

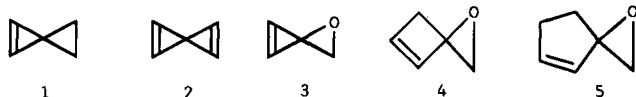
Spectral Characterization and Rearrangement of an Oxaspiropentene

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Received August 1, 1994

Spiropentene (**1**) is a reactive molecule with strain energy ~ 90 kcal mol⁻¹ that polymerizes in the condensed phase at low temperature, but it has been characterized spectroscopically at 0 °C and trapped by Diels–Alder addition to cyclopentadiene and furan.¹ Not surprisingly, spiro-pentadiene (**2**), prepared by



vacuum gas–solid reaction, is even less stable although it has provided a ¹H NMR spectrum at –105 °C and been intercepted from addition of 2 molar equiv of cyclopentadiene.² In comparison to these simple hydrocarbons, oxygen-substituted analogues have received little attention. While oxaspiropentane and its derivatives are well-known and used as cyclobutanone equivalents,³ neither oxaspiropentene (**3**) nor oxaspirohexene (**4**) has been recorded and, to the best of our knowledge, their derivatives are unknown. The smallest spiro-fused oxirane to contain unsaturation of which we are aware is 1-oxaspiro[2.4]hept-4-ene (**5**).⁴ We now report the spectral characterization and rearrangement of the first oxaspiropentene derivative, namely, the novel ring-annulated 3',3'-diphenylspiro[1*H*-cyclopropa[*b*]naphthalene-1,2'-oxirane] (**7**).

Thirty years ago Anet and Anet recorded the first synthesis of a cyclopropene,⁵ and the developments⁶ in the chemistry of this fascinating class of compounds have provided the wherewithal to address the oxaspiropentene question. The formally simple cyclopropenes have been transformed⁷ into a range of stable, colored crystalline 1-alkylidene-1*H*-cyclopropenes, e.g., **6**, that are of special interest because of their novel physicochemical properties.⁸ We have found that epoxidation of 1-diphenylmethylene-1*H*-cyclopropa[*b*]naphthalene (**6**) with dimethyldioxirane yields the highly strained oxaspiropen-

tene **7** that has been characterized spectroscopically prior to its thermal rearrangement to the diphenylcyclobuta[*b*]naphthalenone **8**.

The interaction of several alkylidenecyclopropenes with various oxidizing agents has been addressed, and under the acidic conditions of peracid epoxidation that were employed at that time only products of ring opening were recorded.⁹ Thus the reaction of **6** with *m*-CPBA gives hydroxyethanone **10** in high (71%) yield. The obtention of this compound is best rationalized from formation of epoxide **7**, which opens (in either direction) under the acidic conditions to diol **9** (Scheme 1). As no cyclopropene carrying a 1-hydroxy function has been isolated,⁶ it is not surprising that facile ring cleavage of **9** (with concomitant relief of strain) gives **10** as the final product of reaction.⁹ In order to circumvent such difficulties, the epoxidation of **6** has now been examined under nonacidic, and hence noncatalytic, conditions.¹⁰

The work of Adam and his co-workers has made dimethyldioxirane a convenient and easily accessible reagent.^{10,11} When treated with an excess (3.5 equiv) of a 0.1 M solution of this reagent in acetone at –65 °C, the bright yellow colored solution of **6** is unaltered even after 1 h. However, within 5 min of removal of the reaction mixture from the cold bath and warming to room temperature, the color begins to fade, and the change is complete in a further 5 min; conventional radial chromatography provides 2,2-diphenylcyclobuta[*b*]naphthalen-1(2*H*)-one (**8**) in 86% yield. The compound is identical to a sample obtained previously in these laboratories by a different route.¹² Under the nonacidic conditions of this reaction, oxaspiropentene **7** is presumed to be the initial product. That it is not isolated is explicable by cyclopropylcarbinyl–cyclobutyl rearrangement in analogy to the known saturated oxaspiropentane analogues.³ Spurred by this result we elected to perform the experiment in the cavity of an NMR spectrometer using perdeuterated oxidant (dimethyldioxirane-*d*₆) that is easily available^{13,14} from acetone-*d*₆; oxygenation with the labeled reagent generates labeled NMR solvent.

After addition of the labeled dioxirane (ca. 1 equiv) at –78 °C, ¹H NMR monitoring¹⁵ showed no changes to the spectrum of **6** even after 2 h save for downfield shifts of the signals from their positions at ambient temperature.¹⁶ On warming to –48 °C the characteristic proton resonances for H2/7 and H3/6 of **6** (δ 7.74, s; 8.01, dd, $J_{3,4} = J_{6,5} = 6.2$ Hz; $J_{3,5} = J_{6,4} = 3.3$ Hz, respectively) began to diminish in intensity with new signals appearing at δ 7.97 (s, H2/7) and 8.09 (dd, $J_{3,4} = J_{6,5} = 6.3$ Hz; $J_{3,5} = J_{6,4} = 3.3$ Hz, H3/6) that are assigned to the annulated oxaspiropentene **7**. A ratio **6**:**7** of 3:1 was noted. Further warming to –33 °C showed ca. 40% of epoxide **7** from the ¹H NMR spectrum, and at this temperature, the ¹³C NMR spectrum (recorded over 45 min) displayed a complete twinning of the

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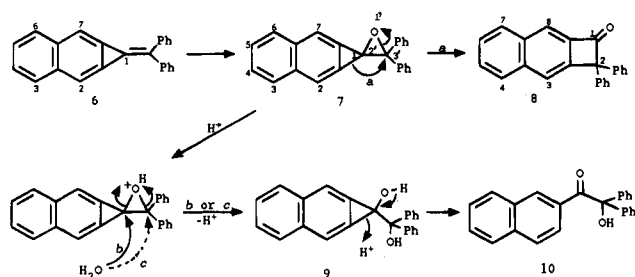
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(15) NMR spectra were recorded at 300 MHz for ¹H and 75 MHz for ¹³C in acetone-*d*₆ and referenced to the central methyl line at 2.00 and 30.00 ppm, respectively.

(16) **6** (room temperature): ¹H δ 7.80 (dd, $J_{3,4} = J_{6,5} = 6.2$, $J_{3,5} = J_{6,4} = 3.3$ Hz, H3/6), 7.57–7.53 (m, 4H), 7.49 (s, H2/7), 7.34 (dd, $J_{4,3} = J_{5,6} = 6.3$, $J_{4,6} = J_{5,3} = 3.3$ Hz, H4/5), 7.33–7.28 (m, 4H), 7.23–7.17 (m, 2H); ¹³C δ 108.30 (C2/7), 112.69 (C1), 120.67 (C8), 127.98 (C1a/7a), 128.04 (2CH), 128.57 (2CH), 128.98 (4CH), 129.64 (4CH), 129.88 (2CH), 139.93 (C2a/6a or 2C_{ipso}) and 140.27 (2C_{ipso} or C2a/6a).

Scheme 1



aromatic methine signals of **6** in the range 127–130 ppm and also the quaternary carbons at ca. 140 ppm. The presence of the same symmetry plane in **6** and **7** is clearly established. Most notable was the appearance of a new characteristically shielded⁶ C2/7 resonance at 114.9 for **7** together with that at 108.1 ppm for **6**; the ratio **6**:**7** was ~1:1. Oxygenation of the exocyclic double bond of **6** shifts C2/7 downfield to a position similar to that in cyclopropa[*b*]naphthalene.⁶ After heating to $-18\text{ }^{\circ}\text{C}$, epoxidation was about 90% complete.

In order to assess the stability of **7** the fully epoxidized material was warmed to $0\text{ }^{\circ}\text{C}$. Much to our surprise the ¹H NMR spectrum showed signals compatible only with the oxirane; the cyclopropylmethyl–cyclobutyl rearrangement had not set in! The ¹³C spectrum of **7** was recorded over 45 min and provided all of the signals save for those due to the oxirane C2'/C3' quaternary carbons.¹⁷ Furthermore, we have found that the rearrangement **7** → **8** is slow at $-5\text{ }^{\circ}\text{C}$ as **8** is formed to the extent of ~30% (¹H NMR) after 120 h. When the ¹³C NMR spectrum was recorded over a further 8 h at $0\text{ }^{\circ}\text{C}$, compound **7** had rearranged but only to an extent of ~50%. More impor-

tantly the oxiranyl quaternary signals were now distinct at 71.7 and 71.0 ppm and the resonances of **8** were also clearly present. After the sample was warmed to room temperature (18 h), the resonances of oxaspiropentene **7** were replaced by those of **8**.¹⁸

The simplicity of using labeled dimethyldioxirane as a reagent for oxygen atom transfer has allowed us to gain the essential evidence to unambiguously establish the existence of the first oxaspiropentene derivative **7**. It is clear that epoxidation of methylenecyclopropene **6** proceeds efficiently in the temperature range $-33\text{--}0\text{ }^{\circ}\text{C}$ and that epoxide **7** has a moderate lifetime in ice. These results may encourage others to search for nonannulated, and presumably more reactive, oxaspiropentenes, especially parent **3**.

Acknowledgment. Financial assistance from the Victoria University of Wellington Fellowships Committee (to M.J.C.) and from the Internal Grants Committee and the New Zealand Lottery Grants Board (Lottery Science Research) for assistance with instrument costs is gratefully acknowledged.

(17) **7** ($0\text{ }^{\circ}\text{C}$): ¹H δ 8.07 (dd, $J_{3,4} = J_{6,5} = 6.3$, $J_{3,5} = J_{6,4} = 3.4$ Hz, H3/6), 7.93 (s, H2/7), 7.57 (dd, $J_{4,3} = J_{5,6} = 6.3$, $J_{4,6} = J_{5,3} = 3.3$ Hz, H4/5), 7.52–7.42 (m, 10H); ¹³C δ 71.04 and 71.71 (C2'/C3'), 114.86 (C2/7), 124.86 (C1a/7a), 127.82 (2CH), 128.68 (4CH), 129.46 (6CH), 129.88 (2CH), 138.61 (C2a/6a or 2C_{ipso}), 139.07 (2C_{ipso} or C2a/6a).

(18) **8** (room temperature): ¹H δ 8.58 (s, H8), 8.22 (s, H3), 8.15 (dd, $J_{4,6} = J_{7,5} = 4.8$, $J_{4,5} = J_{7,6} = 8.2$ Hz, H4/7), 7.73 (ddd, $J_{6,4} = 1.2$, $J_{6,5} = 7.0$, $J_{6,7} = 8.3$ Hz, H6), 7.61 (ddd, $J_{5,7} = 1.1$, $J_{5,6} = 6.9$, $J_{5,4} = 8.2$ Hz, H5), 7.55–7.52 (m, 4H), 7.38–7.33 (m, 4H), 7.25 (tt, $J_{\text{meta}} = 1.2$, $J_{\text{ortho}} = 7.3$ Hz, 2H_{para}); ¹³C δ 81.82 (C2), 122.54 (C3), 123.42 (C8), 127.42 (2C_{para}), 127.48 (4C_{ortho}), 127.71 (C7), 129.28 (4C_{meta}), 129.50 (C5), 129.78 (C6), 131.57 (C4), 135.21 (C7a), 139.18 (C3a), 142.44 (C1'1''), 144.87 (C8a), 151.75 (C2a), 192.01 (C1). The assignments follow from ¹H–¹H and ¹H–¹³C COSY and HMBC experiments on the sample in chloroform-*d* where chemical shifts are generally ca. 1.5 ppm upfield.