Battered benzene and twisted ethene

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Abstract - Strained compounds, besides providing valuable information
about the structure of 'normal' compounds, are of significance as
materials for the discovery of new synthetic methods and procedures
(ref. 1). We have been interested for some time in the preparation of
benzenoid systems strained by in-plane distortions (ref. 2) and have
shown that such compounds have unusual, but predictable, chemistry
(refs. 3,4). These compounds, cyclopropabenzocyclobutenes and related
systems, were initially prepared to determine whethr bond delocalization
towards one cyclohexatriene structure might be observed, the modern
interpretation of the Mills-Nixon effect (ref. 5), but the physical
properties of the compounds indicated that they were still benzenoid in
character. The lack of bond alternation has also been observed in
annelated 15,16-dimethyldihydropyrenes (ref. 6), but bond alternation
is observed in extended biphenylenes (ref. 7). No systems have so far
been reported in which benzene is strained by both in-plane and out-of-
plane distortions and such systems, besides being intrinsically
structurally interesting, may have a rich and distinctive chemistry.
This paper describes our present approach to such systems and also the
application of the incremental strain approach to the synthesis of
highly hindered alkenes (ref. 8).

CYCLOPROPACYCLOPHANES

Our proposed synthetic route to these systems is shown in Scheme 1. A suitably substituted
cyclopropene was to be the dienophile component in a Diels-Alder reaction with a cyclic
1,3-diene. The resulting adduct would then be converted to the cyclopropacyclophane by
elimination, preferably under the mildest conditions possible and certainly excluding
protic or Lewis acids. Silylated derivatives seemed most attractive since these could be
removed by fluoride under mild conditions.

Scheme 1
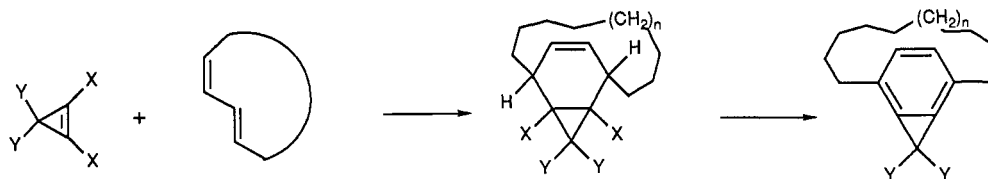
Silylcyclopropenes

A number of trimethylsilylcyclopropenes are known (ref. 9), usually prepared by
trimethylation of a preformed cyclopropane or cyclopropene. We examined carbene additions
to trimethylsilylacetylenes and also the route from halocyclopropanes. Treatment of
iodomethylmercuric iodide and diphenylmercury with bis(trimethylsilyl)acetylene gave
1,2-bis(trimethylsilyl)cyclopropene in low yield as a labile substance. Trapping with
1,3-diphenylisobenzofuran gave the adduct in 35% yield based on the starting material
(ref. 10). Treatment of bis(trimethylsilyl)acetylene with chlorotrimethylsilane in the

presence of lithium 2,2,6,6-tetramethylpiperidine gave 1,2,3-tris(trimethyl)cyclopropene, again in low yield but more stable than the 1,2-derivative. 3,3-Dibromo-1,2-bis-(trimethylsilyl)cyclopropene was prepared in 40% yield by treatment of bis(trimethylsilyl)-acetylene with phenyl(tribromomethyl)mercury in benzene at 80 °C. The dichloro analogue could not be prepared by this method and reaction with sodium trichloroacetate gave only a cyclobutenone derivative (Scheme 2).

Scheme 2
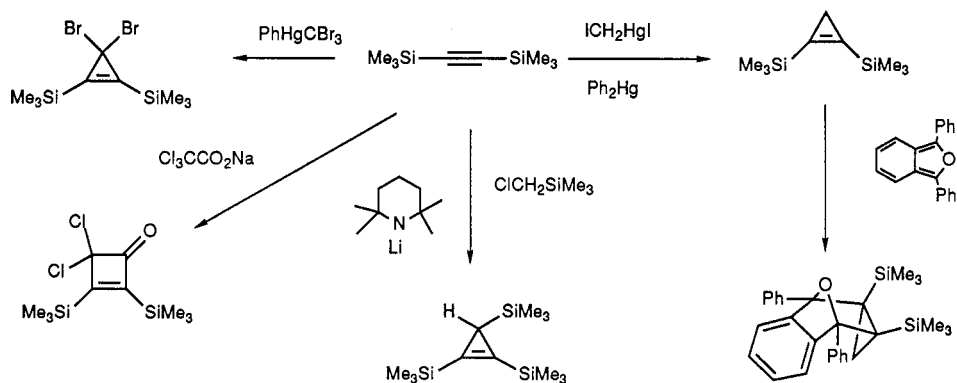
1-Bromo-2-trimethylsilylcyclopropene was prepared by modification of the reported method. Treatment of 1,1,2-tribromo-2-trimethylsilylcyclopropane with butyllithium at -78 °C for 2 min gave the cyclopropene in 13% yield (Scheme 3). The corresponding 1-chloro derivative could be prepared in an analogous manner. 3,3-Dimethyl-1-trimethylsilylcyclopropene was prepared from 3,3-dimethyl-1,1,2-tribromocyclopropane by treatment with butyllithium followed by trimethylchlorosilane. The cyclopropenes in Scheme 3 had been prepared previously by other methods and our compounds were identical in all respects with the reported data.

Scheme 3
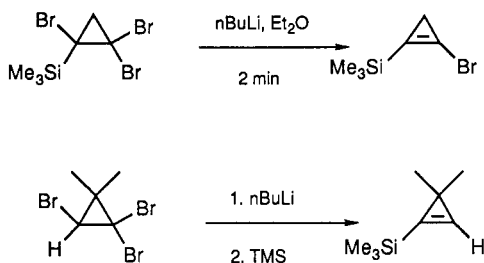
The chemistry of these trimethylsilylcyclopropenes was investigated: dimerisation of 1-chloro-2-trimethylsilylcyclopropene was effected, although in very poor yield, as was dimerisation of 3,3-dimethyl-1-trimethylsilylcyclopropene in 57% yield, somewhat higher than that previously reported (Scheme 4) (ref. 11). 1,2-Bis(trimethylsilyl)cyclopropene dimerized through an ene reaction.

Diels-Alder reactions of cyclopropenes and cyclic dienes

Diels-Alder reactions of these trimethylcyclopropenes with dienes were disappointing. Whereas 1,2-bis(trimethylsilyl)cyclopropene reacted with 1,3-diphenylisobenzofuran (see above), neither 1,2,3-tris(trimethylsilyl)cyclopropene or 3,3-dibromo-1,2-bis-(trimethylsilyl)cyclopropene reacted, even at elevated temperatures. Despite these rather discouraging findings, 3,3-dibromo-1,2-bis(trimethylsilyl)cyclopropene was treated with E,Z-dodeca-1,3-diene at 100 °C when the desired adduct was obtained in 10% yield, together with unreacted diene (Scheme 5). The ^{1}H NMR spectrum was similar in comparable respects to the in-out adducts of the diene prepared by Gassman and his co-workers (ref. 12). We

Scheme 4
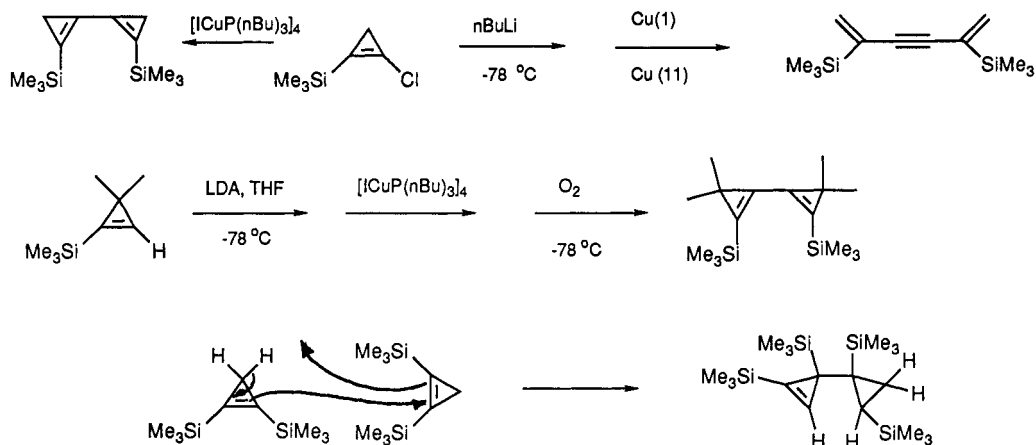
were not able to obtain adducts with the other trimethylsilylcyclopropenes so we examined the reaction of the diene with 1,2-dibromocyclopropene, generated from 1,1,2-tribromo-2-trimethylsilylcyclopropene and tetrabutylammonium fluoride, at low temperature. The desired adduct was obtained in 26% yield, and a similar adduct was obtained in 44% yield with E,Z-undeca-1,3-diene. The ^{1}H NMR spectrum of both of these adducts again correlated well with the relevant absorptions reported by Gassman (ref. 12).

Some preliminary experiments were carried out on the elimination of HBr from these latter adducts in order to give the desired cyclopropacyclophanes, but no material was identified. These compounds do have considerable promise as precursors to cyclopropacyclophanes and the method could readily be adapted to prepare cyclophanes with other aromatic rings or even two strained rings.
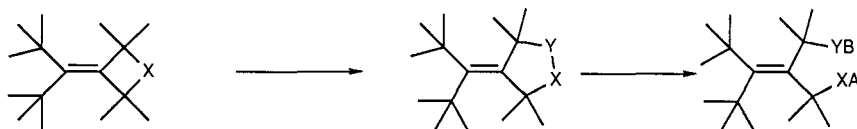
Scheme 5

n = 0, 1   n = 0, 1
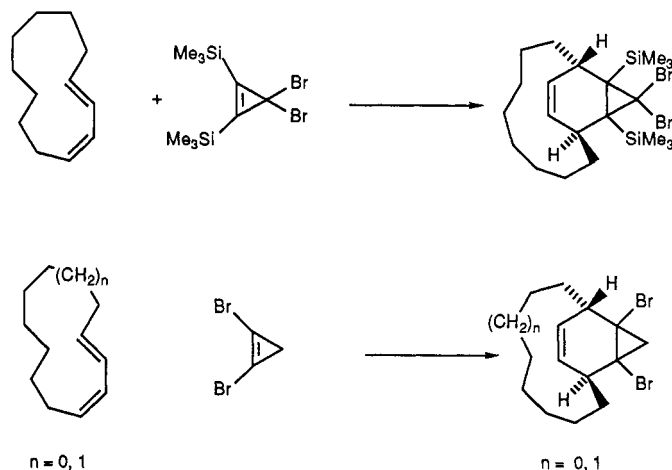
STRAINED ALKENES

Considerable effort has been expended on attempts to synthesize tetra-*tert*-butylethene (ref. 13) which, although unsuccessful, has provided a rich variety of strained alkenes and has been the impetus to new synthetic methodology. Our approach to this molecule and related systems has been to prepare a hindered alkene with a ring as one substituent and then increase the strain by ring expansion, seeking to use a method which would ultimately allow the ring to be converted to an acyclic system (Scheme 6). The compound we chose as our target molecule for these transformations was a substituted 3-methylenecyclobutanone and this was prepared by the Barton-Kellog reaction as illustrated in Scheme 7. Following

Kreb's analysis, this substituted alkene should be capable of preparation, the 4-membered ring tying back the interfering methyl groups.

Scheme 6

Scheme 7
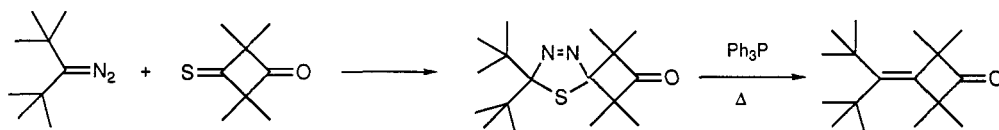
The yield of this cyclobutanone was low, probably due to rearrangement to other products. Our next object was to increase the steric interactions by expanding the ring. Reaction of the methylenecyclobutanone with *m*-chloroperoxybenzoic acid gave, however, not the desired Baeyer-Villiger product but the oxirane in 86% yield, the alkene, despite the bulky substituents, still reacting faster than the ketonic group (Scheme 8). A number of other oxidizing agents were then investigated and finally it was found that potassium *tert*-butylperoxide in the presence of 18-crown-6 gave the desired lactone in 79% yield. The IR spectrum shows a band at 1765 cm^{-1} and the ^{13}C NMR spectrum shows signals for the two alkene carbons and the ester carbonyl carbon. Lithium aluminium hydride reduction of the lactone gave the corresponding lactol in 72% yield. The IR spectrum shows bands at 3614 and 3415 cm^{-1} and the ^{13}C NMR spectrum shows signals for two alkene carbons but none for a carbonyl carbon. No evidence was found to suggest that any of the ring opened hydroxyaldehyde was present and prolonged treatment with excess lithium aluminium hydride over long periods of time gave none of the corresponding diol. The lactone did not react with *m*-chloroperoxybenzoic acid but it did react with methyllithium to give the hemiacetal in 92% yield. Again, no evidence for the presence of any hydroxyketone could be adduced. The acetal did react with hydrogen peroxide in the presence of sulphuric acid to give the hydroperoxide in 96% yield but this did not undergo a Criegee fragmentation to give the diol, decomposition giving a variety of products but not the desired one. Clearly there is considerable resistance to ring opening in these compounds presumably because of the increase in steric crowding that would result.

Scheme 8
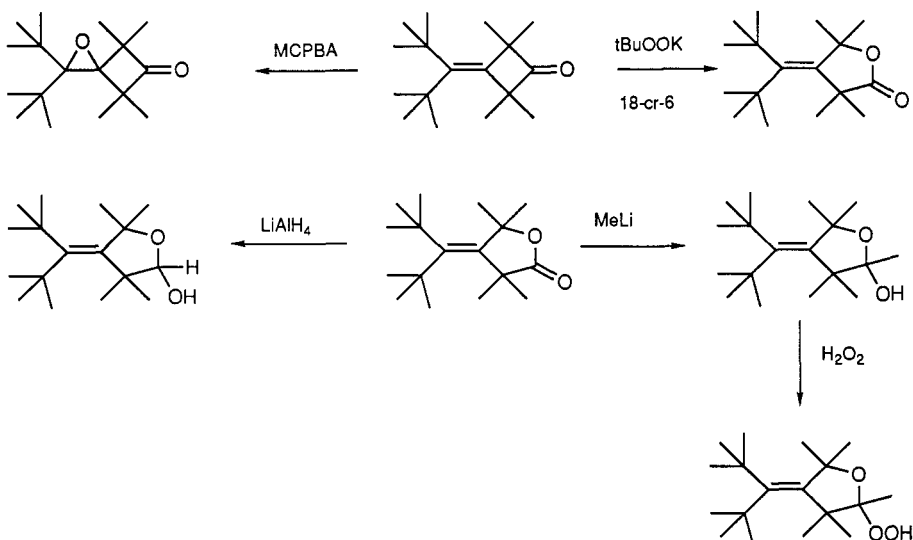
The failure of the lactone to react with *m*-chloroperoxybenzoic acid is indicative of a strained bond with reduced double bond character. This is borne out by the X-ray crystallographic structures of the lactone and lactol (Figures 1 and 2). Both compounds show that the molecules have highly twisted double bonds, the lactone having an alkene bond length of 136 pm with a bond angle of 33.8° and the lactol with a bond length of 137 pm and a bond angle of 37.6°. These molecules are clearly highly strained by steric crowding and it is not surprising that ring opening is precluded. The degree of bond twist begins to suggest that a decoupled biradical might be accessible by an increase in substitution on β-position of the ring in compounds of this type. Unfortunately, suitable crystals for X-ray analysis of the hemiacetal could not be grown so we presently do not know what quantitative effect introducing this substituent had.
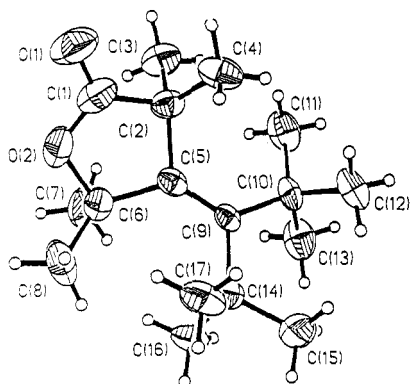
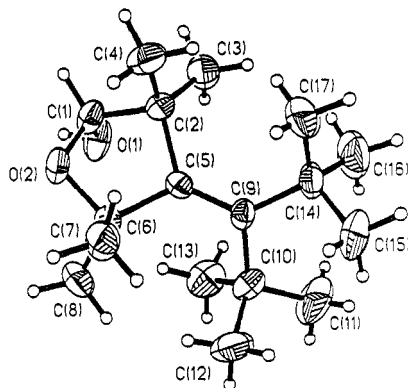Fig. 1. ORTEP drawing of the lactone showing thermal ellipsoids.

Fig. 2. ORTEP drawing of the lactol showing thermal ellipsoids.

The methylene cyclobutanone is a potential precursor to 'skipped' dienes and polynes of the type shown in Scheme 9. We have investigated a number of methods of coupling the cyclobutanone but these were unsuccessful, leading to rearranged products or, in the case of the McMurry reaction, simply to the corresponding alcohol. Routes via other related systems were also unsuccessful but we are currently exploring routes to less substituted derivatives of these systems in the hope that these may have interesting physical and electrical properties.

Scheme 9
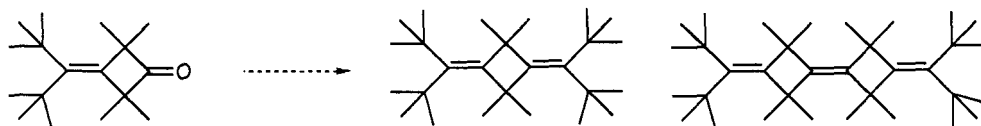
Acknowledgements

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