# Highly Functionalised Methylenecyclopropanes from Cyclopropenes

Mark S. Baird,* M. Fiona Shortt, Helmi H. Hussain and Juma'a R. Al Dulayymi
*Department of Chemistry, University of Wales, Bangor, Gwynedd, UK LL57 2UW*

Reaction of a number of halogenocyclopropenes with benzenesulfenyl chloride leads to 2-bromo-2-phenylthio-1-methylenecyclopropanes

Although the chemistry of simple cyclopropenes has been well studied, that of those substituted with electron-releasing groups at C-1 and C-2 has received much less attention.[1] There are reports of the preparation of 1-alkoxy-2-phenyl-[2] and 1-trialkylsilyloxy-2-trimethylsilyl-cyclopropenes.[3] Although tetra-substituted 1-alkylthio- and 1-dialkylamino-cyclopropenes have been produced by trapping of cyclopropenium ions by nucleophiles,[4] the preparation and chemistry of less substituted examples is reported infrequently, *e.g.*, 1-methylthio-[5] and 1-ethylthio-3,3-dimethylcyclopropene.[6] 1-Alkylthiocyclopropenes, *e.g.* **1a**, have been obtained by the trapping of a 1-lithiocyclopropene by methyl methanethiolsulfonate.[7]

Me Me

a X = MeS, Y = SiMe₃
b X = Me, Y = SMe
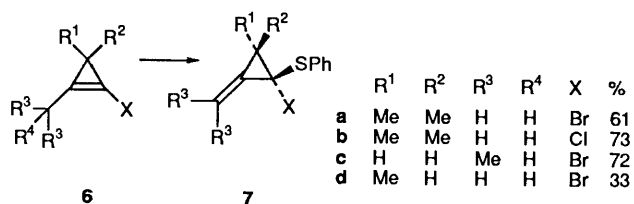c X = Me, Y = Li

1
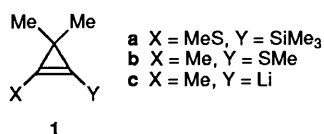
However, in our hands this reaction required temperatures around ambient to proceed—conditions under which the products were not always stable—and separation of the products was not always easy. Thus **1b**† (prepared from **1c**‡ and MeSSO₂Me in 15 min at 20 °C) was very unstable, so that if the reaction was allowed to proceed for 18 h at 20 °C before work-up the product was the open-chain compound, 1-methyl-thio-2,3-dimethylbutadiene.§ In order to develop an alternative approach, we have examined the addition of benzenesulfenyl chloride to a 1-halogenocyclopropene,‡ and the subsequent dehalogenation to the 1-phenylthiocyclopropene. In the case of 1-bromo-2-methylcyclopropene¶ addition of benzenesulfenyl chloride did lead to the expected cyclopropane **2** (63%);‖ the stereochemistry of the addition was assigned as *trans*- by analogy with the addition of benzenesulfenyl chloride to alkylcyclopropenes, which has been explained in terms of the formation and subsequent ring-opening of an episulfonium ion such as **3**.[8]

The cyclopropane **2** was dehalogenated by reaction with meth-yllithium in diethyl ether, and the derived cyclopropene **4** was
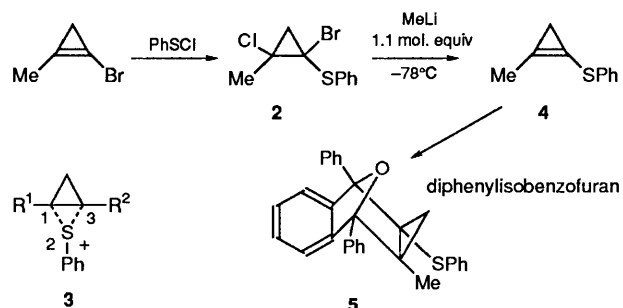
characterised as its cycloadduct **5** with diphenylisobenzofuran.** In contrast, however, addition of benzenesulfenyl chloride to either **6a** or **6b** led to methylenecyclopropanes **7a, b** (61, 73%).

	R¹	R²	R³	R⁴	X	%
a	Me	Me	H	H	Br	61
b	Me	Me	H	H	Cl	73
c	H	H	Me	H	Br	72
d	Me	H	H	H	Br	33

6 **7**

The products were rather unstable to chromatography on silica gel, elution with light petroleum and diethyl ether leading to 2-halogeno-3-phenylthiobutadienes, *e.g.* **9**, in a reaction which may formally involve cyclopropyl–allyl ring-opening with loss of halide ion to produce a 1-methylene-substituted allyl cation **8**, which is trapped by halide ion.

7a **8** **9**
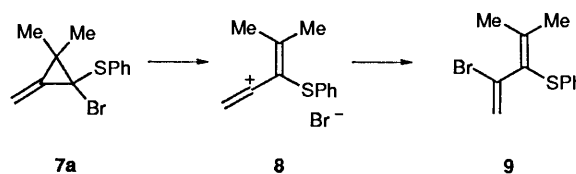
In the same way, the addition of benzenesulfenyl chloride to cyclopropenes **6c, d** led to the corresponding methylenecyclopropane **7c, d**; in the latter case a single epimer at C-3 was obtained at short reaction times, but, if the reactions were prolonged, a minor isomer (*ca.* 1:12) was also observed. The major isomer was assigned as having the 3-hydrogen and the 2-bromine *trans*- as the signal for this hydrogen occurred at higher field in the ¹H NMR spectrum.[10] The formation of methylenecyclopropanes in these reactions may occur by deprotonation of the 3-alkyl group in the intermediate episulfonium ions **3** (R¹ = halogen), in which attack on C-1 or C-3 is hindered by the presence of the substituents on C-4 or

---

† This showed δ_H 1.15 (6 H, s), 1.9 (3 H, s) and 2.3 (3 H, s).

‡ 1-Bromo- and 1-lithio-cyclopropenes were prepared from the corresponding 1,1,2-tribromo- or 1,1-dibromo-2-chlorocyclopropane by reaction with 1.1 or 2.1 mol equiv. of methyllithium, respectively (M. S. Baird and W. Nethercott, *Tetrahedron Lett.*, 1983, 605; M. S. Baird, H. H. Hussain and W. Nethercott, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1845).

§ The crude yield was 86%, but column chromatography led to extensive decomposition. The diene was characterised by addition to tetracyanoethene (37% from 1,1,2-tribromo-2,3,3-trimethylcyclopropane, the precursor of 1-lithio-2,3,3-trimethylcyclopropene). It may arise by ring-opening to a 1-(methylthio)vinylcarbene, followed by a 1,4-hydrogen shift. Similar ring-opening of cyclopropene 1-sulfoxides has been reported to occur at ambient temperature (M. Franck-Neumann and J. J. Lohmann, *Angew. Chem., Int. Edn. Engl.*, 1976, **16**, 323.
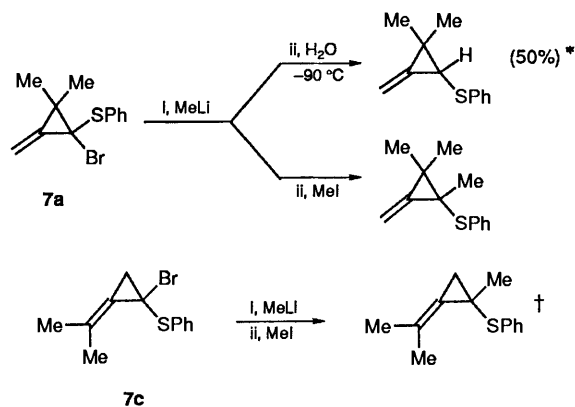
¶ Prepared by reaction of 1,1,2-tribromo-2-methylcyclopropane with 1.1 mol equiv. of methyllithium in diethyl ether, as per references given in footnote ‡.

‖ Compound **2**, m.p. 65–68 °C; showed δ_H 7.1–7.5 (5 H, complex), 1.9 (1 H, d, *J* 7.5), 1.89 (3 H, s) and 1.7 (1 H, d, *J* 7.5); δ_C 150.3, 129.2, 128.0, 126.7, 50.9, 43.7, 34.6 and 25.0.

** The crude cyclopropene was set aside with diphenylisobenzofuran for 18 h at 20 °C in diethyl ether. The adduct showed δ_H 6.8–8.0 (19 H, complex multiplet), 2.77 (1 H, d, *J* 5.4), 1.25 (3 H, s) and 1.16 (1 H, d, *J* 5.4); δ_C included 89.6, 88.6, 45.8, 41.0, 28.9 and 14.1. The stereochemistry is assigned by analogy with other cycloadducts of cyclopropenes.[9]

branching at the C-3 alkyl group. It is interesting to note that, although 1 mol equiv. of HCl is formally liberated in these reactions no products of addition of this to the cyclopropene or the methylenecyclopropane were isolated. The *tert*-butyl derivative 6 ($R^1 = R^2 = H$, $R^3 = R^4 = Me$, X = Br), which has no hydrogen adjacent to the ring, gave a complex mixture of products.

The 2-bromo-1-methylenecyclopropanes could be lithiated by reaction with methyllithium at -90 °C, and trapped with electrophiles although the reaction was not successful with bulky species such as trimethylsilyl chloride. Since 1-halogeno-

cyclopropenes are readily available,‡ this may provide a simple and flexible route to a wide range of methylenecyclopropanes. 2-Phenylthio-1-methylenecyclopropane has been obtained previously by dehydrohalogenation of 1-bromo-1-methyl-2-phenylthiocyclopropane, and has been oxidised to the sulfoxide and sulfone;[11] it has also been produced by lithiation of methylenecyclopropane at the ring methylene group and trapping by diphenyl disulfide.[12]

The addition of benzenesulfenyl chloride to 1,2-dichloro-3,3-dimethylcyclopropene 10 followed a rather different course, leading to the diene 11[13] (43%) of unknown stereochemistry, which was characterised by cycloaddition to tetracyanoethene.[14] The origin of the diene 11 is not certain, but may involve either formation of the appropriate episulfonium ion 3 followed by rearrangement with proton elimination, or the known ring-opening of 10 to the vinylcarbene 12,[15] trapping of this by attack on the sulfur of benzenesulfenyl chloride, and then elimination of HCl.
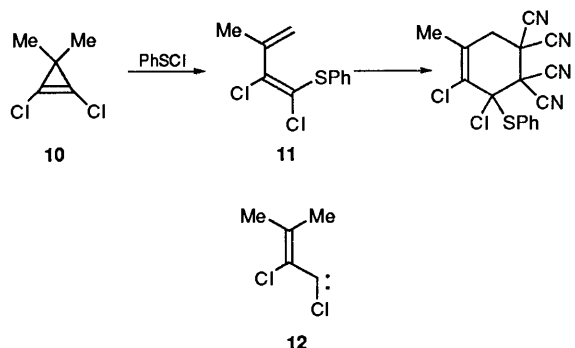
Experimental

Preparation of 2-Bromo-2-phenylthio-3,3-dimethyl-1-methylenecyclopropane.—1,1,2-Tribromo-2,3,3-trimethylcyclopro-

pane (5.0 g, 0.016 mol) was stirred in dry diethyl ether (20 cm³) under argon at -78 °C and methyllithium (11.73 cm³, 1.1 equiv.) was added dropwise to it. The flask was allowed to warm to room temperature, when the solution became clear. The solution was cooled again to -78 °C and water was added to it. The water was frozen out (-60 °C). The ethereal solution was cooled to -78 °C and benzenesulfenyl chloride (2.30 g, 0.016 mol) was added dropwise (under argon). The solution was allowed to reach room temperature. After 25 min, magnesium sulfate was added to the ethereal solution and then was filtered off; the diethyl ether was then removed under reduced pressure to leave a yellow oil. The product, purified by placing it under very high vacuum at 45 °C, was purple–brown (2.6 g, 61%) (Found: C, 53.8; H, 4.8. $C_{12}H_{13}BrS$ requires C, 53.73; H, 4.89%); v_{max}(NaCl)/cm^{-1} 3058m, 2992m, 2922m, 2861m, 1583m, 1479s, 1439s and 1366m; δ_H 1.45 (3 H, s, Me), 1.55 (3 H, s, Me), 5.5 (1 H, s, H), 5.7 (1 H, s, H) and 7.3 (5 H, m, Ph); δ_C 22.23 (CH_3), 26.48 (CH_3), 39.6, 44.1, 106.41, 126.45, 128.26, 128.86, 129.38 and 136.53.

References

1 M. S. Baird, *Functionalised Cyclopropenes as Synthetic Intermediates*, Topics in Current Chemistry, 1988, **144**, 137; B. Halton and M. G. Banwell, *Cyclopropenes, in 'The Chemistry of Functional Groups'*, Cyclopropanes, vol. 2, 1224, ed. Z. Rappoport, Wiley, New York.

2 I. Crossland, *Acta Chem. Scand.*, 1987, **41**, 310; I. Sotofte and I. Crossland, *Acta Chem. Scand.*, 1989, **43**, 168.

3 I. Ryu, Y. Hayama, A. Hirai, N. Sonoda, A. Orita, K. Ohe and S. Murai, *J. Am. Chem. Soc.*, 1990, **112**, 7061.

4 H. Yoshida, M. Kato, T. Ogata and K. Matsumoto, *J. Org. Chem.*, 1985, **50**, 1145; Y. Yoshida, H. Sano, T. Ogata and K. Matsumoto, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 4341; Y. Yoshida, H. Kinoshito, T. Kato, N. Kanehira, T. Ogata and K. Matsumoto, *Synthesis*, 1987, 393; H. Yoshida, Y. Takahashi, H. Kinoshito, S. Ukishima, T. Ogata and K. Matsumoto, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 3565; H. Yoshida, H. Sano, M. Kato, T. Ogata and K. Matsumoto, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2833.

5 T. C. Shields, B. A. Loving and P. D. Gardner, *J. Chem. Soc., Chem. Commun.*, 1967, 556.

6 M. Franck-Neumann and J. J. Lohmann, *Tetrahedron Lett.*, 1978, 3729; 1979, 2397.

7 M. A. Kirms, H. Primke, M. Stohlmeier and A. de Meijere, *Rec. Trav. Chim. Pays-Bas*, 1986, **105**, 462.

8 V. R. Kartashov, N. F. Akimkina and E. V. Skorobogatova, *Zh. Org. Khim.*, 1979, **15**, 753; V. R. Kartashov, N. F. Akimkina and E. V. Skorobogatova, *Zh. Org. Khim.*, 1980, **16**, 889; V. R. Kartashov, N. F. Akimkina and E. V. Skorobogatova, *Zh. Org. Khim.*, 1982, **18**, 38; V. R. Kartashov, N. F. Akimkina, E. V. Skorobogatova and E. P. Trub, *Kinet. Katal.*, 1980, **21**, 1330; E. V. Skorobogatova, N. F. Akimkina and V. R. Kartashov, *Zh. Org. Khim.*, 1979, **15**, 753.

9 M. S. Baird, in Cyclopropanes, Houben-Weyl, in press; Y. Apeliog, *Tetrahedron Lett.*, 1987, 5917; P. Mueller, G. Bernardinelli, J. Pfyffer, D. Rodriguez and J.-P. Schaller, *Helv. Chim. Acta*, 1988, **71**, 544.

10 See P. Weyerstahl, *Dihalocyclopropanes, in 'The Chemistry of the Carbon Halogen Bond'*, Suppl. D, eds. S. Patai and Z. Rappoport, Suppl. D, Wiley, New York.

11 A. Weber and M. Neuenschwander, *Angew. Chem., Int. End. Engl.*, 1981, **20**, 774; A. Weber, G. Sabbioni, R. Galli, U. Stampfli and M. Neuenschwander, *Helv. Chim. Acta*, 1988, **71**, 2026; A. Weber, U. Stampfli and M. Neuenschwander, *Helv. Chim. Acta*, 1989, **72**, 29.

12 M. Stepp, Dissertation, Universitat Kaiserslautern, 1989.

13 Compound 10 showed δ_H 2.0 (3 H, s), 5.25 (1 H, br s), 5.30 (1 H, br s), 7.2–7.4 (5 H, m).

14 Compound 11 showed δ_H 2.15 (3 H, s), 3.30 (1 H, d, *J* 18.5), 3.47 (1 H, d, *J* 18.5), 7.1–8.0 (5 H, complex m).

15 See *e.g.*, M. S. Baird and H. H. Hussain, *Tetrahedron*, 1989, **45**, 6221.

---

* This showed δ_H 1.26 (3 H, s), 1.39 (3 H, s), 2.67 (1 H, t, *J ca.* 2), 5.48 (2 H, br d) and 7.29 (5 H, complex); δ_C 19.0, 24.3, 25.0, 27.7, 104.3, 125.1, 126.3, 128.6, 138.3 and 147.4.

† This showed δ_H 1.45 (1 H, dm, *J ca.* 8), 1.63 (1 H, dm, *J ca.* 8), 1.85 (6 H, br s), 1.55 (3 H, s) and 7.2–7.6 (5 H, m).

‡ See footnote ‡ on preceding page.