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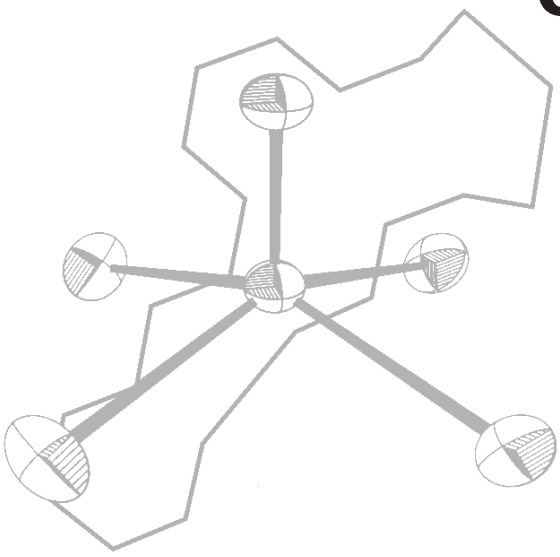

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Studies in the Cycloproparene Series: Oxygen Transfer to 1-Diphenylmethylidene-1*H*-cyclopropabenzene

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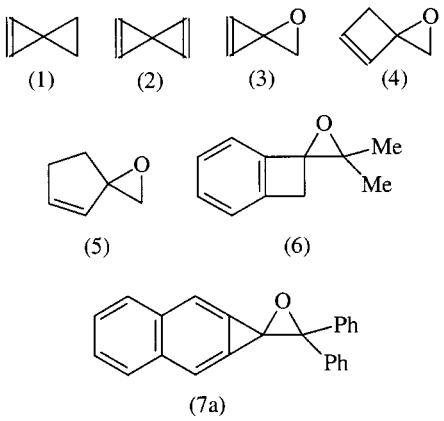
Oxygen transfer from dimethyldioxiran to 1-diphenylmethylidene-1*H*-cyclopropabenzene (8b) proceeds to give the corresponding epoxy derivative (7b), the simplest and most stable oxaspiropentene yet recorded. The compound has been characterized spectroscopically prior to ring expansion and rearrangement to the cyclobutenone (9b) above 20°C; this is the sole product isolated when the reaction is performed at or above room temperature. If the oxygenation reaction is performed under conditions other than strictly anhydrous, the rearrangement (7b) → (9b) competes with protonation of the oxygen atom and sequential opening of the three-membered ring to provide the hydroxyethanone (11b) via the diol (10b).

Despite major advances in the chemistry of the cycloproparenes,[1–4] many simple aspects of their behaviour remain to be explored, and the existence and stabilities of a range of conceptually simple derivatives have yet to be assessed. In this context we have reported already on the ease with which the alkylidenecyclopropparenes undergo oxidation under both acidic and neutral conditions.[5] However, controlled oxygen transfer has been applied previously only to the cyclopropa[*b*]naphthalene derivative (8a) whereupon the first oxaspiropentene, the naphtho-annelated derivative (7a), was characterized.[6] We now report upon comparable experiments involving the simpler cyclopropabenzene* derivative that lead to the homologous oxaspiropentene (7b), the second, simplest, and most stable derivative of the ring system so far known. Oxygen atom transfer to the bridge of (8b) is not observed.

While spiropentene (1) is well recognized as a reactive molecule (strain energy *c.* 375 kJ mol^{-1}) that polymerizes in the condensed phase at low temperature, it has been characterized spectroscopically at 0°C and trapped by Diels–Alder addition to cyclopentadiene and furan.[7] Spiropentadiene (2) was prepared more recently by vacuum gas–solid reaction and it is even less stable; it has provided a ^{1}H n.m.r. spectrum at −105°C and been intercepted from addition of 2 mol. equiv. of cyclopentadiene.[8] In comparison to these simple hydrocarbons, their oxygen-substituted analogues (Scheme 1) have received surprisingly little attention. Saturated oxaspiropentanes are recognized



Scheme 1

* Under rule A-21.3, IUPAC names the parent compound as bicyclo[4.1.0]hepta-1,3,5-triene. For convenience in making comparison with the higher homologues the term 1*H*-cyclopropabenzene is employed throughout the discussion. [*Editor's note.* Under the 1998 IUPAC recommendation FR-0, 'no restriction is placed on when fusion nomenclature may be applied'; this means that 1*H*-cyclopropabenzene is now allowed as a formal name.]

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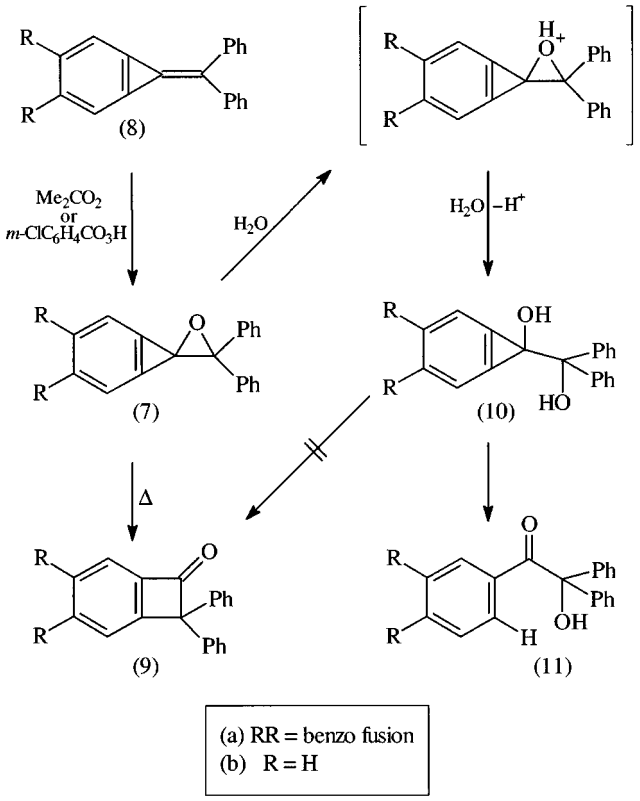
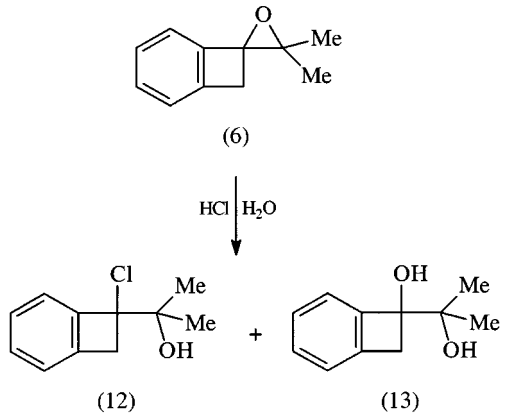
as cyclobutanone equivalents *par excellence*,[9] but the alkene homologues 1-oxaspiro[2.2]pentene (3) and 1-oxaspiro[2.3]hexene (4) have been neither recorded nor intercepted. The simplest spiro-fused oxiran to contain unsaturation appears to be 1-oxaspiro[2.4]hept-4-ene (5),[10*] but the smaller and more highly strained benzo-fused 1-oxaspiro[2.3]hex-4-ene (6) has also been prepared recently;[11] epoxides (5) and (6) are stable compounds at room temperature.



Scheme 2

The formally simple cyclopropparenes can be transformed[1,3,12] into a range of stable, coloured, crystalline 1-alkylidene-1*H*-cyclopropparenes, e.g. (8), that are of special interest because of their novel physicochemical properties.[13] Previously we found[6] that epoxidation of 1-diphenylmethylidene-1*H*-cyclopropa[*b*]naphthalene (8a) with dimethyldioxiran yields the highly strained oxaspiropentene (7a) (Scheme 2) that is stable below 0°C. Under the acidic conditions of peroxy acid epoxidation only products of ring opening were recorded.[5] Thus the reactions of both (8a) and (8b) with *m*-chloroperoxybenzoic acid give the corresponding hydroxyethanone (11a) and (11b), respectively, in high yield (71 and 83%). The formation of these compounds under the acidic conditions is easily rationalized as proceeding via the epoxides (7a,b) that are protonated and then open in either direction to give the diols (10a,b) (Scheme 2). As no cyclopropparene carrying either a hydroxy or a halogen substituent at the 1-position has been isolated,[2–5] it is expected that (10) will undergo easy σ bond cleavage to provide (11) as the final product of reaction with the release of the *c.* 285 kJ mol^{-1} of strain energy[3] of the cyclopropparene ring system.[5] While it is possible for diol (10) to eliminate water with concomitant ring expansion to give cyclobutarenone (9), this last product has never been observed under the acidic reaction conditions employed.[5,6] Not surprisingly, the behaviour of (7) differs from that of the isolable cyclobutarene homologue (6). This compound reacts with aqueous HCl to give chloro alcohol (12) and diol (13) (Scheme 3) with retention of the cyclobutarene ring skeleton; diol (13) was the minor product of reaction.[11]

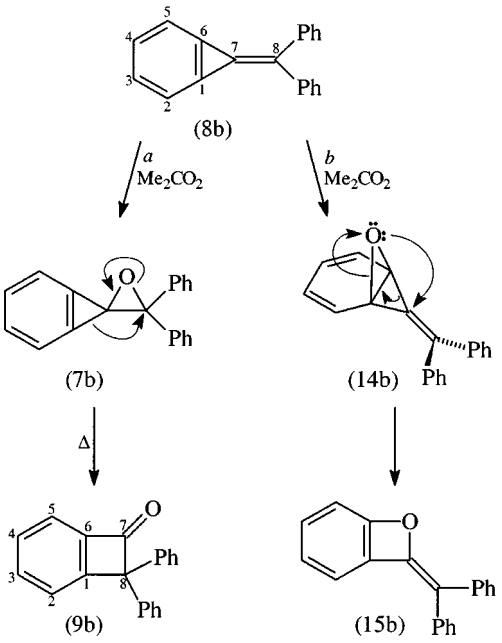


Scheme 3

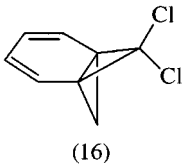
Adam and his coworkers have made dimethyldioxiran a convenient and easily accessible reagent for use in the organic chemistry laboratory.[14,15] When treated with an excess of this reagent at 0°C the pale yellow solution of (8b)[16] lost its colour, and when the mixture was allowed to warm to room temperature conventional workup afforded the cyclobutenone (9b) in modest (30%) yield, but at 50°C this is doubled to almost 60%. The sample is identical to one previously prepared by a different route in these laboratories.[17] Under the neutral conditions of the reaction, epoxide (7b) is presumed to be the initial product that undergoes cyclopropylcarbinyl–cyclobutyl ring expansion (path *a*, Scheme 4). However, this contrasts with the behaviour of (8b) with dienes in Diels–Alder cycloadditions where only a norcaradiene product is formed from reaction across the *bridge bond*.[18] It is the cyclopropanaphthalene homologue (8a) that reacts with dienes by way of the *exocyclic* double bond.[19] These observations suggest, therefore, that the oxygen transfer to olefin (8b) could be to the bridge and not the exocyclic double bond. Such addition would afford the tricyclic oxiran (14b) (path *b*, Scheme 4) which is expected to undergo ring expansion to the oxacyclobutabenzene (15b) by

* The authors of the 1998 communication[10] claim use of 1-oxaspiro[2.4]hept-4-ene but do not provide data for it. The 1985 paper[10] provides data only for 4-methyl-1-oxaspiro[2.4]hept-4-ene.

way of a bicyclobutane–cyclobutene rearrangement as is observed for (16), the product of dihalocarbene addition to parent cyclopropabenzene.[20] The results of the present study are inconsistent with such a pathway but compatible with oxygen transfer to the exocyclic double bond of (8b) to give oxiran (7b).



Scheme 4



(16)

This last fact is substantiated by repetition of the oxygen transfer employing perdeuterated reagent [prepared from an excess of (D_6)acetone and used directly in this solvent[21,22]] at *c.* −30°C in the cavity of an n.m.r. spectrometer. After *c.* 50 min at this temperature oxygen transfer was >90% complete as judged by the presence of only a very weak n.m.r. resonance for the substrate C 2/5 atoms at 111·8 ppm. After 1 h at −10°C reaction was complete, and ^{1}H and ^{13}C n.m.r. spectra obtained were of the primary product of oxygen transfer only. The data (Experimental section) are fully compatible with epoxidation occurring at the exocyclic double bond of (8b) to give the benzo-fused oxaspiropentene (7b) with the same symmetrical aromatic frame and nine distinct ^{13}C resonances. The ^{1}H n.m.r. spectrum displayed a well separated AA′ component of an AA′BB′ pattern in the range 7·65–7·70 ppm with the remaining resonances appearing as a complex multiplet from 7·41–7·54 ppm. The typically shielded cyclopropabenzenyl C 2/5 atoms (C 2/7 for the naphtho compounds) are deshielded in comparison to those of the substrate alkene (8b) to a similar extent as are those for (7a) compared with (8a) [(8a)/(7a) 108·1/114·9; (8b)/(7b) 111·8/116·5 ppm]. The quaternary ^{13}C n.m.r. resonances at δ 70·1 and 71·5 match closely those recorded for the oxiranyl carbons of (7a) (71·0 and 71·7 ppm), and, when comparison is made with the n.m.r. data of the isolable oxiran (6) and its derived diol (13) (Fig. 1), it becomes clear that high-field chemical shifts recorded from oxygen transfer to both (7a) and (7b) are consistent with those recorded for (6) and not the ring-opened diol (13). The three benzylic oxiranyl carbon atoms resonate in the range 70·1–72·2 ppm whereas that of the benzylic alcohol (13) is at 85·2 ppm and those of benzpinacol [$Ph_2C(OH)C(OH)Ph_2$] are at 83·11 ppm.[23] These are some 12–13 ppm downfield of the resonances recorded for (7a) and (7b) and therefore substantiate further the argument that diol (10) (Scheme 2) is not involved in the formation of ketone (9).

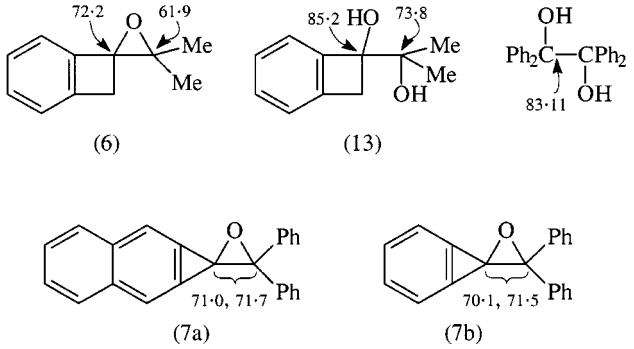


Fig. 1. N.m.r. resonances (in ppm) for selected quaternary carbon atoms bonded to oxygen.

Oxiran (7b) appears to be more stable than its naphtho analogue (7a) for there is little change in its n.m.r. spectra even after standing at 10°C for more than an hour—(7a) exhibits[6] an onset of rearrangement at 0°C which is some 50% complete after 8 h. After almost 1 h at 20°C evidence for decomposition of (7b) becomes evident in the ^{1}H spectrum with new signals appearing in the 7·8–8·2 ppm range; after only 5 min at 35°C these signals become clear. However, it is only from heating at 50°C for a further 30 min that the ^{13}C spectrum shows convincing evidence for significant change with new signals at δ 122·6 and 125·3 of similar intensity to that of C 2/5 of the epoxide (7b) at δ 116·5. A further period of heating for 1 h at this temperature essentially completes the process and the major product of reaction is identified as the cyclobutenone (9b) from its spectroscopic data (see above). The changes recorded in the ^{13}C spectra in proceeding from (8b) → (7b) → (9b) are shown in Fig. 2.

The ^{1}H n.m.r. spectrum of (9b) recorded above displays signals extraneous to both itself and its precursor

(7b). Noteworthy is the presence of a singlet at δ 6·2 and a multiplet in the range δ 7·92–7·96 in a 1 : 2 ratio that is consistent with hydroxyethanone (11b); integration indicates that (11b) is present to the extent of *c.* 10%. This product is known[5] to result from reaction of (7b) with *m*-chloroperoxybenzoic acid and aqueous workup, but we have now found, as expected, that it is formed in 74% yield when (7b) (generated as described above) reacts with aqueous sulfuric acid and in 53% yield with water alone (see Experimental section). In the acid-catalysed reaction (1 h at room temperature) *none* of cyclobutenone (9b) was detected while in the slower

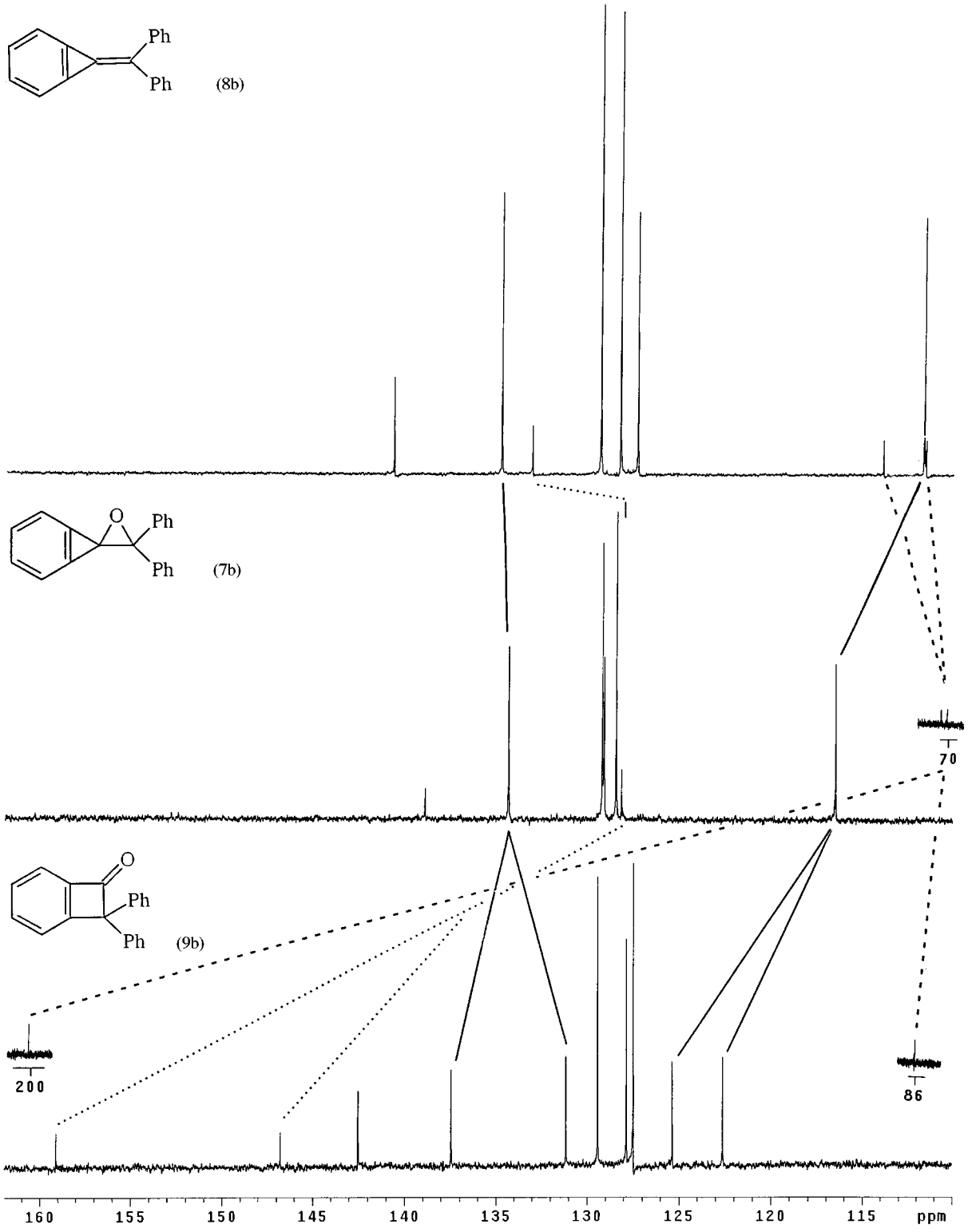


Fig. 2. ^{13}C n.m.r. spectra of cycloproparene (8b) (upper), oxiran (7b) (centre) and cyclobutenone (9b) (lower). Correlations from (8b) are for the eight methylidenecyclopropabenzene carbon atoms.

uncatalysed hydrolysis (14 h at room temperature) this ketone was isolated but only in 9% yield. As discussed above, the conversion of (7b) into hydroxyethanone (11b) must proceed by way of diol (10b) (Scheme 2). The appearance of cyclobutenone (9b) only from the uncatalysed aqueous hydrolysis is therefore much more consistent with a slow thermal rearrangement from (7b) competing with hydrolysis to (10b), rather than with complete hydrolysis to diol (10b) and subsequent partial conversion into ketone (9b) (Scheme 2).

Experimental*

General methods have been described previously.[24] ^{1}H and ^{13}C n.m.r. spectra were recorded for (D_6)acetone solutions on a Varian Associates Unity Inova 300 instrument with the chemical shifts (δ) referenced[25] to the residual methyl signal at δ 2·04(5) and the central line of its ^{13}C septet resonance at δ 29·8. Short- and long-range ^{1}H–^{13}C correlations were determined with gradient-enhanced inverse-detected HSQC and HMBC experiments, and the data now provided for the known compounds (8b), (9b) and (11b) are unpublished. The one-dimensional TOCSY experiments were performed with shaped-pulse-selective excitation and spin lock mixing times of 15–60 ms.

7-Diphenylmethylidenebicyclo[4.1.0]hepta-1,3,5-triene (8b)

The compound was prepared according to literature methods.[16] ^{1}H n.m.r. δ 7·30, br t, J 7·3 Hz, 2H, H 12; 7·38–7·41, BB′ of AA′BB′, 2H, H 2/5; 7·44, br t, J 6·5 Hz, 4H, 2×H 11/13; 7·58–7·61, AA′ of AA′BB′, 2H, H 3/4; 7·65, br d, J 8·5 Hz, 4H, 2×H 10/14. ^{13}C n.m.r. δ 111·7, C 8; 111·8, C 2/5; 114·1, C 7; 127·5, 2×C 12; 128·4, 2×C 10/14; 129·5, 2×C 11/13; 133·2, C 1/6; 134·9, C 3/4; 140·8, 2×C 9.†

Dimethyldioxiran

Dimethyldioxiran was prepared from acetone [or (D_6)acetone] according to the method of Adam *et al.*[14,15] employing the monopersulfate $2KHSO_5.KHSO_4.K_2SO_4$. The filtered solution so obtained was assumed[14] to be *c.* 0·1 M and was used within 48 h of its preparation. The ^{1}H n.m.r. spectrum of the solution of the labelled reagent in (D_6)acetone at 0°C displayed a water proton signal commensurate with that recorded for the labelled solvent alone.

Reactions of 7-Diphenylmethylidenebicyclo[4.1.0]hepta-1,3,5-triene (8b) with Dimethyldioxiran

(a) 8,8-Diphenylbicyclo[4.2.0]octa-1,3,5-trien-7-one (9b)

Olefin (8b) (100 mg, 0·39 mmol) and anhydrous potassium carbonate were placed in a round-bottomed flask (25 ml) equipped with a magnetic stirring bar and the whole mixture was cooled to 0°C. To the flask, purged with dry nitrogen, was added dimethyldioxiran (10 ml, *c.* 1·0 mmol) and after 5–10 min the initially bright yellow solution became colourless. In one reaction the contents were warmed to room temperature and stirred for several hours, while in a second run the mixture was stirring at 50°C for 2 h. The resultant mixture was cooled to room temperature, filtered through anhydrous potassium carbonate, and the filtrate dried (Na_2SO_4/K_2CO_3, 3 : 1), filtered through Celite (30–80 mesh), and concentrated in vacuum to a cream-coloured solid. Radial chromatography (1 : 1 dichloromethane/light petroleum elution) gave a cream-coloured oil which on trituration afforded the title compound as cream crystals (20°C: 32 mg, 30%; 50°C: 61 mg, 57%), m.p. 104–105°C (lit.[17] 104–105°C). ^{1}H n.m.r. δ 7·26, apparent tt, J_{ave} 7·2, 1·7 Hz, 2H, H 12; 7·35 m, 4H, H 11/13; 7·45, m, 4H, H 10/14; 7·59 apparent dt, J_{ave} 7·6, 1·1 Hz, 1H, H 5; 7·65, apparent td, J_{ave} 7·7, <1 Hz, 1H, H 4; 7·83, td, J 7·6, 1·2 Hz, 1H, H 3; 8·16, dt, J 7·6, 1·0 Hz, 1H, H 2. ^{13}C n.m.r. δ 81·4, C 8; 122·6, C 5; 125·3, C 2; 127·5, C 10/14; 127·9, C 12; 129·4, C 11/13; 131·1, C 4; 137·4, C 3; 142·5, C 9; 146·8, C 6; 159·1, C 1; 190·2, C 7. Confirmation of the H 2–H 5 resonances has been obtained from TOCSY experiments which correlate H 2 at 8·16 ppm in sequence with the 7·83 (H 3), 7·65 (H 4), and 7·59 ppm (H 5) resonances, in that order with increasing mixing times.

(b) 3′,3′-Diphenylspiro[bicyclo[4.1.0]hepta-1,3,5-triene-7,2′-oxiran] (7b)

To cycloproparene (8b) (15 mg, 0·06 mmol) in (D_6)acetone (100 μl) contained in an n.m.r. tube sealed with a septum cap and at −90°C was added, by syringe, the solution of (D_6)dimethyldioxiran (600 μl, 0·06 mmol). The solution was monitored by variable-temperature n.m.r. spectroscopy, and after 10 min at −30°C changes in the ^{1}H spectrum were evident. After a further 50 min at this temperature oxygen transfer was complete to >90% as judged from the ^{13}C spectrum. Warming to −10°C for 50 min resulted in spectra fully compatible with the presence of the *title epoxide (7b)* only (see Fig. 2). ^{1}H n.m.r. δ 7·41–7·54, complex m, 12H; 7·65–7·70, AA′ of AA′BB′, 2H, H 3/4. ^{13}C n.m.r. δ 70·1, C 7 or C 3′; 71·5, C 3′ or C 7; 116·4(5), C 2/5; 128·1, C 1/6; 128·4, 4×CH; 129·1, C *para*; 129·2, 4×CH; 134·3, C 3/4; 138·9, C *ipso*. An HSQC experiment in a separate run established the H–C connectivities quoted.

At 0°C the spectra were still of epoxide (7b) after 10 min, but warming to 20°C and holding this temperature for 70 min gave a ^{1}H spectrum which showed changes that became clear after 5 min at 35°C; these were, however, almost undetectable in the ^{13}C mode. Heating to 50°C for 30 min resulted in a ^{13}C n.m.r. spectrum that displayed signals of almost the same intensity for C 2/5 of epoxide (7b) (δ 116·5) and C 2 and C 5 of cyclobutene (9b) (δ 125·3 and 122·6, respectively). After a further 60 min at this temperature the reaction was complete and the spectroscopic data matched those for ketone (9b) described above. Extraneous signals in this last ^{1}H n.m.r. spectrum have been assigned to hydroxytriphenylethanone (11b) (see below) and account for *c.* 10% of the product mixture.

(c) 2-Hydroxy-1,2,2-triphenylethanone (11b)

Olefin (8b) was allowed to react with dimethyldioxiran as described in *(a)* above at −20°C for 60 min. This was followed by two separate procedures: (i) the addition of sulfuric acid; (ii) the addition of ice-cold water.

(i) The addition of sulfuric acid (0·5 ml, 2 M) at the same temperature and then stirring for a further 60 min to attain room temperature, followed by conventional workup and recrystallization (hexane), afforded the α-hydroxy ketone (11b) as colourless needles (84 mg, 74%), m.p. 85–86·5°C (lit.[26] 86–87°C), identical to a sample prepared previously in these laboratories.[5] ^{1}H n.m.r. δ 6·03, br s, OH; 7·29–7·40, complex m, 8H; 7·41–7·52, complex m, 5H; 7·94, br d, J 8·4 Hz, 2H. ^{13}C n.m.r. δ 86·4, Ph_2**C**(OH); 128·2(4), 4×CH; 128·2(7), 2×CH; 128·6, 2×CH; 128·8, 4×CH; 131·4, 2×CH; 133·0, CH *para*; 137·0, C *ipso*; 144·5, 2×C *ipso*; 200·9, Ph**C**O.

(ii) The addition of ice-cold water (0·5 ml) and then stirring for 14 h, during which time room temperature was attained, followed by conventional workup, afforded cyclobutenone (9b)

* Formal von Baeyer nomenclature is employed in this section so that 1*H*-cyclopropabenzene becomes bicyclo[4.1.0]hepta-1,3,5-triene; the atom numbers C 2/5 referred to in the text are the same under both naming systems.
† Atoms C 9–C 14 and H 10–H 14 belong to the phenyl groups. (C 8 is the methylidene carbon.)

(8 mg, 7·5%), m.p. 103–105°C (lit.[5] 104–105°C), as the most mobile component from radial chromatography (1 : 1, dichloromethane/light petroleum elution), and the title α-hydroxy ketone (11b) as the second component (60 mg, 53%) identical to the sample described in (i) above.

Acknowledgments

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Note Added in Proof

The synthesis and spectroscopic characterization of oxaspiropentene (3) have been reported since submission of this paper—see Billups, W. E., Saini, R. K., and Daniels, A. D., *Org. Lett.*, 1999, **1**, 115.