers of **2**-d_1, then the corresponding band in the protio dimers of **2** should be at ~2930 cm^{-1}, a reasonable position for such a stretching vibration.[12]

Several bridged *trans*-cyclooctenes show C=C stretching frequencies between 1600 and 1655 cm^{-1}.[13-20] No bridged *trans*-cycloheptenes have been previously observed in the infrared, although bicyclo[3.2.0]hept-1-ene (**7**) has a band at 1645[21] and *trans*-cyclohept-2-enone at 1558 cm^{-1}.[22] Thus our observed shift of 63 cm^{-1} from 1-methylcycloheptene (1673 cm^{-1})[23] appears reasonable.

Table I presents the heats of formation and strain energies (calculated using Allinger's 1973 force field)[25] of several bridgehead olefins which have been reported or mentioned in the literature.[2-5,9,13-20,24,26-29] Data for related strained olefins (**7**,[21] **8**,[30,31] and **9**[32]) are included. A complete table of all bridgehead olefins reported or mentioned in the literature can be obtained as supplementary material. Empirical force field calculations on some of these compounds have been reported previously;[24a,25,33-35] noteworthy are the anti-Bredt olefin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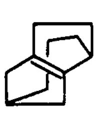
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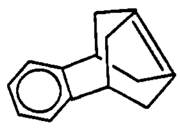
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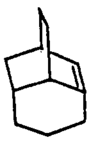
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Table I. Calculated Heats of Formation ($\Delta H_f°$) and Strain Energies of Bridgehead Olefins and the Related Polycycloalkanes[a]

compd[b]	$\Delta H_f°$, calcd[a]	strain energy[a]	Δ strain[c]	ref
bicyclo[2.2.2]oct-1-ene (**1**)	+42.72	50.6	40.4	2, 26
adamantene (**3**)	+32.26[d]	43.0	39.5	4, 26
bicyclo[2.2.1]hept-1-ene	+47.67[d]	50.0	34.9	26
bicyclo[3.2.1]oct-1-ene	+31.03[d]	38.9	28.6	28
bicyclo[3.2.1]oct-1(7)-ene	+29.64[d]	37.5	27.2	28
tricyclo[3.3.2.0^{3,7}]dec-3(7),9-diene (**9**)[e]	+60.35	45.0	25.0	32
bicyclo[4.4.1]undec-1(11)-ene	+14.85	39.5	22.3	20c
tricyclo[6.3.0.0^{4,11}]undec-1(11)-ene (**8**)[f]	+30.94	49.5	21.1	30, 31
homoadamant-3-ene (**2**)	+18.92	35.3	20.3	3, 9
bicyclo[3.2.2]non-1(7)-ene (**5**)	+22.17[d]	35.6	20.7	5
bicyclo[3.2.2]non-1-ene (**4**)	+21.06[d]	34.5	19.5	5
bicyclo[5.1.1]non-1-ene	+42.74[d]	56.2	17.5	24a
bicyclo[5.1.1]non-1(8)-ene	+39.74[d]	53.2	14.5	24a
bicyclo[3.2.0]hept-1-ene (**7**)	+44.47	46.7	13.9	21
bicyclo[3.3.1]non-1-ene	+10.73[d]	24.2	15.2	14, 15, 26
bicyclo[4.2.1]non-1-ene	+16.55[d]	30.0	14.1	16
bicyclo[4.2.1]non-1(8)-ene	+11.51[d]	25.0	9.1	16
tricyclo[5.3.1.0^{3,8}]undec-1-ene (**10**)	+9.14	25.5	12.5	13
bicyclo[4.2.2]dec-1-ene	+9.45	28.5	8.2	19
bicyclo[4.2.2]dec-1(8)-ene	+9.19	28.2	7.9	19
bibyclo[3.3.2]dec-1-ene	+6.19	25.2	4.7	24b
bicyclo[4.3.1]dec-1(9)-ene	−1.46	17.6	3.0	29
bicyclo[4.4.1]undec-1-ene	−8.95	15.7	−1.5	20c

[a] In kilocalories/mole. Calculated using N. L. Allinger's MMI MOLECULAR MECHANICS program (Program 318, Quantum Chemistry Program Exchange, Indiana University, 1975) and Allinger's 1973 force field. See ref 25. [b] Calculations refer to the most stable geometry of each compound; where necessary, various conformations were tested. See ref 24b, 25, 33–35. [c] Difference in strain energies of alkene and related alkane. These often do not correspond to the same conformation. For alkane data, see ref 25c and supplementary material. [d] See ref 33. Where our energies are lower, a more stable conformation probably was found. [e] For the calculations, the benzene ring in **9** was replaced by a double bond. [f] Incorrectly named in ref 31.

studies by Burkert[33] and Ermer.[24]

The strain energy of a bridgehead olefin is a composite of the extra strain associated with the double bond and the residual strain of the carbon skeleton.[27] The latter can be approximated by the strain energy of the parent alkane. Experimental estimates of the extra strain of some isolable bridgehead olefins are available.[20b,27,28] Such calculated alkene-alkane strain energy differences (Δ strain, Table I) indicate the *thermodynamic* driving force for conversion of a given olefin to an alkane. Nevertheless, these Δ strain values appear to correspond well with observed chemical stabilities and reactivities of strained olefins.[36] Three classes of behavior can be recognized.

There is evidence for the fleeting existence of **1**,[2] **3**,[4,26] **8**,[30,31] **9**,[32] bicyclo[2.2.1]hept-1-ene,[26] and the bicyclo[3.2.1]oct-1- and -1(7)-enes,[29] but these olefins have not been observed directly. All have Δ strain values in excess of 21 kcal/mol. Olefins like **2**,[3,9] **4**,[5] and **5**[5] can be detected at low temperatures, but dimerize upon warming. Lower Δ strain values, ~20 kcal/mol, are calculated for this set. Bridgehead olefins isolable at room temperature, like **7**,[21] the bicyclo[5.1.1]non-1- and -1(7)-enes,[24b] bicyclo[3.3.1]non-1-ene,[14,15] the bicyclo[4.2.1]non-1- and -1(8)-enes,[16] and the olefins listed toward the bottom of Table I, have still lower Δ strain values, <18 kcal/mol. Because of possible errors in the calculations and the nature of the assumptions involved, such reactivity indexes can only be approximate. Nevertheless, the Δ strain criterion appears to be more reliable and to have wider applicability than the numerous qualitative "rules" for bridgehead olefins proposed in the past.[26]

Acknowledgments. We thank O. Ermer, K. B. Becker, and U. Burkert for helpful comments.

Supplementary Material Available: Spectra showing the appearance of the 2155-cm^{-1} band at the expense of the 2218-cm^{-1} band are available, as is a greatly expanded Table I in which calculated heats of formation and strain energies of *all* known or mentioned bridgehead olefins and the related polycycloalkanes can be found (3 pages). Ordering information is given on any current masthead.

References and Notes

(1) We thank the National Science Foundation for support of this work at Princeton through Grant CHE-77-24625. One of us (D.J.M.) is indebted to the National Cancer Institute for support. The Fonds der Chemischen Industrie, the Deutscheforschungsgemeinschaft, and a NATO grant facilitated the work at Erlangen.

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(36) Calculated differences between the heats of formation of alkene and of alkane (corresponding to the heats of olefin hydrogenation) provide an alternative, but equivalent index.

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Adamantene

Sir:

The severely distorted anti-Bredt olefin, adamantene (**1**), has been sought repeatedly.[1-5] So far, the evidence for generation of **1** has been only indirect. For instance, self-trapping produced a mixture of [2 + 2] dimers,[1-3] and trapping with dienes[1,2,4] and methanol[5] produced the expected adducts. We now report a direct spectroscopic observation of **1**.

The method used for the generation of **1** is based on the "sodium flame" technique developed by Polanyi[6] for kinetic studies of gas-phase dehalogenation of organic halides with alkali metal vapors. Our experimental arrangement is different in that the gas-phase products are carried in a stream of argon to a cold (10 K) window where they are trapped in an argon matrix.[7] In this fashion, alkyl halides produce radicals, readily identified by their ESR spectra.[8]

1-Bromoadamantane reacts with either Na or K vapor in this manner to produce the known ESR spectrum of the 1-adamantyl radical.[9] 2-Bromoadamantane and Na or K similarly produce an ESR spectrum which even under optimum conditions (45 K) consists only of a broad doublet ($a_H \simeq 23$ G) with indications of further unresolved splitting. We assign it to the 2-adamantyl radical and the large splitting constant to the α proton. The spectra of both radicals are very intense and disappear in ~1 h upon warming to 50 K under reduced pressure of argon, which prevents rapid sublimation of the matrix.

In organic dihalides, one can expect the initial formation of a monohalo radical, followed either by fragmentation or by further dehalogenation reaction with metal. This has indeed been observed. For instance, 1,3-diiodopropane produces a mixture of cyclopropane and propene[8] and benzylic 1,2- or 1,4-dihalides produce the expected polyolefins.[7] We now find that the use of either 1,2-dibromoadamantane (**2**) and K vapor or 1,2-diiodoadamantane (**3**) and either Na or K vapor produces only very weak ESR signals. The dihalides were prepared by the method of ref 2 and were free of monohalides as judged by gas-liquid chromatography. The ESR signals are identical with those of the 1-adamantyl radical and disappear upon warming in the same fashion. We have found no evidence for the presence of halogen-containing radicals in the spectra. Since so little paramagnetic material is produced from **2** and **3**, which ought to be at least as reactive as the corresponding monohaloadamantanes, the bulk of the reaction products is likely to be diamagnetic, similarly as in the case of other dihalides.

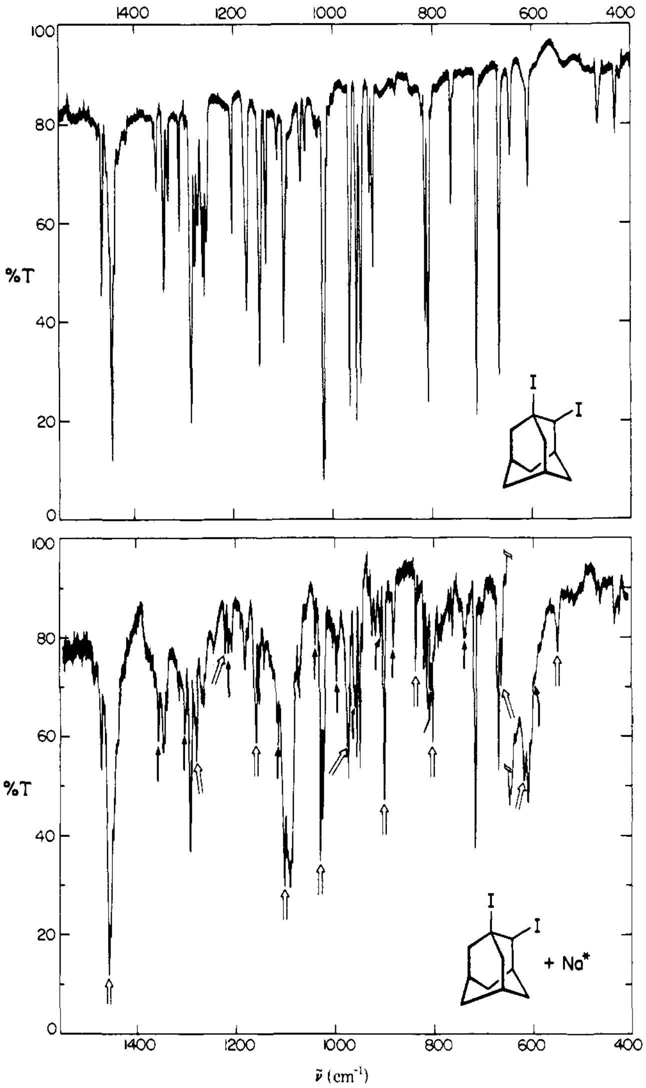

Figure 1. IR spectrum of **3** (top) and of a reaction mixture from **3** and excited Na vapor (bottom), argon 10°. The principal absorptions assigned to **1** are indicated by double arrows. Weaker absorptions probably also associated with **1** are indicated by single arrows.

IR spectra (Figure 1) reveal that about half of **3** is converted into a single new product using either K vapor or microwave-discharged[7] Na vapor. Both reactions produce the same product, characterized by about a dozen strong absorptions. These differ from the known[10] absorptions of adamantene dimers and biadamantyls. The strongest among these are also observed starting with **2**, and we conclude that the product contains neither halogen nor metal atoms. It survives for at least 1 h at 70 K[11] under reduced argon pressure without an appreciable change, proving that it is distinct from the radicals observed in the ESR experiments. The positions of the IR absorptions are compatible with an assignment of the new