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The cycloaddition of cyclopropenes to enones

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Abstract

A number of 1- and 1,2-disubstituted cyclopropenes undergo [4+2]-cycloaddition to methyl vinyl ketone or acrolein at ambient temperature to produce 2-oxabicyclo[4.1.0]hept-3-enes. When 1-phenyl-2-trimethylsilyl-cyclopropene is treated with 0.4 mol. equiv. of *m*-chloroperbenzoic acid, the derived ring-opened enone undergoes [4+2]-cycloaddition to the remaining starting material at ambient temperature. © 2000 Elsevier Science Ltd. All rights reserved.

It was reported recently that 1-phenyl-2-trimethylsilylcyclopropene **1** is converted into the crystalline tetramer **2** in remarkably high yield (85%) when allowed to stand at ambient temperature under vacuum for three weeks.¹ Some of us observed that when **1** was kept at 5°C for an extended period without taking precautions to exclude air, a different crystalline material was obtained.² The formation of this compound appeared to occur most rapidly when **1** was purified by chromatography over silica and then allowed to stand alone at 20°C, when crystals had begun to be deposited after 18 h; after 7 days NMR of the crude products showed the almost complete reaction of the cyclopropene and the formation of a single product. The same product was formed more slowly when **1** was kept in D-chloroform at 20°C, about 10% reaction occurring in 7 days.[†] The product gave a microanalysis consistent with a structure formed from two molecules of cyclopropene and one oxygen atom; its NMR spectrum included two trimethylsilyl signals at δ -0.2 and -0.3, two cyclopropane hydrogens as an AB pattern (J 5.2 Hz) at 1.31 and 1.40 and a second AB system (J 17.0 Hz) at 2.31 and 2.74, together with ten phenyl hydrogens. Its structure was confirmed as being **3** by means of a single crystal X-ray study,³ the result of which is shown in Fig. 1.

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† No tetramer **2** was detected by NMR under either of these conditions.

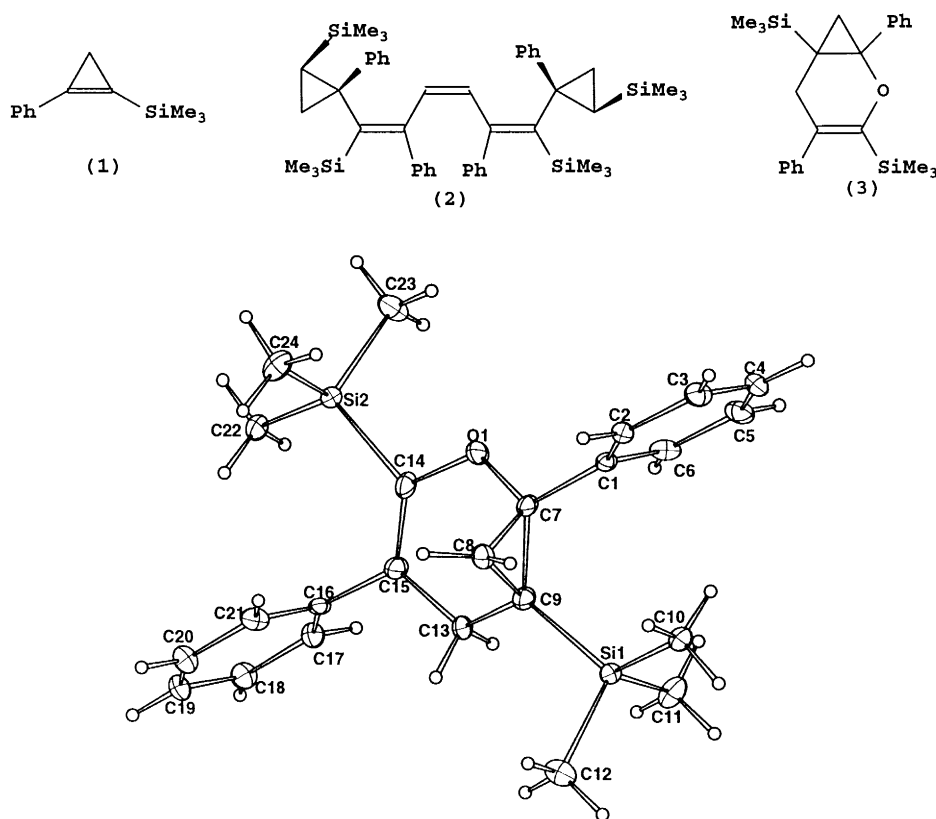
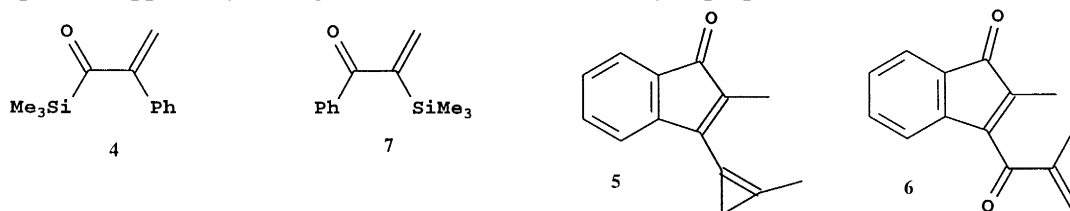
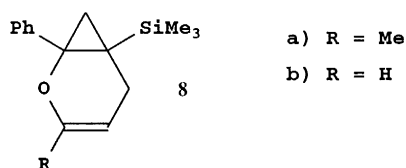


Fig. 1. Single crystal X-ray structure determination of **3**

This formation of compound **3** appeared to be explained by the [4+2]-cycloaddition of the cyclopropene **1** and the enone **4**, to produce a six-membered heterocycle in the boat conformation with atoms C7 and C9 in *RS* and *SR* configurations, respectively. The ring-opening of cyclopropenes to give related enones on reaction with oxygen is known; thus the indenone **5** is converted into compound **6** with the more electron withdrawing group on the 1-position of the enone.⁴ Presumably the cyclopropene **1** must absorb enough oxygen during work-up or chromatography, or in storage, to be oxidised; nonetheless, none of the dimer was observed when oxygen was bubbled through a solution of **1** in D-chloroform for 18 h. However, in support of the above mechanism, the oxidation of **1** by 1 mol. equiv. of *m*-chloroperbenzoic acid⁵ for 10 min at -40°C led to a mixture of **4** together with a minor isomer **7** (70%; ratio 1.7:1);⁶ when the oxidation of **1** was carried out with 0.4 mol. equiv. of the peracid, the NMR spectrum of the product initially showed the presence of **4** and **7** together with unreacted **1**; after standing for 18 h at 20°C , the spectrum showed the signals for compound **3**, and **7** remained unreacted; the major isomer **4** was no longer present, apparently having reacted with the excess of cyclopropene.



There are many examples of cycloaddition of cyclopropenes to dienes, in many cases even at ambient temperature or below.⁷ There are also many examples of the addition of alkenes to enones and enals; with simple alkenes these usually occur at relatively high temperature, although in some cases, and particularly in the presence of a Lewis acid catalyst they occur at ambient temperature and below.⁸ However, the formation of **3** as described above would represent the first example of the [4+2]-addition of a cyclopropene to an enone.⁷ Although there are a number of examples of 2-oxabicyclo[4.1.0]hept-3-enes,⁹ most of these are further functionalised with a ketone at C-5; others are derived from 4*H*-pyrans¹⁰ or 4*H*-pyran-4-ones¹¹ by cyclopropanation. The cyclopropene **1** was therefore treated with an excess of methyl vinyl ketone in chloroform for 4 h at 20°C; the adduct **8a** was isolated in 91% crude yield (87% after rapid column chromatography);¹² a similar product **8b** was isolated when **1** was treated with acrolein (86%). In contrast, when **1** was allowed to stand with *trans*-but-2-en-1-al or 4-methylpent-3-en-2-one, no products of [4+2]-cycloaddition were observed and instead the cyclopropene was slowly oxidised to give **3**.



In order to establish whether this reaction could be applied more widely, a number of other cyclopropenes¹³ were treated with methyl vinyl ketone or acrolein at 20°C; the results are presented in Table 1.¹⁴

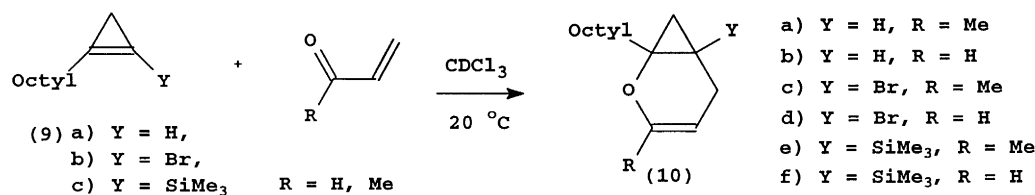


Table 1
Reactions of cyclopropenes with enones to give 2-oxabicyclo[4.1.0]hept-3-enes at 20°C

Cyclopropene	Enone	Reaction Time	Product	Yield (after chromatography)
(1)	Methyl vinyl ketone	4	(8a)	86
	Acrolein	4	(8b)	86
	Crotonaldehyde	18		0
	Mesityl oxide	18		0
(9a)	Methyl vinyl ketone	18	(10a)	89
	Acrolein	4	(10b)	92
(9b)	Methyl vinyl ketone	18		0
(9c)	Methyl vinyl ketone	4	(10e)	87
	Acrolein	4	(10f)	86
	Crotonaldehyde	18		0

Under these conditions, no reaction was observed with either mesityl oxide or *trans*-crotonaldehyde.

2-Bromo-1-octylcyclopropene did not react with any of the enones, nor did 3-methyl-3-phenylcyclopropene. In this latter case the steric hindrance caused by the 3-substituents to cycloaddition to the cyclopropene π -bond has been noted on a number of occasions.⁷

The use of an appropriate catalyst and of high pressure to promote the [4+2]-cycloaddition with less reactive enones and cyclopropenes is being examined.

References

1. Lee, G.-A.; Chang, C.-Y. *Tetrahedron Lett.* **1998**, *39*, 3013.
2. Hussain, H. H.; Alhourani, B. J.; Al Alhabashna, M. Y. Unpublished results.
3. Crystal data for **3**: Formula C₁₂H₁₆O_{0.5}Si, MW=196.34, triclinic, space group P1 (no.1), $a=6.038$ (2), $b=9.898$ (2), $c=10.640$ (2) Å, $\alpha=108.49$ (3), $\beta=103.01$ (3), $\gamma=103.23$ (3)°, $U=555.7$ (2) Å³, $Z=2$, $D_c=1.173$ Mg/m³, $\mu(\text{Mo-K}\alpha)=0.171$ mm⁻¹, $F(000)=212$, crystal size=0.35×0.125×0.125 mm, T=150(2) K. Intensity data were collected on a Nonius KappaCCD area detector diffractometer. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares (non-H anisotropic, H-atoms isotropic) to final $R_1=0.0397$ and $wR_2=0.1253$ for 3999 unique data and 251 parameters. Full details have been deposited with the Cambridge Crystallographic Data Centre (CCDC141103).
4. Padwa, A.; Austin, D. J.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 4103.
5. Baird, M. S.; Hussain, H. H. *Tetrahedron Lett.* **1986**, *27*, 5143.
6. Further oxidation of the mixture of **4** and **7** with MCPBA for 18 h at 20°C led to the epoxidation of the alkene bond of **4**, but left **7** unchanged.
7. For a review, see: Baird, M. S. *Cyclopropanes from Cyclopropenes, in Three and Four Membered Carbocyclic Compounds*; de Meijere, A., Ed.; Houben Weyl E17a, 1996; p. 114.
8. See for example: Yamauchi, M.; Katayama, S.; Baba, O.; Watanabe, T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3041; Takaki, K.; Okada, M.; Negoro, K. *J. Org. Chem.* **1982**, *47*, 1200; Weichert, A.; Hoffmann, H. M. R. *J. Org. Chem.* **1991**, *56*, 4098; Wada, E.; Kanemasa, S.; Tsuge, O. *Chem. Lett.* **1989**, 675; Conrads, M.; Mattay, J. *Chem. Ber.* **1991**, *124*, 1425; Bakker, C. G.; Scheeren, J. W.; Nivard, R. J. F. *Rec. Trav. Chim. Pays Bas* **1981**, *100*, 13; Bridges, A. J.; Fisher, J. W. *J. Org. Chem.* **1984**, *49*, 2954; Snider, B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 3685; Jao, E.; Slifer, P. B.; Lalancette, R.; Hall, S. S. *J. Org. Chem.* **1996**, *61*, 2865; Seebach, D.; Stucky, G.; Pfammatter, E. *Chem. Ber.* **1989**, *122*, 2377; Takaki, K.; Yamada, M.; Negoro, K. *J. Org. Chem.* **1982**, *47*, 5246; Weinstein, B.; Lin, L.-C. C.; Fowler, F. W.; *J. Org. Chem.* **1980**, *45*, 1657; Alder, K.; Ruden, E. *Chem. Ber.* **1941**, *74*, 920; Alder, K.; Offermans, H.; Ruder, E. *Chem. Ber.* **1941**, *74*, 905; Smith, G. W.; Norden, D. G.; Ballard, S. A. *J. Am. Chem. Soc.* **1951**, *73*, 5267, 5270.
9. Dolejs, L.; Mironov, A.; Sorm, F. *Coll. Czech. Chem. Commun.* **1961**, 1015.
10. See for example: Dimroth, W. *Chem. Ber.* **1966**, *99*, 2351, 2357, 2358; Bischofberger, N.; Frei, B.; Wirz, J. *Helv. Chim. Acta* **1983**, *66*, 2489; Frei, B.; Wolf, H. R.; Jeger, O. *Helv. Chim. Acta* **1979**, *62*, 1645.
11. Yamaoka, H.; Mishima, I.; Miyamoto, M.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 469; Yamaoka, H.; Mishima, I.; Hanafusa, T.; *Chem. Lett.* **1980**, 411.
12. A minor product observed in the NMR spectrum of the crude product was provisionally identified as the regioisomeric adduct. Compound **8a** showed δ_{H} 7.3–7.7 (5H, m), 4.43 (1H, m), 2.43 (1H, d (J 14.7 Hz) of narrow m), 2.19 (1H, d (J 14.7 Hz) of narrow m), 1.72 (3H, narrow m), 1.34 (1H, d, J 5.3 Hz), 1.30 (1H, br.d, J 5.3 Hz), –0.31 (9H, s); irradiation of the signal at 1.72 reduced the signal at 4.43 to a dd (J 2.8, 4.6 Hz) and those at 2.43 and 2.19 each to a dd (J 16.8, 2.8 and 16.8, 4.6 respectively); δ_{C} 147.0, 140.3, 129.8, 128.1, 92.2, 68.2, 23.2, 20.4, 15.3, 13.3, –3.0.
13. Baird, M. S.; Hussain, H. H.; Nethercott, W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1845; Baird, M. S.; Dale, C. M.; Al Dulayymi, J. R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1373.
14. The regiochemistry of **10a** and **10b** was confirmed by the presence an additional couplings in the ¹H NMR signal for one of the hydrogens on C-5 to the cyclopropane hydrogen on C-6. The regiochemistry of **10e** and **10f** was assigned by analogy to **8**.