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PROPELLANES—XV

SYNTHESIS OF 3-THIA[3.2.2]PROPELLANE AND ATTEMPTED RING CONTRACTION OF 5-MEMBERED THIOETHER RINGS TO CYCLOBUTANES.[1]

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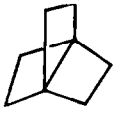
Abstract—3-Thia[3.2.2]propellane has been synthesized. The Stevens rearrangement was executed for a number of model compounds in the hope that a thiacyclopentane sulfonium salt would be converted into a substituted cyclobutane ring. The reaction took the course of ring-opening to compounds containing exo-methylene groups. Thus the synthesis of [2.2.2]propellane by this route failed.

IN ATTEMPTING to synthesize small-ring propellanes such as [2.2.2]propellane **1**, it appears *a priori* that the innate strain in the desired target would require the use of rather delicate reaction conditions the closer one gets to the synthetic goal. Thus, our hope that the symmetrical triketone **2**, could be induced to decarbonylate stepwise and yield **1** was a too highly optimistic one despite the fact that the theoretical quantity of carbon monoxide could indeed by obtained by mercury-sensitized photodecarbonylation. The highly symmetrical **2** has a high m.p. and a low vapour pressure so that the minimal temperature required for technical reasons to maintain a sufficient amount of **2** in the vapour phase was too high and even if **1** were indeed formed alongside the carbon monoxide, it did not survive and only hydrocarbon polymer was obtained on the walls of the quartz reaction chamber.[2]



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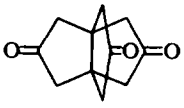

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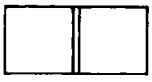


3

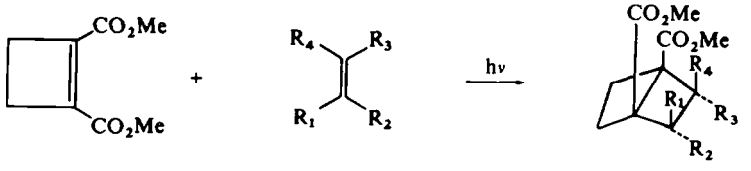
A more rational scheme might be the low temperature photochemical addition of ethylene to the heretofore unisolated bicyclohexene **3**. Although a number of authors including ourselves, have attempted the synthesis of **3**,[3] only one report describes partial success.[3c] Although **3** has not been isolated, it may perhaps be used *in situ* to prepare **1**.

We wish to report smooth photochemical syntheses of several bicyclo[2.2.0] hexane derivatives, **4**. Of a number of methods now known for the synthesis of such compounds,[4] we chose to explore the possibility of photocycloaddition of ethylenes to 1,2-dicarbomethoxycyclobutene since such reactions of olefins are well documented[5] and since the diester undergoes both photodimerization[6] and photoaddition.[7] Incidentally, Bloomfield has recently published an independent synthesis of **4a**[8] along lines that are similar to ours.

1,2-Dicarbomethoxycyclobutene underwent [2 + 2] photochemical cycloaddition with ethylene, with *trans*-1,2-dichloroethylene and with ketene di (2-methoxyethyl)

acetal, leading respectively to the bicyclo[2.2.0]hexane derivatives **4a**, **4b** and **4c**. The products were always accompanied by the photodimer **7** which has already been described.[6,7] A determination of the dimensions of the unit cell by x-ray crystallography indicated, albeit not conclusively, that **7** may have the *anti*-configuration.[9]* NMR spectroscopy supports this formulation as do further chemical reactions and the properties of subsequent products (*vide infra*).

The ethylene adduct **4a** was formed in 65–70% yield when irradiation was conducted at −30°. Attempted purification by distillation in a high vacuum resulted in ring opening and the formation of 2,5-dicarbomethoxyhexa-1,5-diene, as already reported.[8] Since we required pure **4a** for further synthetic manipulation we devised a purification scheme consisting of column chromatography on florisil at −10° to −5° followed by low temperature crystallization from pentane. The pure product exhibited the AA′XX′ pattern of cyclobutane protons at τ 7·48 and the methyl singlet of the ester group at τ 6·30 in complete accord with Bloomfield's product.[8] Of the three possible photoadducts, A-C, of *trans*-1,2-dichloroethylene, **4b** only A and B were formed in a 2:1 ratio, respectively. This composition indeed indicates a stepwise radical photoaddition mechanism similar to that proposed for the addition of the dichloroethylenes, to cyclopentenone.[5a] Their structure follows from the NMR spectra. Component B of the product **4b** exhibited a highly symmetrical AA′XX′ pattern centered at τ 7·35 for the cyclobutane protons in the unsubstituted ring, a singlet at 6·28 for the methyl protons and a singlet for the deshielded methine protons at 4·72 indicating the *trans*-arrangement of the carbomethoxy groups and the chlorine atoms. In contradistinction, A has a complex multiplet for the cyclobutane protons in the unsubstituted ring, two singlets for the methyl groups one being deshielded by a halogen atom and the methine protons comprise an AB quartet (see Experimental).



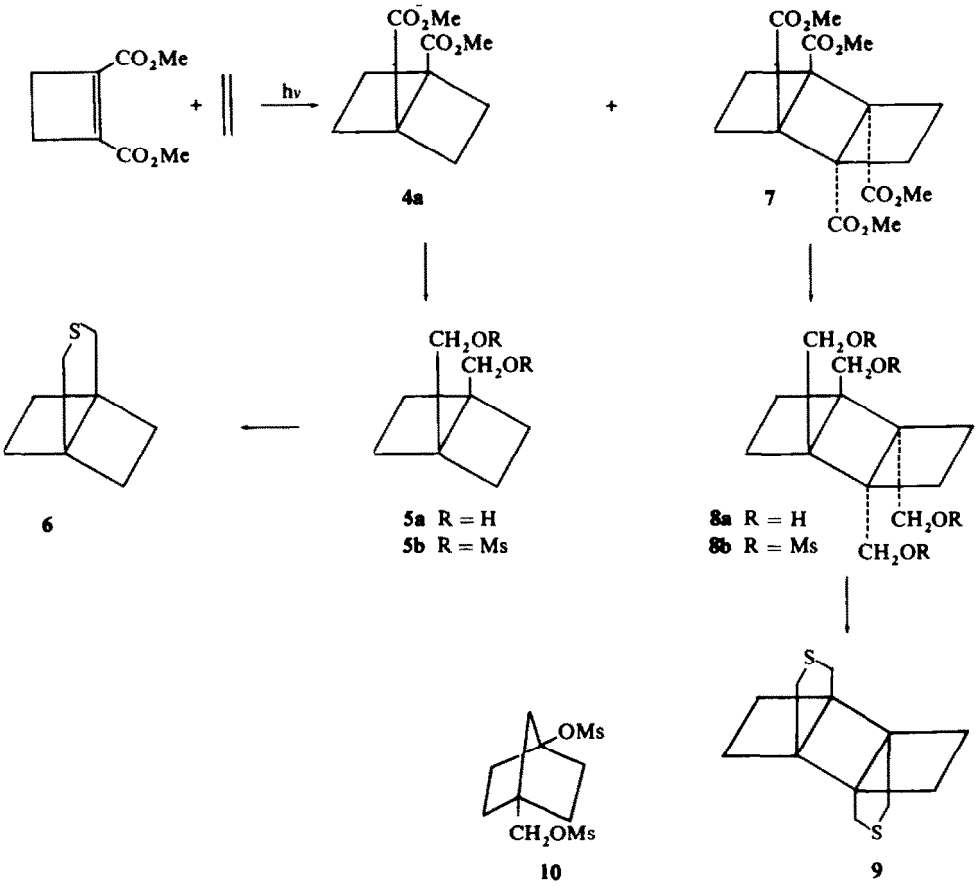
$R_1 = R_3 = Cl$; $R_2 = R_4 = H$
$R_1 = R_2 = H$; $R_3 = R_4 = OCH_2CH_2OMe$

4a $R_1 = R_2 = R_3 = R_4 = H$
4b A: $R_1 = R_3 = Cl$; $R_2 = R_4 = H$
B: $R_2 = R_3 = Cl$; $R_1 = R_4 = H$
C: $R_1 = R_4 = Cl$; $R_2 = R_3 = H$
4c $R_1 = R_2 = H$; $R_3 = R_4 = OCH_2CH_2OMe$

LAH reduction of **4b** was carried out at low temperature. Although the ester functions were reduced, hydrogenolysis of the chlorine atoms did not occur. The resulting diols were unstable even at 0° and were therefore discarded as intermediates. In the case of the ethylene adduct **4a**, however, and that of the dimer **7**, LAH reduction afforded the diol **5a** and the tetrol **8a**, respectively, both of which were stable at room temperature (Scheme 1).

* The late Professor Gerhard Schmidt who had a certain interest in this compound expressed the opinion that it is the *anti*-dimer.

SCHEME 1



These were converted, respectively, into the dimesylate **5b** and the tetramesylate **8b**. Treatment of each of these with Na_2S afforded the thiapropellanes **6** and **9**, respectively. Such compounds may lend themselves to sulfur extrusion reactions which would lead to ring contraction of the 5-membered sulfur-containing ring to a 4-membered ring either *via* the sulphone,[10] the α-chlorosulfone,[11] or the sulphonium salt.[12]*

Comparison of the NMR spectra of **5a** and **8a** presented evidence for the *anti*-stereochemistry of the dimer **7**. The cyclobutane protons in **5a** exhibit a well resolved AA′XX′ symmetrical multiplet centred at τ 7·90 in addition to the singlet for the methylene protons of the hydroxymethyl groups (τ 6·50). The multiplicity of the former indicates grossly different environments for protons *syn*- or *anti*- to the angular substituents. It is clear from molecular models that a similar situation would prevail for **8a**, were it of *syn*-configuration. However, the cyclobutane protons in **8a** in fact exhibit a broad singlet at τ 7·90, indicating the collapse of the AA′XX′ system. This would indeed be expected by the near-equivalence of protons located above and below the molecular plane as is the case in the *anti*-configuration. Further, a *syn*-tetrol would be expected to

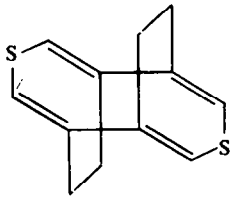
* We are grateful to Professor Boekelheide for his suggestions and results communicated to us before publication.

afford an ortho-ester readily but such a compound could not be obtained even under forcing conditions.

Particular care must be taken for the preparation of the dimesylate **5b**. The mildest feasible conditions were used in order to avoid its rearrangement to the [2.2.1]bicycloheptane derivative **10**. Such rearrangement is complete when crude **5b** is heated to 70–80° for a few minutes. The structure of **10** is easily distinguishable from **5b** through the NMR spectra. Whilst **5b** exhibits a symmetrical pattern for the cyclobutane protons centred at τ 7·80 and the methylene and methanesulfonyl protons give singlets at 5·80 and 6·96 respectively in the ratio of 8:4:6, for **10**, eight of the corresponding ring protons appear at 8·0 as a symmetrical multiplet with two more as a broad doublet at 8·35. The methylene and methanesulfonyl protons appear at 5·75 and 6·95, respectively, in the ratio of 2:6.

The NMR spectra of **6** and **9** again support these formulations. The former exhibits a symmetrical multiplet centred at τ 7·85 for the cyclobutane protons and a singlet at 7·20 for the methylene protons adjacent to sulfur. The spectrum of **9** is slightly more complex. The cyclobutane protons again form a symmetrical multiplet centred at 7·70 but since the methylene protons adjacent to sulfur now comprise some that differ in environment from others (flanked either by a cyclobutane ring or a bicyclohexane ring system), they exhibit an AB quartet at 7·45 and 6·75. The rather large difference in chemical shift involved here points to the rigidity of the pentacyclic structure, part of the methylene protons being forced into the deshielding cone of the σ framework of the fused cyclobutane ring.

After **9** was crystallized the mother liquor was examined for the presence of a possible isomer which might have arisen if some *syn*-isomer were carried through the synthetic sequence in company with **8a** and **8b**. An additional compound was indeed isolated by prep. TLC, albeit in very low yield. Its molecular weight was 220, i.e. 4 mass units less than **9**. From the NMR and UV data (see experimental section) and assuming that no far-reaching skeletal rearrangements had taken place, it may be that oxidative cyclization of **8b** also occurs affording **11** which has a framework containing two parallel transoid-diene systems. Thus we would tentatively prefer **11** on the basis of the UV spectrum.

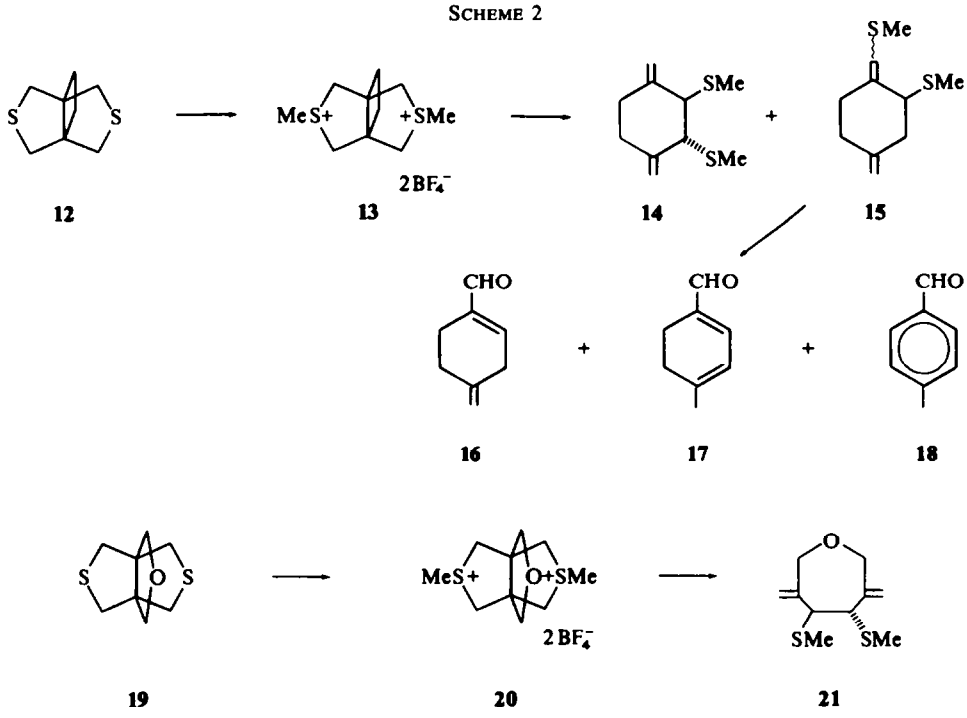


11

The successful application of the Stevens rearrangement in the preparation of several metacyclophanes by Boekelheide *et al.*[12] as well as successful urging by Professor Boekelheide himself, caused us to investigate this method as a possible route to [2.2.2]propellane. Sulphonium salts of 3,7-dithia[3.3.2]propellane **12**[13] and the related 3-oxa-7,10-dithia[3.3.3]propellane **19** which we had available[14] were prepared and subjected to the conditions of the rearrangement (Scheme 2).

Rearrangement of **13** gave a mixture of four compounds; the two major components were separated by column chromatography and GLC techniques and identified as **14** and **15**. The NMR spectrum of **14** shows the vinylic protons at τ 5·0 as a quartet ($J = 2$Hz), the methine protons as a singlet at 6·55, the cyclohexane protons as a multiplet spreading from 7·2 to 7·8 and the thiomethyl protons exhibit a singlet at 8·00. The vinylic protons in **15**, however, appear at 4·20 and 5·25, the single methine proton comprises a multiplet at 5·90 coupled to the allylic protons at 7·56 and the two differently situated thiomethyl groups manifest their protons as singlets at 7·75 and 8·05, for the thioenol ether methyl group and for the thiomethyl group, respectively.

SCHEME 2



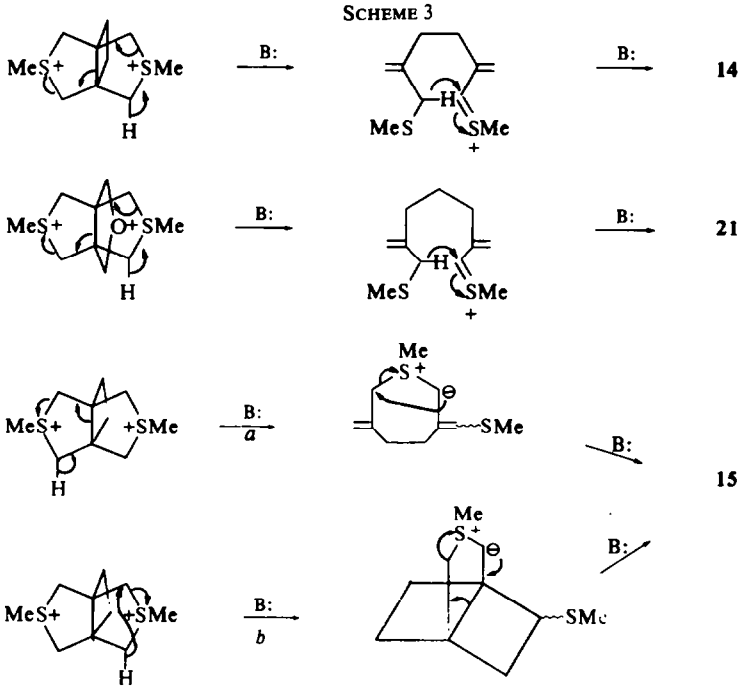
12 **13** **14** **15** **16** **17** **18** **19** **20** **21**

In order to obtain support for the location of the thiomethyl groups, the rearrangement products were subjected to mercuric chloride-assisted hydrolysis. Under such conditions a thioenol group affords a carboxaldehyde and the β-thiomethyl groups are eliminated yielding an α,β-unsaturated aldehyde.[15] We were able to isolate **16**, formed by hydrolysis of **15**, its isomer **17** and *p*-tolualdehyde **18** resulting from oxidation of the latter.

Rearrangement of **20** produced a single isolable product **21** whose structure was again clearly indicated by NMR spectroscopy: vinylic protons at τ 5·0, an AB quartet at 5·53 and 5·89 for the protons adjacent to the ether linkage, a singlet for the methine protons at 6·30 and a singlet for the thiomethyl protons at 7·96.

The isolation of **14** and **21** on the one hand and of **15** on the other appears to indicate a dual mechanism in operation for the rearrangement. Clearly, the desired ring contraction of a five- to a four-membered ring has not occurred and relative relief of strain has been

SCHEME 3

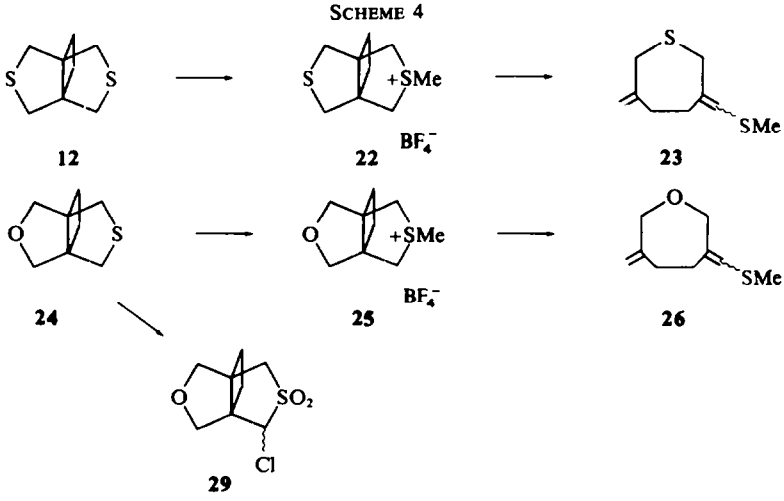


achieved by the formation of the above products rather than that of a [2.2.2]propellane derivative.

The formation of **14** and **21** appears to require a simultaneous cleavage of both charged rings with subsequent recyclization as shown in Scheme 3.

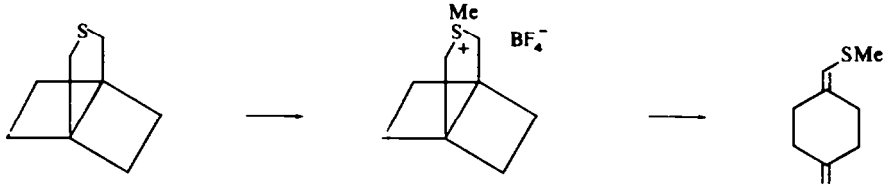
The formation of **15** may be rationalized either *via* route *a* or route *b*. The first route appears the more reasonable since the incipient carbanion is stabilized by a thioenol ether group. In route *b* the prior formation of the bicyclo[2.2.0]hexane nucleus is required.

SCHEME 4



In order to obtain further potential support for either of these routes the monosulphonium derivatives **22** and **25**, of **12** and of 3-oxa-7-thia[3.3.2]propellane, **24**,[16] respectively, were prepared and subjected to the rearrangement conditions. The results are summarized in Scheme 4.

These results are in accord with route *a* proposed above for the Stevens rearrangement in these tricyclic systems and were further substantiated by the preparation of **28** from 3-thia[3.2.2]propellane **6**:



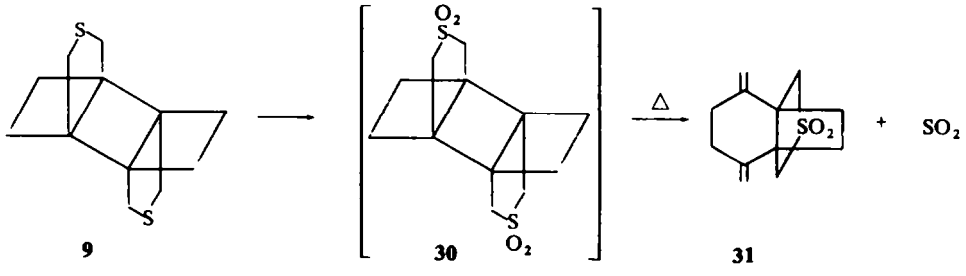
6 **27** **28**

Since we had compounds **23** and **26** in hand, they appeared to be heaven-sent substrates for potential [3,3]sigmatropic rearrangement. Disappointingly, however, over the range of −60° to 160°, no evidence for such rearrangement was observed in their 60 MHz and 90 MHz NMR spectra.

Attempts to apply the Ramberg–Bäcklund reaction and other SO_2 extrusion reactions were also made. Paquette *et al.* have explored these methods much more widely.[11]

For example, the α-chlorosulphone **29** was prepared from **24** but attempts to effect the rearrangement under basic conditions with concurrent ring contraction ended merely in epimerization of **29**.

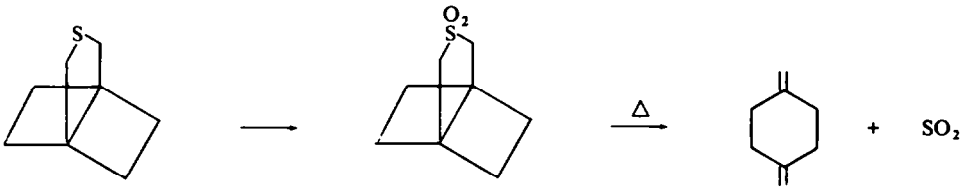
The disulphone of **9** could not be isolated from the reaction of **9** with *m*-chloroperbenzoic acid or hydrogen peroxide and the product **31** actually formed was obtained by thermal SO_2 extrusion from the unisolated disulphone **30**.



9 **30** **31**

Treatment of **9** with ozone at low temperature, however, resulted in the precipitation of a highly insoluble colourless product, probably the disulphone **30** which upon warming to room temperature spontaneously extruded SO_2 and again afforded the stable monosulphone **31** identical with the product obtained above.

The monosulphone **32** was similarly obtained by treatment of **6** with ozone. It displayed two singlets in its low temperature NMR spectrum at τ 6·73 and 7·45, respectively, in the ratio of 1 : 2, as expected for this structure. This product, however, also decomposed on warming and gave 1,4-dimethylenecyclohexane **33** rather than the desired [2.2.2]propellane. The half-life of **32** at 25° is *ca.* 2·5 hr.

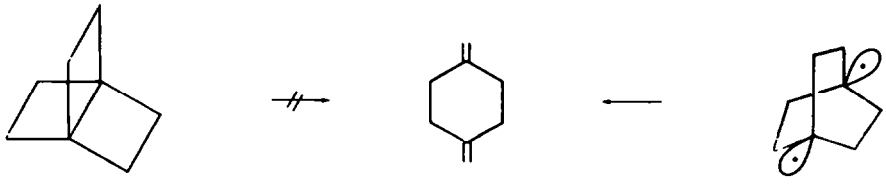


6 32 33

Irradiation of **31** in acetone solution at −25° resulted in an intractable mixture of products. Irradiation of **32** in hexane solution at −45° in an all quartz apparatus with an 80 W Hanovia medium arc for 10 hr resulted in recovery of starting material.

We have written polar intermediates in our cases of the Stevens rearrangement of sulphonium salts. It should be pointed out for its own sake as well as in connection with the following discussion of theoretical predictions made by Hoffman and Stohrer,[17] that results recently published raise the possibility that radicals may be intermediates in the Stevens rearrangement. CIDNP effects have been observed in the Stevens rearrangement of sulphonium ylides[18a] as well as in that of amine imides.[18b] In the latter case intermediate radicals have been trapped by scavengers.[18c] A warning has been published regarding the possibility that such CIDNP effects may be artifacts and thus cannot be taken as conclusive evidence for the actual intermediacy of radicals in the rearrangement steps itself. This warning appears justified for the particular case cited.[18d]

Hoffmann and Stohrer[17] have discussed the electronic structure of [2.2.2]propellane and other small ring propellanes. They point out that the $2_s + 2_s$ fragmentation of **1** to give **33** is forbidden but the conversion of the diradical **34** to **33** is symmetry-allowed and indeed may be thermodynamically favoured. The intramolecular recombination of **34** to give **1** is also a symmetry forbidden process. Their CNDO/2 and INDO calculations predict that **1** is more stable than **34**. All this taken together has the synthetic consequence that if **34** were generated it would not constitute an intermediate *en route* to **1** but, rather, it would be likely to undergo the thermodynamically favoured fragmentation to 1,4-dimethylenecyclohexane **33**.



1 33 34

The foregoing discussion does not, of course, prove that we are dealing with radical intermediates in certain stages of our Stevens rearrangements but we have nevertheless been rather successful in synthesizing compounds containing exocyclic methylene groups analogous to **33**, rather than attaining the extremely desired and highly elusive **1**.*

* W. Shakespeare, "Troilus and Cressida," 3, 2 (1602): "that the will is infinite, and the execution confined; that the desire is boundless, and the act a slave to limit."

EXPERIMENTAL

All m.ps are uncorrected. NMR spectra were measured on a Varian A-60A spectrophotometer unless otherwise stated, IR spectra on a Perkin–Elmer 237 instrument and mass spectra on an Atlas CH-4 mass spectrometer employing a heated inlet system with electron energy maintained at 70 eV and ionization current at 20 μA. GLC data were collected on a Varian Aerograph model 90-P instrument employing a 5′ × ¼″ analytical column of SE-30 substrate 3% on Varaport-30 stationary phase and a 6′ × ¼″ preparatory column of SE-30, 5% on Chromosorb W. Such data are listed in the sequence: retention time, °C(column), ml/min helium flow. Irradiations were conducted in all-pyrex assembly using an Hanovia 450 W immersion lamp under a nitrogen atmosphere except in cases involving ethylene.

1,4-*Dicarbomethoxybicyclo*[2.2.0.]*hexane*,4a. A solution of dimethyl cyclobutene-1,2-dicarboxylate[6] (1 g) in hexane (500 ml) was irradiated at −30° to −25° for 8 hr. whilst a constant flow of ethylene was conducted through the solution. The volume of hexane was reduced to 50 ml at the water pump without external heating. The photodimer **7** crystallized (0·35 g) m.p. 139°. Lit.[7] m.p. 135–136°. GLC analysis of the volatile components in the mother liquor showed the presence of starting material (5%), **4a** (85%) and an unidentified product (10%). (1·0, 1·8 and 1·4 min, respectively/120°/120 ml/min). Purification was effected by placing 0·65 g of the crude oil obtained upon removal of the above solvent on 40 g florisil in a column equipped with a cooling jacket and elution of the photoadduct at 0° with pentane–CH_2Cl_2 (70:30). Low temp crystallization yielded pure **4a**, as long colourless needles, m.p. 0–5° (pentane). IR (neat): 1740, 1130 cm^{-1}. NMR ($CDCl_3$, τ): 6·30 (s, $OC\underline{H}_3$), 7·48(AA′XX′ mult, $4C\underline{H}_2$).

1,4-*Dicarbomethoxy*-2,3-*dichlorobicyclo*[2.2.0]*hexane*, **4b.** The cyclobutene diester (1·26 g) and *trans*-dichloroethylene (18 g) in cyclohexane (450 ml) were irradiated at room temp for 24–30 hr. After disappearance of the starting diester (as observed by GLC), the volume of solvent was reduced to 25 ml at the water pump and **7** was allowed to crystallize overnight at 5°, usually yielding 0·15 g per run. Removal of solvent from the mother liquor then afforded **4b** as an oil (1·3–1·5 g) which was shown by NMR to contain 65% of A (*trans*) and 35% of B (*cis*-), (6·0 and 8·5 min/120°/120, respectively). The analytical sample of the mixture was obtained by bulb to bulb distillation at 110–115°/0·06 mm. (Found: C, 44·79; H, 4·50; Cl, 25·79; MW 266. $C_{10}H_{12}O_4Cl_2$ requires C, 45·10; H, 4·50; Cl, 26·30%; MW 267·11). IR (neat): 1750–1720, 1220 cm^{-1}. NMR ($CDCl_3$, τ): (A) 4·90, 5·50 (AB quartet, $C\underline{H}Cl$ J = 7 Hz), 6·22 (s, $OC\underline{H}_3$), 6·28 (s, $OC\underline{H}_3$), 7·40 (m, 2 $C\underline{H}_2$). (B) 4·72 (s, $C\underline{H}Cl$), 6·28 (s, $2OC\underline{H}_3$), 7·35 (m, $2C\underline{H}_2$).

1,4-*Dicarbomethoxybicyclo*[2.2.0.]*hexane di* (2-*methoxyethylketal*),**4c.** The cyclobutene diester (1·25 g) and ketene bis(2-methoxyethyl)acetal[19] (9·26 g) were irradiated in cyclohexane (400 ml) for 35 hr. After crystallization of **7** (see above) the pure photoadduct **4c** was obtained by prep. GLC (7·5 min/160°/120). Found: C, 55·54; H, 7·23; MW, 346. $C_{16}H_{26}O_8$ requires C, 55·48; H, 7·57%; MW 346·37). IR (neat): 1745–1735, 1200, 1110 cm^{-1}. NMR ($CDCl_3$, τ): 6·75 (s, $2OC\underline{H}_2C\underline{H}_2O$), 6·37 (s, $CO_2C\underline{H}_3$), 6·40 (s, $CO_2C\underline{H}_3$), 6·58 (s, $OC\underline{H}_3$), 7·55 (m, $3C\underline{H}_2$).

1,4-*Bishydroxymethylbicyclo*[2.2.0]*hexane*,**5a.** The diester **4a** (0·54 g) was dissolved in dry ether (30 ml) and a solution of LAH (3·3 ml of 1·25 molar solution in THF) was added at −30°. After 2 hr a mixture of ether (30 ml) and MeOH (5 ml) was added followed by NH_4Cl aq (10%, 2 ml). After 30 min stirring the inorganic precipitate was removed by filtration. Evaporation of the filtrate at reduced pressure afforded a viscous oil. This was dissolved in $CHCl_3$, the solution was dried (Na_2SO_4) and the volume was reduced to 3–4 ml. Dilution with pentane and standing afforded the diol (210 mg), m.p. 140–142° (1·2 min/120°/120). The mother liquors were evaporated in a sublimation apparatus and the residue was sublimed at 55°/0·03 mm. After crystallization of the sublimate an additional 80 mg was obtained, overall yield 75%. (Found: M^+–OH; 125. $C_8H_{14}O_2$–OH requires 125·19). IR (KBr): 3300, 1030 cm^{-1}. NMR ($CDCl_3$, τ): 6·35 (br s, 2 $O\underline{H}$), 6·50 (s, $2C\underline{H}_2O$), 7·90 (AA′XX′ mult, $4C\underline{H}_2$).

Dimesylates **5b** and **10**. A solution of the diol **5a** (100 mg) in pyridine (2·5 ml) was slowly injected by means of a syringe into a solution of MsCl (0·69 g) in pyridine (5 ml) at −20°. The temp was then allowed to rise to 0° and stirred at 0° for 90 min and then refrigerated overnight. The whole was poured on ice and conc. HCl (2·5 ml) and stirred for 20 min. The creamy precipitate was removed by filtration and the solid was taken up in $CHCl_3$. Addition of an equal volume of pentane afforded the dimesylate **5b** (150 mg; 71%), m.p. 110–112° ($CHCl_3$–pentane). (Found: C, 40·42; H, 5·98; S, 21·41. $C_{10}H_{18}O_6S_2$ requires C, 40·27; H, 6·08; S, 21·45%). IR (KBr): 1165, 1030 cm^{-1}. NMR ($CDCl_3$, τ): 5·80 (s, $2C\underline{H}_2O$), 6·96 (s, $2SO_2C\underline{H}_3$), 7·80 (AA′XX′ mult $4C\underline{H}_2$). In an attempt to dry crude **5b** at 70°/0·02 mm the solid melted and the rearranged compound **10** was then obtained apparently quantitatively, by crystallization, m.p. 103–104·5° ($CHCl_3$–pentane). (Found: $M^+ - SO_3CH_3$; 203. $C_{10}H_{18}O_6S_2 - SO_3CH_3$ requires 203·20). IR (KBr): 1165,

1030 cm^{-1}. NMR ($CDCl_3$, τ): 5·75 (s, $C\underline{H}_2O$), 6·95 (s, $2SO_2C\underline{H}_3$), 8·00 (AA'XX' mult, $4C\underline{H}_2$), 8·35 (br m, $1C\underline{H}_2$).

Anti-1,2,5,6-*Tetrakishydroxymethyl*[4.2.$0^{1,6}$.$0^{2,5}$]*octane*, **8a**. The photodimer **7** (1·14 g) was reduced with LiAl(OMe)$_3$H (0·35 g; 27 mmol) prepared *in situ* in anhydrous THF (80 ml) at 0° or with LAH solution (9 ml, 1·25 molar in THF) at −30°. After 2 hr NH_4Cl aq (10%, 5 ml) was added and the mixture stirred overnight. The inorganic precipitate was removed by filtration and the filtrate dried ($MgSO_4$). Removal of solvent afforded the colourless *tetrol* (0·55 g; 72%), m.p. 240–244°. The analytical sample of **8a** had m.p. 245–246° (dioxan). (Found: C, 63·72; H, 8·74. $C_{12}H_{20}O_4$ requires C, 63·14; H, 8·83%). IR (KBr): 3250, 1020 cm^{-1}, NMR (DMSO-d_6, τ): 5·75 (t, J = 5 Hz, 4 O$\underline{H}$), 6·40 (d, J = 5 Hz, $4C\underline{H}_2O$), 7·90 (br s, $4C\underline{H}_2$). After D_2O exchange: 6·20(s), 6·40(s), 7·90(s).

Tetramesylate, **8b**. A solution of the tetrol (0·50 g) in dry pyridine (5 ml, dist from KOH) was added during 15 min at −20° to a solution of MsCl (3·45 g) in dry pyridine (10 ml). The mixture was stirred throughout and allowed to warm to 0° during 2 hr and further to room temp by standing overnight. After workup similar to the above (30 ml conc HCl, 60 g ice); a cream coloured solid tetramesylate (1·06 g; 90%) was obtained, m.p. 155–157°. The analytical sample had m.p. 168–170° (MeCN). (Found: S, 23·64. $C_{16}H_{28}O_{12}S_4$ requires S, 23·70%). IR (KBr): 1360, 1180 cm^{-1}. NMR (DMSO-d_6, τ): 5·52 (s, $4C\underline{H}_2O$), 6·80 (s, $4SO_2C\underline{H}_3$), 7·70 (br s, 4 $C\underline{H}_2$).

3-*Thia*[3.2.2.]*propellane*, **6**. The dimesylate **5b** (316 mg) in DMSO (50 ml) was treated with Na_2S nonahydrate (962 mg) and stirred for 96 hr at 48° under N_2. Water (150 ml) was added and the whole was extracted with pentane (6 × 25 ml). Evaporation without external heating at the water pump gave practically pure **6** as an oil (110 mg, 76%, 3·5 min/100°/120). (Found: C, 68·56; H, 8·70; S, 22·48, MW 140. $C_8H_{12}S$ requires C, 68·54; H, 8·63; S, 22·83%; MW 140·18). IR (neat): 1440 cm^{-1}. NMR ($CDCl_3$, τ): 7·20 (s, $2C\underline{H}_2S$), 7·80 (AA'XX', $4C\underline{H}_2$).

Pentacyclo[5.3.2.$0^{1,7}$.$0^{2,6}$.$2^{2,6}$]-4,9-anti-*dithiatetradecane*, **9**. A mixture of the tetramesylate **8b** (2·70 g), Na_2S nonahydrate (7·0 g), and DMSO (300 ml) was stirred under N_2 for 48 hr at 69°. Water (1·2 l) was added and the whole was extracted with pentane (7 × 60 ml). The combined extracts were dried ($MgSO_4$) and the solvent was removed. Crystallization afforded colourless **9** (0·71 g; 64%), m.p. 208–209° ($CHCl_3$-MeOH, 1 : 1). (Found: C, 63·90; H, 7·22; S, 28·46; MW 224. $C_{12}H_{16}S_2$ requires C, 64·27; H, 7·19; S, 28·54%; MW 224·25). IR (KBr); 1450, 1230 cm^{-1}. NMR ($CDCl_3$, τ): 6·75, 7·45 (AB quartet, J = 10 Hz, $4C\underline{H}_2S$), 7·70 (AA', XX', $4\underline{C}H_2$).

The mother liquor after crystallization yielded additional solid (130 mg). This was placed on a prep TLC plate (SiO_2) and the plate was developed with hexane (1×) and hexane–CCl_4 (2 : 1, 2×). The second fraction contained an additional product, **11**, m.p. 138–140°. (Found: MW 220. $C_{12}H_{12}S_2$ requires MW 220·22). IR (KBr): 1150–1050, 910, 860, 790 cm^{-1}. UV (hexane): $\lambda\lambda_{max}$ 242, 250 nm; $\varepsilon\varepsilon_{max}$ 7300, 5300. NMR ($CDCl_3$, τ): 3·20 (s, 4 vinylic H), 7·00 (s, $4C\underline{H}_2$).

Preparation of sulfonium salts

3,7-*Bismethylsulfonium*[3.3.2]*propellane difluoroborate*, **13**. A solution of BF_3-etherate (1·3 ml) in CH_2Cl_2 (6 ml) was added dropwise with stirring to freshly distilled trimethyl orthoformate (5·5 ml) at −30°.[20] The temp was brought to 0° and stirring continued for 15 min. After cooling again to −30°, solid 3,7-dithia[3.3.2]propellane, **12**[13] (1·0 g) was added all at once and the mixture allowed to warm to room temp. Immediate precipitation occurred. Stirring was continued overnight and the solid was collected by filtration. A practically quantitative yield of **13** was obtained. The analytical sample had m.p. 202–203° (MeCN–acetone, 1 : 3). (Found: S, 16·90. $C_{10}H_{18}S_2$. $2BF_4$ requires S, 17·05%). IR (KBr): 1100–1000 cm^{-1}. NMR (DMSO-d_6, τ): 6·20 (*q*, J = 12 Hz, 4 $C\underline{H}_2S^+$), 6·80 (s, 2 $S^+C\underline{H}_3$), 7·87 (s, $2C\underline{H}_2$).

3-*Oxa*-7,10-bis *methylsulfonium*[3.3.3]*propellane difluoroborate*, **20**. Dimethoxycarbonium fluoroborate (25 mmol) was prepared *in situ* as described above. A solution of 3-oxa-7,10-dithia[3.3.3]propellane, **19**[14] (676 mg) in CH_2Cl_2 (5 ml) was added with stirring at 0° and the mixture stirred overnight at room temp under N_2. The solid precipitate was removed by filtration, affording the bissulfonium salt **20** (760 mg; 54%), m.p. 225–227° (acetone–MeCN, 2 : 1). (Found: C, 31·12; H, 4·42; S, 16·14. $C_8H_{18}OS_2$. 2 BF_4 requires C, 30·60, H, 4·59; S, 16·35%). IR (KBr): 1100–1000 cm^{-1}. NMR (DMSO-d_6, τ): 5·5–6·5 (3 overlapping quartets: $2C\underline{H}_2S^+$ and $C\underline{H}_2O$), 6·75 (s, $2S^+C\underline{H}_3$).

3-*Oxa*-7-*methylsulfonium*[3.3.2]*propellane fluoroborate*, **25**. A solution of 3-oxa-7thia[3.3.2]propellane, **24**[16] (350 mg) in CH_2Cl_2 (5 ml) was added at 25° to a solution of dimethoxycarbonium fluoroborate (5·0 mmol), prepared *in situ*. The mixture was allowed to warm to room temp, stirring was continued for 2 hr and the precipitate collected (440 mg; 77%), m.p. 173–175° (MeOH). (Found: C, 41·46; H, 5·62; S, 12·06.

$C_9H_{15}OS.BF_4$ requires C, 41·90; H, 5·81; S, 12·40%). IR (KBr): 1100–1000 cm^{-1}. NMR (DMSO-d_6, τ): 6·25 (s, $2C\underline{H}_2O$), 6·28 (q. $J = 9$ Hz, $2C\underline{H}_2S^+$), 6·95 (s, $S^+C\underline{H}_3$), 8·00 (s, $2C\underline{H}_2$).

3-Methylsulfonium[3.2.2]*propellane fluoroborate*, **27.** 4-Thia[3.2.2]propellane **6** (56 mg) was injected at 0° with the aid of a syringe into a solution of dimethoxycarbonium fluoroborate (2·0 mmol) prepared *in situ* in CH_2Cl_2 (5 ml). Stirring was maintained at 0° for 30 min and at room temp for 2 hr. The solvent was removed and the oily residue taken up in a minimal volume of MeOH. Addition of ether afforded **27** (60 mg; 73%), mp. 97–98° (Found: S, 13·17%, $C_9H_{15}S.BF_4$ requires S, 13·25%). IR (KBr): 1100–1000 cm^{-1}. NMR (DMSO-d_6, τ): 6·20 (q, $J = 4$ Hz, $S^+C\underline{H}_2$), 6·80 (s, $S^+C\underline{H}_3$), 7·55–7·75 (br s, $4C\underline{H}_2$).

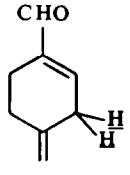
3-Thia-7-methylsulfonium[3.3.2]*propellane fluoroborate*, **22.** Trimethyloxonium fluoroborate[21] (369 mg) was covered with $MeNO_2$ (5 ml) in a 50 ml round bottom flask, stoppered with a serum 6 stopper and cooled to 0° in a dry box. A solution of 3,7-dithia[3.3.2]propellane **12** (390 mg) in CH_2Cl_2 (5 ml) was added all at once and the solution stirred at 0° for 5 hr. The solvent was removed in a vacuum, affording a crystalline residue. It was taken up in acetone and hot $CHCl_3$ was added to the nearly boiling acetone solution. Colourless needles of **22** (320 mg; 51%) were obtained, m.p. 157–158° (acetone–$CHCl_3$ 1:3). (Found: C, 39·64; H, 5·44; S, 22·66. $C_9H_{15}S_2.BF_4$ requires C, 39·40; H, 5·47; S, 23·40%). IR (KBr): 1100–1000 cm^{-1}. NMR (DMSO-d_6, τ): 6·40 (q, $J = 12$ Hz, $4S^+C\underline{H}_2$), 6·70 (s, $S^+C\underline{H}_3$), 7·20 (q, $J = 12$ Hz, $4CH_2S$), 8·00 (s. $4C\underline{H}_2$).

Conditions for the Stevens rearrangement. NaH (200 mg, 4 mmol as 50% dispersion in oil) was placed in a thoroughly dried three-neck flask under N_2. It was washed with pentane (3 × 10 ml) by decantation, covered with DMF (10 ml) and cooled to 0°. The sulfonium compound (1·0 mmol) was dissolved in DMF (10 ml) and added to the NaH suspension through a syringe. The mixture was stirred for 1·5–2 hr and diluted with water to a total volume of *ca.* 75 ml. The whole was extracted with hexane (5 × 25 ml), the combined extracts dried ($MgSO_4$) and the solvent removed under reduced pressure.

Application of the above procedure to **13** afforded a mixture of four products in the ratio 40:10:40:10. Lowering the reaction temp to −30° altered the product distribution to 45:10:40:5 (3·0, 3·6, 4·3 and 4·6 min, respectively/120°/120 ml/min). The analytical sample was prepared by collecting all four compounds on the prep column. (Found: C, 60·16; H, 7·63; S, 32·23. $C_{10}H_{16}S_2$ requires C, 60·01; H, 8·00; S, 32·00%). Chromatography of 257 mg of the oily mixture of these compounds on a florisil column using pentane as eluent yielded a 1:1 mixture of the two major components, **14** and **15** (150 mg). IR (neat): 3070, 1620, 1610 cm^{-1}. NMR (CCl_4, τ): 4·20, 5·13, 5·25, 5·9, 6·66, 7·56, 7·76, 8·05, 8·08. The two major components were further separated by GLC.

14 (3·0 min/120°/120): IR (neat), 3070, 1630 cm^{-1}. NMR (CCl_4, τ): 5·15 (d, $J = 6$ Hz, $2 = C\underline{H}_2$), 6·64 (s, 2CHS), 7·30–8·0 (m, $2C\underline{H}_2$), 8·08 (s, $2SC\underline{H}_3$). *m/e*: M^+, 200; M^+—CH_3, 185; M^+—CH_3S, 153; M^+—CH_3SH, 152; M^+—CH_3SH—CH_3, 137; M^+—$2CH_3SH$, 104. $M^+ \xrightarrow{m^*} 152 \xrightarrow{m^*} 137$.

15 (4·3/120°/120): IR (neat): 3070, 1640, 1610 cm^{-1}. NMR (CCl_4, τ): 4·20 (br s, $=C\underline{H}$), 5·25 (br s, $=C\underline{H}_2$), 5·90 (m, $C\underline{H}S$), 7·56 (m, $C\underline{H}_2CHS$), 7·75 (s, $=CSC\underline{H}_3$), 8·05 (s, $SC\underline{H}_3$). The CH_2 protons show a multiplet upfield from 7·30 mainly hidden by the other signals. Irradiation at 7·56 collapses multiplet at 5·90 to singlet. *m/e*: M^+, 200; 185, 153, 152, 137, 105, 104. $185 \xrightarrow{m^*} 137$. $152 \xrightarrow{m^*} 137$.

$HgCl_2$ treatment of products resulting from **13**. A solution of the oil (150 mg) in MeCN (4 ml) was added to $HgCl_2$ (800 mg) covered with water (2 ml). A cream coloured precipitate formed immediately. The whole was stirred at 50° for 30 min. Enough Na_2S was added to destroy any unreacted complex and the mixture was filtered through a column of celite (5 cm ht). It was extracted with $CHCl_3$ (4 × 25 ml) and the combined extracts dried ($MgSO_4$). Removal of solvent under reduced pressure gave an oil (90 mg) which was submitted to prep TLC using CCl_4 as eluent. The second band (R_f 0·70) yielded unreacted **14** (10 mg), the next two (overlapping) bands afforded a mixture of **16** and **17** (4:1, R_f 0·6–0·4). NMR of **16** (CCl_4, τ): 0·5 (s, $C\underline{H}O$), 3·20 (m, $=CH$), 5·10 (s, $R=C\underline{H}_2$), 6·80 (m, ), 7·60 (s, $2C\underline{H}_2$).

Repeated reaction with 576 mg of the oil with $HgCl_2$ (3 g) in MeCN (20 ml) and water (3 ml) at 70° for 90 min, after decomposing the complexes with Na_2S and filtration over celite afforded 240 mg oil. Prep TLC

using hexane (1×), CCl_4-hexane (1:1, 2×) and CCl_4 (1×) as eluents yielded **14** (20 mg), **17** (1·4 min/120/120; 80 mg) and **18** (1·3 min/120/120; 15 mg).

IR of **17** (neat): 3020, 1680, 1590 cm^{-1}. NMR ($CDCl_3$, τ): 0·5 (s, C<u>H</u>O), 3·20, 4·00 (AB quartet, J = 6 Hz, ), 7·60 (br s, $2C\underline{H}_2$), 8·03 (br s, $C\underline{H}_3$). Its *semicarbazone* had m.p. 206–207° (Lit.[22] m.p. 204–204·5°).

Compound **18** was found to be identical with *p*-tolualdehyde by IR and NMR. Its semicarbaxone had m.p. 216–217° (Lit.[23] m.p. 221°) and showed no m.p. depression on admixture with an authentic specimen.

Stevens rearrangement of **20** gave **21** (8 min/130°/110) in 70% yield, m.p. 67–68° (pentane). (Found: C, 55·06; H, 7·80; S, 28·98. $C_{10}H_{16}OS_2$ requires C, 55·52; H, 7·46; S, 29·64%). IR (KBr): 3070, 1630 cm^{-1}. NMR ($CDCl_3$, τ): 4·95 (m, $=C\underline{H}_2$), 5·53, 5·89 (AB quartet, J = 13 Hz, $2C\underline{H}_2O$), 6·40 (s, 2C<u>H</u>S), 7·96 (s, $2SC\underline{H}_3$). *m/e*: M^+, 216, M^+—CH_3, 201; M^+—CH_3S, 169; M^+—CH_3SH, 168; M^+—CH_3SH—CH_3, 153; M^+—CH_3S—CH_2O, 139; M^+—CH_3SH—CH_3S, 121.

Stevens rearrangement of **22** afforded **23** as an oil (4 min/120°/120) in 80% yield. (Found: C, 58·26; H, 7·21; S, 34·60. $C_9H_{14}S_2$ requires C, 58·10; H, 7·52; S, 34·40%). IR (neat): 3050, 1620, 1590 cm^{-1}. NMR (CCl_4, τ): 4·20 (s, $=C\underline{H}$), 5·10 (s, $=C\underline{H}_2$), 6·60 and 6·90 (s, $C\underline{H}_2S$), 7·64 (s, $2C\underline{H}_2$), 7·74 (s, $SC\underline{H}_3$). *m/e*: M^+, 186; M^+—CH_3, 171; M^+—CH_3S, 139, M^+—CH_3S—CH_2S, 93. Variable temp NMR from −60° to 160° gave no evidence for a sigmatropic rearrangement in **23**.

Stevens rearrangement of **25** gave **26** in 85% yield (2·2 min/120°/120) as a roughtly 1:1 mixture of isomers. (Found: C, 63·16; H, 8·20; S, 19·12. $C_9H_{14}OS$ requires C, 63·49; H, 8·29; S, 18·86%). IR (neat): 3060, 1630, 1600 cm^{-1}. NMR (Brucker 90 MHz, CS_2 τ): 4·36 (m, $=C\underline{H}$), 5·29 (s, $=CH_2$), 5·94 (d, J = 2 Hz, C<u>H</u>O), 6·09 (br s, C<u>H</u>O and $C\underline{H}_2O$), 7·71 (two s, $C\underline{H}_2C\underline{H}_2$), 7·80 (2s, 2 $SC\underline{H}_3$). *m/e*: M^+, 170; M^+—CH_3, 155; M^+—CH_3S, 123; M^+—CH_3SH, 122. Variable temp NMR from −60° to 160° gave disappointing results. No evidence was found for the existence of a sigmatropic rearrangement in **26**.

Stevens rearrangement of **27** gave **28** as an oil in 63% yield (4·6 min/120°/120). IR (neat): 3070, 1650, 1630 cm^{-1}. NMR ($CDCl_3$, τ): 4·35 (s, $=C\underline{H}$), 5·30 (s, $=C\underline{H}_2$), 7·73 (s, $8C\underline{H}_2$), 7·77 (s, $SC\underline{H}_3$). *m/e*: M^+, 154; M^+—CH_3, 139; M^+—CH_3S, 107; M^+—CH_3SH, 106.

Sulfone of 3-*oxa*-6-*chloro*-7-*thia*[3.3.2]*propellane*, **29**. N-Chlorosuccinimide (730 mg; 1·0 eq) was added in one portion to a solution of 3-oxa-7-thia[3.3.2]propellane, **24** (850 mg) in CCl_4 (50 ml). After 3 hr stirring an additional quantity of NCS (150 mg) was added and stirring was continued overnight. The solvent was removed and replaced with an ethereal solution of perphthalic acid (22 mmol peracid). The whole was stirred at 0° for 3 hr and then at room temp overnight. $CHCl_3$ (50 ml) was added and the whole was washed thrice with $NaHCO_3$ aq, with saturated NaCl aq solution and then dried ($MgSO_4$). Evaporation of solvent yielded an oil (1·01 g) which was chromatographed on neutral alumina (30 g). The *α-chlorosulphone*, **29**, was obtained from a benzene–$CHCl_3$ fraction of the eluent (260 mg, 6·7 min/160°/120), m.p. 158·5–159° (EtOAc). (Found: C, 44·61; H, 5·17; Cl, 16·00. $C_8H_{11}O_3SCl$ requires C, 43·30; H, 4·93; Cl, 15·90%). IR (KBr): 1325, 1125, 780 cm^{-1}. NMR ($CDCl_3$, τ): 5·05 (s, C<u>H</u>Cl), 5·80–6·80 (3 overlapping q, $C\underline{H}_2SO_2$, $C\underline{H}_2$—O—$C\underline{H}_2$), 7·70–7·85 (m, $C\underline{H}_2C\underline{H}_2$).

Epimerization of **29**. A mixture of NaH (200 mg), compound **29** (150 mg) and THF (25 ml) was heated under reflux for 2·5 hr whilst monitoring the course of the reaction by GLC. After cooling ether–MeOH (8:2; 10 ml) was added, followed by water (20 ml). The whole was extracted with $CHCl_3$ (4 × 25 ml) and the combined extracts were dried ($MgSO_4$). Removal of solvent afforded an oil which upon crystallization gave the *epimer* of **29** (80 mg), m.p. 152–153·5° (CCl_4). (Found; C, 44·39; H, 5·17; Cl, 15·95. $C_8H_{11}O_3SCl$ requires C, 43·30; H, 4·93; Cl, 15·90%). IR (KBr): 1325, 1145, 1060, 750 cm^{-1}. NMR ($CDCl_3$, τ): 5·30 (s, C<u>H</u>Cl), 5·70–6·70 (4 overlapping q), 7·70–8·00 (m, $C\underline{H}_2C\underline{H}_2$).

Preparation of sulfone **31**. (a) Compound **9** (40 mg) was heated with AcOH (5 ml) and H_2O_2 (30%; 0·118 ml) at 50° for 30 min. The solvent was removed, $NaHCO_3$ aq was added and the whole was extracted with $CHCl_3$. Removal of the solvent afforded an oil whose properties were identical with those of the product obtained in (b).

(b) Ozone was passed through a solution of **9** (100 mg) in CH_2Cl_2 (25 ml) at −78° for 2 hr. After removal of the CH_2Cl_2 at −10° the insoluble colourless residue was allowed to stand overnight at room temp. The oil was then placed on a prep TLC plate (SiO_2) and eluted with CCl_4. The main band (R_f 0·4) yielded the colourless crystalline *sulfone* **31** (30 mg), m.p. 75–76° (hexane). (Found: C, 64·11; H, 7·19; S,

14·94. $C_{12}H_{16}O_2S$ requires C, 64·30; H, 7·14; S, 14·29%). IR (KBr): 3060, 1630, 1300, 1120 cm^{-1}. NMR ($CDCl_3$, τ): 5·00 and 5·20 (s, 2=CH_2), 6·75 (s, $SO_2C\underline{H}_2$), 7·60 (AA'XX' q, $C\underline{H}_2$). *m/e*: M^+, 224; M^+—C_2H_4, 196; M^+—SO_2, 160; M^+—SO_2—C_2H_4, 132.

Attempted preparation of **32**. Ozone was passed through a solution of 3-thia[3.2.2]propellane (50 mg) in CH_2Cl_2 (20 ml) at −78° for 1·5 hr. When the solvent was removed at −30°/1 mm and the residual oil was taken up in $CDCl_3$ and its NMR spectrum was measured at −30°, it corresponded to that expected for the sulphone **32**. Singlets were observed at τ 6·73 and 7·45, $C\underline{H}_2SO_2$ and $C\underline{H}_2C\underline{H}_2$ protons, respectively, in a ratio of 1:2.

When the solution was allowed to warm up towards the normal room temp operation of the NMR probe. two new singlet signals appeared at τ 5·30 and 7·80, corresponding to the vinylic and allylic protons of **33**, respectively[24]. From these measurements $t_{\frac{1}{2}}$ for the reaction **32** → **33** is *ca.* 2·5 hr at 25°.

Several low temp irradiations gave intractable mixtures.

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