J. Am. Chem. Soc. 1984, 106, 3698-3699

Synthesis of Methylenecyclopropene

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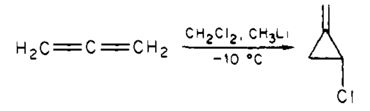
Received December 30, 1983
Revised Manuscript Received April 4, 1984

As the simplest cross-conjugated cyclic hydrocarbon, methylenecyclopropene (**1**) and its derivatives have been the object of considerable research effort.[1] Physical evidence for the parent hydrocarbon is, however, completely lacking despite the intense theoretical interest in this molecule.[2] We now wish to report the synthesis and characterization of this compound.

1

The starting material **2**[3] was prepared from allene and chlorocarbene (CH_2Cl_2, CH_3Li).[4] The bromide **3** is an equally attractive precursor, although purification of this compound is somewhat more tedious.[5]



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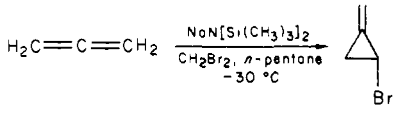
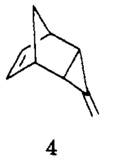


3

The synthesis of methylenecyclopropene can be effected under a variety of conditions. For example, the adduct **4**[1g] along with **5** and unchanged **2** could be isolated when **2** was added under vacuum (0.50 torr) to a solution of potassium *tert*-butoxide in tetrahydrofuran at -40 °C and the volatiles were collected in a liquid-nitrogen trap containing cyclopentadiene. *This result shows conclusively that methylenecyclopropene can be generated and transferred in vacuo and thus studies of its chemical and physical properties carried out.*



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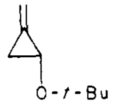


5

An important consideration in using this route is the choice of temperature. Below -40 °C methylenecyclopropene experiences addition of *tert*-butoxide yielding **5** faster than it can be removed from the reaction medium. Above -40 °C the solvent and precursor are, of course, too volatile for the reaction to be carried out in vacuo.

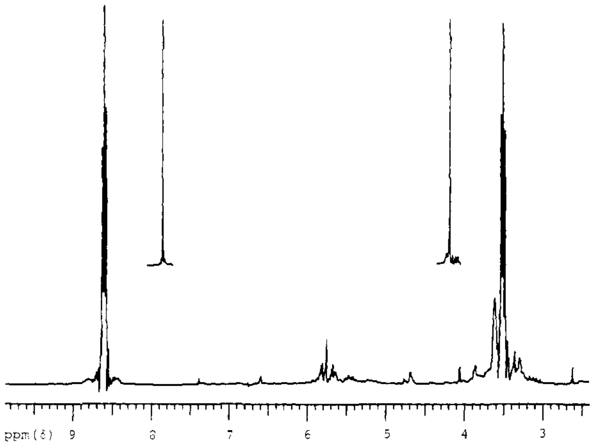


Figure 1. 90-MHz ^1H NMR spectrum and decoupled spectrum of methylenecyclopropene obtained by passing **2** over potassium *tert*-butoxide supported on Chromosorb W.

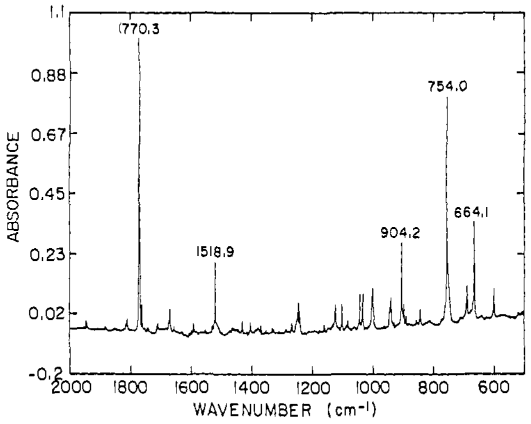
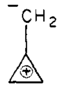


Figure 2. Infrared spectrum of methylenecyclopropene recorded at 15 K in an argon matrix.

When **2** was passed through a vertical 3.5-cm i.d. column packed with 4 cm of potassium *tert*-butoxide on Chromosorb W at 240 °C and 10 mtorr,[6] methylenecyclopropene nearly free of **5** and unreacted **2** could be collected in a liquid-nitrogen trap. This route can be used to generate 15–20 mg (30–40%) of the hydrocarbon. Solutions of methylenecyclopropene prepared in this way were stable at -98 °C for at least 24 h but decomposed above ~-75 °C.

The ^1H NMR spectrum, recorded at -98 °C, of **1** in tetrahydrofuran-d_8 (Figure 1) displayed two triplets ($J = 2.2$ Hz) at δ 3.47 (exocyclic protons) and 8.61 (ring protons). These chemical shifts suggest that **1a** contributes significantly to the resonance hybrid.



1a

This effect is also seen in the ^{13}C NMR spectrum where the exocyclic carbon appears at δ 59.57 ($^1J_{CH} = 161.5$ Hz) and the two equivalent ring carbons at δ 132.9 ($^1J_{CH} = 228.5$ Hz).

The infrared spectra of several substituted methylenecyclopropenes exhibit two distinctive bands which appear in the region

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[1] Review: (a) Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1975**, *57*, 1. For synthetic approaches to the parent hydrocarbon, see: (b) Shields, T. C.; Gardner, P. D. *J. Am. Chem. Soc.* **1967**, *89*, 5425. (c) Krull, I. S.; D'Angelo, P. F.; Arnold, D. R.; Hedaya, E.; Schissel, P. O. *Tetrahedron Lett.* **1971**, 771. (d) Chapman, O. L. *Pure Appl. Chem.* **1974**, *40*, 511. (e) Billups, W. E.; Blakeney, A. J.; Chamberlain, W. T. *J. Org. Chem.* **1976**, *41*, 3771. (f) Billups, W. E.; Blakeney, A. J.; Rao, N. A.; Buynak, J. D. *Tetrahedron* **1981**, *37*, 3215. (g) Weber, A.; Neuenschwander, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 774; *Angew. Chem.* **1981**, *93*, 788.

[2] For some recent references, see: (a) Dewar, M. J. S.; Kohn, M. C. *J. Am. Chem. Soc.* **1972**, *94*, 2699. (b) Gayoso, J.; Boucekkine, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1974**, *71*, 182. (c) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941. (d) Johnson, R. P.; Schmidt, M. W. *Ibid.* **1981**, *103*, 3244. (e) Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *Ibid.* **1981**, *103*, 5292. (f) Buemi, G.; Raudino, A.; Zuccarello, F. *THEOCHEM* **1981**, *1*, 285. (g) Rosenstock, H. M.; Dannacher, J.; Liebman, J. F. *Radiat. Phys. Chem.* **1982**, *20*, 7.

[3] Compound **2**, bp 69–71 °C, was produced in ~10% yield: NMR ($CDCl_3$) δ 0.70–1.90 (m, 2 H), 3.40–3.60 (m, 1 H), 5.56–5.64 (m, 1 H), 5.76–5.90 (m, 1 H); mass spectrum *m/e* calcd for C_4H_5Cl 88.0080, 90.0050, found 88.0078, 90.0051.

[4] Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1960**, *82*, 5723.

[5] Martel, B.; Hiriart, J. M. *Synthesis* **1972**, 201.

[6] Denis, J. M.; Niamayoua, R.; Vâta, M.; Lablache-Combier, A. *Tetrahedron Lett.* **1980**, *21*, 515. In this study two dry ice–acetone traps placed in series were used to collect any high-boiling impurities, e.g., *tert*-butyl alcohol, **5** or **2**. Methylenecyclopropene and a small amount of isobutylene which results from the dehydration *tert*-butyl alcohol were collected in a liquid-nitrogen trap.

0002-7863/84/1506-3698$01.50/0

1810–1880 cm^{-1} and 1510–1550 cm^{-1}. Although a detailed analysis has not yet been performed, it has been suggested that these absorptions originate from strong coupling of the double bonds. The infrared spectrum of methylenecyclopropene itself was obtained by slowly introducing the hydrocarbon and argon onto a polished copper surface cooled to 15 K with a closed-cycle helium refrigerator. The spectrum (Figure 2) was recorded on an IBM Model 98 FT IR spectrometer. Although several impurity peaks including those of isobutylene[6] could be subtracted, we are still unable to associate the weak absorptions with methylenecyclopropene. Concentration studies did, however, show that the five strongest peaks of the spectrum arise from methylenecyclopropene.[7] It is interesting that the high-energy transition of methylenecyclopropene is shifted to 1770.3 cm^{-1}, which is also consistent with the dipolar structure (enhanced single-bond character) **1a**.

The mass spectrum of methylenecyclopropene (20 eV) shows a parent molecular ion (also base peak) at *m/e* 52; high-resolution mass spectrum, *m/e* calculated for C_4H_4 52.0313, found 52.0312.

Finally, quantities of this heretofore inaccessible hydrocarbon are now available for additional studies of its properties, many of which have already been anticipated by theoreticians.[2] These studies will be reported later.

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation (Grant C-490) for support of this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also acknowledge many stimulating discussions with Professor S. Staley who has independently synthesized methylenecyclopropene.

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(7) We thank Drs. Robert Hauge, Zakya Kafafi, and Judy Chu for assistance in securing this spectrum.

Synthesis and Direct Observation of Methylenecyclopropene

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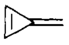
Received February 3, 1984
Revised Manuscript Received April 24, 1984

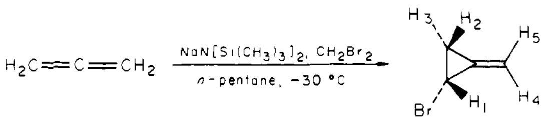
Methylenecyclopropene (**1**) occupies a central position in organic structural chemistry as the simplest member of a family of cross-conjugated nonalternant hydrocarbons known as the fulvenes.[1] Both the exceptional polarity of the π system expected from this structural arrangement (**1** ↔ **1a**) as well as the high strain imparted by the three-membered ring, which raises the energies of the σ orbitals and lowers those of the σ^* orbitals, are expected to have unusual chemical and spectroscopic consequences. We now report the synthesis and direct observation of this molecule, which had previously only been trapped in situ.[2]



1

1a

The immediate precursor for **1** was 2-bromomethylenecyclopropane (**2**), prepared by the addition of bromocarbene[3] to allene.



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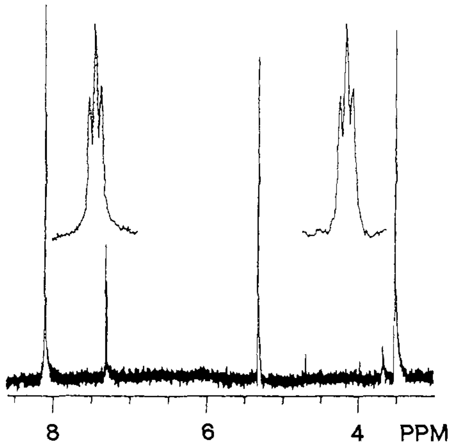


Figure 1. 360-MHz ^1H NMR spectrum of methylenecyclopropene in CD_2Cl_2 at −90 °C. The apparent triplets shown at the top are expansions of the peaks at δ 3.60 and 8.18. The peak at δ 5.41 is the solvent ($CHDCl_2$); the smaller signal at δ 7.4 is unidentified.

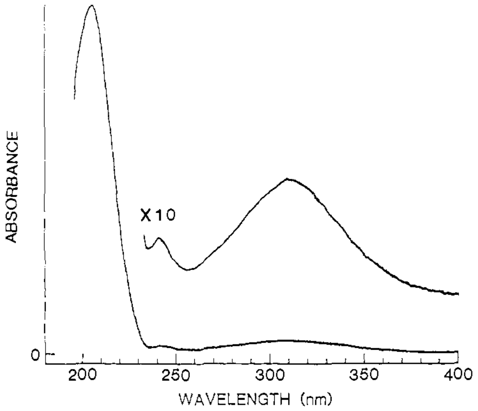
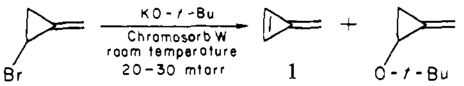


Figure 2. Ultraviolet spectrum of methylenecyclopropene in *n*-pentane at −78 °C.

The 360-MHz NMR of **2** (purified by gas chromatography on a 10% Carbowax 20M on Chromosorb W column at 90 °C) in $CDCl_3$ was reproduced by computer synthesis with the following parameters: δ 3.51 (H_1), 1.84 (H_2), 1.49 (H_3), 5.81 (H_4), 5.64 (H_5), $J_{12} = 8.02$, $J_{13} = 3.81$, $J_{14} = 0.90$, $J_{15} = 1.56$, $J_{23} = 10.85$, $J_{24} = J_{34} = 2.86$, $J_{25} = J_{35} = 2.14$, $J_{45} < 0.6$ Hz.

When **2** was passed through a horizontal half-filled 1.0 cm i.d. × 35 cm column of potassium *tert*-butoxide on Chromosorb W at room temperature and 20–30 mtorr,[4] unchanged **2** and 2-*tert*-butyoxymethylenecyclopropane (**3**)[2b] were trapped at −78 °C whereas methylenecyclopropene (**1**) was trapped as a white solid in a second trap cooled with liquid nitrogen. It has proven difficult to perform this reaction so as to produce more than several milligrams of **1**. Treatment of **2**-*2-d* under these conditions afforded **1**, which displayed a ^1H NMR spectrum (see below) that was identical with that of **1** generated from unlabeled **2**. This is consistent with H/D exchange occurring at the ring carbons in **1** under the conditions of this reaction.



2 1 3

The 360-MHz ^1H NMR spectrum of **1** in CD_2Cl_2 at −90 °C (Figure 1) displayed two equivalent apparent triplets (line separation = 2.2 Hz) at δ 3.60 (exocyclic protons) and 8.18 (ring protons). It is clear that this spectrum displays evidence for a significant contribution from resonance form **1a**. We believe that hydrogen bonding is also important, as evidenced by an interesting

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(1) Review: Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1975**, *57*, 1.

(2) (a) Weber, A.; Neuenschwander, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 774. (b) Billups, W. E.; Blakeney, A. J.; Rao, N. A.; Buynak, J. D. *Tetrahedron* **1981**, *37*, 3215.

(3) Martel, B.; Hiriart, J. M. *Synthesis* **1972**, *201*.

(4) Denis, J. M.; Niamayoua, R.; Vâta, M.; Lablache-Combier, A. *Tetrahedron Lett.* **1980**, *21*, 515.

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