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The Use of Chlorosubstituted Cyclopropenium Cations for the Synthesis of Substituted Cyclopropenones.

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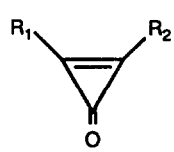
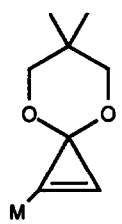
Abstract 2-chlorocyclopropenyl cations (3) which are readily prepared from the corresponding 2-chlorocyclopropenes (4) by reaction with triphenylcarbenium tetrafluoroborate are converted to cyclopropenones (7) in high yield upon treatment with aqueous sodium bicarbonate.

Cyclopropenones (1) represent an interesting class of compounds that have attracted much attention over past years, providing challenges to both synthetic and theoretical chemists.[1-3] This unique structure is also present in compounds of biological origin[4,5], in particular the antibiotic Penitricin[4] is a simple hydroxymethyl substituted cyclopropenone. These compounds undergo a diverse range of reactions giving rise to many and varied compounds of potential use to synthetic chemists, and thus present themselves as very useful synthetic intermediates[6-8]. However, to date the synthetic potential of these compounds has been largely unexploited, due in part to the difficulties encountered in their synthesis. One of the most successful general synthesis of substituted cyclopropenones reported involves the alkylation of metallated cyclopropenone acetals[9] (2) followed by deprotection. This approach provides access to both mono and disubstituted cyclopropenones in fair to good overall yields.

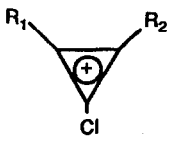


(1)



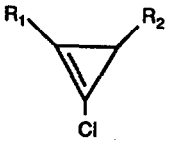
(2)

We chose to explore the potential of chloro-substituted cyclopropenium cation salts (3) as intermediates for the synthesis of the corresponding cyclopropenones. These cations exist at the same level of oxidation as the corresponding cyclopropenones, and can be envisaged undergoing facile hydrolysis in the presence of a weak base (Scheme 1) to produce the corresponding cyclopropenones (7).



(3)

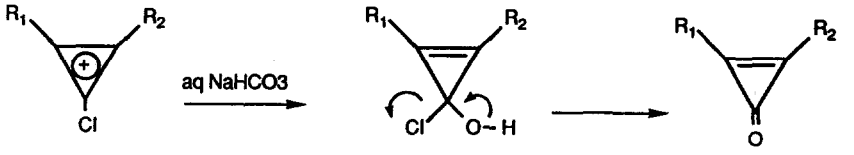
a) R_1,R_2 = Pr
b) R_1,R_2 = Bu
c) R_1,R_2 = -$(CH_2)_6$-



(4)

a) R_1,R_2 = Pr
b) R_1,R_2 = Bu
c) R_1,R_2 = -$(CH_2)_6$-

Scheme 1.



(3)

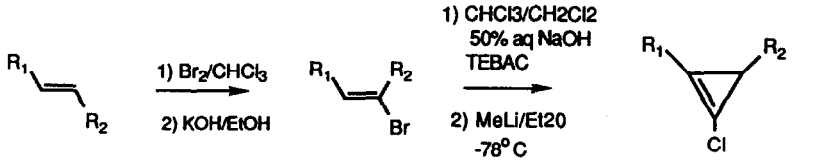
(7)

a) R_1,R_2 = Pr
b) R_1,R_2 = Bu
c) R_1,R_2 = -$(CH_2)_6$-

The cations (3) were anticipated to be prepared by hydride abstraction from the readily prepared[10] 2-chlorosubstituted cyclopropenes (4) using the reagent, triphenylcarbenium tetrafluoroborate.[11]

The cyclopropenes (4a,b) were synthesized according to scheme 2, which is based on the methodology developed by Baird[10], whereas the fused cyclooctyl cyclopropene (4c) was prepared as previously reported[12].

Scheme 2.

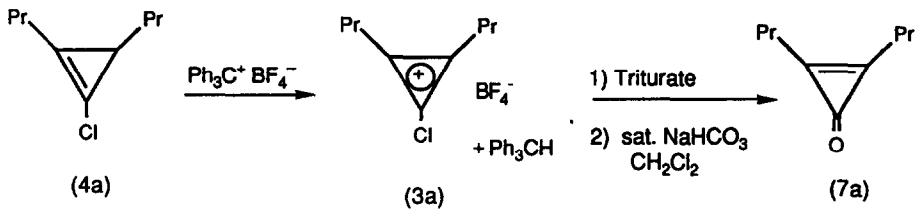


(4)

a) R_1,R_2 = Pr
b) R_1,R_2 = Bu

Treatment of (4a) with one equivalent of triphenylcarbenium tetrafluoroborate in dichloromethane at 0° resulted in essentially complete conversion to the cyclopropenium cation (3a) and triphenylmethane.

Separation of these two can be readily achieved by trituration with dry petroleum to remove the triphenylmethane and leaves the cation as a dark viscous moisture sensitive oil which is pure, as shown by N.M.R (^{13}C δ 165.87, 159.57, 27.79, 19.02, 13.61; ^{1}H δ 2.97 (4H t, J = 7.4 Hz), 1.88 (4H, sext., J = 7.4 Hz), 1.08 (6H, t, J = 7.4 Hz) . Treatment of a solution of the cation (6) in dichloromethane with saturated aqueous sodium bicarbonate afforded dipropylcyclopropenone (5a) (^{13}C δ 160.16, 159.40, 27.65, 19.25, 73.24; ^{1}H δ 2.59 (4H, t, J = 7 Hz) 1.6-1.9 (4H, m), 1.04 (6H, t, J = 7 Hz), υ_{max} (thin film) 1840 (s), 1630 (s) cm^{-1} in an 80% overall yield.



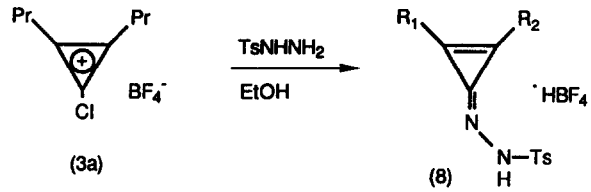
We have applied this approach to the synthesis of three disubstituted cyclopropenones, the results of which are presented below.

Cyclopropenes (4a-c)	Yields of Cyclopropenones (7a-c)[13]
4a	85%
4b	75%
4c	69%

This strategy constitutes a useful synthesis of substituted cyclopropenones. Furthermore this methodology should also apply to other 2-halosubstituted cyclopropenes and indeed, any cyclopropene substituted at the 2-position with a good leaving group might be considered as a potential precursor to the corresponding cyclopropenones.

The intermediate chlorocyclopropenium cations (3) themselves can be considered as potential synthetic equivalents to the corresponding cyclopropenones (7), for example treatment of dipropylcyclopropenium tetrafluoroborate (3a) with a solution of tosyl hydrazine resulted in the quantitative conversion to the tosyl hydrazone salt (8)[14] (Scheme 3).

Scheme 3.



We are currently investigating alternative methods of generating the cations (3) using different hydride abstracting oxidising agents to expand the scope of this synthesis, and are also investigating the synthetic utility of the intermediate cations (3), in particular their ability to react as a synthetic equivalent to a cyclopropenone. This work was supported by the Australian Research Council small grants scheme.

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13) ^{13}C δ ($CDCl_3$) (7b); 160.40, 159.83, 28.00, 25.68, 22.02, 13.28; (7c); 162.12, 158.55, 34.15, 26.11, 22.02.

14) ^{13}C δ ($CDCl_3$) (8); 154.75, 148.51, 148.34, 145.37, 132.91, 130.04, 128.09, 57.88, 26.35, 26.13, 21.31, 19.14, 18.87, 17.52, 13.40, 13.29.

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