# Sterically Crowded Alkenes. Synthesis of 4-(Di-*tert*-butylmethylene)tetramethyldihydro-2(3*H*)-furanone and Furanols by Ring Expansion of 3-(Di-*tert*-butylmethylene)tetramethylcyclobutanone

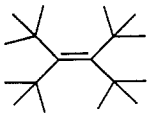
Peter J. Garratt,* David Payne, and Derek A. Tocher

*Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, U.K.*

*Received September 22, 1989*

3-(Di-*tert*-butylmethylene)tetramethylcyclobutanone (**5**), prepared by the Barton–Kellog reaction from 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**3**) and di-*tert*-butyldiazomethane (**2**), is epoxidized with *m*-chloroperoxybenzoic acid but undergoes the Baeyer–Villiger reaction with potassium *tert*-butyl peroxide to give the lactone **9**. The lactone **9** is reduced with $LiAlH_4$ to the lactol **10** and reacts with methyllithium to give the the hemiacetal **12**. X-ray crystallographic studies on **9** and **10** show that the double bond is twisted by more than 30° in both cases. All attempts to reductively ring open the lactol **10** and hemiacetal **12** failed, presumably indicative of the further torsional strain that would accrue from such ring opening. The cyclobutanone **5** did not give the corresponding cyclobutanethione **16** when treated with $P_2S_5$ or Lawesson's reagent but rearranged to the cyclopentenone **18**. On attempted double extrusion from the bis(thiadiazolidine) **21**, derived from the cyclobutane-1,3-dithione **20**, partial reversion and rearrangement occured to give the cyclobutanethione **22**. The same compound was obtained on attempted extrusion from the monothiadiazoline **23**. The McMurry reaction of **5** gave only the corresponding alcohol **26**.

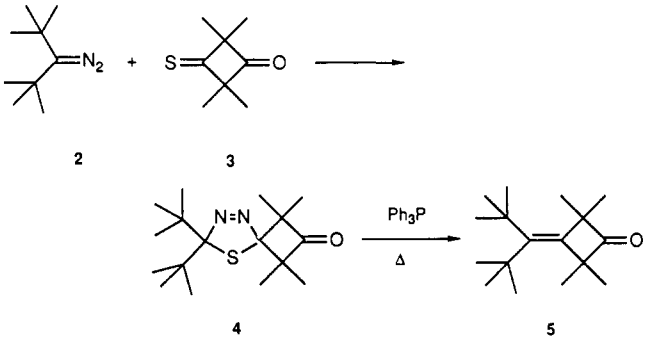
The introduction of bulky substituents onto the carbon atoms of ethene leads to both 1,1- and 1,2-steric interactions. Since any relaxation of the bond angle between two nonbonded atoms leads to the compression of the bond angle between these atoms and two other nonbonded atoms, highly sterically congested alkenes must seek relief in bond lengthening or bond twisting, or in a combination of both. Tetra-*tert*-butylethene (**1**) has been both a synthetic target and a subject for theoretical discussion for many years and, although it has not been prepared, many highly hindered alkenes have been synthesized in approaches to it.[1] Two synthetic methods have, in the main, been used: the joining together of two highly substituted moeities in a double-bond-forming reaction or the formation of a highly substituted alkane to be followed by the introduction of the unsaturation. Numerous variations and modifications have been made to these two basic approaches: groups have been tied back as rings for release after coupling or groups have been introduced that could later be removed, again with an increase in nonbonded interactions. We have investigated a route based on the coupling approach in which one of the moieties is a functionalized ring that could be expanded before being ring opened. We intended to take advantage of the information, largely provided by Krebs and his co-workers,[2] on the limits to ring size and degree of substitution allowed for the alkene to be formed. The preparation of a number of highly substituted, twisted ethenes by this method is described.[3]



**1**

## Results and Discussion

The ketone **5** was chosen as the initial target system since the alkene should be capable of formation according to Krebs observations and the cyclobutanone carbonyl group should be readily manipulated to allow the ring size to be increased prior to ring opening. The ketone **5** also had potential as a precursor to "skipped" polyethenes, another area in which we were interested. Treatment of 2,2,4,4-tetramethyl-3-oxocyclobutanethione (**3**) with di-*tert*-butyldiazomethane (**2**) in ether at −78 °C gave the thiadiazoline **4** in 81% yield as a white, crystalline solid.




**2** **3** **4** **5**

The $^{13}C$ NMR spectrum showed a signal at $\delta$ 219.3, characteristic for a carbonyl and not a thiocarbonyl carbon,[4] and the IR spectrum showed an absorption at 1787 $cm^{-1}$, characteristic of a cyclobutanone carbonyl.[5] The 2-fold extrusion of nitrogen and sulfur from **4** did not proceed easily and considerable experimentation was required until optimum conditions were found: even then, only a 23% yield of the desired cyclobutanone **5** was obtained. The thiadiazoline **4** was heated with triphenyl-

(1) (a) Barton, D. H. R.; Guziec, F. S., Jr.; Shahak, I. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1974. Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *Ibid.* **1976**, 2079. (b) Olah, G. A.; Surya Prakash, G. K. *J. Org. Chem.* **1977**, *42*, 580. (c) Guziec, F. S., Jr.; Murphy, C. J. *Ibid.* **1980**, *45*, 2890. (d) Lenoir, D.; Burghard, H. *J. Chem. Res. Synop.* **1980**, 396. Lenoir, D.; Dauner, H.; Frank, R. M. *Chem. Ber.* **1980**, *113*, 2636. (e) Cullen, E. R.; Guziec, F. C., Jr.; Murphy, C. J. *J. Org. Chem.* **1982**, *47*, 3563. (f) Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. *J. Am. Chem. Soc.* **1982**, *104*, 2326. (g) Krebs, A.; Born, W.; Kalleta, B.; Nickel, W.-U.; Rüger, W. *Tetrahedron Lett.* **1983**, *24*, 4821. Krebs, A.; Nickel, W.-U.; Tikwe, L.; Kopf, J. *Ibid.* **1985**, *26*, 1639. (h) Dannheim, J.; Grahn, W.; Hopf, H.; Parrodi, C. *Chem. Ber.* **1987**, *120*, 871.

(2) Krebs, A.; Kaletta, B.; Nickel, W.-U.; Rüger, W.; Tikwe, L. *Tetrahedron* **1986**, *42*, 1693 and references therein.

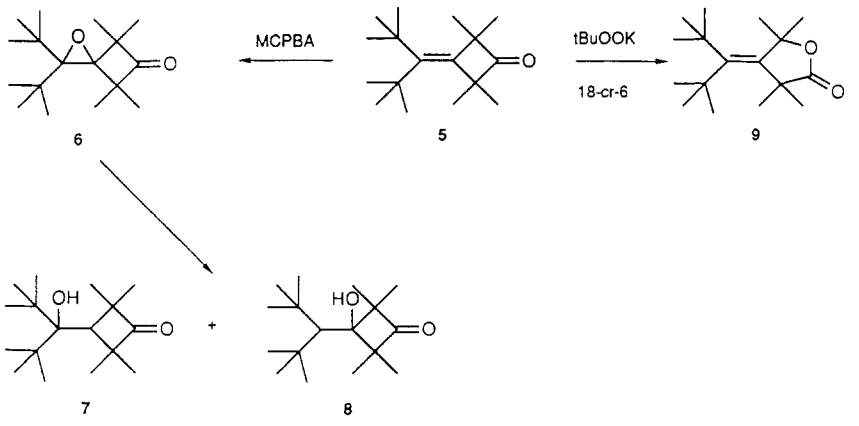
(3) Part of this work was reported at the 6th International Symposium on Novel Aromatic Compounds, Toyonaka, Japan, August 20–25, 1989.

(4) Jaythirtha Rao, V.; Muthuramu, K.; Ramamurthy, V. *J. Org. Chem.* **1982**, *47*, 127.

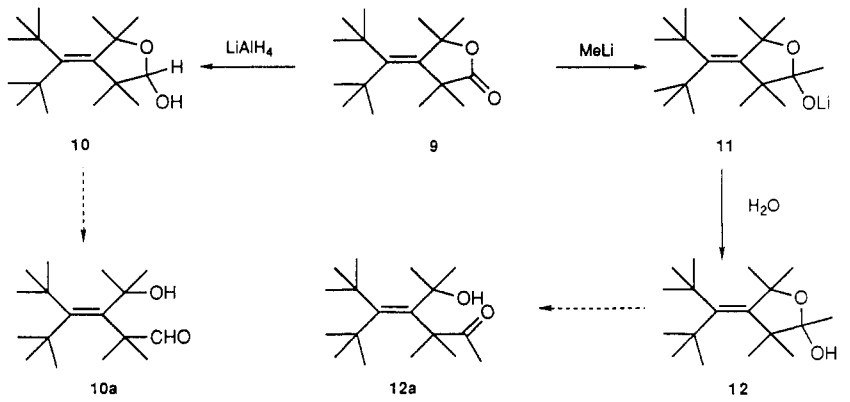
(5) See: Nakanishi, K. *Infrared Absorption Spectroscopy*; Holden-Day: San Francisco, Tokyo, 1962.

0022-3263/90/1955-1909$02.50/0 

**Scheme I**




**Scheme II**




phosphine at 140 °C for 8 h, monitoring the reaction by $^1$H NMR spectroscopy. The mass spectrum of **5** showed no molecular ion peak but there were ion peaks at $M^+ - 15$ and $M^+ - 57$. The $^1$H NMR spectrum showed two signals, $\delta$ 1.32 and 1.44, corresponding to the *tert*-butyl and methyl groups, respectively, and the $^{13}$C NMR spectrum showed signals at $\delta$ 225.5, 153.7, and 143.7 for the carbonyl and alkene carbons, together with four other absorptions.

Treatment of **5** with *m*-chloroperoxybenzoic acid gave not the desired lactone but the oxirane **6**. The $^1$H NMR spectrum of **6** showed two signals attributed to methyl groups but only one signal attributed to the *tert*-butyl group, and the $^{13}$C NMR spectrum showed no signals in the region for double-bond carbons. The IR spectrum showed an absorption at 1782 cm$^{-1}$, a position consistent for a cyclobutanone carbonyl stretch.[5] Treatment of **6** with an equimolar amount of $LiAlH_4$ at room temperature gave a mixture of the ketols **7** and **8** (Scheme I). The composition of this mixture was substantiated by mass spectral and analytical data and the two compounds could be separated by HPLC. The structural assignments to the two isomers are tentative, resting on NOE experiments with the $^1$H NMR spectra.

Presumably, the double bond is still sufficiently accessible that its high nucleophilicity directs the reaction of the *m*-chloroproxybenzoic acid toward it rather than toward the carbonyl group. A number of other, less electrophilic oxidizing reagents were examined and it was eventually found that oxidation with potassium *tert*-butyl peroxide[6] in toluene containing 18-crown-6 gave the desired lactone **9** in 79% yield. The $^1$H NMR spectrum showed two different types of methyl and *tert*-butyl groups and the $^{13}$C NMR spectrum showed the signals for two alkene carbon atoms at $\delta$ 145.5 and 156.2 and a signal for the carbonyl carbon at $\delta$ 181.5. The IR spectrum showed an absorption at 1765 cm$^{-1}$, a position characteristic for the carbonyl stretching frequency of a $\gamma$-lactone.[5] The structural assignment was confirmed by an X-ray crystallographic analysis, which is discussed below.

It has previously been shown that as alkenes become more crowded, they become less susceptible to oxidation by peroxyacids.[7] This is true for the lactone **9** for, by contrast with the cyclobutanone **5**, is is not epoxidized with *m*-chloroperoxybenzoic acid.

Treatment of the lactone with $LiAlH_4$ in ether gave the lactol **10** in 72% yield as a crystalline solid, mp 151–154 °C (Scheme II). The IR spectrum had no absorption at 1765 cm$^{-1}$ but there were absorptions at 3614 and 3415 cm$^{-1}$, attributed to free and intermolecularly bonded OH stretching vibrations. The $^1$H NMR spectrum showed two *tert*-butyl and four methyl signals and the $^{13}$C NMR spectrum showed signals at $\delta$ 151.3 and 153.3 for the alkene carbon atoms together with 11 signals at higher field. The structural assignment was confirmed by an X-ray crystallographic analysis, which is described later.

In an attempt to further reduce and thus ring open the lactol, it was treated with a 4-fold excess of $LiAlH_4$ in boiling THF or diglyme over long periods but was recovered unchanged. This resistance to reduction suggests that none of the lactol exists in the ring-open form **10a**, presumably due to the large increase in steric compression that would ensue, or, less likely, that the resulting diol is so sterically demanding that it is not formed.

In an alternative approach to opening the lactone ring, it was treated with methyllithium in an attempt to form

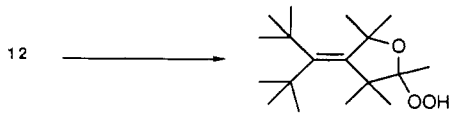
(6) Curci, R.; Di Furia, F. *Int. J. Chem. Kinet.* **1975**, *7*, 341.

(7) Krebs, A.; Rüger, W.; Nickel, W. U.; Wilke, M.; Burkert, U. *Chem. Ber.* **1984**, *117*, 310.

the oxyanion **11**, which might then ring open to the hydroxy ketone **12a**. A colorless oil was obtained in 93% yield, which slowly solidified on standing and was identified as the hemiacetal **12**. In the IR spectrum there was again no signal in the 1765 $cm^{-1}$ region but there was an absorption at 3606 $cm^{-1}$, attributable to an OH stretch. The $^1H$ NMR spectrum showed five signals attributable to a methyl group, two signals for the *tert*-butyl groups, and a singlet for the OH proton. The $^{13}C$ NMR spectrum showed two signals for the alkene carbons at $\delta$ 152.8 and 153.7 and 12 signals at higher field. Again, no evidence could be obtained for the presence of any of the ring-opened form, the hydroxy ketone **12a**.

This addition of methyllithium nicely illustrates the effect of steric strain in this system: thus although the methyllithium can add to the carbonyl group of the lactone the resulting oxyanion does not ring open but survives to be protonated. This behavior now resembles that of a thiolactone, which does not fragment because of the lower bond strength of the C=S bond and the greater stability of the sulfur anion.[8]

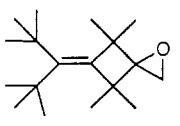
A possible method of cleaving the hemiacetal **12** would be via a Criegee rearrangement involving fragmentation of the hydroperoxide **13**.[9] Treatment of the hemiacetal




13

**12** with $H_2O_2$ and acetic acid in THF gave only recovered starting material. Replacing the acetic by sulfuric acid rapidly gave the desired peroxide **13** in 96% yield as a colorless oil. The $^1H$ NMR and $^{13}C$ NMR spectra were in accord with the proposed structure but the material decomposed even at −10 °C. No evidence for fragmentation to the diol could be obtained.

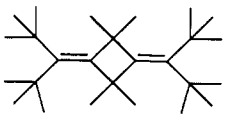
Although the Baeyer–Villiger reaction had not led to ring-opened products, it had illustrated that a ring expansion method is a useful approach to highly hindered alkenes. We attempted to extend its use by first expanding the ring by the introduction of a carbon atom and following this by a Baeyer–Villiger oxidation to the $\delta$-lactone. Diazomethane has been used to ring expand tetramethylcyclobutane-1,3-dione to 2,2,4,4-tetramethylcyclopentane-1,3-dione and this appeared a reasonable analogy for the cyclobutanone **5**.[10] Accordingly, **5** was treated with ethereal diazomethane at −25 °C and then at ambient temperature. Four compounds were observed after workup and HPLC, the starting material **5** vastly predominating. An attempt was then made to form the epoxide **14** by




14

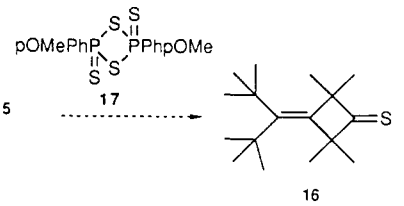
treatment with dimethyloxosulfonium methylide, but again only starting material was recovered. Highly strained oxiranes have been prepared from $\beta$-hydroxy sulfides.[11] Consequently, **5** was treated with [(phenylthio)methyl]-lithium at 0 °C and the mixture was then warmed to ambient temperature for 18 h, but again only starting material was recovered. Finally, since 2,2,4,4-tetramethylcyclobutane-1,3-dione is known to react twice with sodium nitromethane to give the corresponding bis($\beta$-nitro alcohol),[12] and such a product is a precursor to the $\beta$-amino alcohol necessary for the Tiffeneau–Demjanov ring expansion, **5** was treated with sodium nitromethane. Again, under a number of conditions, including the presence of 15-crown-5, only starting material was recovered. The attempt to extend the ring expansion method in this way was therefore abandoned.

Attention was then turned to the preparation of the "skipped" diene **15**, for which the cyclobutanone **5** would seem an ideal precuror. The diene **15** is the first member



15

of a potential series of "skipped" polyenes in which the double bonds are are linearly arranged, unlike those of conjugated dienes, and the nonbonded $sp^2$ atoms are only 218 pm apart. With the methyl substituents acting as a lipophilic insulation, interesting one-dimensional electronic properties might be observed in long polymers. Freund and Hünig[13] have examined the redox properies of systems in which a quinone is linked to the cyclobutanone, but no other work has been reported. Our initial route involved the conversion of the cyclobutanone **5** into the corresponding cyclobutanethione **16**. Treatment of **5** with Lawesson's reagent, **17**,[14] in boiling toluene for 3 h gave a new product, which was not the desired cyclobutanethione **16**. Mass spectral and analytical data revealed that

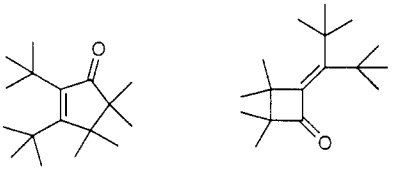



16

the new compound was isomeric with the starting material and clearly a rearrangement had occured. The IR spectrum showed a band at 1727 $cm^{-1}$, at significantly lower frequency than that expected for a cyclobutanone, and the $^1H$ NMR spectrum showed four signals at $\delta$ 1.04, 1.26, 1.31, and 1.36, in the ratio 2:2:2:3, indicative of two types of methyl and two types of *tert*-butyl groups. The $^{13}C$ NMR spectrum had a signal at $\delta$ 207.7, attributable to the carbon of a carbonyl group, and signals at $\delta$ 166.7 and 155.6, attributable to alkene carbons. We assign the structure **18** to this product but have not completely excluded the possibility of **19**. A complete correlation of the $^{13}C$ NMR spectral values with those of model compounds[15] gave a much closer fit with the values for **18** than for those of **19**, but there were some discrepancies: thus the value for the $\alpha$-carbon atom was at 9 ppm lower field than the range value for this carbon in known 2-cyclopentenones, but the

(8) See: Nicolaou, K. C.; McGarry, D. G.; Somers, P. K.; Veale, C. A.; Furst, G. T. *J. Am. Chem. Soc.* **1987**, *109*, 2504.
(9) See: Ziegler, F. E.; Wester, R. T. *Tetrahedron Lett.* **1984**, *25*, 617.
(10) Krapcho, A. P.; Rao, D. R.; Silvon, M. P.; Abegaz, B. *J. Org. Chem.* **1971**, *36*, 3885.
(11) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097.
(12) Organic Syntheses; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. 4, p 221, note 1, ref 3.
(13) Freund, W.; Hünig, S. *J. Org. Chem.* **1987**, *52*, 2154. See also: Novak, J. A.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 7618.
(14) Pedersen, B.; Scheibye, S.; Willsson, N.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.
(15) C-13 NMR Data Base, FIZ, Karlsruhe, Leopoldshafen 2, FRG.

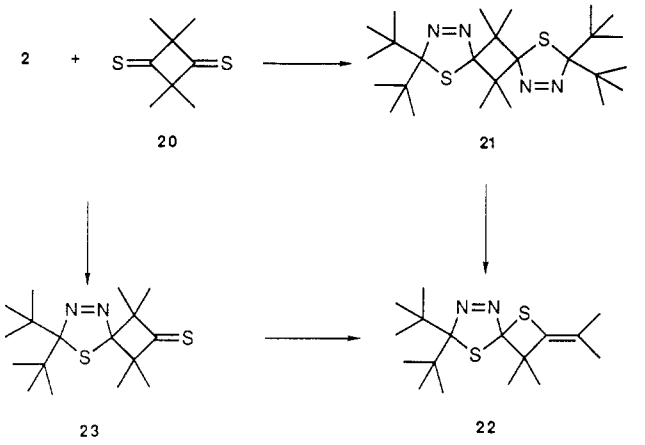
discrepancy was much worse for the 2-methylenecyclobutanone. Attempts to distinguish between **18** and **19** by ozonolysis were unsuccessful, the compound resisted oxidation, and suitable crystals for X-ray crystallographic analysis could not be obtained.



18 19

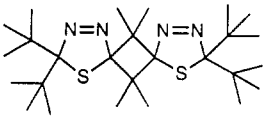
A variety of other methods were tried in order to convert **5** into **16**: these gave the same rearranged product or, in the case where **5** was treated with $H_2S$ and HCl gas in methanol in the presence of trimethyl orthoformate, at least four new products were formed, none of them corresponding to the rearranged product and none appearing to be the desired cyclobutanethione.

An alternative route was therefore examined: the reaction of the dithione **20** with di-*tert*-butyldiazomethane (**2**). Treatment of **20** with 2 molar equiv of **2** at −78 °C



20 21 23 22

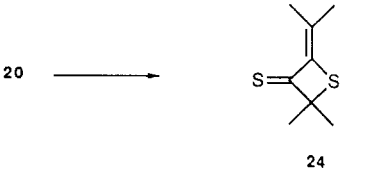
and warming to room temperature gave **21** in 68% yield. The addition of the 2 mol was confirmed by analysis and the $^{13}C$ NMR spectrum showed only six types types of carbons present, indicating that only one isomer had been formed. The $^1H$ NMR spectrum, which has only two signals corresponding to the *tert*-butyl and methyl groups, shows that this isomer is the symmetric anti isomer **21** rather than the asymmetric syn isomer **21a**. Attempted



21a

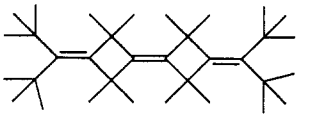
2-fold extrusion from **21** was unsuccessful. Treatment of **21** with 2.5 mol equiv of $Ph_3P$ in boiling toluene gave four unidentified products, whereas heating **21** as a melt with $Ph_3P$ at 85 °C or 100 °C gave no reaction. At 140 °C, **21** was completely consumed and at least 11 products were formed, one of which was identified as **22**. The same compound was obtained by heating **21** at its melting point (187–189 °C) for 2 min. This product can be produced conceptually by partial reversion to **23**, cleavage of the cyclobutane ring, and readdition of dimethylthioketene in the reverse sense. In a further attempt to obtain **15**, the monothiadiazoline **23** was prepared by treatment of the dithione **20** with 1 molar equiv of **2**. The thiadiazoline **23**, which was formed as a product in a number of previously discussed reactions, was isolated in 53% yield as a crystalline, orange solid. Analysis confirmed that only one di-*tert*-butyldiazomethane had added and this was supported by the mass spectrum, which showed a molecular ion at *m/e* 326. The thiadiazoline **23** was heated to 140 °C with triphenylphosphine. Some nitrogen appeared to be evolved, but on isolation of the product only the rearranged compound **22**, previously observed in the reactions of **21**, was isolated. The microanalytical composition was in accord with the assigned structure and the mass spectrum showed a peak at *m/e* 326, corresponding to the molecular ion. The $^{13}C$ NMR spectrum showed signals at $\delta$ 175.9 and 177.4, corresponding to two alkene carbon atoms, and the $^1H$ NMR spectrum showed five signals in the ratio 3:3:2:1:1, assigned to the two different *tert*-butyl groups, the ring methyl groups, and the two different alkene geminal groups, respectively.

The rearrangement in this case is not unexpected, since the dithione **20** itself has been reported to slowly undergo a similar rearrangement to **24** when heated to 125 °C.[16] Rearrangement of **23** appears to be more facile, since when heated to 100 °C for 10 min it is completely converted into **22**.



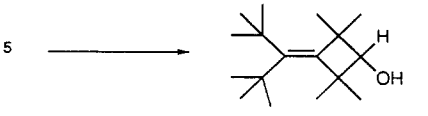
20 24

Unable to prepare the diene **15**, we turned our attention to the triene **25**. This might be expected to be formed by coupling the cyclobutanone **5**, success having been reported in coupling other hindered ketones by the McMurry method using low-valent titanium salts.[1d,17] The cyclo-



25

butanone **5** was added to a mixture of $TiCl_3$ and $LiAlH_4$ in THF and the mixture boiled. Three compounds were isolated, the starting cyclobutanone and the reduced secondary alcohol **26** being characterized. The alcohol could be conventionally prepared by reduction of **5** with $LiAlH_4$. The IR spectrum showed no absorption at 3632 $cm^{-1}$ and there was no absorptions in the carbonyl region. The mass spectrum showed peaks both for the molecular ion and $M^+ + 1$, and in the $^1H$ NMR spectrum two different methyl proton signals were observed.



5 26

It had previously been reported that reduction could occur under the conditions employed[17] and that the $TiCl_3$/potassium reagent gave higher yields of coupled products in the case of hindered ketones. The coupling of **5** with the $TiCl_3$/potassium reagent was therefore investigated: the mixture was heated to reflux for 16 h in

(16) Elam, E. U.; Davis, H. E. *J. Org. Chem.* **1967**, *32*, 1562.
(17) McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1976**, *41*, 896.

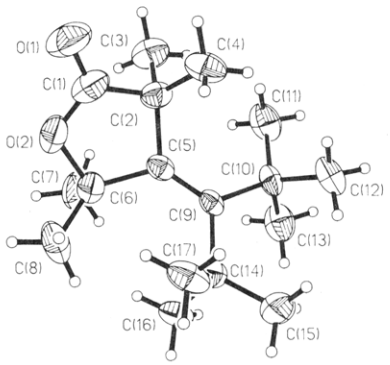



**Figure 1.** ORTEP drawing of **9** showing thermal ellipsoids.

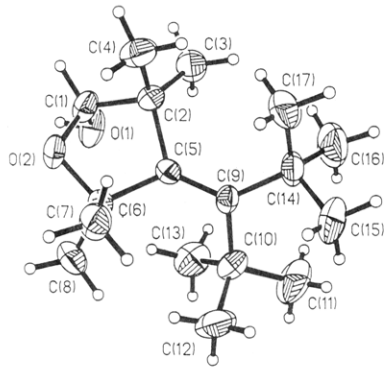



**Figure 2.** ORTEP drawing of **10** showing thermal ellipsoids.

THF and two compounds were isolated, one of which was identified as the alcohol **26**.

## X-ray Crystallographic Analysis of the Lactone 9 and Lactol 10

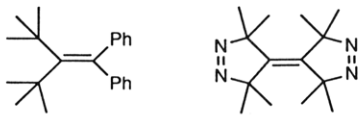
Crystals of the lactone **9** suitable for X-ray crystallographic analysis were prepared from 5% EtOAc in pentane. A view of the molecular structure is shown in Figure 1. The strain induced by the nonbonded interactions is minimized by a lengthening of the alkene bond (135.7 pm) compared to the "normal" value (133.7 (6) pm) and, more strikingly, by the relative twisting of the terminal substituents by 33.8°. Some lengthening of all the single bonds from the "normal" values also occurs (see supplementary material). The $C(sp^2)$–$C(sp^3)$–$C(sp^3)$ interbond angles are also increased with respect to the "normal" tetrahedral angle. Despite these adjustments, there are still some short nonbonded distances between atoms.

Crystals of **10** suitable for X-ray crystallographic analysis were obtained from benzene. A view of the molecular structure is shown in Figure 2. Again the alkene bond is lengthened (136.7 (5) pm) and the substituents on the alkene are twisted from each other (37.5°), the torsional distortion being greater than that found for the lactone (see supplementary material). Similar distortions of single bond lengths and interbond angles occur as observed for the lactone.

In both cases the five-membered rings are puckered, that of the lactol being greater than that for the lactone.

Force-field calculations were made using the MM2 program.[18] With no constraints this gave a low energy structure for **9** with a greatly lengthened alkene bond (137.9 pm) but with little torsional distortion. Restricting the value for the lenghth of the alkene to that derived from the X-ray structure gave only a slightly more twisted structure. A search was then made for alternative minima, again with the X-ray crystallographic data bond length, but none could be found.

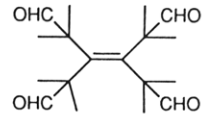
Structures have been derived for a number of highly substituted alkenes by X-ray crystallographic analysis. Both lengthening of the alkene bond (e.g. 136.0 for **27**,[19] 135.6 for **28**[20]) and twisting (24.0° for **28**, 28.6° for **29**)[2] have been observed, but the combination of values for the lactone and, particularly, the lactol indicate that these are two of the most distorted alkyl-substituted alkenes known.




27




28




29

## Experimental Section

$^1H$ NMR spectra were recorded at 60, 200, or 400 MHz. $^{13}C$ NMR spectra were recorded at 50 or 100 MHz. IR spectra were obtained as KBr disks. Melting points were recorded either on a hot-stage or oil bath apparatus and are uncorrected. Flash chromatography was performed on Woelm silica (32–63 μm) as the stationary phase.

**Preparation of Di-*tert*-butyldiazomethane (2).** This was prepared by the method of Barton et al.[1a] from pivalonitrile and *tert*-butyl chloride in 25% yield.

**Preparation of 2,2,4,4-Tetramethyl-3-oxocyclobutanethione (3).** This was prepared by the method of Elam and Davis[16] from 2,2,4,4-tetramethyl-1,3-cyclobutanedione and phosphorus pentasulfide in 44% yield, mp 54–55 °C (lit.[16] mp 57–59 °C).

**Preparation of Thiadiazolidine 4.** Di-*tert*-butyldiazomethane (**2**) (0.67 g, 4.35 mmol) in ether (10 mL) was added to a stirred solution of the thione **3** (0.67 g, 4.29 mmol) in ether (10 mL) at −78 °C. The red color discharged and the solution was allowed to equilibrate to room temperature and was stirred for a further 16 h. The ether was removed under reduced pressure to give a white solid, recrystallized from ethanol as **4**, 1.09 g, 3.5 mmol (82%): mp 141–143 °C dec; MS, *m/e* (rel intensity) 253 ($M^+$ − 57, 13), 57 (100); $^1H$ NMR δ 1.15 (s, 18 H), 1.28 (s, 12 H); $^{13}C$ NMR δ 19.6, 23.6, 30.8, 42.9, 67.4, 111.4, 130.7, 219.4; IR 2969, 2930, 2870, 1787 $cm^{-1}$. Anal. Calcd for $C_{17}H_{30}N_2SO$: C, 65.81; H, 9.68; N, 9.03; S, 10.32; O, 5.16. Found: C, 65.57; H, 9.74; N, 8.99; S, 10.45.

**Preparation of Cyclobutanone 5.** Thiadiazoline **4** (10.0 g, 32 mmol) and triphenylphosphine (16.0 g, 61 mmol) were stirred together as a melt at 140 °C for 8 h. The mixture was allowed to cool and was then dissolved in benzene (50 mL) and treated with iodomethane (10 mL, 108 mmol). The mixture was filtered and the solvent removed from the filtrate under reduced pressure to give a red solid (14.2 g). The solid was extracted with 5% EtOAc in petroleum ether (3 × 15 mL) and the combined extracts were added to a silica gel column (400 g) and eluted with the same solvent mixture. A solid (5.62 g) was recovered from the eluant and rechromatographed on silica (200 g), eluting with 1:1 $CH_2Cl_2$/petroleum ether. A white solid was recovered from the eluant, which was recrystallized from ethanol and the crystals were then sublimed to give **5**, 1.83 g, 7.32 mmol (22.7%): mp 115–116 °C; MS, *m/e* (rel intensity) 235 ($M^+$ − 15, 0.14), 193 ($M^+$ − 57, 1.1), 57 (100); $^1H$ NMR δ 1.32 (s, 18 H), 1.44 (s, 12 H); $^{13}C$ NMR δ 26.4, 34.5, 38.7, 64.2, 143.7, 153.7, 225.5; IR 3056, 2958, 2925, 2870, 1787 $cm^{-1}$. Anal. Calcd for $C_{17}H_{30}O$: C, 81.60; H, 12.00; O, 6.40. Found: C, 81.43; H, 12.16; O, 6.50.

**Treatment of 5 with *m*-Chloroperoxybenzoic Acid. Preparation of Oxirane 6.** Cyclobutanone **5** (0.50 g, 2.0 mmol) in $CH_2Cl_2$ (2 mL) was added dropwise to a stirred solution of *m*-chloroperoxybenzoic acid (0.865 g, 80%, 4.0 mmol) in $CH_2Cl_2$ (15 mL) under nitrogen. The reaction vessel was then covered with aluminum foil and the mixture was stirred for 16 h when

(18) Allinger, N. L.; Yuh, Y. H. *QCPE Program* **1980**, No. 395.

(19) Mugnoli, A.; Simonetta, M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1831.

(20) Bushby, R. J.; Pollard, M. D.; McDonald, W. S. *Tetrahedron Lett.* **1978**, 3851.

a precipitate had formed. The mixture was diluted with $CH_2Cl_2$ (20 mL), washed with saturated $Na_2SO_3$ solution (3 × 30 mL) and saturated $NaHCO_3$ solution (3 × 30 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue added to a column of silica gel (20 g) and eluted with 5% EtOAc in petroleum ether to give **6** as a white solid, 0.46 g, 1.73 mmol (86%). For analytical purposes a small sample was recrystallized from methanol and sublimed, mp 64–66 °C: MS, *m/e* (rel intensity) 266 ($M^+$, 0.25), 251 ($M^+ - 15$), 209 ($M^+ - 57$, 2.0), 57 (100); $^1H$ NMR δ 1.17 (s, 18 H), 1.27 (s, 6 H), 1.44 (s, 6 H); $^{13}C$ NMR δ 20.3, 23.9, 31.4, 38.1, 63.9, 79.1, 80.7, 223.7; IR 3058, 2961, 2927, 2873, 1782 $cm^{-1}$. Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.69; H, 11.28; O, 12.03. Found: C, 76.56; H, 11.39; O, 12.02.

**Treatment of 6 with Lithium Aluminum Hydride.** $LiAlH_4$ (0.066 g, 1.76 mmol) was added to oxirane **6** (0.47 g, 1.76 mmol) in ether (5 mL) and the mixture stirred for 2.5 h. The mixture was cooled in ice–water and saturated $NH_4Cl$ solution (10 mL) was added. The mixture was extracted with ether (3 × 10 mL), the ethereal extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a white solid, 0.24 g, mp 129–131 °C, a mixture of the ketols **7** and **8**: MS, *m/e* (rel intensity) 253 ($M^+ - 15$, 11.9), 57 (100); $^1H$ NMR δ 1.38, 1.31, 1.18, 1.17, 1.15, 1.14. Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.01; O, 11.92. Found: C, 75.96; H, 12.17; O, 11.84.

HPLC of the mixture, eluting with 10% EtOAc in petroleum ether, gave **7** and **8**. Compound **7**: $^1H$ NMR δ 1.30, 1.17, 1.13 (5.9:7.6:18.5). Compound **8**: $^1H$ NMR δ 1.38, 1.17, 1.15 (5.8:6.7:19.5).

**Treatment of 5 with Potassium *tert*-Butyl Peroxide. Preparation of Lactone 9.** Potassium *tert*-butyl peroxide (2.56 g, 20.0 mmol) was dissolved after prolonged stirring in toluene (100 mL) containing 18-crown-6 (5.26 g, 20 mmol) under nitrogen. Cyclobutanone **5** (0.050 g, 2.0 mmol) in toluene (10 mL) was then added dropwise with stirring and the stirring was continued for 72 h. The mixture was washed with water (2 × 250 mL), the aqueous washings were extracted with $CH_2Cl_2$ (100 mL), and the combined organic layers were dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue chromatographed on silica gel (40 g), eluting with 5% EtOAc in petroleum ether to give two materials. The first was identified as **5**, 0.07 g (14%), and the second compound, obtained as a white crystalline solid, was the desired lactone **9**, 0.42 g, 1.58 mmol (79%). A small sample of lactone was recrystallized from ether for analytical purposes, mp 166–168 °C: MS, *m/e* (rel intensity) 267 ($M^+ - 1$, 0.2), 209 ($M^+ - 57$, 9.5), 57 (100); $^1H$ NMR δ 1.38 (s, 9 H), 1.39 (s, 9 H), 1.63 (s, 6 H), 1.78 (s, 6 H); $^{13}C$ NMR 30.0, 32.9, 35.4, 36.3, 40.1, 41.3, 50.0, 89.3, 145.5, 156.2, 181.5; IR 3015, 2957, 2925, 2872, 1765, 1203, 1165 $cm^{-1}$. Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.69; H, 11.28; O, 12.03. Found: C, 76.25; H, 11.45; O, 12.28.

**Treatment of 9 with *m*-Chloroperoxybenzoic Acid.** Lactone **9** (0.030 g, 0.113 mmol) in $CH_2Cl_2$ (1 mL) was added dropwise to a stirred solution of *m*-chloroperoxybenzoic acid (0.050 g, 80%, 0.29 mmol) in $CH_2Cl_2$ (5 mL) under nitrogen. The reaction vessel was then wrapped in aluminum foil and the mixture stirred for 120 h. The mixture was worked up as above but only unchanged lactone (0.030 g) was recovered.

**Treatment of 9 with Lithium Aluminum Hydride. Preparation of Lactol 10.** Lactone **9** (0.32 g, 1.24 mmol) in ether (2 mL) was added dropwise to a stirred slurry of lithium aluminum hydride (0.188 g, 4.96 mmol) in ether (10 mL) under nitrogen. Effervescence occured on addition of the lactone and the mixture was monitored by TLC, all starting material appearing to have been consumed after 3 h. Saturated $NH_4Cl$ solution (10 mL) was added dropwise to the mixture, which was then filtered through Kieselguhr. The organic and aqueous layers were separated, the aqueous layer was extracted with ether (2 × 10 mL), and the combined organic layers were dried ($MgSO_4$). The solvent was removed under reduced pressure to give a white residue (0.26 g) that was chromatographed on silica gel (10 g), eluting with 1:1 $CH_2Cl_2$/petroleum ether to give **10** as a white solid, 0.24 g, 0.89 mmol (72%). A small amount of lactol was recrystallized from 5% EtOAc in petroleum ether for analytical purposes, mp 151–154 °C: MS, *m/e* (rel intensity) 251 ($M^+ - 17$, 0.02), 235 ($M^+ - 33$, 0.7), 211 ($M^+ - 57$, 16), 57 (100); $^1H$ NMR δ 1.30 (s, 3 H), 1.34 (s, 9 H), 1.42 (s, 9 H), 1.45 (s, 3 H), 1.46 (s, 3 H), 1.84 (s, 3 H), 2.27 (br s, 1 H), 4.68 (d, 1 H); $^{13}C$ NMR δ 25.3, 27.5, 34.3, 34.7, 35.4, 36.6, 40.1, 42.4, 51.9, 88.9, 107.3, 151.3, 153.3; IR 3614, 3415, 3011, 2975, 2927, 1201, 1153 $cm^{-1}$. Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.12; H, 11.94; O, 11.94. Found: C, 75.86; H, 12.14; O, 12.08.

**Treatment of Lactol 10 with Lithium Aluminum Hydride.** Lactol **10** (0.040 g, 0.15 mmol) in THF (1 mL) was added dropwise to a stirred slurry of $LiAlH_4$ (0.022 g, 0.6 mmol) in THF (5 mL) under nitrogen. The mixture was boiled for 3 h, cooled, and worked up as above. Only the lactol (0.040 g) was isolated (TLC, $^1H$ NMR spectrum). Repetion of the reaction but boiling for 1 week also gave recovered starting material, as did attempting the reduction in boiling diglyme for 72 h.

**Treatment of Lactone 9 with Methyllithium. Preparation of Hemiacetal 12.** Methyllithium (1.20 mL, 1.4 M, 1.68 mmol) in ether was added dropwise to a stirred solution of **7** (0.17 g, 0.64 mmol) in THF (10 mL) under nitrogen at −78 °C. The mixture was allowed to come to room temperature over 6 h and stirring was continued for a further 18 h. Saturated $NH_4Cl$ solution solution was then added dropwise followed by ether (20 mL). The mixture was then separated and the organic layer was washed with saturated $NaHCO_3$ solution (2 × 10 mL) and brine (2 × 10 mL) and then dried ($Mg_2SO_4$). The solvent was removed under reduced pressure and the residue chromatographed on silica (20 g), eluting with 5% EtOAc in petroleum ether, to give the acetal **12** as a colorless oil, 0.16 g, 0.57 mmol (93%), which crystallized slowly on standing: MS, *m/e* 265 (rel intensity) ($M^+ - 17$, 38), 225 ($M^+ - 57$, 10), 207 ($M^+ - 75$, 13) 57 (100); $^1H$ NMR δ 1.27 (s, 3 H), 1.31 (s, 3 H), 1.36 (s, 3 H), 1.37 (s, 9 H), 1.44 (s, 9 H), 1.46 (s, 3 H), 1.89 (s, 3 H), 2.21 (s, 1 H); $^{13}C$ NMR δ 21.9, 25.0, 26.1, 34.2, 34.8, 35.3, 36.8, 40.3, 42.7, 53.9, 86.3, 109.1, 152.8, 153.7; IR 3606, 2971, 2925, 1393, 1381 $cm^{-1}$.

**Treatment of 12 with Hydrogen Peroxide. Preparation of Peroxide 13.** Hydrogen peroxide (0.05 mL, 30% v/w, 1.63 mmol) containing concentrated $H_2SO_4$ (1 drop) was added to a stirred solution of **12** (0.09 g, 0.32 mmol) in THF (5 mL) under nitrogen at 0 °C. The mixture was allowed to warm to room temperature and was monitored by TLC, all starting material being consumed after 10 min. Ether (10 mL) was added and the mixture washed with saturated $NaHCO_3$ (3 × 10 mL) and brine (2 × 10 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give **13** as a colorless oil, 0.09 g, 0.30 mmol (96%), which slowly solidified on standing. An attempt at further purification by base extraction failed and **13** slowly decomposed on storing at −10 °C: MS, *m/e* (rel intensity) 265 ($M^+ - 33$, 55), 117 (100); $^1H$ NMR δ 1.24 (s, 3 H), 1.37 (s, 9 H), 1.42 (s, 3 H), 1.44 (s, 3 H), 1.45 (s, 9 H), 1.51 (s, 3 H), 1.92 (s, 3 H), 7.43 (br s, 1 H); $^{13}C$ NMR δ 15.7, 25.1, 25.5, 34.0, 34.2, 34.9, 37.0, 40.1, 42.2, 53.9, 87.6, 116.7, 150.7, 152.2.

**Treatment of 13 with Acetic Anhydride.** 4-(Dimethylamino)pyridine (0.037 g, 0.30 mmol) was added to a stirred solution of **13** (0.09 g, 0.30 mmol) and acetic anhydride (0.20 mL, 0.27 mmol) in $CH_2Cl_2$ (5 mL) under nitrogen. The reaction was monitored by TLC and all the peroxide was consumed after 20 min. The mixture was poured onto water (20 mL), ether (40 mL) was added, and the complete mixture was extracted with saturated $MgCO_3$ solution (2 × 20 mL). The organic layer was dried ($MgSO_4$) and the solvent removed under reduced pressure. HPLC on silica, eluting with 1% EtOAc in petroleum ether, gave four products, none of which was identified further and none corresponded to **13**.

**Treatment of 5 with Lawesson's Reagent (17).** Cyclobutanone **5** (0.10 g, 0.40 mmol) and **17** (0.097 g, 0.24 mmol)[14] were added to toluene (10 mL) and the mixture was stirred and heated to reflux under nitrogen for 3 h. The mixture was then cooled and filtered and the solvent was removed from the filtrate under reduced pressure. The residue was chromatographed on silica (10 g), eluting with 1:1 $CH_2Cl_2$/petroleum ether, to give **18** as a white solid, 0.070 g, 0.28 mmol (70%), mp 75–76 °C: MS, *m/e* (rel intensity) 250 ($M^+$, 0.2), 235 ($M^+ - 15$, 0.1), 151 (100); $^1H$ NMR δ 1.04 (s, 6 H), 1.26 (s, 6 H), 1.31 (s, 9 H), 1.36 (s, 9 H); $^{13}C$ NMR δ 20.6, 26.3, 34.1, 40.6, 41.7, 44.4, 60.7, 155.6, 166.7, 207.7. Anal. Calcd for $C_{17}H_{30}O$: C, 81.60; H, 12.00; O, 6.40. Found: C, 81.49; H, 12.15; O, 6.62.

Similar treatment of **5** with $PCl_5$ or bis(tricyclohexyltin) sulfide and $BCl_3$ also gave **18**.

**Preparation of 2,2,4,4-Tetramethylcyclobutane-1,3-dithione (20).** Compound **20** was prepared from the 2,2,4,4-

tetramethylcyclobutane-1,3-dione and $P_2S_5$ in 46% yield by the method of Elam and Davis.[16]

**Preparation of the Bis(thiadiazoline) 21.** Di-*tert*-butyldiazomethane (**2**) (0.574 g, 3.7 mmol) in ether (10 mL) was added to a stirred solution of **20** (0.319 g, 1.85 mmol) in ether (10 mL) at −78 °C. There was a rapid loss of the red color of the solution and a white precipitate appeared. The mixture was allowed to warm to room temperature and was stirred for 16 h. The solvent was removed under reduced pressure to give a white crystalline solid, recrystallized from $CCl_4$ as **21**, 0.63 g, 1.31 mmol (68%), mp 187–89 °C: MS, *m/e* (rel intensity) 395 ($M^+$ − 85, 0.35), 57 (100); $^1H$ NMR δ 1.18 (s, 36 H), 1.34 (s, 12 H); $^{13}C$ NMR δ 24.8, 31.0, 43.2, 55.5, 116.4, 130.2; IR 2965, 2925, 1387, 1367 $cm^{-1}$. Anal. Calcd for $C_{26}H_{48}N_4S_2$: C, 64.94; H, 10.06; N, 11.65; S, 13.33. Found: C, 64.31; H, 10.00; N, 11.64; S, 13.18.

**Attempted Preparation of 15.** Compound **21** (0.0432 g, 0.09 mmol) was heated to 190 °C until the evolution of nitrogen ceased (ca. 2 min). The yellow-brown resinous residue was separated by HPLC, eluting with 25% EtOAc in petroleum ether and then petroleum ether. Eleven products were observed and one was identified as **18**, identical by MS and $^1H$ NMR spectral data with the sample described above. Heating **21** with $Ph_3P$ in THF or as a melt at 85 °C, 100 °C, or 140 °C led to recovered **21**, slow reaction, and reaction with the formation of **18**, respectively.

**Preparation of Thiadiazolinethione 23.** Di-*tert*-butyldiazomethane (**2**) (0.178 g, 1.16 mmol) in ether (4 mL) was added dropwise to a stirred solution of the dithione **20** (0.20 g, 1.16 mmol) in ether (10 mL) at room temperature. The red color of the solution was partially discharged and the solution was stirred for 16 h. The solvent was removed under reduced pressure and the orange residue was chromatographed on silica (50 g), eluting with 5% EtOAc in petroleum ether. Removal of the solvent under reduced pressure gave orange crystals, recrystallized from ethanol as **23**, 0.20 g, 0.61 mmol (53%), mp 122–23 °C: MS, *m/e* (rel intensity) 326 ($M^+$, 0.1), 269 ($M^+$ − 57, 5), 57 (100); $^1H$ NMR δ 1.21 (s, 18 H), 1.39 (s, 12 H); $^{13}C$ NMR δ 23.5, 27.6, 30.7, 42.9, 69.9, 115.4, 130.8, 280.6; IR 2973, 2927, 2874, 1389, 1368, 1152 $cm^{-1}$. Anal. Calcd for $C_{17}H_{30}N_2S_2$: C, 62.57; H, 9.20; N, 8.59; S, 19.63. Found: C, 62.33; H, 8.96; N, 8.59; S, 19.73.

**Treatment of 23 with Triphenylphosphine.** The cyclobutanethione **23** (0.50 g, 1.53 mmol) and $Ph_3P$ (2.05 g, 7.82 mmol) were stirred together as a melt at 100 °C for 8 h. The mixture was allowed to cool and dissolved in benzene (10 mL). Iodomethane (3 mL) was added to the solution, which was stirred at room temperature for 12 h. The mixture was filtered and the filtrate evaporated under reduced press at 30 °C to give a yellow solid. HPLC, eluting with 25% $CH_2Cl_2$ in petroleum ether and then 5% $CH_2Cl_2$ in petroleum ether, gave six products, two of which were identified. The first product, recrystallized from ethanol as a yellow solid, was identified as **22**, 0.202 g, 0.62 mmol (40%), mp 74–75 °C: MS, *m/e* (rel intensity) 326 ($M^+$, 11), 269 ($M^+$ − 57, 26), 57 (100); $^1H$ NMR δ 1.29 (s, 9 H), 1.37 (s, 9 H), 1.67 (s, 6 H), 1.89 (s, 3 H), 1.95 (s, 3 H); $^{13}C$ NMR δ 21.8, 26.2, 27.8, 30.0, 41.1, 42.3, 50.8, 124.8, 136.1, 175.9, 177.4; IR 3474, 3216, 3196, 2860, 2722, 2553, 2499, 2401, 2357, 2330, 2102, 2025, 1895, 1817, 1728, 1689, 1571, 1558, 1554, 1551, 1541, 1369, 1302, 1225, 1147, 1120, 997 $cm^{-1}$. Anal. Calcd for $C_{17}H_{30}N_2S_2$: C, 62.57; H, 9.20; N, 8.59; S, 19.63. Found: C, 62.86; H, 9.37; N, 8.59; S, 19.59.

The second product was obtained as a yellow oil and identified as **24**, 0.08 g, 0.47 mmol (30%): MS, *m/e* (rel intensity) 172 ($M^+$, 52.5), 96 ($M^+$ − 76, 71); $^1H$ NMR δ 1.43 (s, 6 H), 1.69 (s, 3 H), 1.82 (s, 3 H); IR 2969, 2925, 2860, 1244, 1162, 1075 $cm^{-1}$.

**Crystal data for 9:** $C_{17}H_{30}O_2$, mol wt = 266.47, monoclinic, $a$ = 9.544 (6) Å, $b$ = 11.826 (5) Å, $c$ = 14.330 (6) Å, $\beta$ = 93.82 (4)°, $V$ = 1614 Å$^3$, $Z$ = 4, space group $P2_1/n$. Cell dimensions were obtained by least-squares refinement using 31 computer-centered reflections in the range 8° < 2θ < 30° on a Nicolet R3m/V diffractometer equipped with a graphite monochromator, λ(Mo $K_\alpha$) = 0.71073 Å.

**Solution and Refinement of 9.** A crystal of dimensions 0.15 × 0.20 × 0.20 mm was used for a $\omega/2\theta$ data collection in the range 5° < 2θ < 50° at $T$ = 19 ± 1 °C. Three check reflections were measured every 97 scans and showed no significant decay during the data collection. The data were corrected for Lorentz and polarization effects. Of the total of 3735 unique reflections, the 1139 with $I > 3\sigma(I)$ were used in calculations.

The structure was solved by direct methods.[21] The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were refined with a common isotropic temperature factor, $U$ = 0.08 Å$^2$. The geometry of the hydrogen atoms was idealized and the C–H bond lengths constrained to be 0.96 Å. In the final cycle of refinement, no parameter shifted by more than 0.05 times its estimated standard deviation and there were no peaks in the difference Fourier above the noise level (0.22 e·Å$^{-3}$). The final agreement factors $R$ and $R_w$ were 0.0645 and 0.0713, respectively.[22]

**Crystal data for 10:** $C_{17}H_{32}O_2$, mol wt = 268.49, monoclinic, $a$ = 15.289 (3) Å, b = 6.788 (1) Å, $c$ = 15.942 (3) Å, $\beta$ = 93.33 (2)°, $V$ = 1651 Å$^3$, $Z$ = 4, space group $P2_1/a$. Cell dimensions were obtained by least-squares refinement using 40 computer-centered reflections in the range 12° < 2θ < 30° on a Nicolet R3m/V diffractometer equipped with a graphite monochromator, λ(Mo $K_\alpha$) = 0.71073 Å.

**Solution and Refinement of 10.** A crystal of dimensions 0.6 × 0.4 × 0.3 mm was used for a $\omega/2\theta$ data collection in the range 5° < 2θ < 30° at $T$ = 19 ± 1 °C. No crystal decay was observed during the data collection. The data were corrected for Lorentz and polarization effects. Of a total of 3732 unique reflections measured, the 1670 with $I > 3\sigma(I)$ were used in the calculations.

The structure was solved by direct methods.[21] Structure refinement exactly paralleled that described for compound **9**. In the final cycle of refinement, no parameter shifted by more than 0.02 times its standard deviation and the largest peak in the final difference Fourier was 0.24 e·Å$^{-3}$. The final agreement factors $R$ and $R_w$ were 0.0690 and 0.0682, respectively.[22]

**Acknowledgment.** D.P. thanks the Science and Engineering Research Council (U.K.) for a studentship, and we also thank them for the provision of the X-ray equipment. We thank Professor F. E. Ziegler (Yale) for valuable discussions regarding the Criegee fragmentation sequence.

**Registry No.** **2**, 54396-68-8; **3**, 10181-59-6; **4**, 124992-69-4; **5**, 124992-70-7; **6**, 124992-71-8; **7**, 124992-72-9; **8**, 124992-73-0; **9**, 124992-74-1; **10**, 124992-75-2; **12**, 125023-15-6; **13**, 124992-76-3; **17**, 19172-47-5; **18**, 124992-77-4; **20**, 10181-56-3; **21**, 124992-78-5; **22**, 124992-79-6; **23**, 124992-80-9; **24**, 124992-81-0; **26**, 124992-82-1; 2,2,4,4-tetramethylcyclobutane-1,3-dione, 933-52-8.

**Supplementary Material Available:** Tables of final atomic coordinates, thermal parameters, and complete listings of bond lengths and angles for **9** and **10** and $^1H$ and $^{13}C$ NMR spectra for compounds **12** and **13** (17 pages). Ordering information is given on any current masthead page.

(21) Sheldrick, G. M. SHELXTL PLUS, an integrated system for solving, refining and displaying crystal structures from diffraction data, University of Göttingen, Federal Republic of Germany, 1986.

(22) $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. $R_w = \sum[w^{1/2}\cdot(|F_o| - |F_c|)]/\sum[w^{1/2}\cdot|F_o|]$.