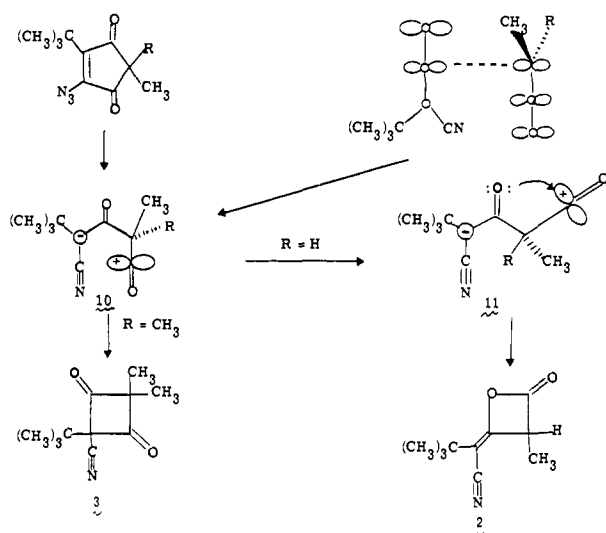


Scheme III



In conclusion, we wish to emphasize the significant points resulting from this study: (1) for the first time, the zwitterion resulting from the interaction of a ketene with a ketene has been independently generated and shown to give the same products as the cycloaddition itself; (2) the fact that zwitterions are formed in the thermolysis of **4** further establishes our earlier prediction and provides a most powerful predictive model for the thermal chemistry of appropriately substituted vinyl azides;<sup>10,11</sup> (3) these results suggest a potentially general mechanistic probe for the investigation of the cycloadditions of a variety of cyano compounds since suitably substituted cyclic vinyl azides can be viewed as precursors to possible cyano substituted zwitterionic intermediates in [2 + 2], [3 + 2], and [4 + 2] cycloadditions.

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- A crude yield of >80% was observed by <sup>1</sup>H NMR analysis. Although <sup>1</sup>H NMR showed little impurity, an appreciable amount of polymeric material was left behind after vacuum distillation of the crude product.
- Dimethylketene was generated by the pyrolysis of commercially available tetramethylcyclobutane-1,3-dione at 580 °C (1 Torr).
- A crude yield of 83% was obtained which showed it to be >90% by <sup>1</sup>H NMR analysis. Again a large amount of polymer remained as a residue after vacuum distillation. When the reaction was followed by IR analysis, one observed the ketene absorption to decrease in intensity as the cyclobutanedione carbonyl absorption at 1763 increased. No higher carbonyl absorption was detected. Thus, it is unlikely that the cycloaddition initially gives a 2-oxetanone which rearranges to the cyclobutanedione, **3**, under the reaction conditions.

- The spectral and analytical properties of all these new compounds are in strict agreement with their molecular formulations.
- The corresponding azido compounds were not purified because of their inherent instability. However, no impurities could be detected by IR or <sup>1</sup>H NMR analysis.
- Prepared independently as described by W. Weyler, Jr., W. G. Duncan and H. W. Moore, *J. Am. Chem. Soc.*, **97**, 6187 (1975).
- Prepared independently from the commercially available isobutanoyl chloride and MeOH.
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- Taken in part from the Ph.D. Thesis of D. Scott Wilbur.

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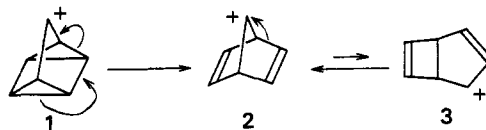
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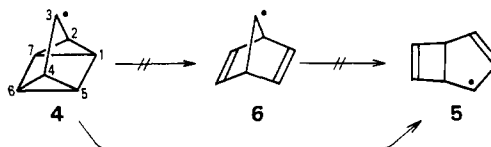
### Fast Rearrangement of 3-Quadricyclyl Radical to Bicyclo[3.2.0]hepta-3,6-dien-2-yl Radical

Sir:

3-Quadricyclyl cation (**1**) rearranges to 7-norbornadienyl cation (**2**) which undergoes a partially degenerate rearrangement; the mechanism proposed for the latter is ring contraction of **2** to bicyclo[3.2.0]hepta-3,6-dien-2-yl cation (**3**) followed by ring expansion back to **2**.<sup>1</sup> In contrast to the cationic ana-



logues, we report here that 3-quadricyclyl radical (**4**) rearranges quite rapidly to bicyclo[3.2.0]hepta-3,6-dien-2-yl radical (**5**); 7-norbornadienyl radical (**6**) is not involved in this rearrangement.



The radical chain reduction<sup>2</sup> of 3-chloroquadricyclane (**7**) by a stannane affords an opportunity to examine rearrangement of **4**. When 0.20 mmol of **7**,<sup>3</sup> 0.11 mmol of tri-*n*-butylstannane, and 0.004 mmol of di-*tert*-butyl peroxide are reacted in 0.15 mL of *n*-hexane in a degassed sealed tube at 130 °C for 6 h, the stannane was consumed as shown by the absence of the absorption at 1810 cm<sup>-1</sup> ( $\nu_{\text{Sn-H}}$ ) in the IR spectrum of the reaction mixture. A GLC analysis of the reacted mixture showed that 0.10 mmol of **7** was consumed and bicyclo[3.2.0]hepta-2,6-diene (**8**)<sup>4</sup> was formed to the amount of 90 mol % of the consumed **7**. No other volatile product (neither quadricyclane nor norbornadiene) was present in >1 mol % of the consumed **7**. A control experiment without the stannane showed that ~80% of **7** persisted under the present reaction condition.<sup>5</sup> These results indicate that most of **4**, generated by homolytic chlorine atom abstraction from **7** by tri-*n*-butylstannyl radical, rearranges to **5** followed by hydrogen atom transfer from the stannane. To trap **4** before the rearrangement, **7** was dechlorinated in tri-*n*-butylstannane solvent in a reaction condition in which >80% of quadricyclane persists in the stannane solvent. When 0.16 mmol of **7** was heated in 0.15 mL (0.58 mmol) of the stannane in the presence of 2 mol % of azoisobutyronitrile at 80 °C for 3 h in a sealed degassed tube, 80% of **7** decayed and **8** was detected to the extent of 15

mol % of the consumed 7.<sup>6</sup> Quadricyclane was formed no more than 1 mol % of the consumed 7, showing that the rearrangement of 4 to 5 is quite fast. Judging from the unsuccessful trial to trap 4, we can estimate the rate of the rearrangement to be faster than the cyclization of hex-5-en-1-yl radical to cyclopentylmethyl radical ( $\sim 10^5 \text{ s}^{-1}$  at 40 °C)<sup>7,8</sup> and to be of similar rate to or even faster than the interconversion between nortricyclyl and norborn-5-en-2-yl radicals ( $\sim 10^8 \text{ s}^{-1}$ ).<sup>8-10</sup>

The rearrangement of 4 to 5 was studied also with ESR technique. Photolysis of an ethane solution of a mixture of 3-bromoquadricyclane,<sup>11</sup> triethylsilane, and di-*tert*-butyl peroxide or of a mixture of quadricyclane and the peroxide at -146 °C in an ESR cavity gave a spectrum consisting of three sets of 1:2:1 triplets (19.9<sub>2</sub>, 14.0<sub>1</sub>, and 1.74 G) split into doublets of 2.71 G at  $g = 2.00267$ , which is identical with the spectrum of 5<sup>12</sup> generated by photolysis of a mixture of di-*tert*-butyl peroxide and bicyclo[3.2.0]hepta-2,6-diene.<sup>4b</sup> An ESR spectrum of 6 was observed during photolysis of an ethane or cyclopropane solution of a mixture of 7-bromonorbornadiene, triethylsilane, and di-*tert*-butyl peroxide.<sup>13</sup> There was no indication of the formation of 5 in the spectra observed in the examined temperature range between -60 and -146 °C. If 4 rearranged to 5 via 6, as one might conceive on the basis of chemistry of cationic analogues, we should have observed 5, not 6, in the latter ESR experiment, but this is not the case.

When 7-bromonorbornadiene<sup>14</sup> (0.22 mmol) was reduced with the stannane (0.13 mmol) in *n*-hexane (0.15 mL) in the presence of di-*tert*-butyl peroxide (0.004 mmol) at 130 °C for 15 min,<sup>15</sup> norbornadiene was formed in 72% yield based on the stannane and 8 was not detected (<1 mol % of the stannane). This result shows that 6 does not rearrange to 5 at higher temperatures either.

These results of present product and ESR studies indicate that 4 rearranges to 5 with a fast rate and that 6 is not involved in this rearrangement. The predominant formation of bicyclo[3.2.0]heptadiene derivatives by the rearrangement of 4 to 5 may provide a diagnostic tool for differentiating homolytic processes from those involving carbonium ion intermediates; the latter give norbornadiene and/or quadricyclane derivatives.<sup>3b,16</sup>

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- When a *n*-hexane solution of 7 was heated at 130 °C for 6 h in a sealed degassed tube, 80% of 7 persisted and 7-chloronorbornadiene was formed to the extent of ~10%. No other olefinic chloride was formed (<5%) as shown by a 220-MHz <sup>1</sup>H NMR spectrum of the residue of this reaction mixture after evaporation of the solvent.
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## Infrared Laser Photochemistry of Matrix-Isolated Molecules

Sir:

Two groups have reported studies of infrared laser induced photochemistry of matrix-isolated species. Turner et al.<sup>1</sup> have examined rearrangements of isotopically labeled carbonyl fragments induced by radiation from a carbon monoxide laser in the 1900-cm<sup>-1</sup> region. These authors have concluded<sup>1b</sup> that "a single molecule requires absorption of only one photon to undergo isomerization". Ambartzumian et al.<sup>2</sup> claim to have observed selective dissociation of <sup>32</sup>SF<sub>6</sub> in argon matrices using a carbon dioxide laser operating in the 940-cm<sup>-1</sup> region. They estimate that each molecule absorbs energy corresponding to about 150 quanta of CO<sub>2</sub> laser radiation.<sup>2b</sup> Some aspects of their reported conclusions appeared unusual to us and we attempted to reproduce their results and extend work in this field.

We were surprised that no dissociated products were detected using infrared spectroscopy,<sup>2b</sup> since for the species that may be produced (SF<sub>4</sub>, S<sub>2</sub>F<sub>10</sub>, and SF<sub>5</sub>) vibrational data are available.<sup>3-5</sup> A reported decrease in absorption due to <sup>32</sup>SF<sub>6</sub> from ~95 to ~55%<sup>2b</sup> would be expected to yield photoproducts having substantial absorbances.

We have carried out a series of experiments involving CO<sub>2</sub> laser irradiation of various matrix-isolated molecules and have not observed any evidence for dissociation or reaction in this medium. Table I shows some of the species studied, the vibrational modes excited, and the laser wavenumbers employed. Matrix ratios were in the range 100:1 to 40 000:1, and slow spray-on techniques were used. Our observations of the effects of irradiation are that no spectroscopic or visual effects were observed (a) for irradiation of pure argon matrices or (b) when the exciting frequency was more than 10 cm<sup>-1</sup> away from an absorption band. Irradiation of the matrix at a guest absorption frequency (or at up to 5 cm<sup>-1</sup> to lower wavenumber) with low energy density (0.4 J cm<sup>-2</sup>) causes "fogging" of the previously glassy matrices, and at higher densities (40 J cm<sup>-2</sup>) causes matrix destruction with complete evaporation. Prolonged photolyses have led to fracturing of the cesium iodide substrate. We are led to the conclusion that the spectra presented by Ambartzumian et al. show no conclusive evidence of dissociative photochemistry but may simply be interpreted in terms of differential evaporation of <sup>32</sup>SF<sub>6</sub> from the matrices.