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THE REGIOSELECTIVE OXIDATION OF 1–TRIMETHYLSILYCYCLOPROPENES TO α–TRIMETHYLSILYL–α,β,–UNSATURATED KETONES

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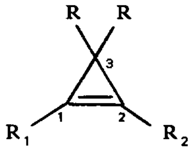
Reaction of the cyclopropenes (3, R_1 = Me, R_2 = Me), (3, R_1 = H, R_2 = Pr^i) and (3, R_1 = H, R_2 = Bu^t) with one equivalent of m–chloroperbenzoic acid leads to the enones (4) and (7, R = Pr^i and Bu^t) respectively, in the last two cases accompanied by about 15% of the regioisomer (8, R = Pr^i or Bu^t). In the case of (3, R_1 = Me, R_2 = H) oxidation with excess reagent led to the formate (9, R = $SiMe_3$) and two intermediates (11) and (10, R = $SiMe_3$) could be identified.

The oxidation of cyclopropenes by peracids has been reported to lead to ring opened α,β– unsaturated ketones or aldehydes in a process believed to involve an intermediate oxabicyclo[1.1.0]butane.[1–4] In a number of cases (1), where $R_1 \neq R_2$, little regioselectivity is observed in the process; however, with R_1 = Ph and R_2 = Bu^t, only a product derived by breaking the C_1-C_3 bond was observed.[3] In contrast, a second study involving (2) showed that exclusive cleavage of the C_2-C_3 bond occurred.[4] The ready availability of substituted cyclopropenes, eg. from the reaction of trihalocyclopropanes with an alkyl lithium,[5] has led us to examine in more detail their possible use in synthesis; we now report that peracid oxidation of 1– trimethylsilylcyclopropenes generally proceeds with high regioselectivity and provides a useful route to α– trimethylsilyl– α,β– unsaturated ketones.



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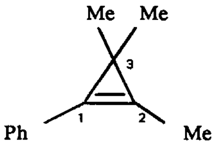

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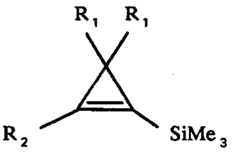

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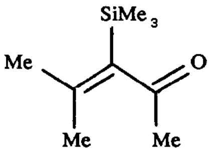

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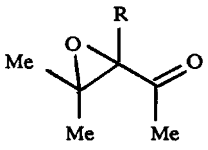
Treatment of (3, R_1 = R_2 = Me)[5] with one mol.equivalent of m– chloroperbenzoic acid in dichloromethane for 10m at 20 °C led to a rapid reaction; the enone (4) was isolated in good yield (73%).[6] This was distinguished from its regioisomer (5, R = $SiMe_3$) on the basis of a carbonyl absorption at 1685 cm^{-1}, the corresponding value for acylsilanes being about 1645 cm^{-1}.[7] Such α–trimethylsilyl–α,β–unsaturated ketones have been shown to be of value in a modified Robinson annulation by trapping with enolates.[10] Indeed (7, R = Me) has been prepared in four steps from vinyl bromide, though the final step, formation of the carbonyl group in (4) by oxidation of the corresponding alcohol, is reported to proceed in relatively low yield.[11,12] The present route proceeds in three steps from readily available starting materials.##



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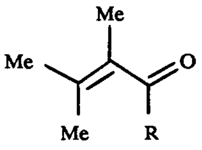

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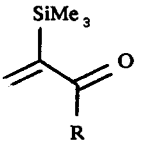

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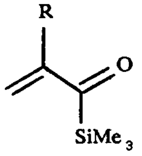

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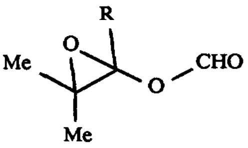
The oxidation of α,β–unsaturated ketones by peracids can lead to migration of either group in a Baeyer–Villiger type reaction, or to formation of the epoxide.[9] Treatment of the enone (4) with a further equivalent of the peracid for 2 h at 20 °C leads to a second clean oxidation, in this case to the acyl–epoxide (6, R = $SiMe_3$)[8] (62% based on (3, R_1 = R_2 = Me)). It is interesting that the peracid oxidation of tetramethylcyclopropene is reported to lead to (5, R = Me) but that this is further oxidized to (6, R = Me), and that the two oxidations occur at comparable rates, reaction with one mol. equiv. of peracid leading to a mixture of alkene and epoxide.[3c]

Oxidation of (3, R_1 = H, R_2 = Bu^t)# with one equivalent of the peracid led principally to (7, R = Bu^t)[13] (66%), although in this case *ca.* 17% of the product was regioisomer (8, R = Bu^t).[14,15] The observation of any (8, R = Bu^t) may reflect the effect of the bulk of the t–butyl group in a reaction which shows considerable steric effects.[2–4] Reaction of (3, R_1 = H, R_2 = Pr^i)** with one equivalent of peracid at -20 to 20 °C for 15 min also led to one major product (7, R = Pr^i) although once again a minor product (ca. 15%) was the regioisomer (8, R = Pr^i).[16] Compounds (7, R = Pr^i and Bu^t) were relatively resistant to further oxidation, surviving unchanged after treatment with a further equivalent of the peracid for 18 h at 20 °C in chloroform.

In the case of the cyclopropene (3, R_1 = Me, R_2 = H) with a hydrogen at C–2, oxidation with one mol. equiv. of m–chloroperbenzoic acid did not lead to complete reaction. However, when 3 mol. equiv. of the peracid were employed for 4 h at 20 °C, a single product, (9, R = $SiMe_3$),[17] was obtained in reasonable yield (74%). When the reaction products were examined with 2 mol. equiv. of the peracid, two intermediates could be identified. The second was obtained pure by column chromatography and was characterised as the formate (10, R = $SiMe_3$);[18] the first was not obtained pure, but on the basis of ^1H n.m.r. could be provisionally identified as the aldehyde (11).[19]



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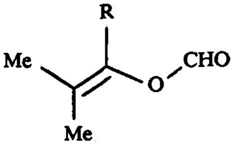

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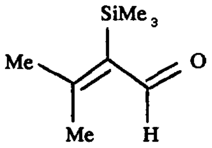

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Although the oxidation of aldehydes by peracids generally leads to the corresponding acid,[9] α,β– unsaturated aldehydes such as citral can be converted to formates in good yield.[20] It is noteworthy that the oxidation of 1,3,3– trimethylcyclopropene is known to lead initially to an *ca.* 2:1 mixture of 2,3– dimethylbut– 2– enal, and mesityl oxide; the aldehyde is again further oxidized, in competition with the reaction of the cyclopropene, to the epoxide (9, R = Me).[3c] The oxidation of (3, R_1 = Me, R_2 = H) thus proceeds rather differently to that of the trimethylcyclopropene, the trimethylsilyl– group appearing to have a much greater effect on the regioselectivity of the ring opening. Although this method is apparently not useful for the preparation of α– silyl– α,β– unsaturated aldehydes, it does provide ready access to formate derivatives of 1– silylepoxides such as (9, R = $SiMe_3$). We are at present examining the chemistry of these species.

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6. Which showed δ_H 2.17 (3H, s), 1.82 (3H, s), 1.72 (3H, s), 0.16 (9H, s); δ_C 210.4s, 144.0s, 143.1s, 31.9q, 23.8q, 23.3q, −0.2q; ν_{max} 1685, 1251, 839 cm^{-1}.
7. See eg., A.G. Brook, J.M. Duff and P.F. Jones, J.Amer.Chem.Soc., 1967, 89, 431; E.J. Corey, D. Seebach and R. Freedman, ibid., 434; J.A. Sonderquist and A. Hassner, ibid., 1980, 102, 1577.
8. Which showed δ_H 2.07 (3H, s), 1.37 (3H, s), 1.20 (3H, s) 0.15 (9H, s); δ_C 213s, 70.5s, 62.9s, 28.3q, 23.4q, 22.7q, − 1.5 q; ν_{max} 2965, 1694, 1357, 1251, 845 cm^{-1}.
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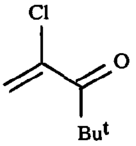
12. A related trapping of 1–metallo–1–trimethylsilyalkenes by anhydrides cuts out the oxidation step, but the yields are very variable (A.G. Brook and J.M. Duff, Can.J.Chem., 1973, 51, 2024).
13. This showed δ_H 5.78 (1H, d, J 2 Hz), 5.61 (1H, d, J 2 Hz), 1.17 (9H, s), 0.15 (9H, s); δ_C 215.4s, 155.7s, 126.6t, 44.1s, 27.4q, –1.0q ; ν_{max} 2963, 1672, 1250, 843 cm^{-1}.
14. This showed δ_H 5.95 (1H, s), 5.64 (1H, s), 1.12 (9H, s), 0.24 (9H, s); ν_{max} 2961, 1610, 1250, 843 cm^{-1}. The carbonyl stretch is in agreement with the assigned structure rather than with (7, R = Bu^t).[7]
15. It is interesting to note that 1–chloro–2–t–butylcyclopropene[5] undergoes a similar oxidative ring cleavage on treatment with one equivalent of m–chloroperbenzoic acid at 20 °C, but that the ratio of products is reversed, (12) and (13) being obtained in a ratio of 1:3.



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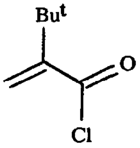

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16. Compounds (7, R = Pr^i) and (8, R = Pr^i) (combined yield 81.5%) showed δ_H 6.36 (1H, dd, J 1.9, 0.4 Hz), 6.05 (1H, d, J 1.9 Hz), 3.18 (14, sep., J 6.9 Hz), 1.05 (6H, d, 6.9 Hz), 0.13 (9H, s) and δ_H 5.96 (1H, d, J 1.1 Hz), 5.91 (1H, s), 2.82 (1H, d.sep., J 1.1, 6.9 Hz), 0.96 (6H, d, J 6.9 Hz), 0.25 (9H, s) respectively.
17. This showed δ_H 7.9 (1H, s), 1.3 (6H, s), 0.2 (9H, s); δ_C 162d, 90.7s, 63.3s, 23.9q, 21.6q, 0.0q; ν_{max} 2967, 1724, 1254, 1174, 844 cm^{-1}.
18. This showed δ_H 8.0 (1H, s), 1.8 (3H, s), 1.62 (3H, s), 0.14 (9H, s); δ_C 160.2d, 147.5s, 137.2s, 20.2q, 18.3q, –0.6q; ν_{max} 1724, 1252, 1164, 843, 760 cm^{-1}.
19. Compound (11) showed δ_H 10.2 (1H, s), 2.1 (3H, s), 2.0 (3H, s), 0.2 (9H, s).
20. N. Prileiaev, Bull.soc.chim.France, 1927, 42, 687.

\# Prepared (91%) by treatment of 1,1–dibromo–2–chloro–2–t–butylcyclopropane (M.S. Baird, W. Nethercott and P.D. Slowey, J.ChemRes., 1985, S370) with 2 mol. equiv. of methyl lithium at –78 °C followed by warming to 0° for 10 min and then quenching with chlorotrimethylsilane at –50°.

\#\# In principle, reaction of trihalocyclopropane with two mol. equiv. of methyl lithium,, quenching of the ethereal solution with chlorotrimethylsilane to form the trimethylsilylcyclopropene,[5] and oxidation with m–chloroperbenzoic acid could be performed in a single pot sequence; however, when this was carried out starting from 1,1–dibromo–3–chloro–2,2,3–trimethylcyclopropane, mixtures of (4) and (6, R = $SiMe_3$) were obtained even with a deficiency of the peracid at –40 °C. This presumably reflects a solvent effect on the differential rates of the two oxidation steps.

** Prepared from 2–chloro–3–methylbut–1–ene by reaction with (i) bromoform–aq NaOH–cetrimide to give 1,1–dibromo–2–chloro–2–(prop–2–yl)cyclopropane (69%) and then (ii) 2 mol. equiv. of methyl lithium at –78 °C, warming to 0° for 10 min and then quenching with chlorotrimethylsilane at –50 °C.

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