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## Thermolysis of Spiro[2,2-dimethylbicyclo[2.2.2]octa-5,7-diene-3,3-cyclopropene]. An Attempt to Synthesize 4,4-Dimethylmethylenecyclopropene

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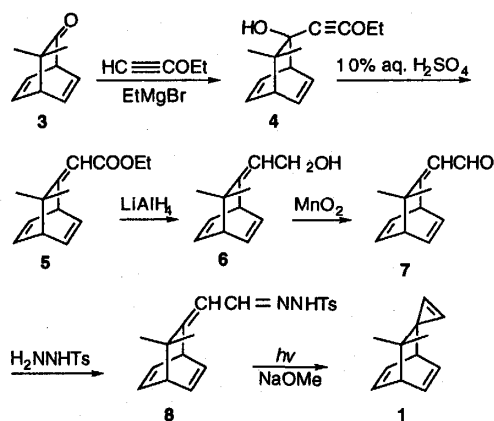
Spiro[2,2-dimethylbicyclo[2.2.2]octa-5,7-diene-3,3-cyclopropene], a potential precursor to 4,4-dimethylmethylenecyclopropene, has been synthesized. Thermolysis of the spirotriene gave isopropylideneacetylene rather than 4,4-dimethylmethylenecyclopropene, exclusively.

After intensive efforts<sup>1-6)</sup> on the preparation of methylenecyclopropenes (triafulvenes), the simplest cross-conjugated cyclic hydrocarbon, Billups<sup>7)</sup> and Staley<sup>8)</sup> have independently succeeded to characterize the parent methylenecyclopropene, which was synthesized from dehydrohalogenation of 2-halogenomethylenecyclopropanes through a column packed with potassium *tert*-butoxide on Chromsorb W at room temperature under reduced pressure. As expected, methylenecyclopropene was a highly reactive compound; dilute solutions in pentane showed a half-life of approximately 20 h at -78 °C.

Other successful studies were the pyrolysis of 2-phenylsulfinylmethylenecyclopropane,<sup>9)</sup> cyclopropenyl diazomethyl ketone,<sup>10)</sup> and 3-methylenetricyclo[3.2.2.0<sup>2,4</sup>]nona-6,8-diene derivatives.<sup>11)</sup> Since in all the previous studies the flash thermolysis technique was applied to introduce the strained double bond in the small ring, we thought that the introduction of the exocyclic double bond by flash thermolysis might be even prospective.

In this paper, we will report the synthesis and the thermal behavior of the title compound (1), spiro[2,2-dimethylbicyclo[2.2.2]octa-5,7-diene-3,3-cyclopropene], a potential precursor to 4,4-dimethylmethylenecyclopropene (4,4-dimethyltriafulvene) (2). Treatment of 3,3-dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (dimethylbarrelenone) (3)<sup>12)</sup> with ethoxy acetylene and ethylmagnesium bromide in dry ether resulted in 68% of carbinol (4).

Shaking of 4 with 10% aq. H<sub>2</sub>SO<sub>4</sub> solution gave the unsaturated ester (5) mp 45 °C, which on LiAlH<sub>4</sub> reduction in dry ether afforded unsaturated alcohol (6), mp 37 °C, in overall yield of 69% from 4. This 6 was oxidized by MnO<sub>2</sub> at room temperature in ether to give the aldehyde (7), mp 75 °C, in 68% yield, then tosylhydrazone (8), mp 217 °C (dec), 88% yield. When a THF solution of 8 and NaOMe was irradiated until the disappearance of the pink color of the solution, the spirotriene (1) was afforded in 56% yield after quick SiO<sub>2</sub> column chromatography with pentane. The structure of 1 was deduced as shown in Scheme 1 from physical data.



Flash thermolysis of 1 was carried out at 400-430 °C under the nitrogen stream in a previously described apparatus.<sup>13)</sup> The pyroly-

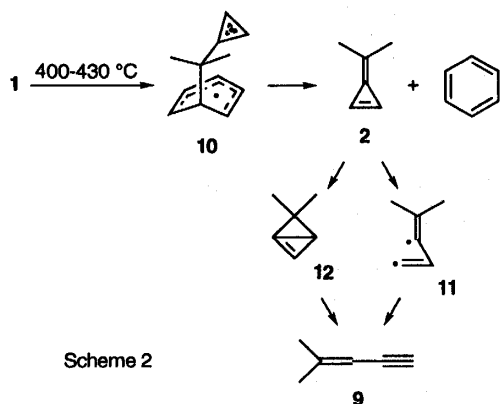
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Dedicated to Professor Hitoshi Takeshita on the occasion of his retirement

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ysate was deposited on the liquid nitrogen-cooled Dewar wall and analyzed by gas-liquid chromatography and NMR spectra comparing with authentic samples.<sup>14</sup> The pyrolysates identified from the reaction at 400–430 °C were shown to be only benzene and 2-methyl-2-penten-4-yne (**9**). No other C<sub>6</sub>H<sub>8</sub> species were detected under these reaction conditions.

The formation of **9** would be explained as shown in Scheme 2. The spirotriene (**1**) would form, by C–C bond fission, the biradical (or zwitter ion) intermediate (**10**), which by the subsequent C–C bond fission would give the desired **2**. Unfortunate ring opening of **2**, however, gave **9** via a biradical (**11**) or even a bicyclo[1.1.0]butene (**12**). These plausible pathways have been already reported in the literatures.<sup>15</sup> The reason why 4,4-dimethylmethylene-cyclopropene could not survive during the reaction course would be attributable to its large heat of formation caused by strain energy.<sup>16</sup>



Scheme 2

### Experimental<sup>17)</sup>

**Preparation of the Carbinol 4.** To an ether solution (45 cm<sup>3</sup>) of ethoxyethylmagnesium bromide prepared from ethoxyacetylene (6 g), Mg (1.95 g), and ethyl bromide (7 cm<sup>3</sup>) under nitrogen atmosphere, an ether solution (39 cm<sup>3</sup>) of **3** (1.1 g) was added in one portion and the solution was stirred for 12 h at room temperature. After the addition of 20% aq. NH<sub>4</sub>Cl solution, the ice-cooled reaction mixture was extracted with ether. The ether layer was washed with 10% aq. NH<sub>4</sub>Cl solution, dried and evaporated. The colorless oil, 1.1 g (68%) was obtained by basic Al<sub>2</sub>O<sub>3</sub> column chromatography.  $\nu$  3400 and 2250 cm<sup>-1</sup>.  $\delta$  0.93 (3H, s), 1.06 (3H, s), 1.36 (3H, t,  $J=7$  Hz), 1.46 (1H, s, exchangeable with D<sub>2</sub>O), 3.10 (1H, m), 3.70 (1H, m), 4.00 (2H, q,  $J=7$  Hz), and 6.20 (4H, m).

**Dehydration of 4 into 5.** The ether solution (25 cm<sup>3</sup>) of **4** (1.36 g) was stirred for 40 h with 10% aq. H<sub>2</sub>SO<sub>4</sub> solution (0.3 cm<sup>3</sup>). The ether solution was washed with saturated aq. NaCl solution, aq. NaHCO<sub>3</sub> solution and H<sub>2</sub>O. Basic Al<sub>2</sub>O<sub>3</sub> column chromatography of the reaction mixture yielded **5**, mp 45 °C, 940 mg (69%), Found:  $m/e$  218.1305. Calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>: 218.1306.  $\nu$  2900, 1715, 1645, and 1175 cm<sup>-1</sup>.  $\delta$  1.10 (6H, s), 1.23 (3H, t,  $J=7$  Hz), 3.28 (1H, m), 4.05 (2H, q,  $J=7$  Hz), 5.40 (1H, s), 5.86 (1H, m), and 6.26 (4H, m).  $\lambda_{\max}$  (hexane) 235 nm ( $\epsilon$ : 13000).

**LiAlH<sub>4</sub> Reduction of 5 to 6.** The anhydrous ether solution (20 cm<sup>3</sup>) of **5** (940 mg) was treated with LiAlH<sub>4</sub> (660 mg) at room temperature to give **6**, mp 37 °C, 750 mg (99%),  $m/z$  176.  $\nu$  3400, 3400, 2960, 1660, 1380, 1360, 1350, and 1040 cm<sup>-1</sup>.  $\delta$  1.03 (6H, s), 2.46 (1H, br s, exchangeable with D<sub>2</sub>O), 3.23 (1H, m), 4.06 (2H, d,  $J=7$  Hz), 4.36 (1H, m), 5.16 (1H, t,  $J=7$  Hz), and 6.16 (4H, m).

**MnO<sub>2</sub> Oxidation of 6 to 7.** The ether solution (30 cm<sup>3</sup>) of **6** (830 mg) was stirred at room temperature for 3 h with MnO<sub>2</sub> (6 g). The mixture was filtered and evaporated the solvent to give **7**, mp 75 °C, 560 mg (68%),  $m/z$  174.  $\nu$  3060, 2950, 2820, 2730, 1675, 1620, 1600, 1150, and 700 cm<sup>-1</sup>.  $\delta$  1.10 (6H, s), 3.35 (1H, m), 5.25 (1H, m), 5.68 (1H, d,  $J=7.5$  Hz), 6.32 (4H, m), and 9.98 (1H, d,  $J=7.5$  Hz). Tosylhydrazone **8** of **7**. mp 217 °C (dec),  $\delta$  1.00 (6H, s), 2.36 (3H, s), 3.33 (2H, br m), 4.60 (1H, m), 5.73 (1H, d,  $J=9$  Hz), 6.40 (4H, m), 7.40 (2H, d,  $J=8$  Hz), 7.73 (2H, d,  $J=8$  Hz), and 8.03 (1H, d,  $J=9$  Hz).

**Irradiation of 8. Synthesis of 1.** The THF solution (15 cm<sup>3</sup>) of **8** (500 mg) and NaOMe (214 mg) was stirred overnight at room temperature. The degassed solution was irradiated in Dry Ice/CCl<sub>4</sub> bath for 6 h until the disappearance of the pink color. After the solid was filtered, the solvent was evaporated at the normal pressure very carefully. The residue was purified by SiO<sub>2</sub> column chromatography with *n*-pentane and the solvent was removed at the normal pressure to give **1**, colorless oil, 127 mg (56%), Found:  $m/z$  158.1092. Calcd. for C<sub>12</sub>H<sub>14</sub>: 158.1095.  $\delta$  0.56 (6H, s) 2.40 (1H, m) 3.23 (1H, m), 6.26 (4H, m), and 6.93 (2H, s).

**Thermolysis of 1.** 92.5 mg of **1** in the glass tube was put in the sublimation zone and heated at 400–430 °C under nitrogen atmosphere. The pyrolysate was collected on the liquid nitrogen-cooled Dewar wall and analyzed by gas-liquid chromatography (SE 30 (7 ft) 15% on Chromsorb WHP 80/100 mesh), finding

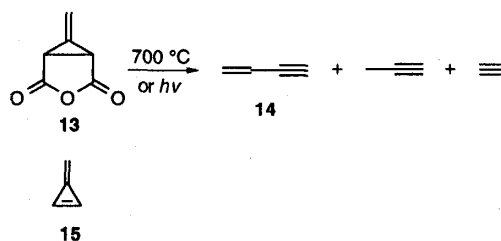
benzene (54-60%) and 2-methyl-2-penten-4-yne (9, 22-24%).  $\nu$  3320, 2980, 2900, 2110, 1625, 1440, 1380, 1330, 1195, 1080, and 818  $\text{cm}^{-1}$ .  $\delta$  1.82 (3H, s), 1.90 (3H, s), 2.83 (1H, d,  $J=2$  Hz), and 5.17 (1H, m).  $\lambda_{\text{max}}$  (pentane) 221 nm ( $\epsilon$ : 10000), which is identical with the authentic sample.

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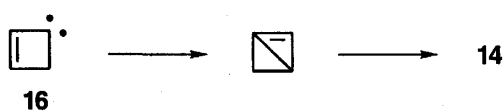
### References and Notes

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1. I. S. Krull, P. F. D'Angelo, D. R. Arnold, E. Hedaya, and P. O. Schissel, *Tetrahedron Lett.*, **1971**, 771.
  2. R. Block, F. Leyendecker, and N. Toshima, *Tetrahedron Lett.*, **1973**, 1025.
  3. M. Neuenschwander and W. K. Schenk, *Chimia*, **29**, 215 (1975).
  4. W. E. Billups, A. J. Blakeney, and W. T. Camberlain, *J. Org. Chem.* **41**, 3771 (1976).
  5. W. E. Billups, A. J. Blakeney, N. A. Rao, and J. D. Buynak, *Tetrahedron*, **37**, 3215 (1981).
  6. A. Weber and M. Neuenschwander, *Angew. Chem.*, **93**, 788 (1981); *Angew. Chem. Int. Ed. Engl.*, **20**, 774 (1981).
  7. W. E. Billups, L-J. Lin, and E. W. Casserly, *J. Am. Chem. Soc.*, **106**, 3698 (1984).
  8. S. W. Staley and T. D. Norden, *J. Am. Chem. Soc.*, **106**, 3699 (1984).
  9. G. Maier, M. Hoppe, K. Lanz, and H. P. Reisenauer, *Tetrahedron Lett.*, **25**, 5645 (1984).
  10. A. Weber, U. Stämpfli, and M. Neuenschwander, *Helv. Chim. Acta*, **72**, 29 (1989).

11. J. Krebs, D. Griggisberg, U. Stämpfli, and M. Neuenschwander, *Helv. Chim. Acta*, **69**, 835 (1986).
12. R. T. Luibrand and E. M. Fujimori, *J. Org. Chem.*, **45**, 958 (1980).
13. a) J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, **48**, 3704 (1970). b) P. de Mayo, *Endeavour*, **31**, 135 (1972).
14. The authentic 2-methyl-2-penten-4-yne was synthesized by P. A. Ashurst and D. R. J. Law's method (*J. Chem. Soc. (C)*, **1966**, 1615.)
15. It has been reported that the products from pyrolysis or photolysis of cis-1-methylenecyclopropane-2,3-dicarboxylic anhydride (**13**) were 1,3-butenyne (**14**) and acetylenes instead of methylenecyclopropene (**15**).<sup>1)</sup>



On the other hand, Shelvin et al. have also obtained **14** from carbene rearrangement of cyclobutenylidene (**16**), which was generated from cyclobutenone and atomic carbon: S. F. Dyer, S. Kammula, and P. B. Shelvin, *J. Am. Chem. Soc.*, **99**, 8104 (1977).



16. N. C. Baird and N. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 3966 (1967).
17. The NMR and IR spectra were measured in  $\text{CCl}_4$  and the chemical shift were expressed in  $\delta$  unit from the internal standard,  $\text{Me}_4\text{Si}$ .