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REACTIONS OF BICYCLOBUTYLIDENE AND 1,3-BIS(TRIMETHYLENE)PROPADIENE

SYNTHESIS OF TRISPIRO[3.0.3.0.2.0]UNDECANE, 9-METHYLENEDISPIRO[3.0.3.1]NONANE, AND BICYCLOBUTYLIDENE-2,2'- AND 2,4'-DIONE

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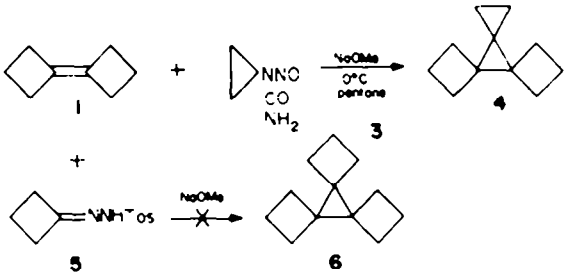
Abstract—A number of reactions of bicyclobutylidene (1) and 1,3-bis(trimethylene)propadiene (2), directed towards the preparation of compounds in which conjugated and steric effects of the cyclobutane ring could be evaluated, are described. Trispiro[3.0.3.0.2.0] undecane (4) was prepared from 1, and 1-cyclobutylidenespiro[3.2]hexane (8b) from 2. Thermolysis of 8b gave 9-methylenedispiro[3.0.3.1]nonane (14). Oxidation of 1 with singlet oxygen gave the "ene" product 17, and an attempted two step conversion to the dioxetane via the bromohydroperoxide 19 also gave 17. Oxidation of 2 with peroxyacids gave products which probably arose from either the allene oxide or the bis-oxirane. The cyclobutane ring does not appear to afford any steric protection to allow the isolation of the dioxetane or allene oxide. Three unsucessful routes directed towards the synthesis of bicyclobutenyl (24) are described, and the syntheses of bicyclobutylidene-2,4'-dione (39) and - 2,2'-dione (40) are reported.

We have recently described the preparation of bicyclobutylidene (1) and 1,3-bis(trimethylene)propadiene (2),[1] and we now discuss some chemistry of these compounds directed towards elucidating the conjugative and steric effects of the 4-membered ring. The conjugative character of the cyclopropane ring has been widely explored,[2] and the theoretical basis for its interaction is reasonably secure.[3,4] The corresponding conjugative interaction of the cyclobutane ring is predicted to be much smaller,[4] and there is little convincing evidence for its operation.[4c] The cyclopropane ring would not be expected to be a particularly good protecting group owing to its high reactivity, but the lesser reactivity of the cyclobutane ring might enable this group to be used to block an otherwise reactive centre. Although the synthesis of higher homologues of 2 did not indicate any great protection of the unsaturated terminus by the cyclobutane ring,[1] this might be due to the coplanarity of the ring and the π-system, and a cyclobutane ring at a potentially reactive sp^3 carbon might afford more steric protection.

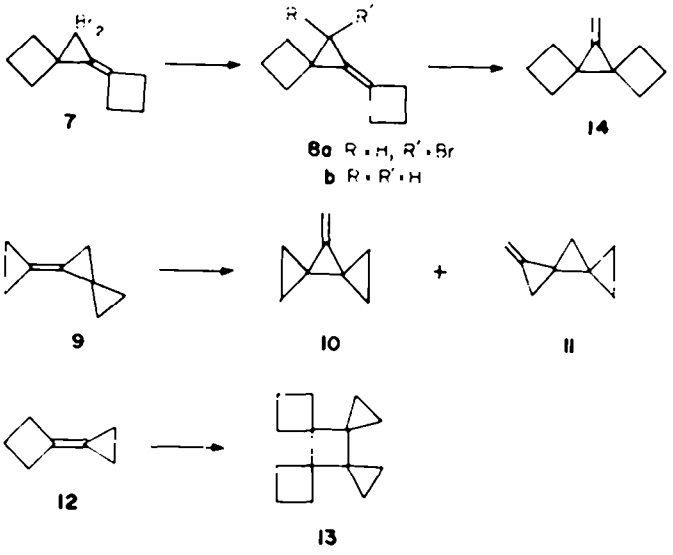
Both 1 and 2 have been shown to react with dihalo carbenes,[1] 2 being prepared from 1 by the Skattebøl allene synthesis.[5] Reaction of 1 with cyclopropylidene and cyclobutylidene would provide a simple synthesis of cyclobutyl substituted cyclopropanes, compounds of which there are few examples. Bicyclobutylidene (1) reacts with cyclopropylidene, prepared from N-nitroso-N-cyclopropyl urea (3) and sodium methoxide,[6] to give trispiro[3.0.3.0.2.0]undecane (4), a colourless liquid, in 32% yield. The NMR spectrum ($CDCl_3$) showed a multiplet at τ 7.80–8.44 for the cyclobutyl protons (12 H) and a singlet at τ 9.46 for the cyclopropyl protons (4 H), and the IR spectrum exhibited a weak cyclopropane absorption at 3030 cm^{-1}. Compound 4 was thermally stable, a property in common with related rotanes.[7]

It has so far been impossible to trap cyclobutylidene from its potential precursors with olefins, but the high reactivity of 1 encouraged us to examine its reaction with cyclobutoxylhydrazone (5), which is believed to give cyclobutylidene via the diazo derivative on treatment with sodium methoxide.[8] However, in accord with previous experience, we were unable to isolate any of the desired trispiro[3.0.3.0.3.0]dodecane (6) under these conditions.



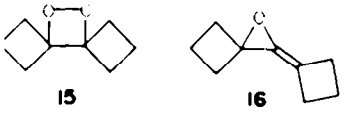
Although 2 reacts with dihalocarbene, we were unable to obtain the methylene addition product by either reaction with diazomethane[9] or by the Simmons–Smith reaction[10] and its modifications.[11] The decrease in reactivity of the allene compared to the corresponding alkene is in agreement with the observations of Rahman and Kuivila,[1,2] who obtained but a low yield of the alkylidenecyclopropane on reaction of 2-methyl-2,3-pentadiene and 2,3-pentadiene under the Simmons–Smith conditions. In order to prepare the desired cyclopropylidenecyclobutane 8b, the mono-dibromocarbene adduct 7[1] was treated with tri-n-butyltin hydride. It was found that using commercial $(nBu)_3SnH$ only one bromine could be replaced and 8a was obtained, but reaction of 7 with excess freshly prepared $(nBu)_3SnH$ for 5 days gave 8b in 58% yield. The NMR spectrum of 8b shows a multiplet at τ 7.02–7.50 (4 H) assigned to the allylic protons, a multiplet at τ 7.58–8.34 (8 H) assigned to the remaining cyclobutyl protons, and a triplet at τ 8.90–9.10 (2 H) assigned to the cyclopropyl protons.

The thermolysis of cyclopropylidenespiropentane (9) at 210° gave a mixture of 10 and 11,[7] while cyclopropylidenecyclobutane (12) dimerised in the liquid phase at 210° to give 13.[13] Either mode of reaction appeared accessible to 8b, although attempts to dimerise 1 had not



been successful.[14] Pyrolysis of **8b** in a flow system[7,15] at 430°, 0.1 mm gave a mixture which, after separation by preparative GLC, yielded **14** (17%) and **8b** (51%). In the NMR spectrum ($CDCl_3$), **14** shows a singlet at τ 4.66 (2 H) assigned to the methylene protons and a multiplet at τ 7.70–8.10 (12 H) assigned to the cyclobutyl protons. The IR spectrum shows a weak band at 1790 cm^{-1}, attributed to the methylenecyclopropane group.[12] Attempts to increase the yield of **14** by prolonging the reaction time were unsuccessful, and **8b** and **14** may be in equilibrium under these conditions. No products which might result from rearrangement of **14** were observed. **8b** was recovered unchanged after heating at 200° in the liquid state, and no evidence for dimer formation was obtained.

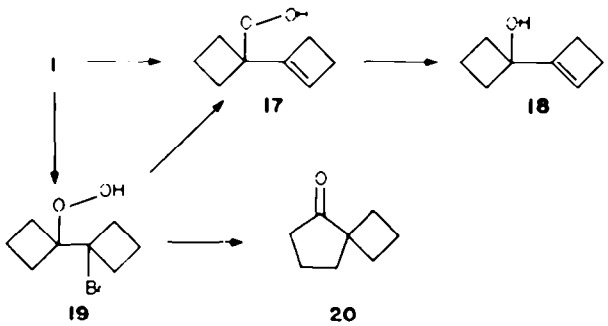
If the cyclobutane ring could act as a steric blocking agent, then it might be possible to isolate the dioxetane **15** derived from **1** and the allene oxide **16** derived from **2**.



The oxidation of **1** with *m*-chloroperoxybenzoic acid had been shown to give the oxirane,[1] and controlled oxidation thus appeared possible. Reaction of **1** with $^1O_2$, produced from H_2O_2 and sodium hypochlorite, gave the "ene"-product **17**, a colourless liquid, in 40% yield. The NMR spectrum (CCl_4) showed a broad singlet at τ 2.06–2.36 (1 H) characteristic of the hydroperoxy proton, a singlet at τ 4.09 (1 H) assigned to vinylic proton and a multiplet at τ 7.4–8.0 (10 H) assigned to the cyclobutyl protons. Reduction of **17** with sodium borohydride gave the alcohol **18**.

Since direct reaction with $^1O_2$ had given the not unexpected "ene" product,[16] an alternative route to **15** was investigated. Reaction of **1** with 1,3 - dibromo - 5,5 - dimethylhydantoin and excess 86% hydrogen peroxide at −70°[17] gave the bromohydroperoxide **19** in 36% yield, the spectral properties being in accord with the assigned structure. Reaction of **19** with KOtBu in THF gave **17** and **18** in 18% and 20% yield, respectively, identical in all observed respects with the previously prepared samples. Reaction of **19** with sodium methoxide gave spiro[3,4]octan-5-one (**20**),[18] a compound previously obtained by pyrolysis of 9-oxatrispiro[3.0.3.1]nonane,[1] which may be an intermediate in this present transformation.[17] Reaction of **19** with methanolic sodium methoxide and EDTA at −30°,[19] or with silver acetate in dichloromethane at various temperatures,[20] also gave **20**.

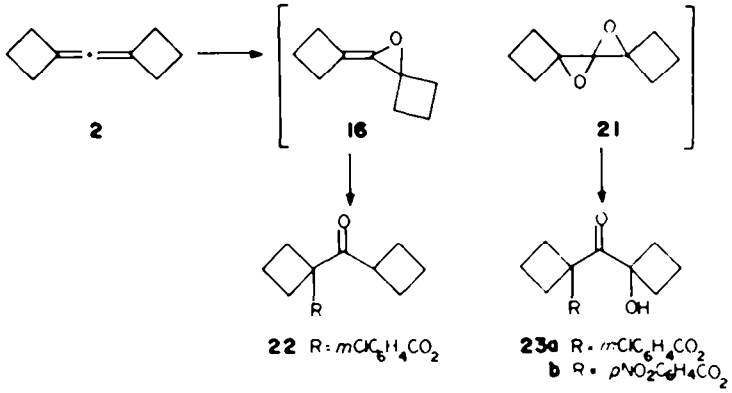
The allene **2** was oxidised with 1.5 equivalents of *m*-chloroperoxybenzoic acid in dichloromethane at 0°, when **22**, a colourless liquid (6%), and **23a**, white crystals, m.p. 98–99° (46%), were obtained. The NMR spectrum ($CDCl_3$) of **22** showed a multiplet at τ 1.90–2.73 (4 H) assigned to the aromatic protons, and a multiplet at τ 7.10–8.25 (13 H) assigned to the cyclobutyl protons, while the IR spectrum showed a strong absorption at 1710 cm^{-1}. The NMR spectrum ($CDCl_3$) of **23a** again had a multiplet in the aromatic region, τ 1.9–2.7 (4 H), to-



gether with a multiplet for the cyclobutyl and hydroxyl proton, τ 6.90–8.36 (13 H), and the IR spectrum showed a broad hydroxyl (3405 cm^{-1}) and a strong carbonyl (1710 cm^{-1}) absorption.

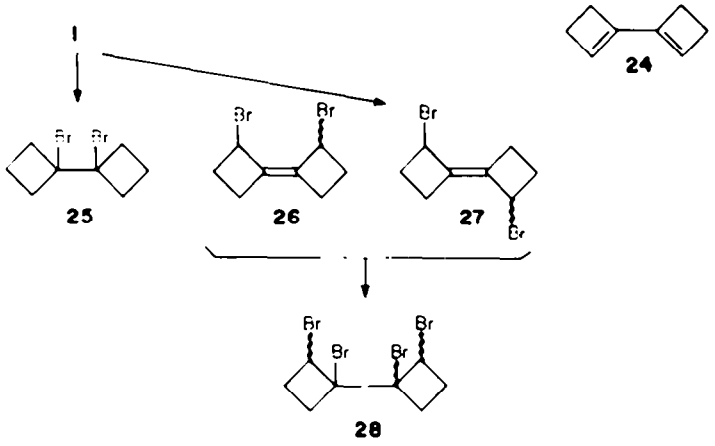
was treated with bromine to give the tetrabromide **28**, but again all attempts at debromination failed.

A second route to **24** from the alcohol **18** was investigated. Reaction of **18** with acetic anhydride gave the



Compounds **22** and **23a** can arise by acid catalysed ring opening of **16** and **21** respectively, a process previously observed by Crandall and co-workers in the epoxidation of tetramethylallene.[21] In an attempt to circumvent this

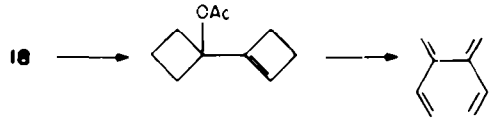
acetate **29** as a colourless liquid in 60% yield. Flow pyrolysis of **29** at 450° and 0.1 mm gave unreacted **29** (28%) and 3,4-diethylene-1,5-hexadiene (**30**) (23%). The tetraene **30** was identical in all observed properties with



ring opening. **2** was treated with *m*-chloroperoxybenzoic acid in the presence of anhydrous sodium carbonate,[21] but only smaller yields of **22** and **23a** were obtained. Oxidation with *p*-nitroperoxybenzoic acid under buffered conditions gave only **23b** in 26% yield as white crystals, m.p. 79–80°.

Thus the cyclobutane ring does not appear to afford steric protection to the dioxetane or allene oxide, and in the first case the observed alternate mode of reaction may be favoured by the relief of cyclobutyl ring strain.

A compound of considerable potential for the synthesis of polycyclobutyl systems would be bicyclobutenyl (**24**), and we have explored a number of routes to the compound. Bromination of **1** in $CHCl_3$ at 0° gave the dibromide **25** in almost quantitative yield, but decomposition occurs rapidly if **25** is stored above −78°. Attempts to dehydrobrominate **25** under a variety of conditions were unsuccessful, either polymeric products or **1** being obtained. The reaction of **1** with *N*-bromosuccinimide gave a mixture of **25** and the allylic bromides **26** and **27**. Reaction of the mixture of allylic bromide with a variety of dehydrobromination again was unsuccessful, only polymeric materials being formed. Consequently the mixture of allylic bromides **26** and **27** those reported by Skattebøl and Solomon.[22] Compound **30** may arise by thermal cleavage of **24**, and a similar cleavage has been observed with the diacetate of 1,2-di(hydroxymethyl)cyclobutane.[23] Heating **29** at lower temperature led to its recovery unchanged.



As a third possible route to **24** we have examined methods of preparing the diols **37** and **38**, which are also potential intermediates to the diones **39** and **40**. The Barton–Kellogg reaction[24,25] of 2-acetoxycyclobutane (**31**) gave the thiirans **33** (30%) and **34** (33%) via **32**. The thiirans were separated and each desulphurised with triphenylphosphine[24] to the corresponding alkenes **35** and **36**. Compound **35**, colourless crystals, m.p. 43–44°, was obtained in *ca.* 50% yield.[26] The NMR spectrum showed a two proton triplet at τ 4.43–4.67 and a fourteen proton multiplet at τ 7.30–8.15, and the IR spectrum

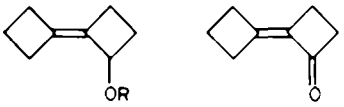
showed a strong band at 1725 cm $^{-1}$. Compound **36**, colourless crystals, m.p. 45–46°, was obtained in similar yield,[26] and showed similar NMR and IR spectra. Hydrolysis of **35** and **36** with methanolic sodium methoxide or potassium carbonate in methanol gave the corresponding diols **37** and **38**. The stereochemical assignments shown for the thiirans and acetates are largely based on the properties of these diols and the diones derived from them.

Diol **37**, m.p. 131–132°, showed in the NMR spectrum ($CDCl_3$, saturated) a signal at τ 8.03 assigned to the hydroxyl proton which shifts on dilution (50%) to τ 8.28. The IR spectrum of **37** as a 0.27 M solution in $CHCl_3$ showed two OH absorptions, the stronger of which we assigned to free OH and the weaker to hydrogen bonded OH. The free OH band remained dominant on dilution to 0.07 M. In contrast, diol **38**, m.p. 63–64°, has its hydroxyl proton at τ 5.81 in the NMR spectrum ($CDCl_3$), which is shifted only to τ 5.88 on dilution, and in the IR spectrum (0.27 M, $CHCl_3$) the free OH band is weaker than the hydrogen bonded OH absorption and virtually disappears on dilution. Diol **37** was consequently assigned the *trans* structure shown, in which intra-molecular hydrogen bonding could not occur, and diol **38** was assigned the *cis* structure, in which it could.

Oxidation of **37** with chromium trioxide pyridine complex[27] give the dione **39** in 36% yield, and a similar oxidation of **38** gave **40**, 26%. In the IR spectra only **40** showed a band at 1670 cm $^{-1}$, attributable to the C=C stretch, and in the electronic spectra compound **39** absorbed at a slightly longer wavelength with higher intensity than **40**, both observations being in accord with the stereochemistry assigned to the diols.

No attempt was made to transform the diols into **24** because of our experience with the thermolysis of the monoacetate **29**. The low yield of the oxidation step precluded an investigation of the chemistry of the diones, which may have interesting photochemical properties and could also act as precursors for other cyclobutyl systems.

In a preliminary investigation to determine if the Wittig reaction might be an alternative route to the diones, **31** was treated with cyclobutyltriphenylphosphonium bromide and n-butyl lithium when a 5% yield of the acetate **41a** was obtained, which was characterised by conversion to the known ketone **42**[28] via the known alcohol **41b**.[28] The low yield is probably due to increased steric interference by the acetate, since hindered alkenes are difficult to prepare by the Wittig method, and the use of this reaction to prepare **35** was therefore not examined.

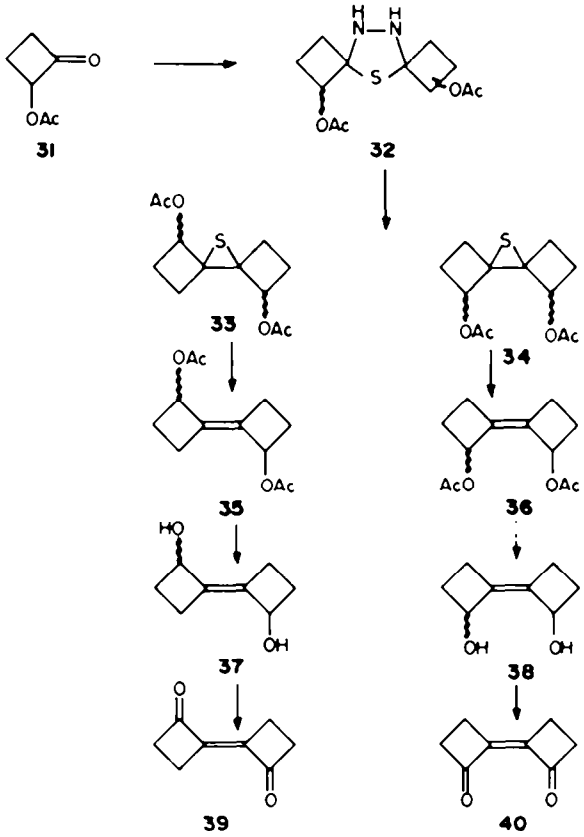


41 a R Ac
b R = H

42

EXPERIMENTAL

NMR spectra were obtained on either a Varian T-60 or HA-100 spectrometer and are recorded in τ units with Me_4Si as internal standard. Mass spectra were taken on either an AEI MS-12 or MS-9 spectrometer. IR spectra were recorded on a Unicam SP-200 spectrometer, only strong and medium bands being reported. Electronic spectra were recorded on a Unicam SP-800



recording spectrometer. M.Ps were taken on a Kofler hot stage microscope and are uncorrected. GLC was carried out on either a Hewlett Packard F and M 5750 or 776 chromatograph.

Silica for preparative TLC was Merck Kieselgel PF_{254}, and for column chromatography Hopkins and Williams MFC silica gel. Solvents were purified by standard methods. Petroleum ether is that fraction boiling below 40°.

Bulb to bulb distillations were carried out at a pressure $< 1 \times 10^{-4}$ mm on a vacuum line.

Synthesis of trispiro[3.0.3.0.2.0]*undecane* (**4**)

Bicyclobutylidene (**1**) (140 mg, 1.30 mmole) was added to dry pentane (20 ml) and the soln cooled to 0° under N_2 and stirred. N-nitroso-N-cyclopropylurea (0.48 g, 3.7 mmole) was then added, followed by NaOEt (2.7 g, 50 mmole) and the mixture was stirred for 6.5 hr. The insoluble material was removed by filtration, and the ppt wash with pentane (2 × 5 ml). The combined filtrate and washings were reduced in volume by distillation, and the remaining solvent then removed by distillation under reduced pressure. The residue was then purified by bulb to bulb distillation under reduced pressure to give *trispiro*[3.0.3.0.2.0]*undecane* (**4**), 60 mg (31%), MS *m/e* 148.1242 ($C_{11}H_{16}$ required 148.1252), 148 (83%), 132, 131, 130, 129, 120, 119 (100%). NMR, see Discussion; IR (liquid film) 2920, 1440, 1010 and 900 cm^{-1}.

Reduction of the dibromide **7**

(i) *With commercial tri-n-butyltin hydride.* The dibromide **7** (0.5 g, 1.7 mmole) was introduced into a 3-necked round bottomed flask fitted with a dropping funnel, stirrer and a condenser, and cooled in an ice bath. Tri-n-butyltin hydride (1.0 g, 3.4 mmole, commercial) was added over 2 hr under N_2 with stirring. The mixture was heated to 35–40° and stirred for 3 days. Preparative TLC on silica of the orange mixture, eluting with petroleum ether, gave, after extraction, a pale yellow oil, which was purified by bulb to bulb distillation to give the colourless *2-cyclobutylidene-3-bromospiro*[3.2]*hexane* (**8a**), 92 mg (26%), MS *m/e* 212.0193 ($C_{10}H_{13}Br$ requires 212.0201), 214, 212 (6%, 1:1, M^+), 186, 184 (12%, 1:1, $M-C_2H_4$), 171, 169, 133, 131, 117 (100%), 105, 104, 103, 96, 91 (100%); NMR ($CDCl_3$), 6.46–6.60 (q, 1 H, cyclopropyl), 7.0–7.3 (m, 4 H, allylic), 7.54–8.20 (m, 8 H, CH_2); IR (liquid film) 2980, 1780, 1440, 1420, 1170 and 675 cm^{-1}.

(ii) *With freshly prepared tri-n-butyltin hydride.* The dibromide **7** (0.89 g, 3 mmole) was put in a 3-necked flask fitted as for (i), and freshly prepared[29] $(nBu)_3SnH$ (2.2 g, 7.5 mmole) was added dropwise over 2 hr to the vigorously stirred compound under N_2. The mixture was then stirred vigorously at 40–45° under N_2 for 5 days, and the mixture was then distilled under reduced pressure to give *1-cyclobutylidenespiro*[3.2]*hexane* (**8b**), 230 mg (55%), b.p. 85°, 10 mm; MS 134.1076 ($C_{10}H_{14}$ required 134.1095), 134 (1%) 119 (14%), 117, 106 (21%, $M-C_2H_4$), 105, 104, 103, 93, 92, 91 (100%); NMR see discussion; IR (liquid film) 2950, 1790, 1440, 1420, 1118 and 1010 cm^{-1}.

Pyrolysis of 1-*cyclobutylidenespiro*[3.2]*hexane* (**8b**). *Synthesis of* 9-*methylenedispiro*[3.0.3.1]*nonane* (**14**)

Compound **8b** (160 mg, 1.2 mmole) was put into a 5 ml round bottomed flask which was then connected to a pyrex column (10 mm × 200 mm) containing glass helices, which was passed through a horizontal cylindrical furnace. The other end of the tube was connected to a flask and an outlet to vacuo. The furnace was heated to 430° (thermocouple in well), the system evacuated to 0.1 mm and the collection flask immersed in liquid N_2. Compound **8b** distilled through the furnace and the products were collected in the flask. Preparative GLC on silcone rubber (6 ft × ¼ in.) at 80° gave, in order of increasing retention time: (i) 9-*methylenedispiro*[3.0.3.1]*nonane* (**14**), 27 mg (17%), colourless liquid; MS *m/e* 134.1090 ($C_{10}H_{14}$ requires 134.1095), 134 (7%), 133 (19%), 131, 119, 117, 115, 107, 106 (31%, $M-C_2H_4$), 105, 103, 93, 91 (100%); NMR, see discussion; IR (liquid film), 3000, 1455 and 905 cm^{-1}; (ii) 1-*cyclobutylidenespiro*[3.2]*hexane* (**8b**), 81 mg (51%).

When a 10 mm × 320 mm furnace tube was used at 410° and 0.1 mm then the ratio of **14**:**8b** was 1:4 (GLC) and some decomposition products were found in the NMR spectrum of the crude product.

Reaction of bicyclobutylidene with hydrogen peroxide and sodium hypochlorite

Synthesis of 1 - (1 - *hydroperoxycyclobutyl*)*cyclobutene* (**17**). Bicyclobutylidene (120 mg, 1.1 mmole) was dissolved in MeOH (30 ml), the soln cooled to 0° and H_2O_2 (30%, 2.6 ml, 0.02 mole) was added. The soln was stirred, cooled and NaOCl (5%, 10.8 ml, 7 mmole) was added dropwise over 30 min. The mixture was stirred for a further 2 hr at 0°, water (30 ml) was added and the mixture extracted with $CHCl_3$ (2 × 20 ml). The combined extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to give a pale yellow liquid, which on bulb to bulb distillation gave 1-(1-*hydroperoxycyclobutyl*)*cyclobutene* (**17**), colourless liquid, 60 mg (40%): MS *m/e* 140 (30%, M^+), 123 (20%, M–OH), 122, 120, 112 (20%, $M-C_2H_4$), 107, 105, 96, 95 (20%, $M-C_2H_3O$), 91, 87, 81, 79, 77, 67 (45%, $M-C_4H_9O$), 65, 55, 53 (100%); NMR, see discussion; IR (liquid film) 3450, 2980, 1670, 1270, 1155, 1110, 880 and 770 cm^{-1}. (Found: C, 68.15; H, 8.66. Calc. for $C_8H_{12}O_2$: C, 68.55; H, 8.63%).

Reduction of **17** *with sodium borohydride*

Synthesis of 1 - (- *hydroxycyclobutyl*)*cyclobutene* (**18**). The hydroperoxide **17** (60 mg, 4.3 mmole) was dissolved in abs EtOH (3 ml), the soln stirred and $NaBH_4$ (50 mg, 1.5 mmole) added in one portion. The mixture was stirred at room temp. for 3 hr under N_2, and water (3 ml) was then added. The soln was made just acidic with 50% HCl aq and extracted with $CHCl_3$ (2 × 10 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent removed by evaporation. The residual oil was purified by bulb to bulb distillation to give 1-(1-hydroxycyclobutyl)cyclobutene (**18**), colourless oil, 40 mg (75%); MS *m/e* 124 (8%, M^+), 122, 112, 107 (57%, M–OH), 104, 96 (26%, $M-C_2H_4$), 95, 81, 80, 79 (52%, $M-C_2H_3O$), 77, 70, 67, 65, 57, 55, 53, 43, 41 (100%); NMR (CCl_4), 4.12 (s, 1 H, olefinic), 7.24–8.03 (m, 11 H, OH and cyclobutyl); IR (liquid film) 3450, 2980, 1730, 1270, 1160, 1090, 980, 930, 880, 820 and 770 cm^{-1}.

Reaction of bicyclobutylidene (**1**) *with hydrogen peroxide and* 1,3-*dibromo*-5,5-*dimethylhydantoin*

Synthesis of 1 - *hydroperoxy* - 2' - *bromobicyclobutyl* (**19**). Bicyclobutylidene (0.22 g, 2 mmole) and H_2O_2 (86%, 1.36 g, 40 mmole) were added to dry ether (20 ml) at − 70° under N_2. The solution was stirred and 1,3 - dibromo - 5,5 - dimethylhydantoin (0.5 g, 2 mmol) was added in small portions over 10 min. The mixture was stirred at − 70° for a further 30 min and then allowed to warm to room temp. The soln was extracted with cold sat $NaHCO_3$ aq (7 ml) and then water (2 × 10 ml). The ethereal layer was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a colourless liquid. Preparative TLC on silica, eluting with petroleum ether–ether (3:1) gave, in order of increasing R_f values: (i) 1-*hydroperoxy*-2'-*bromobicyclobutyl* (**19**), colourless liquid, 160 mg (36%); MS *m/e* 220.1068 ($C_8H_{13}O_2Br$ requires 220.1078), 222, 220 (1:1, 4%), 205, 203 (1:1, 14%, M–OH), 178, 176, 163, 161, 151, 149, 141, 135 (80%), 133 (1:1, $M-C_4H_7O_2$), 124, 123, 121, 87 (100%); NMR ($CDCl_3$), 1.27–1.57 (bs, 1 H, hydroperoxy), 7.0–7.9 (m, 12 H, cyclobutyl); IR (liquid film) 3450, 2970, 1470, 1260 and 810 cm^{-1}, (ii) 1,1'-*dibromobicyclobutyl* (**25**), 10 mg (2%), identical in all observed respects to an authentic sample (see below).

Reaction of **19** *with potassium t-butoxide*

Compound **19** (90 mg, 0.4 mmole) was dissolved in dry THF (8 ml) and the solution stirred under N_2. t-BuOK (220 mg, 2 mmole) was added in one portion and the mixture stirred at room temp. for 1.5 hr. Water (5 ml) was added and the mixture extracted with ether (2 × 8 ml). The combined ethereal layers were dried ($MgSO_4$) and the solvent removed by evaporation to give an oil. Preparative TLC on silica, eluting with petroleum ether–ether (4:1) gave in order of increasing R_f value: (i) the alcohol **18**, 10 mg (20%), identical in all observed respects to the previous sample; (ii) the hydroperoxide **17**, 10 mg (18%), identical in all observed respects to the previous sample.

Reaction of **19** *with sodium methoxide*

(i) Compound **19** (100 mg, 0.45 mmole) was dissolved in dry ether (20 ml), the soln cooled to 0° under N_2 and stirred. NaOMe (0.5 g, 9.8 mmole) was added in one portion and the mixture then stirred for 2 hr at 0°. A ppt formed which was removed by filtration and washed with ether (10 ml). The combined ether layers were reduced by evaporation to give *spiro*[3,4]*octan*-5-*one*, 20 mg (36%), identical in all observed respects with an authentic sample.

(ii) Compound **19** (60 mg, 0.27 mmole) was dissolved in dry MeOH (2 ml) and stirred at −30° under N_2. Freshly prepared NaOMe in MeOH (1 ml, 0.63 M, 0.54 mmole) containing EDTA (2 mol% based on NaOMe) was added over 10 min and the mixture then stirred at −30° for a further 2 hr. Ice cold water (2 ml) was added and the soln was extracted with cold CCl_4 (2 × 7 ml). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give an oil (20 mg). The NMR and IR spectra indicated the presence of **20** and unchanged **19**.

Reaction of **19** *with silver acetate*[29]

A soln of **19** (150 mg, 0.68 mmole) in CH_2Cl_2 (2 ml) was added to a rapidly stirred slurry of AgOAc (0.44 g, 2.6 mmole) in CH_2Cl_2 (2 ml) at −10° under N_2. The mixture was stirred at −10° for 15 min and the solids removed by filtration. The filtrate was washed with ice water (3 ml) and Na_2CO_3aq (10%, 3 ml) and dried ($MgSO_4$). The solvent was removed at 0° under reduced pressure to give an oil, identified as *spiro*[3,4]*octan*-5-*one* (**20**), 60 mg (71%) by comparison with an authentic sample. Reaction at other temps. gave essentially the same result.

Reaction of 1,3-*bis*(*trimethylene*)*propadiene* (**2**) *with* m-*chloroperoxybenzoic acid*

(i) The allene **2** (130 mg, 1.1 mmole) was dissolved in dry CH_2Cl_2 (15 ml), the soln stirred, cooled to 0° under N_2 and a soln of *m*-chloroperoxybenzoic acid (330 mg, 1.9 mmole) in dry CH_2Cl_2 (6 ml) was added dropwise over 10 min. The mixture was then allowed to warm to room temp. and stirred for a further 12 hr. The mixture was extracted with sat Na_2CO_3aq (2 × 10 ml), water (3 × 10 ml) and dried ($MgSO_4$). The solvent was removed by evaporation to give an oil which, by preparative TLC on silica, eluting with petroleum-ether–ether (4:1) gave, in order of increasing R_f value: (i) 1 - (m - *Chlorobenzoxy*) - 1,3 - *bis*(*trimethyl*) - 3 - *hydroxypropan* - 2 - *one* (**23a**), 150 mg (45%), white crystals, m.p. 98–99°: MS *m/e* 310 (2%, M^+), 308, 292, 280 (44%, $M-C_2H_4$), 252, 238 (100%), 210, 209, 181, 153 (100%, $M-CO_2C_6H_4mCl$); NMR see Discussion; IR (KBr) 3405, 2901, 1710, 1575, 1430, 1300, 1250, 1135 and 680 cm^{-1}. (Found: C, 62.08; H, 5.38; Cl, 11.23. Calc. for $C_{16}H_{17}O_4Cl$: C, 62.24; H, 5.55; Cl, 11.48%); (ii) 1 - (m - *chlorobenzoxy*) - 1,3 - *bis*(*trimethylene*)*propan* - 2 - *one* (**22**), 20 mg (6%), oil; MS *m/e* 293, 292 (M^+, 43%), 237, 222, 209, 181, 156, 153 (100%); NMR, see Discussion; IR (liquid film) 2901, 1710, 1575, 1430, 1300, 1250, 1135, 982, 818, 760 and 680 cm^{-1}. (Found: C, 65.99; H, 6.04; Cl, 11.61. Calc. for $C_{16}H_{17}O_3Cl$: C, 65.65; H, 5.85; Cl, 12.11%); (iii) A mixture of **2** (120 mg, 1.0 mmole), *m*-chloroperoxybenzoic acid (130 mg, 0.76 mmole) and anhyd. Na_2CO_3 (160 mg, 1.5 mmole) in dry CH_2Cl_2 (30 ml) was stirred at room temp. under N_2 for 2 days. The insoluble material was removed by filtration, and the filtrate evaporated under reduced pressure to give an oil. Preparative TLC, as for (i), gave **23a**, 11 mg (4%) and **22**, 2 mg (1%), together with the allene **2**, 60 mg (50%).

Reaction of 1,3-*bis*(*trimethylene*)*propadiene* (**2**) *and* p-*nitroperoxybenzoic acid*

A mixture of **2** (60 mg, 0.5 mmole), *p*-nitroperoxybenzoic acid (180 mg, 1.0 mmole) and anhyd. Na_2CO_3 (100 mg, 1.0 mmole) in dry CH_2Cl_2 (30 ml) was stirred under N_2 at room temp. for 1.5 hr. The insoluble material was then removed by filtration, and the filtrate evaporated under reduced pressure to give an oil. Preparative TLC on silica, eluting with CH_2Cl_2, gave 1 - (p - *nitrobenzoxy*) - 1,3 - *bis*(*trimethylene*) - 3 - *hydroxypropan* - 2 - *one* (**23b**), 40 mg (26%), white crystals, m.p. 79–80°; MS, *m/e* 319 (3%, M^+)), 291 (9%, $M-C_2H_4$), 250, 249, 219, 218, 191, 153, 152, 151, 150 (100%); NMR ($CDCl_3$), 1.51–1.97 (m, 4 H, aromatic), 6.91–8.35 (m, 13 H, cyclobutyl and hydroxyl); IR (KBr) 3408, 2905, 1720, 1605, 1538, 1350, 1300, 883, 850 and 722 cm^{-1}. (Found: C, 59.82; H, 5.32; N, 4.27. Calc. for $C_{16}H_{17}O_6N$: C, 60.18; H, 5.37; N, 4.39%).

Bromination of bicyclobutylidine (**1**)

A soln of Br_2 (1.60 g, 10 mmole) in dry $CHCl_3$ (10 ml) was added dropwise over 30 min to a vigorously stirred soln of **1** (1.08 g, 10 mmole) in dry $CHCl_3$ (10 ml) at 0° under N_2. After completion of addition the solvent was removed under reduced pressure and the residual oil was bulb to bulb distilled at 20° to give 1,1'-*dibromobicyclobutyl* (**25**), colourless liquid, 1.63 g (61%, pure by GLC (silicon rubber, 6 ft × ¼ in.); MS, 270, 268 (3%), 266 (1:2:1); 242, 240 (4%) 238 (1:2:1 $M-C_2H_4$); 214, 212 (7%), 210 (1:2:1, $M-C_4H_8$), 189, 187 (7%, 1:1, M–Br), 79 (100%); NMR (CCl_4), 7.11–7.94 (m, 10 H), 8.20–8.39 (m, 2 H); IR (liquid film) 2950, 1430, 1250, 1100 and 1035 cm^{-1}. (Found: C, 36.31; H, 4.56; Br, 59.94. Calc. for $C_8H_{12}Br_2$: C, 35.86; H, 4.51; Br, 59.14%).

Reaction of bicyclobutylidene (**1**) *with* N-*bromosuccinimide*

Recrystallised benzoyl peroxide (0.05 g, 0.2 mmole) was added to a vigorously stirred suspension of N-bromosuccinimide (3.5 g, 20 mmole) and **1** (1.08 g, 10 mmole) in boiling benzene (10 ml). Heating was continued until NBS was no longer detectable (KI/starch), the mixture was cooled, the insoluble material removed by filtration, and the residue washed with cold benzene (2 × 5 ml). The combined filtrates were evaporated under reduced pressure to give a brown mass which was trituated with ether (20 ml) and filtered; the residue being washed with petroleum ether (3 × 5 ml). The combined filtrates were evaporated under reduced pressure to give an oil which on bulb to bulb distillation gave a pale yellow oil. Preparative GLC on silicon gum rubber SE-30 (10 ft × ¾ in.) at 145° gave, in order of increasing retention time, (i) bromobenzene (0.3 g); (ii) 1,1'-*dibromobicyclobutyl* (**25**), 1.29 (48%), identical in all respects with an authentic sample; (iii) 2,2'- (**26**) *and* 2,4'-*dibromobicyclobutylidene* (**27**), 0.74 g (28%), pale yellow oil; MS, 268, 266 (12%) 264 (1:2:1, M^+); 242, 240 (7%) 238 (1:2:1, $M-C_2H_2$); 214, 212 (8%), 210 (1:2:1, $M-C_4H_6$); 187, 185 (1:1, M–Br, 30%), 79 (100%); NMR (CCl_4) 4.80–5.26 (m, 2 H, methine) 6.50–7.90 (m, 8 H, methylene); IR (liquid film) 2950, 1430, 1250, 1205, 1170 and 870 cm^{-1}. (Found: C, 35.75; H, 3.71; Br, 59.64. Calc. for $C_8H_{10}Br_2$: C, 36.13; H, 3.79; Br, 59.94%).

Bromination of the mixture of **26** *and* **27**

The mixture of **26** and **27** (53 mg, 0.2 mmole) was dissolved in dry $CHCl_3$ (1 ml), the soln stirred and cooled to 0° under N_2. A soln of Br_2 (32 mg, 0.2 mmole) in dry $CHCl_3$ (0.5 ml) was added dropwise over 30 min, and the mixture stirred at 0° until the brown colour was discharged. The solvent was removed by distillation under reduced pressure to give a brown oil, which on bulb to bulb distillation gave *tetrabromobicyclobutyl* (**28**), pale yellow oil, 85 mg (100%), which contained 5% of (**26**, **27**) by GLC; MS *m/e* 425.7436 ($C_8H_{10}Br_4$ requires 425.7417); 430, 428, 426 (2%) 424, 422 (1:4:6:4:1) 349, 347 (62%) 345, 343 (1:3:3:1, M–Br), 105 (100%); NMR (CCl_4) 4.60–5.68 (m, 2 H, methine); 6.30–7.88 (m, 8H, methylene); IR (liquid film) 2950, 1435, 1250, 1195, 1065, 870 and 840 cm^{-1}.

Acetylation of 1 - (1 - *hydroxycyclobutyl*)*cyclobutene* (**18**)

Ac_2O (1.5 ml, 15 mmole) was added to **18** (40 mg, 0.3 mmole) and the mixture was heated to reflux for 1 hr. Preparative TLC on silica, eluting with petroleum ether–ether (4:1) gave 1-(1-*acetoxycyclobutyl*)*cyclobutene* (**29**) colourless liquid, 30 mg (60%), MS *m/e* 166 (4%, M^+), 157, 138 (11%, M–CO), 124, 123 (11%, $M-CH_3CO$), 109, 107, 106, 105, 96 (100%); NMR (CCl_4) 4.33–4.69 (m, 1 H, olefinic), 7.09–8.06 (m, 13 H, CH_3CO, cyclobutyl); IR (liquid film) 2980, 1740, 1450, 1395, 1260, 1090 and 1030 cm^{-1}.

Pyrolysis of the acetate **29**

The acetate **29** (50 mg, 0.3 mmole) was put into a 5 ml flask which was attached to a Pyrex column (10 mm × 200 mm) filled

with glass helices. The column was passed through a cylindrical funnel and a collection flask with a vacuum outlet fitted to the end. The furnace was heated to 450° (thermometer in well), the apparatus evacuated to 0.1 mm and the collecting flask cooled in liquid N_2. The pyrolysate was collected and purified by preparative GLC on carbowax (6 ft × ¼ in.) at 100° to give, in order of increasing retention time: (i) *3,4-dimethylene-1,5-hexadiene* (**30**)[22] 7 mg (22%); NMR ($CDCl_3$) 3.60 (q, 2 H, vinyl), 4.67–5.06, (3 multiplets, 8 H, methylene); IR (CCl_4) 990, 917 and 898 cm^{-1}; λ_{max} 216 nm; (ii) acetic acid; (iii) acetate **29** (14 mg, 28%). Using 30 mg of **29** under the same conditions resulted in complete conversion to **30**. Thermolysis at 350° or 400° at 0.1 mm gave unchanged **29**.

Preparation of the thiadiazoline **32**

H_2S was passed through **31** (9.20 g, 72 mmole) at 25° for 15 min. Aqueous hydrazine (6 ml, 7.5M, 37.5 mmole) was then added dropwise over 45 min to the vigorously stirred soln at - 25°, the passage of H_2S being continued. After completion of addition H_2S was passed for a further 15 min, and the mixture was then extracted with CH_2Cl_2 (50 ml). Sat NaCl aq (10 ml) was added to the aqueous layer, and this was then extracted further with CH_2Cl_2 (2 × 25 ml). The combined organic extracts were dried ($MgSO_4$), and the solvent removed under reduced pressure to give a pale yellow oil. The oil was dissolved in ether (25 ml), poured through a short silica (50 g) packed column and eluted with ether (200 ml). The combined ethereal eluant was evaporated under reduced pressure at 0° to give **32**, a mixture of isomers, 9.4 g (91%), colourless oil; MS *m/e* 252.1113 (M–H_2S), ($C_{12}H_{16}N_2O_4$ requires 252.1110); 252 (15%), 226, 210, 200, 166, 160, 158, 151, 150 (100%); NMR ($CDCl_3$) 4.44–5.38 (m, 2 H, methine), 5.50–6.43 (m, 2 H, NH), 7.58–8.32 (m, 14 H); IR (liquid film) 3280, 2940, 1785, 1730, 1440, 1380, 1240, 1070, 1020, 900 and 820 cm^{-1}.

Oxidation of **32** *with diethyl azidocarboxylate*

The thiadiazolidine **32** (6.7 g 0.023 mol) was dissolved in dry benzene (20 ml), the soln stirred and cooled to 0° under N_2. A soln of diethyl azodicarboxylate (4.0 g, 0.023 mol) in dry benzene (50 ml) was then added dropwise over 30 min, and after addition the soln was stirred at 0° for 3 hr. The mixture was then heated to 40° for 18 hr and finally heated to reflux for 30 min. The mixture was allowed to cool, petroleum ether (40 ml) was added and the mixture stood for 2 hr at 0°, when a white crystalline ppt of diethyl hydrazinodicarboxylate formed. This was removed by filtration, the ppt washed with petroleum ether (2 × 10 ml) and the combined filtrates were evaporated under reduced pressure to give an orange oil. Column chromatography of the oil on silica eluting with petroleum ether–ether (3:2) gave in order of increasing R_f value: (i) *1,8 - diacetoxy - 9 - thiadispiro[3.0.3.1]nonane* (**34**), white crystals, m.p. 75–76°, 1.7 g (28%); MS *m/e* 256 (6%), 213, 171, 170, 154, 153, 129, 128 (100%); NMR (CCl_4) 4.60–4.78 (m, 2 H, methine), 7.40–7.92 (m, 8 H, methylene), 8.08 (s, 6 H, CH_3CO); IR (KBr) 2950, 1735, 1720, 1440, 1385, 1240, 1105, 1085, 1050, 970, 935 and 900 cm^{-1}. (Found: C, 56.11; H, 6.33; O, 24.93; S, 12.46. Calc. for $C_{12}H_{16}O_4S$: C, 56.24; H, 6.29; O, 24.97; S, 12.51%). (ii) A mixture of **34** and **33**, 1.5 g (25% and (iii) 1.6 - *diacetoxy - 9 - thiadispiro[3.0.3.1]nonane* (**33**), white crystals, m.p. 71–72°, 1.3 g, (22%); MS *m/e* 256 (M^+, 20%), 213, 171, 170, 154, 153, 129, 128 (100%); NMR (CCl_4) 4.68–4.77 (t, 2 H, methine), 7.46–7.98 (m, 8 H, methylene), 8.09 (s, 6 H, CH_3CO); IR (KBr) 2950, 1750, 1435, 1380, 1240, 1215, 1180, 1090, 975, 945, 920 and 895 cm^{-1}. (Found: C, 56.23; H, 6.33; O, 24.87; S, 12.56. Calc. for $C_{12}H_{16}O_4S$: C, 56.24; H, 6.29; O, 24.97; S, 12.51%).

Desulphurisation of **33** *and* **34**

Compound **33** (0.77 g, 3 mmole) was added with dry triphenylphosphine (1.3 g, 5 mmole) and the mixture was stirred and heated to 100° for 3 hr under N_2. The cooled mixture was triturated with petroleum ether (2 × 10 ml), the insoluble material removed by filtration, the ppt washed with petroleum ether (2 × 10 ml) and the combined filtrate evaporated under reduced pressure to a volume of *ca.* 2 ml. Column chromatography on silica gave, in order of increasing R_f: (i) triphenylphosphine sulphide, 40 mg; (ii) *2,4'-diacetoxybicyclobutylidene* (**35**), 0.57 g (85%),[26] colourless crystals, m.p. 43–44° (petroleum ether–ether); MS *m/e* 224 (M^+, 3%), 182, 181, 164, 140, 139, 138, 122, 121, 79 (100%); NMR (CCl_4), 4.43–4.67 (t, 2 H, methine), 7.30–8.15 (m, 14 H, methylene, $COCH_3$); IR (KBr) 1725, 1380, 1240, 1110, 1075 and 945 cm^{-1}. (Found: C, 63.95; H, 7.13. Calc. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19%). A similar procedure with compound **34** gave *2,2'-diacetoxybicyclobutylidene* (**36**) (80%),[26] colourless crystals, m.p. 45–46° (petroleum ether–ether); MS *m/e* 224 (M^+, 5%), 182, 181, 164, 140, 139, 138, 122, 121, 79 (100%); NMR (CCl_4) 4.51–4.74 (m, 2 H, methine), 7.33–8.18 (m, 14 H, methylene, $COCH_3$); IR (KBr), 2950, 1725, 1375, 1250 and 1065 cm^{-1}. (Found: C, 64.57; H, 7.25. Calc. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19%).

Hydrolysis of **35** *and* **36**

A freshly prepared soln of NaOMe in MeOH (0.2 M, 15 ml) was added to an ice-cold, stirred soln of **35** (224 mg, 1 mmole) in MeOH (5 ml) under N_2. The soln was stirred at 0° until none of **35** could be detected (2 hr) and soln of AcOH (0.25 g, 4 mmole) in EtOH (2 ml) was then added. The mixture was evaporated under reduced pressure, sat NaCl aq (5 ml) was added and the mixture extracted with CH_2Cl_2 (5 ml). The aqueous fraction was decanted from the solid and extracted with CH_2Cl_2 (5 ml), and the combined organic layer were dried (Na_2CO_3). Evaporation of the solvent under reduced pressure gave *bicyclobutylidene-2,4'-diol* (**37**), white crystals, 155 mg (69%), m.p. 131–132°; MS *m/e* 140 (M^+, 0.6%), 139, 125, 123, 122 (M–H_2O, 35%), 121, 111, 107, 97, 96 (100%); NMR ($CDCl_3$) 5.10–5.40 (m, 2 H, methine), 7.08–8.36 (m, 10 H, methylene, OH); IR (KBr) 3320, 3245, 2990, 2945, 1435, 1325, 1235, 1185, 1125, 1095, 1075 and 960 cm^{-1}. (Found: C, 68.70; H, 8.66. Calc. for $C_8H_{12}O_2$: C, 68.54; H, 8.63%). Similar hydrolysis of **36** gave *bicyclobutylidene-2,2'-diol* (**38**), (66%), white crystals, m.p. 63–64°; MS *m/e* 140 (M^+, 0.3%) 139, 125, 123, 122 (M–H_2O, 100%); NMR ($CDCl_3$) 4.96–5.34 (m, 2 H, methine); 5.81 (s, 2 H, OH), 7.38–8.24 (m, 8 H, methylene); IR (KBr) 3250, 2900, 1440, 1230, 1115, 1110 and 820 cm^{-1}. (Found: C, 68.49; H, 8.65. Calc. for $C_8H_{12}O_2$: C, 68.54; H, 8.63%).

Oxidation of **37** *and* **38**

Finely ground CrO_3 (0.24 g, 24 mmole) was slowly added to a vigorously stirred soln of dry pyridine (0.38 g, 4.8 mmole) in dry CH_2Cl_2 (6 ml) at 20° under N_2. The resulting soln was stirred at 20° for 1 hr, then cooled to 0° and a soln of **37** (28 mg, 0.2 mmole) in CH_2Cl_2 (1 ml) added. The mixture was stirred at 0° under dry N_2 for 20 min, the mixture filtered through Kieselguhr, the residue triturated with CH_2Cl_2 (2 × 10 ml) and the combined filtrate refiltered. The resulting filtrate was washed with NaOH aq (20 ml, 1 M) and water, (20 ml), and dried. Preparative TLC on silica, eluting with petroleum ether–ether (1:9) gave *bicyclobutulidene-2,4'-dione* (**39**), 9.8 mg (36%), yellow crystals, m.p. 123–125°; MS *m/e* 136.0521 ($C_8H_8O_2$ requires 136.0524); 136 (M^+, 100%), 108, 80, 79 (100%); NMR ($CDCl_3$) 6.74–7.27 (m); IR (KBr) 2920, 1735, 1230, 1095 and 1075 cm^{-1}; λ_{max} (EtOH) 255 sh nm (ε 8300), 266 (10,200), 274 sh (9120). Similar oxidation of **38** gave *bicyclobutylidene-2,2'-dione* (**40**) (26%), yellow crystals, m.p. 107–108°; MS *m/e* 136.0520 ($C_8H_8O_2$ requires 136.0524); 136 (M^+, 80%), 108, 80, 79, 77, 66 (100%); NMR ($CDCl_3$) 6.78–7.08 (m, 4 H), 7.23–7.52 (m, 4 H); IR (KBr) 2900, 1745, 1670, 1120 and 1070 cm^{-1}; λ_{max} (EtOH), 252 sh nm (ε 6130), 263 (7580), 271 sh (7050).

Reaction of **31** *with cyclobutyltriphenylphosphonium bromide*

Cyclobutyltriphenylphosphonium bromide (54.7 g, 0.09 mmole) was suspended in dry THF (600 ml), stirred, and n-BuLi (68 ml, 1.97 M in n-hexane, 0.13 mmole) was added. After 15 min all of the bromide had dissolved, and a soln of **31** (11.5 g, 0.09 mmole) in dry THF (200 ml) was then added dropwise over 45 min to the deep red soln. The mixture was stirred for a further 30 min at room temp. and then heated to 60–65° with stirring for 12 hr. The soln was cooled, filtered and CH_2Cl_2 (250 ml) added to the filtrate. The mixture was extracted with water (5 × 100 ml) and the organic layer dried ($MgSO_4$). The solvent was removed by evaporation under reduced pressure to give a dark oil which was

triturated with petroleum ether (200 ml). The ppt of triphenylphosphine oxide which formed was removed by filtration, the ppt washed with petroleum ether (2 × 15 ml) and the combined filtrates concentrated by evaporation. Fractional distillation of the residue gave 2-*acetoxybicyclobutylidene* (**41a**), colourless oil, 0.74 mg (5%); MS *m/e* 166 (3%, M^+), 161, 157, 139, 138, 123 (20%), 55 (100%); NMR ($CDCl_3$) 4.21–4.63 (m, 1 H methine), 7.09–8.30 (m, 13 H); IR (liquid film) 2950, 1730, 1380, 1240 and 1060 cm^{-1}. (Found: C, 68.13, H, 8.59. Calc. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%).

Hydrolysis of **41a** with freshly prepared sodium methoxide in methanol gave 2-*hydroxybicyclobutylidene* (**41b**) (57%);[28] MS, *m/e* 124 (8%, M^+); NMR ($CDCl_3$) 5.06–5.42 (m, 1 H, methine), 6.84–8.21 (m, 11 H); IR (liquid film) 3350, 2950, 1700, 1440 and 1110 cm^{-1}. Oxidation of **41b** with chromium trioxide-pyridine as for the diols gave *bicyclobutylidene*-2-*one* (**42**) (21%), having identical NMR, IR and electronic spectra to those reported.[28]

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