4. Generation and Trapping of Triafulvene[1][2])

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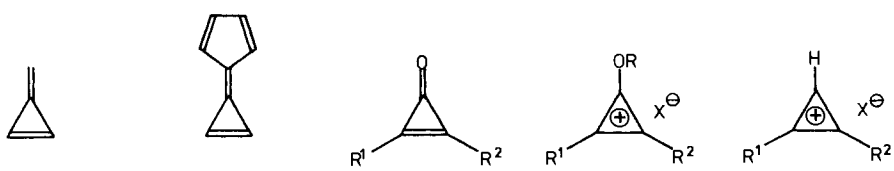
Substituted methylidenecyclopropanes **12a–d**, being easily available from 1,1-dibromo-2-(phenylthio)-cyclopropane (**9a**), are attractive precursors of triafulvene (2-methylidene-1-cyclopropene; **1**). Both the sulfoxide **12b** and the sulfone **12c** react with an excess of alkoxides (*t*-BuOK and NaOMe) to give **12e** and **12f**, respectively, while the sulfinyl group of **12b** may be replaced by the $PhCH_2S$ substituent in the presence of $PhCH_2SH$/*t*-BuOK. These reactions *(Scheme 4)* may be explained by assuming **1** as a reactive intermediate, although an alternative sequence including carbene **20** *(Scheme 6)* is not completely ruled out. D-labelling experiments *(Scheme 5)* do not give conclusive evidence due to D scrambling, but deprotonation/methylation sequences show that H–C(2) of **12a–c** is the most acidic proton. Final evidence for **1** results from the reaction of **12d** with cyclopentadienide *(Scheme 7)*: the reaction of **1** with cyclopentadiene produces the expected [4 + 2]-cycloaddition product **23**, while some mechanistic insight results from the sequence **12d**→**24**→**25**.

1. Introduction. – Although a considerable number of substituted triafulvenes and calicenes have been described since 1963, parent calicene (**2**) is unknown so far, while spectroscopic evidence for triafulvene (**1**) was not available until 1984 [3] [4]. Based on theoretical calculations [5] (of the parent system) and spectroscopic investigations (mainly of substituted compounds), **1** and **2** are expected to be olefinic molecules with strongly alternating bond lengths. Due to the fact that several cyclopropenylium salts or cyclopropenones are available today, most synthetic strategies so far started from an electrophilic three-membered ring system as well as with a nucleophilic Me or cyclopentadienyl equivalent.



1 **2** **3** **4** **5**

For example, the first synthesis of stabilised triafulvenes [6–8] involves a substituted cyclopropenone **3** which is reacted with an acidic methylene compound (*e.g.* malonodinitrile) in the presence of Ac_2O. Other appropriate starting materials are alkoxy-cyclopropenylium salts **4** ([9–13]) as well as highly alkylated or phenylated cyclopropenylium salts **5** [14] [15].

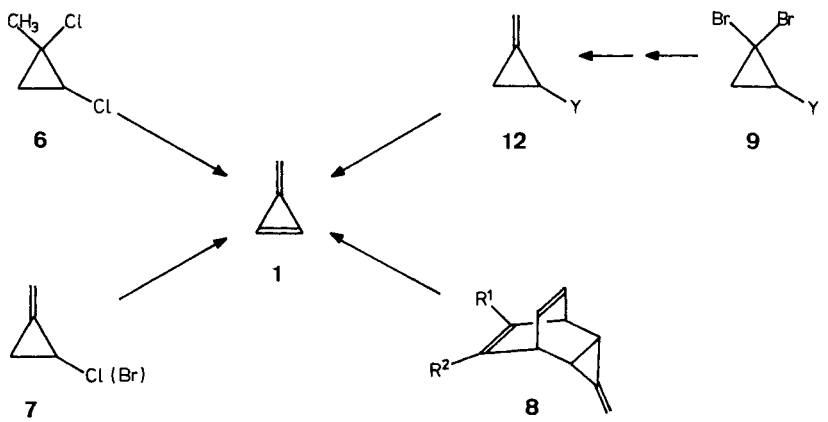
[1]) Fulvene, Fulvalenes, Part 55; Part 54: [1].

[2]) Short communication: [2].

Several early attempts towards the parent systems **1** and **2** starting from unsubstituted cyclopropenone [16] or cyclopropenylium salts [17] have been unsuccessful for various reasons, in most cases because of predominant side reactions or because of the thermal instability of key intermediates. So, the method using acetoxy-chloroalkanes as synthons [18] [19], which allowed the isolation of pure heptafulvene and sesquifulvalene [20], cannot be applied to triafulvene and calicene because of an easy decomposition of acetoxy-cyclopropenylium-tetrafluoroborate even at −100° [17].

Some recent synthetic attempts for triafulvene (**1**) are summarised in *Scheme 1*. Elimination experiments on 1,2-dichloro-1-methylcyclopropane (**6**) with alkoxides resulted in the formation of 1-alkoxy-2-methylidenecyclopropanes and led *Billups et al.* [21] to assume **1** as reactive intermediate. On the other hand, we showed that trifunctional cyclopropanes **9** with two different types of potential leaving groups are easily converted into 1-methylidene-2-Y-cyclopropanes **12** and isolated the first *Diels-Alder* product of **1** [2][2]) (*cf.* later). Very recently, direct spectroscopic evidence for the parent system **1** has been obtained at low temperature by *Billups et al.* [3] and *Staley* and *Norden* [4], eliminating HCl and HBr from precursors **7** by means of flash vacuum pyrolysis. On the other hand, *Maier et al.* [22] have observed the typical IR bands of **1** [3] [23] in the pyrolysis products of either **12b** or cyclopropenyl diazomethyl ketone. Finally, potential *retro-Diels-Alder* precursors **8** for triafulvene have been prepared by our group [24].

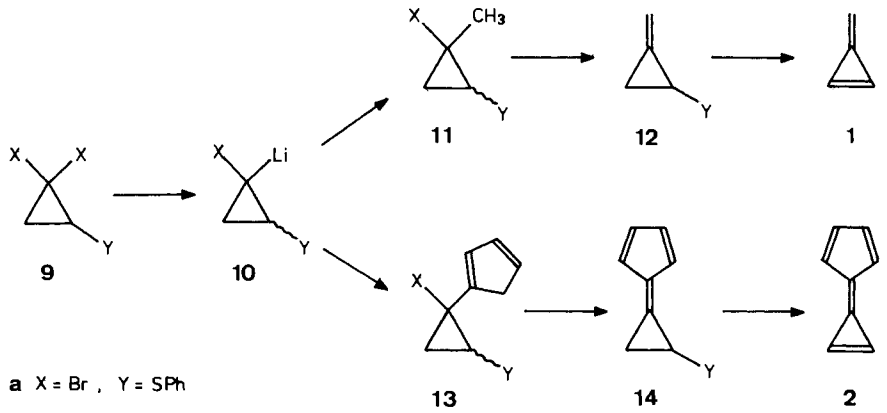
Scheme 1. *Recent Strategies for the Synthesis of* **1**



Trisubstituted cyclopropanes **9** should be attractive precursors of triafulvene (**1**) and calicene (**2**) [25] *(Scheme 2)*. In contrary to the classical procedures, they are not transformed into an electrophilic species. Metalation by halogen-Li exchange gives a nucleophile **10** which should be reacted with an electrophilic Me or cyclopentadienyl equivalent. Subsequent elimination of the leaving groups X and Y could, in principle, give fulvene **1** and fulvalene **2**, respectively.

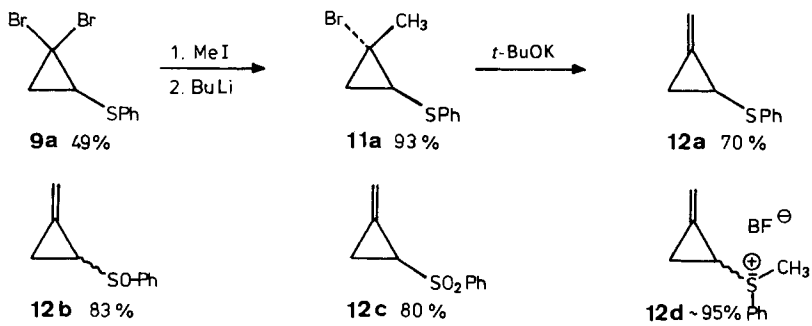
At a first stage of our experiments a series of trisubstituted cyclopropanes has been prepared [1], mainly by carbene addition to the appropriate olefins [26]. 1,1-Dibromo-2-(phenylthio)cyclopropane (**9a**) proved to be especially attractive because halogen-Li

Scheme 2. *Planned Synthesis of* **1** *and* **2**



exchange **9a**→**10a**, followed by methylation **10a**→**11a**, was nearly quantitative, and base-induced elimination **11a**→**12a** gave **12a** in a 70% yield. The key precursor **12a** was later transformed into the corresponding sulfoxide **12b**, sulfone **12c**, and sulfonium-tetrafluoroborate **12d** by subsequent oxidation and methylation [1]. In this way, a set of attractive triafulvene precursors **12a–d** became available in high yields *(Scheme 3)*.

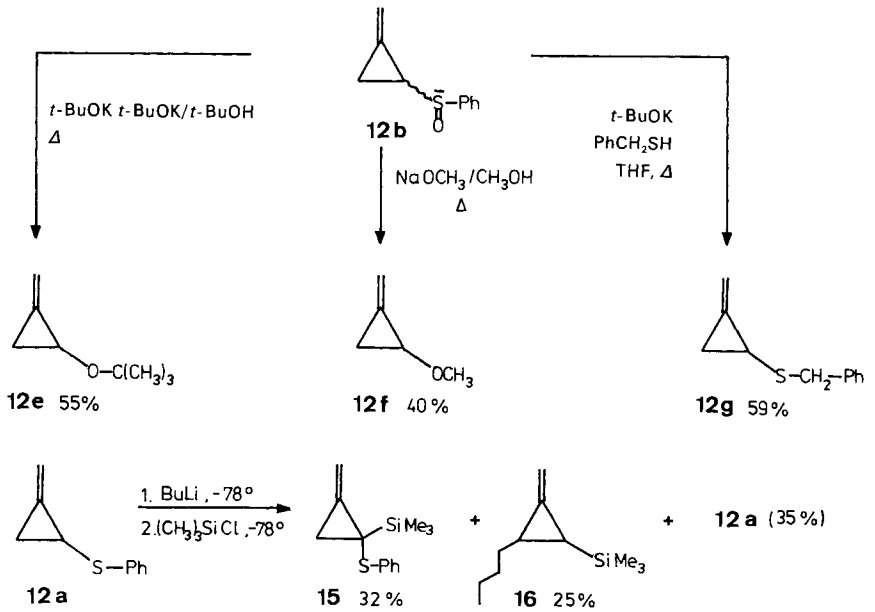
Scheme 3. *Synthesis of Triafulvene Precursors* **12** *from* **9**



Here, we report the results of a series of elimination experiments with precursors **12a–d** in the presence of trapping agents like nucleophiles and cyclopentadiene.

2. Elimination/Trapping Experiments with 12a–12c. – To gain some evidence for the instable intermediate **1**, trapping experiments are very important. In *Scheme 4*, reactions which may be interpreted *via* an elimination-addition sequence are summarised. Both the sulfoxide **12b** and the sulfone **12c** react with 1 equiv. of strong bases such as *t*-BuOK or LDA in THF between −20° and −80°. In this way, diphenyl disulfide is formed from the sulfoxide **12b**, indicating the cleavage of the leaving group. However, the expected three-membered-ring product could not be isolated or detected spectroscopically, most probably because of polymerisations. If the basic elimination of the leaving group from

Scheme 4



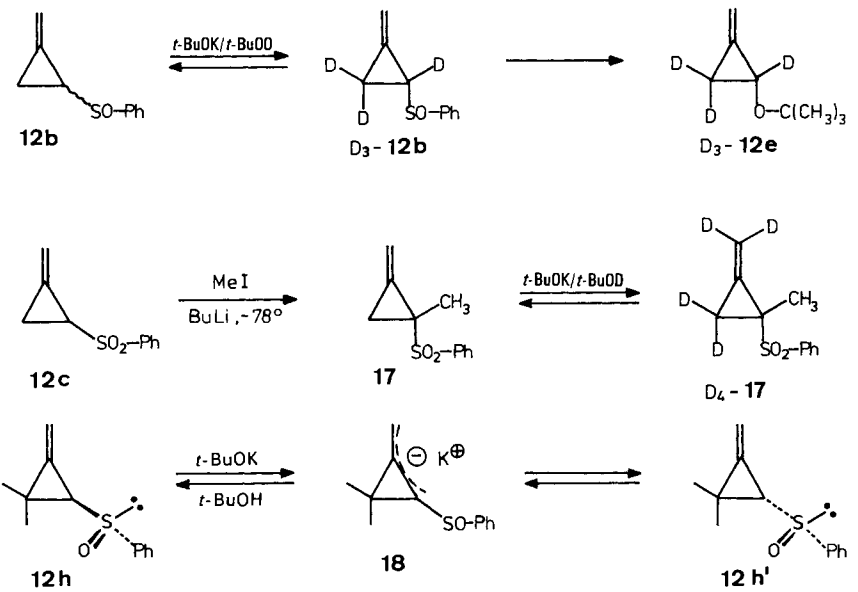
the sulfoxide **12b** (or the sulfone **12c**) is performed in the presence of high concentrations of a protic trapping reagent such as *t*-BuOH or MeOH, then the expected addition products **12e** and **12f** are isolated in fairly good yields. Even more convincing is the realised exchange of the sulfinyl group of **12b** against the $PhCH_2S$ group **12b**→**12g**, if **12b** is reacted with 1 equiv. of $PhCH_2Sh$ and 2 equiv. of *t*-BuOK in THF. It is important to note that benzyl thiolate does not react with **12b** in the absence of a strong base. Another interesting sequence is observed in the attempted deprotonation/silylation of **12a** with BuLi/Me_3SiCl: the formation of **15** demonstrates that H–C(2) is the most acidic proton of **12a**. Product **16** is best explained by assuming the formation of (trimethylsilyl)triafulvene as a reactive intermediate, followed by nucleophilic attack of BuLi.

Considering the fact that S_N2-type reactions of substituted cyclopropanes are predominantly observed in bicyclic systems [27] and only in very reactive cyclopropanes [28], all the reactions indicated in *Scheme 4* are easily interpreted in terms of *triafulvene* (**1**) (or of (trimethylsilyl)triafulvene for **15**→**16**) *as a reactive intermediate* being trapped by a nucleophile. However, some surprising aspects of most elimination/addition reactions of methylidene-cyclopropanes **12** have to be mentioned: contrary to expectations, only for the conversion of **12b** with the weakest nucleophile (benzylthiol or -thiolate) equivalent amounts of nucleophile are adequate for trapping of **1**. All the elimination/additions of alcohols or alkoxides need very high concentrations of the nucleophile, if good yields of **12e** and **12f** are envisaged. Similarly, although the sulfoxide **12b** and the sulfone **12c** are reacting easily in the presence of equivalent amounts of LDA or numerous other amides, no amino adduct of type **12** has ever been isolated neither by us nor by *Billups et al.* [21]. Furthermore, highest yields of addition products **12e, f, g** seem to result in cases of small reaction rates. In terms of the postulated intermediate **1**, a reasonable explanation of that

surprising behaviour is that *1)* the high reactivity of **1** demands relatively low concentrations of **1**, and *2)* that **1** tends to anionic polymerisations which are favoured by the increasing nucleophilicity of the trapping reagent.

Due to the fact that the intermediary formation of **1** is very reasonable but not beyond any doubt according to the results of the reactions indicated in *Scheme 4*, a series of labelling experiments *(Scheme 5)* were carried out.

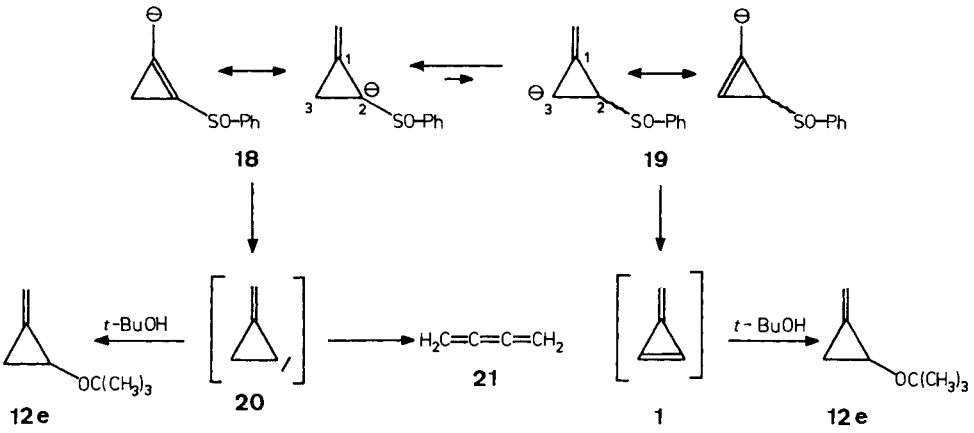
Scheme 5



If one assumes that the sequence **12b**→**12e** involves **1** as reactive intermediate, then subsequent addition of *t*-BuOD (or of *t*-BuO$^-$ followed by deuteration) is expected to give 1-(*tert*-butoxy)-2-methylidene[3-$^2H_1$]cyclopropane. Our experiments show, however, that D_3-**12e** is formed with D-labels mainly at C(2) and C(3): in the ^{1}H-NMR spectrum ($CDCl_3$, 80 MHz) of D_3-**12e** the vinylic protons display signals at 5.60 and 5.48 ppm (of at *ca.* 80% intensity due to some D incorporation), while the *singlet* of the *t*-BuO group absorbs at 1.26 ppm. Deprotonation and methylation of the sulfoxide **12c** (to give **17**) clearly demonstrates that H–C(2) of **12c** is considerably more acidic than H–C(3). Treatment of **17** with *t*-BuOK in a large excess of *t*-BuOD gives D_4-**17**, so that all the positions of the supposed allylic anion intermediate are deuterated. Allylic anions of type **18** are reasonable intermediates explaining the observed equilibration between diastereoisomers **12h** and **12h'** in the presence of strong bases. These results show that in the presence of *t*-BuOK/*t*-BuOD partial (**12b**) or complete (**17**) D scrambling takes place, thus, preventing reliable conclusions concerning **1** as an intermediate.

A rationalisation of protonation and alkylation experiments is depicted in *Scheme 6*. Under kinetic control, deprotonation of methylidenecyclopropanes reasonably takes place at the most acidic position (H–C(2)), however, an equilibrium of type **18**⇄**19** (**18** is

Scheme 6



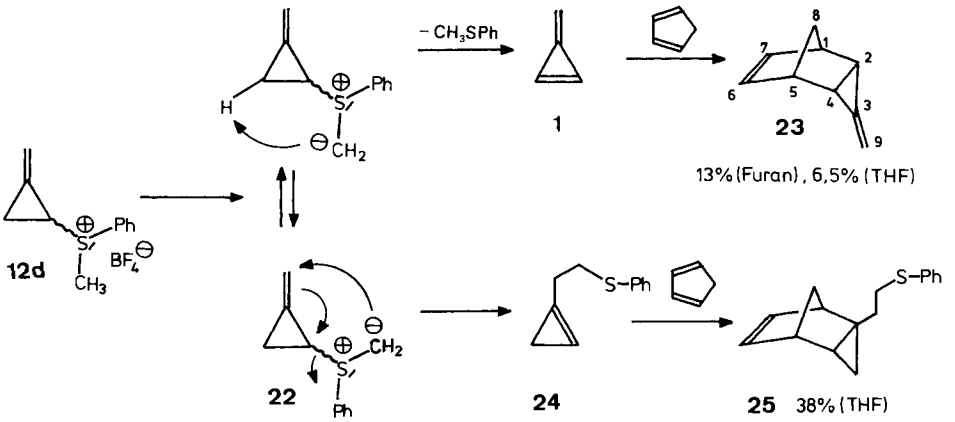
favoured) gives D scrambling over C(2) and C(3) and over the exocyclic CH_2-group. With respect to the elimination of the leaving group, there is not much doubt that the easiest way for anion **19** to form **12e**, in the presence of alkoxide/alcohol, is the sequence **19**→**1**→**12e**.

Some doubt still exists, since the thermodynamically favoured anion **18** has the alternative **18**→**20**→**12e**, thus forming the methylidene-cyclopropyl-carbene **20** after extrusion of the leaving group. Insertion of this carbene into the O–H bond of *t*-BuOH could explain the formation of **12e** as well. It has to be mentioned, however, that carbenes of type **20** very easily rearrange to cumulenes **21** and enynes [21], products which could not be observed (at least not in considerable amounts) in the NMR spectra of the crude reaction mixture.

3. Final Proof of 1 by *Diels-Alder* Reaction with Cyclopentadiene. – Numerous examples in the literature demonstrate that the safest proof for the discrete existence of reactive intermediates are products formed by synchroneous cycloaddition reactions. Without any doubt, several efforts in this direction have been undertaken in previous attempts to prepare triafulvene [29] [21], but there exists only one hint of an attempted trapping of **1** with butadiene [30]. At the beginning of our experiments with substituted methylidenecyclopropanes **12**, several trapping reagents such as furan (as solvent), diphenylisobenzofurane, and *N*-phenyl-1,2,4-triazoline-3,5-dione have been unsuccessfully tested in the presence of strong bases. With *t*-BuOK the only detectable product (besides the reactants and untractable polymeric material) was **12e**.

This failure as well as the observation that, in the presence of nucleophilic bases like LDA, the amount of polymeric material was considerably increased (supporting the idea of an easy anionic polymerisation) promoted us to try cyclopentadienide as base. We hoped to eliminate methyl phenyl sulfide from **12d** and to generate **1** as well as cyclopentadiene at the same time *(Scheme 7)*. Even if **1** is supposed to be extremely sensitive to polymerisations, the close proximity of **1** and cyclopentadiene should strongly increase the chance of trapping **1** as [4 + 2]-cycloaddition product **23**. In fact, methyl phenyl sulfide is easily eliminated from the sulfonium salt **12d** under very mild conditions. If **12d**

Scheme 7. *Trapping Experiments with Cyclopentadiene*



is reacted with 1 equiv. of Na-cyclopentadienide in furan for 40 min at room temperature, then **23** is isolated in a 13% yield[3]) after LPC and preparative gas chromatography of the crude reaction mixture. This result definitely proves that triafulvene (**1**) occurs as intermediate in elimination experiments of methylidenecyclopropanes of type **12**.

The spectroscopic data *(Fig.)* are consistent with structure **23**: the number of lines in the ^{1}H- and ^{13}C-NMR spectra corresponds to the symmetry of the molecule. The ^{1}H-NMR signals at 5.81 ppm (H–C(6)/H–C(7)) and 3.00 ppm (H–C(1)/H–C(5)) are characteristic for norbornenes, while the *multiplet* at 4.98 ppm (2 H–C(9)) appears at almost the same δ's as the exocyclic CH_2-group of **16** (5.1 ppm). The assignment of the signals at 1.93 (H–C(2)/H–C(4)) and 1.84 ppm (2 H–C(8)) follows from decoupling experiments, as well as the *endo*-configuration of **23**. In the ^{13}C-NMR spectrum, C(6)/C(7) at 133.4 and C(1)/C(5) at 45.0 ppm absorb in the norbornene region, while the signals of the exocyclic double bond are in a range typical for methylidenecyclopropanes (C(3) at 142.9, C(9) at 102.2 ppm). The very low chemical shift (20.7 ppm) of C(2)/C(4) is characteristic for cyclopropanes. Compared with norbornenes, C(8) at 63.7 ppm absorbs at substantially higher frequencies. This chemical shift has been found to be very characteristic for *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-enes and establishes the *endo*-configuration of **23** [31][4]).

Some more insight into the mechanism of the elimination sequence of **12d** in the presence of bases[5]) stems from the isolation of another *Diels-Alder* adduct: the same reaction of **12d** with Na-cyclopentadienide in THF (where the yield of **23** is reduced to 6.5%) gives the cycloaddition product **25** in a surprisingly high yield (38%) compared to **23**. Furthermore, crude (more than 80% pure) cyclopropene **24** may be isolated after reaction of **12d** with BuLi in THF (*ca.* 25% yield). In the ^{1}H-NMR spectrum of **24** (80

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[3]) The yield of **23** is remarkably solvent-dependent: 13% in furan, 6.5% in THF. Only traces of **23** are observed in Et_2O.

[4]) In tricyclo[3.2.1.$0^{2,4}$]oct-6-ene, C(8) absorbs at 63.7 ppm for the *endo*-isomer, but at 37.7 ppm for the *exo*-isomer [31].

[5]) Prof. *A. Krief* (personal communication) supposed **22** to be important in the elimination sequence **12d**→**1**, long before we had experimental evidence by the process **12d**→**24**.

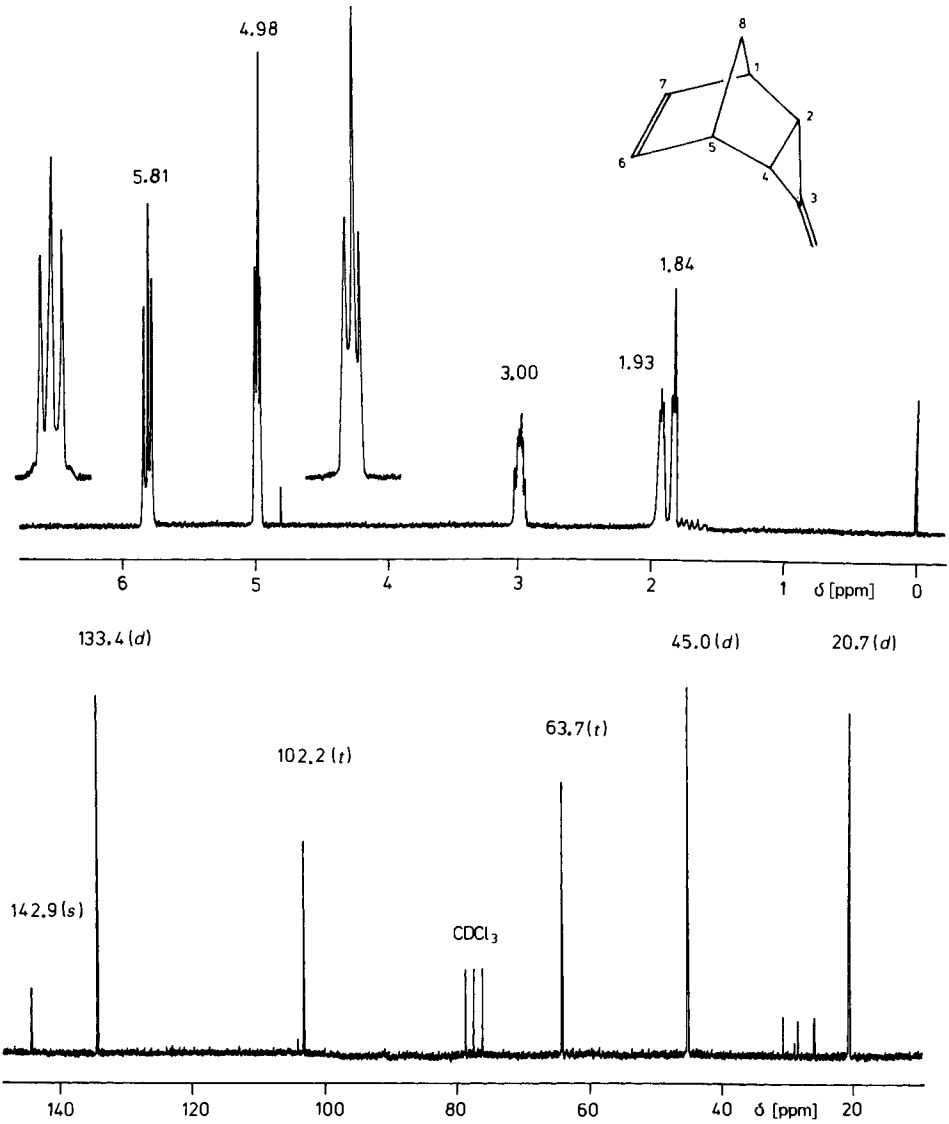

Figure. *^{1}H-NMR Spectrum* (100 MHz, $CDCl_3$, left) *and ^{13}C-NMR spectrum* (25 MHz, $CDCl_3$, right) *of* **23**

MHz, $CDCl_3$), vinylic H–C(2) absorbs as a narrow *multiplett* at 6.53 ppm, while 2 H–C(3) produce a sharp *doublet* (J = 1.75 Hz) at 0.94 ppm. The A_2B_2-type *multiplets* of the protons of the side chain appear at 3.13 and 2.86 ppm. Finally, the complex *multiplet* of 5 aromatic protons is centered at 7.23 ppm.

The formation of **24** and **25** implies a deprotonation of **12d** to give the ylide **22**[5]) which seems to be a key intermediate in the formation of both **1** and **24**: internal proton abstraction from C(3) of **12d** followed by elimination of methyl phenyl sulfide gives **1**,

which is then trapped by cyclopentadiene, while nucleophilic attack at the exocyclic CH_2 group followed by double-bond shift and cleavage of the C–S bond gives **24**.

In summary methylidenecyclopropanes **12** are attractive precursors of triafulvene (**1**). While elimination/trapping experiments *(Scheme 4)* give some evidence for the formation of **1** as an intermediate, isolation of the first [4 + 2]-cycloaddition product of **1** removes any doubts[6]), while the mechanistic importance of ylide **22** is emphasised by the sequence **12**→**24**→**25**.

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Experimental Part

General. All the reactions have been realised in abs. solvents under an atmosphere of dry N_2. THF has been distilled from $LiAlH_4$ immediately prior to use. The cyclopropanes **12a–d** were prepared as described in [1]. IR spectra were measured on a *Perkin-Elmer 399B* spectrometer. The NMR spectra were measured at amb. temp. in $CDCl_3$ with *Bruker WP-80, Varian EM-360L,* and *Varian XL-100* spectrometers. MS spectra were recorded on a *Varian-Mat CH5-DF.*

1. *1-(*tert*-Butoxy)-2-methylidenecyclopropane* (**12e**). A soln. of 178 mg (1 mmol) of **12b** and 672 mg (6 mmol) of *t*-BuOK in *t*-BuOH (3 ml) was vigorously stirred for 3 h at 60°. The yellow suspension was then hydrolysed with 10 ml of H_2O, cooled to 0°, and extracted with $CFCl_3$ (3 × 5 ml). The org. phase was washed twice with 10 ml of H_2O, dried ($MgSO_4$), and carefully concentrated *in vacuo* (0°/200 Torr) to give a yellow oil which was immediately distilled at −10°/10^{-3} Torr: 60 mg (55%) of **12e** as a colourless oil. IR (CCl_4/CS_2): 3068*w*, 3042*w*, 2979*s*, 2936*w*, 2865*w*, 1520*m*, 1387*m*, 1363*m*, 1331*m*, 1258*m*, 1232*m*, 1193*m*, 1158*s*, 1117*m*, 1097*w*, 1079*w*, 1020*w*, 935*w*, 909*m*, 896*s*, 775*w*, 735*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.62 (*m*, 1 H); 5.47 (*m*, 1 H); 3.74–3.55 (*m*, 1 H); 1.44–1.09 (*m*), 1.27 (*s*) (total 11 H). MS: 69 (3), 59 (8), 58 (5), 57 (100), 56 (15), 55 (3), 53 (4), 41 (38), 39 (7).

2. *1-Methoxy-2-methylidenecyclopropane* (**12f**). The sulfoxide **12b** (178 mg, 1 mmol) was dissolved in 3 ml of a freshly prepared NaOMe soln. (5.8M in MeOH). After refluxing at 100° for 5 h, 10 ml of H_2O were added. The soln. was cooled to 0° and extracted twice with 5 ml of $CFCl_3$. The org. phase was washed with H_2O (10 ml) and separated: 4.5 ml of a $CFCl_3$ soln. of **12f** practically free of MeOH. The yield (40%) was determined by ^{1}H-NMR by comparing the signals of **12f** with those of an added amount of pyrazine. The very volatile product was distilled together with the solvent at −10°/10 Torr and separated by prep. VPC (10% *Carbowax 20M,* 4 m, injector temp. 80°, oven temp. 50°). IR ($CHCl_3$): 2996*m*, 2935*m*, 2900*w*, 2828*m*, 1650*w*, 1460*w*, 1444*m*, 1423*w*, 1325*m*, 1151*s*, 1113*m*, 1018*m*, 905*s*, 859*w*. ^{1}H-NMR (80 MHz, $CDCl_3/CFCl_3$): 5.69 (*m*, 1 H); 5.45 (*m*, 1 H); 3.62 (*m*, 1 H); 3.36 (*s*, 3 H); 1.50–1.10 (*m*, 2 H). Irradiation of the olefinic signals gives an *ABX* system with H_A: 1.20, H_B: 1.30, and H_X: 3.62; J_{AB} = 10.5, J_{AX} = 2.9 and J_{BX} = 6.6. MS: 84 (7, $M^{+\cdot}$), 83 (100), 69 (36), 56 (12), 55 (75), 54 (16), 53 (21), 52 (6), 51 (14), 50 (13), 45 (32), 44 (8), 43 (12), 41 (38), 40 (8), 39 (75), 38 (8).

3. *1-(Benzylthio)-2-methylidenecyclopropane* (**12g**). To a magnetically stirred suspension of *t*-BuOK (390 mg, 3.5 mmol) in THF (5 ml), 210 mg (1.7 mmol) of neat $PhCH_2SH$ were added in one portion at r.t. After 30 min, a soln. of 290 mg (1.6 mmol) of **12b** in THF (1 ml) was added. The resulting suspension was refluxed for 6 h, then cooled, and treated with 20 ml of H_2O and 30 ml of Et_2O. The org. phase was washed with H_2O (3 × 10 ml), salt-water (brine) (10 ml), then dried ($MgSO_4$), and concentrated in a rotary evaporator at 40°. Chromatography of the yellow residue over silica gel (pentane/CH_2Cl_2 3:1) and distillation of the resulting pale yellow oil at 25°/0.01 Torr furnished 170 mg (59%) of colourless oil **12g**. IR ($CHCl_3/CS_2$): 3080*m*, 3060*m*, 2995*s*, 2975*s*, 2925*m*, 2870*m*, 1601*w*, 1494*m*, 1452*m*, 1418*w*, 1397*m*, 1382*m*, 1350*m*, 1296*w*, 1225*m*, 1196*w*, 1150*m*, 1113*s*, 1071*m*, 1026*m*, 998*w*, 935*w*, 890*s*, 768*m*, 755*m*, 710*m*, 696*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.25 (*m*, 5 H); 5.41 (*m*, 2 H); 3.78 (br. *s*, 2 H); 2.40, 1.55, 1.14 (*ABX*, J_{AB} = 8.75, J_{AX} = 7.75, J_{BX} = 4.25). MS: 161 (3), 144 (3), 143 (25), 142 (3), 129 (3), 128 (6), 92 (8), 91 (100), 89 (3), 85 (27), 77 (3), 65 (19), 63 (3), 51 (4), 45 (11), 39 (5).

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[6]) Very recently, *Billups et al.* [3], after proving the existence of **1** in solution at low temperature by spectroscopic methods, made use of the sequence **1** + cyclopentadiene→**23** for the chemical characterisation of **1**.

4. *2-Methylidene-1-(phenylthio)-1-(trimethylsilyl)cyclopropane* (**15**). To a soln. of **12a** (162 mg, 1 mmol) in Et_2O (5 ml) was added at −10° 1 equiv. of BuLi (1.48M in hexane). After 90 min stirring at −10°, the orange soln. was treated with 120 mg (1.1 mmol) of Me_3SiCl and stirred for another h at −10°. The mixture was then hydrolysed with H_2O (10 ml), and the org. phase separated and dried ($MgSO_4$). Solvent evaporation left a yellow oil, which was purified by chromatography over silica gel (elution with pentane/CH_2Cl_2 10:1) to give 174 mg (75%) of **15**. IR (CCl_4/CS_2): 3078*m*, 3062*m*, 3000*w*, 2960*m*, 2900*w*, 1735*m*, 1478*m*, 1440*m*, 1249*s*, 1111*m*, 1085*m*, 1026*m*, 907*m*, 885*m*, 842*s*, 737*m*, 690*m*, 645*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.59–7.17 (*m*, 5 H); 5.43 (*m*, 2 H); 1.73 (*td*, J = 1.9, J = 8.2, 1 H); 1.55 (*td*, J = 2.2, J = 8.2, 1 H); −0.03 (*s*, 9 H).

5. *1-Butyl-2-methylidene-3-(trimethylsilyl)cyclopropane* (**16**). To the neat sulfide **12a** (324 mg, 2 mmol) was added at −78° 1 equiv. of BuLi in hexane. After 2 h, the yellow soln. was treated with 240 mg (2.2 mmol) of Me_3SiCl and stirred for another h at −78°. The cooling bath was removed, and the mixture was allowed to warm up to r.t. before adding water (10 ml) and Et_2O (30 ml). The Et_2O layer was separated, dried ($MgSO_4$), and concentrated *in vacuo* to leave a residue containing **12a**, **15**, and **16** in a ratio of *ca.* 1.4:1.3:1. Pure **16** was isolated by chromatography on silica gel (elution with pentane) and bulb-to-bulb distillation at 20°/10^{-3} Torr. Yield: 93 mg (25%). IR (CCl_4/CS_2): 3065*w*, 2994*m*, 2958*s*, 2922*m*, 2872*m*, 2854*m*, 1731*w*, 1467*m*, 1458*m*, 1440*w*, 1379*w*, 1258*m*, 1247*s*, 1180*w*, 1130*w*, 1098*m*, 952*m*, 938*w*, 862*s*, 858*m*, 840*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.24 (*m*, 1 H); 5.09 (*m*, 1 H); 1.59–0.69 (*m*, 11 H); −0.04 (*s*, 9 H). ^{13}C-NMR (25 MHz, $CDCl_3$): 140.5 (*s*); 98.7 (*t*); 34.0 (*t*); 32.0 (*t*); 22.5 (*t*); 19.4 (*d*); 14.1 (*q*); 12.5 (*d*); −2.2 (*q*). MS: 167 (4), 139 (7), 111 (4), 99 (3), 97 (5), 85 (4), 83 (4), 74 (8), 73 (100), 59 (23), 45 (10), 43 (7), 40 (8).

6. *1-(*tert*-Butoxy)-2-methylidene-[1,3,3-$^2H_3$]cyclopropane* (D_3-**12e**). To a magnetically stirred soln. of **12b** (244.5 mg, 1.37 mmol) in *t*-BuOD (3 ml), small portions of *t*-BuOK (totally 910 mg, 8.11 mmol) are added. The brown suspension is then stirred at 60° for 5 h. After cooling at 0°, ice-water (15 ml) and *Freon 11* (= $CFCl_3$, 30 ml) are added. After washing with ice-water (3 × 10 ml), the org. layer is dried ($MgSO_4$) and filtered, and the solvent is then removed at r.t./200 Torr. Distillation of the yellow oil at −20°/0.04 Torr gives 89.5 mg (51%) of D_3-**12e** as a colourless oil. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.60 (br. *s*, *ca.* 1 H); 5.48 (br. *s*, *ca.* 1 H); 1.26 (br. *s*, *ca.* 11 H)[7]).

7. *Phenyl 1-Methyl-2-methylidenecyclopropanesulfonate* (**17**). A cold (−78°), magnetically stirred soln. of **12c** (403.6 mg, 2.1 mmol) and MeI (1.06 g, 11.2 mmol) in THF (7 ml) was treated dropwise with 3.18 mmol of BuLi in hexane. The yellow suspension was stirred for 4 h at −78° and for 2 h at 25°, and then hydrolysed with H_2O (20 ml). After addition of 20 ml of Et_2O, the org. phase was separated and dried ($MgSO_4$). Solvent evaporation left a yellow oil that solidified in the refrigerator. Recrystallisation from pentane afforded 323.4 mg (75%) of colourless **17**. M.p. 28–29°. IR ($CHCl_3/CS_2$): 3060*w*, 3010*m*, 2970*w*, 2930*w*, 2865*w*, 1475*w*, 1446*m*, 1377*w*, 1316*m*, 1307*s*, 1290*m*, 1180*m*, 1140*s*, 1080*m*, 1042*m*, 1000*w*, 899*m*, 858*m*, 830*m*, 754*m*, 721*m*, 689*m*, 629*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.94–7.33 (*m*, 5 H); 5.54 (*m*, 2 H); 2.33 (*m*, 1 H); 1.57–1.29 (*m*), 1.45 (*s*) (total 4 H). Irradiation of the olefinic *m* leaves an *AB* system of the cyclopropane protons at 2.33 and 1.40 with J_{AB} = 9.75. MS: 208 (27, M^+), 129 (9), 128 (3), 126 (14), 125 (51), 97 (9), 91 (5), 83 (8), 78 (20), 77 (30), 67 (52), 66 (13), 65 (38), 55 (3), 53 (3), 52 (6), 51 (31), 50 (7), 43 (57), 42 (3), 41 (100), 40 (11), 39 (47).

8. *1,1-Dimethyl-2-methylidene-3-(phenylsulfinyl)cyclopropane* (**12h**, **12h'**). 2-Methyl-1-(phenylthio)-1-propene (prepared from NaSPh and β-methallyl chloride, followed by isomerisation with EtONa in EtOH [32]) was treated with *t*-BuOK and $CHBr_3$ in pentane to give the corresponding dibromocyclopropane in 10% yield. This compound was converted into a mixture of the diastereoisomeric sulfoxides **12h** and **12h'** according to the procedure described in [1]. When a mixture of these two isomes (ratio *ca.* 3:1) was heated in *t*-BuOH in the presence of 5 equiv. of *t*-BuOK for 7 h at 60°, the same sulfoxide was recovered (83%), but the ratio of the diastereoisomers was completely different (*ca.* 1:5). The two sulfoxides were identified by their ^{1}H-NMR: 1st isomer: 7.62 (*m*, 5 H); 5.52 (*m*, 1 H); 5.22 (*m*, 1 H); 2.73 (*m*, 1 H); 1.60 (*s*, 3 H); 1.30 (*s*, 3 H). ^{1}H-NMR: 2nd isomer: 7.62 (*m*, 5 H); 5.78 (*m*, 1 H); 5.60 (*m*, 1 H); 2.73 (*m*, 1 H); 1.48 (*s*, 3 H); 1.18 (*s*, 3 H).

9. endo-*3-Methylidenetricyclo[3.2.1.$0^{2,4}$]oct-6-ene* (**23**). To a suspension of 2 mmol of **12d** in furan (10 ml) were added dropwise within 40 min 2 ml of Na cyclopentadienide in THF (1,6M), whereby the yellow mixture turned to red-brown. After being stirred for 4 h, the suspension was stored at 0° overnight, then treated with H_2O (10 ml) and extracted with pentane (3 × 15 ml). The combined pentane phases were dried ($MgSO_4$) and concentrated at 0°–20°/200 Torr. The oily residue was at first purified by chromatography over silica gel (pentane) and then purified by prep. VPC (10% *Carbowax 20M*, 4 m, 40 ml N_2/min, injector temp. 90°, over temp. 60°, t_R (**23**) 36

[7]) Integral ratio unexact probably due to partial deuteration at the exocyclic C-atom.

min) to give 30.7 mg (13%) of **23**. IR (CS_2): 3064*m*, 3016*m*, 2978*s*, 2959*m*, 2922*m*, 2859*m*, 1750*w*, 1725*w*, 1650*w*, 1330*m*, 1259*w*, 880*s*, 841*m*, 760*m*, 732*m*, 707*w*. ^{1}H-NMR and ^{13}C-NMR: see the *Figure*. MS: 118 (16, M^+), 117 (100), 116 (13), 115 (53), 103 (10), 102 (3), 92 (3), 91 (41), 89 (10), 79 (22), 78 (12), 77 (24), 66 (4), 65 (18), 63 (11), 62 (5), 57 (5), 53 (4), 52 (12), 51 (14), 50 (6), 39 (18).

10. *1-[2-(Phenylthio)ethyl]cyclopropene* (**24**). A suspension of **12d** (485.6 mg, 1.8 mmol) was treated in THF (9 ml) at 0° with 3.29 mmol of BuLi in hexane. After stirring for 6 h at 0°, 20 ml of ice-water and Et_2O (20 ml) were added. The H_2O layer was extracted with Et_2O (10 ml), and the combined org. layers were washed with H_2O (10 ml), salt water (10 ml), dried ($MgSO_4$), and evaporated. The yellow oil was purified by chromatography on neutral alumina (activity III; elution with pentane/CH_2Cl_2 10:1). Solvent evaporation provided a colourless oil, which was dried for 5 h at 0°/0.01 Torr to remove methyl phenyl sulfide: 90.7 mg of **24** as a colourless oil (purity > 80% (^{1}H-NMR)), which rapidly polymerises on standing in $CDCl_3$ at r.t. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.50–6.96 (*m*, 5 H); 6.53 (*m*, 1 H); 3.13 (*m*, 2 H); 2.86 (*m*, 2 H); 0.94 (*d*, J = 1.75, 2 H).

11. *2-[2-(Phenylthio)ethyl]tricyclo[3.2.1.0^{2,4}]oct-6-ene* (**25**). To a suspension of 190.1 mg (0.7 mmol) of **12d** in THF (5 ml) was added dropwise 1 mmol of Na cyclopentadienide in THF at 25°. The brown soln. was stirred for 6 h, then treated with H_2O (10 ml) and extracted with pentane (2 × 10 ml), dried ($MgSO_4$), and evaporated. Chromatography of the yellow residue on silica gel (pentane) provided 65.9 mg (38%) of **25** as a colourless oil. IR ($CHCl_3$/CS_2): 3070*m*, 2970*s*, 2940*m*, 2876*m*, 1590*m*, 1524*m*, 1514*m*, 1488*s*, 1445*s*, 1430*m*, 1340*m*, 1296*w*, 1314*w*, 1248*w*, 1240*w*, 1227*w*, 1212*w*, 1139*w*, 1114*w*, 1092*m*, 1068*w*, 1048*m*, 1025*m*, 954*w*, 942*w*, 909*w*, 886*w*, 838*m*, 758*m*, 746*m*, 736*s*, 723*m*, 689*m*. ^{1}H-NMR (80 MHz, $CDCl_3$): 7.41–6.94 (*m*, 5 H); 5.91–5.56 (*m*, 2 H); 3.15–2.43 (*m*, 4 H); 2.40–1.40 (*m*, 4 H); 1.40–1.00 (*m*, 1 H); 0.68–0.40 (*m*, 2 H). MS: 242 (8, M^+). 163 (8), 156 (5), 138 (4), 137 (27), 136 (5), 135 (5), 133 (19), 132 (27), 131 (20), 125 (3), 124 (9), 123 (81), 119 (26), 118 (11), 117 (97), 116 (4), 115 (9), 112 (5), 111 (4), 110 (28), 109 (9), 106 (7), 105 (28), 104 (27), 103 (9), 92 (8), 91 (100), 86 (3), 79 (32), 78 (19), 77 (34), 67 (9), 66 (8), 65 (16), 55 (7), 54 (3), 53 (7), 51 (9), 45 (49), 41 (32), 39 (10).

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