6. Generation and Trapping of Cyclopropenes from 2-Alkoxy-1,1-dichlorocyclopropanes

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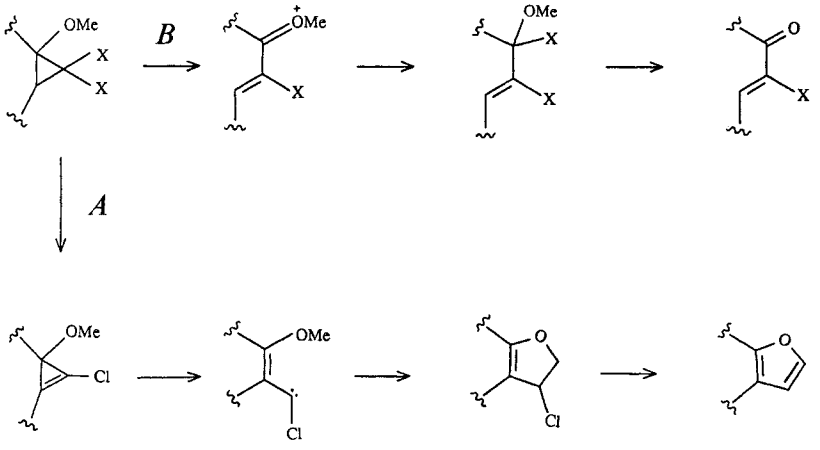
In presence of crown ether, 2-alkoxy-1,1-dichlorocyclopropanes react with *t*-BuOK/THF preferentially *via* ring opening to 2-chloroalk-2-en-1-ones and alkynones or to chlorocyclopropenes. The latter may be intercepted with 1,3-diphenylisobenzofuran, but in the absence of trapping agent, the rearrangement to vinylcarbenes does not occur.

Introduction. – With base, 1,1-dichlorocyclopropanes react by hydro,chloro-elimination to chlorocyclopropenes which can be intercepted with nucleophiles [1] [2] or with furans and isobenzofurans [3] [4]. In the absence of trapping agents, they may undergo rearrangements at or below room temperature to vinylcarbenes, which yield cyclopropane adducts with alkenes [4] [5] or products derived from inter- or intramolecular insertion into activated CH bonds [2] [6] [7] (*Path A, Scheme 1*). The intramolecular cap-

Scheme 1



ture by insertion into C–H bonds of vinylcarbenes derived from dichlorocyclopropanes according to *Path A* has been exploited for the synthesis of some phenanthrofurans and phenanthrocyclopentadienes from appropriately substituted phenanthrenes [7].

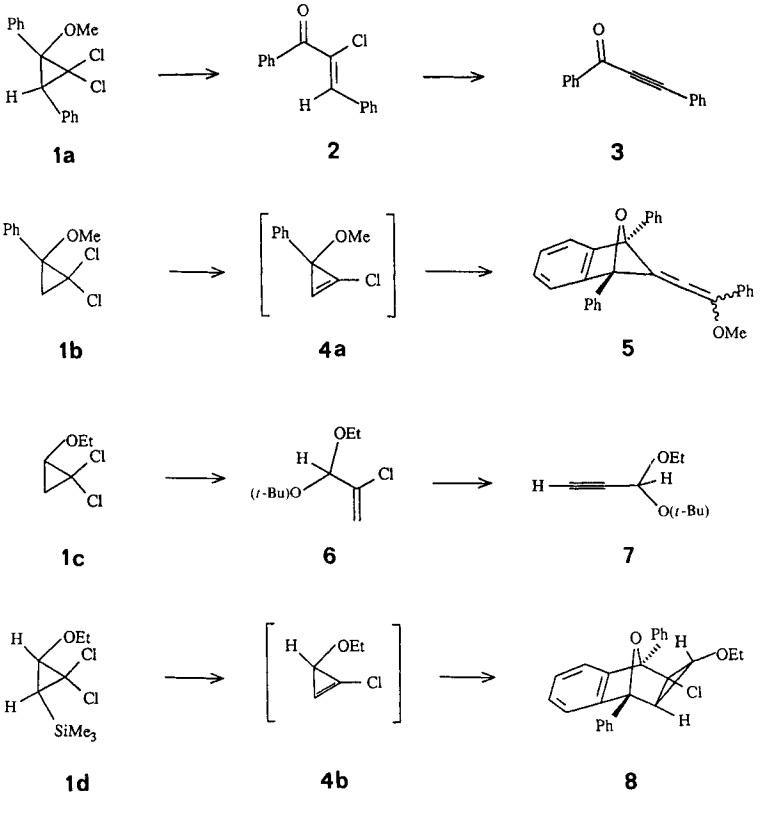
A competitive pathway (*Path B*) available to dichlorocyclopropanes consists in an electrocyclic opening of the cyclopropane ring, assisted by the departure of one of the

halides [8]; the intermediary allylic cation is intercepted by an appropriate nucleophile such as the leaving group or the solvent. Hydrolysis of the allylic substituents of the trapped product finally results in the formation of 2-chloroprop-2-enones or, if sufficiently basic conditions are used, in prop-2-ynones. This pathway typically occurs when dihalocarbenes are added to cyclic enamines. The adducts may not be isolated, and ring-enlarged α-halocycloalkenones are obtained instead [9].

We have investigated the base-induced hydro,chloro-elimination of several 2-alkoxy-1,1-dichlorocyclopropanes with the objective of developing a simple general furan synthesis according to the scheme outlined above.

Results and Discussion. – The (*Z*)-1-methoxy-1,2-diphenylethene (α-methoxy-*trans*-stilbene) [10] forms a moderately stable adduct **1a** with dichlorocarbene which is structurally analogous to the one leading to phenanthrofuran [7], but **1a** does not undergo the expected reaction to give a furan. When it was treated with strong base (2 equiv. *t*-BuOK, THF, dicyclohexano[18]crown-6, −50°), 1,3-diphenylprop-2-yne-1-one [11] (**3**) was formed in 43% yield (*Scheme 2*). This product arises from base-induced hydro,chloro-elimination of an intermediate (*Z*)-2-chloro-1,3-diphenylprop-2-en-1-one [12] (**2**), which is formed according to *Path B*. Experiments to trap eventual cyclopropene intermediates

Scheme 2



derived from **1a** failed. The chloropropenone **2** was also formed as a side-product during the dichlorocarbene addition to methoxystilbene.

Treatment of the dichlorocarbene adduct **1b** [13] with *t*-BuOK in THF and crown ether at −40° afforded no identifiable products, but when the reaction was carried out in the presence of 1,3-diphenylisobenzofuran, an intermediate **4a** was trapped (33%) as a *ca.* 1:1 mixture (by NMR) of two stereoisomers **5** (*Scheme 2*). One of the unstable isomers could be isolated. MS indicated a molecular formula $C_{30}H_{22}O_2$, which does not correspond to the expected adduct of cyclopropene **4a**, but to an adduct having lost HCl. The allenic structure of **5** is indicated by the ^{13}C-NMR signal at 197.97 ppm and the IR stretching vibration at 2040 cm^{-1}. The presence of the enol ether follows from the ^{13}C signal at 108.7 ppm.

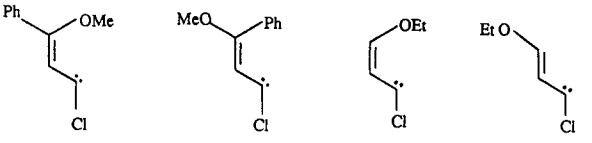
We ascribe the different reactions of the cyclopropanes **1a** and **1b** to the increased stabilization, by the additional Ph group, of the intermediate allylic carbenium ion derived from **1a** on one hand, and to the easier access to the cyclopropane H-atoms of **1b** by the base, which favors cyclopropene formation, on the other.

Cyclopropane **1c** [14] [15] reportedly yields chloro acetals of type **6** with various bases in protic solvents and, under more vigorous conditions, prop-2-ynal acetals of type **7** [16] (*Scheme 2*). Since cyclopropene formation takes place under aprotic conditions with **1b**, the same reaction was expected to occur with **1c**. However, for unknown reasons, this was not the case, and **1c** reacted to **6** also with *t*-BuOK/THF. In order to enforce formation of a cyclopropene, the silylated cyclopropane **1d** was synthesized from ethoxy(trimethylsilyl)acetylene [17] *via* catalytic hydrogenation [18] and subsequent dichlorocarbene addition [19]. Fluoride-induced elimination [20] of **1d** produced only unidentifiable products. However, a cyclopropene **4b** was definitely formed as evidenced by its trapping with 1,3-diphenylisobenzofuran. The structure of adduct **8**, isolated in 30% yield, follows from the analytical and spectral data.

The low-field ^{1}H-NMR signal at 4.38 ppm (^3J = 1.6 Hz) due to deshielding by the O-atom, is indicative for an *'exo'* addition, with H–C(3) of the original cyclopropene **4b** oriented *'syn'* to the O-bridge. For comparison, H–C(2) of the cyclopropanes **1c** and **1d** resonates at 3.56 and 3.65 ppm, respectively. The small vicinal coupling (^3J = 1.6 Hz) in **8** is characteristic for *trans*-arranged protons [21] and supports the proposed structure.

'exo'-Addition is the normal mode for cycloadditions of halocyclopropenes to furans [22]. Comparison of the products derived from **1a** and **1c** suggests, that in both cases *Path B* is followed. In principle, a sequence involving an intermediate 1-chloro-2-ethoxycyclopropene could also lead from **1c** to **6** *via* an ethoxy-stabilized vinylcarbene, but this pathway seems less likely in the light of the observation that the cyclopropenes **4a** and **4b** do not yield analogous acyclic products.

Ring-opening of the cyclopropenes **4a** and **4b** may give two stereoisomeric vinylcarbenes **9a,b** and **10a,b**, respectively, but only **9a** and **10a** can react further to form a furan. The absence of furan products from **4b** is understandable, because *cis*-configuration of the carbene and EtO group such as realized in **10a** is required for intramolecular insertion, while the corresponding *trans*-isomer **10b** would be thermodynamically more stable than **10a**. This argument does not apply to the vinylcarbenes **9a,b** derived from **4a** where the more stable isomer **9a** has the appropriate configuration for a CH insertion into the alkoxy group. Furthermore, **9b**, if formed, could react by a formal CH insertion into the *o*-position of the *cis*-positioned Ph group. The fact that such insertion products are

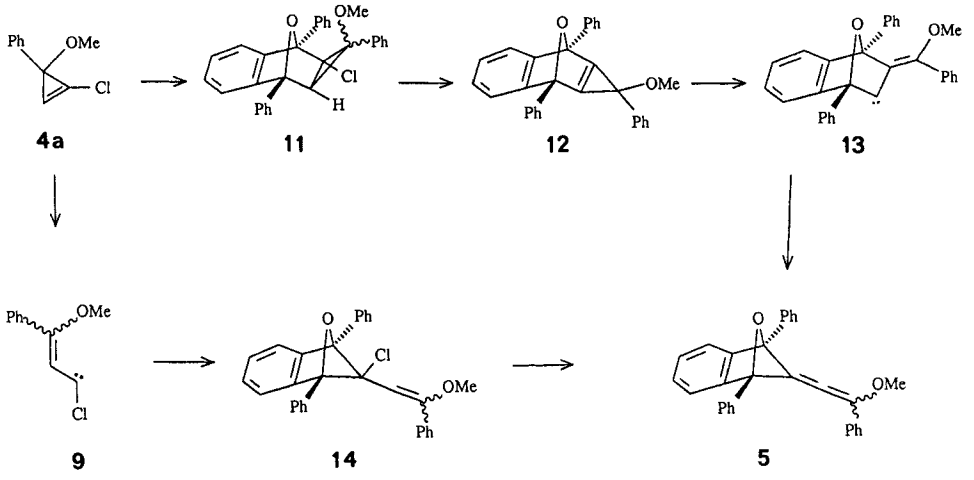


9a **9b** **10a** **10b**

observed neither from **4a** nor from **4b** suggests that these cyclopropenes do not open to vinylcarbenes under the reaction conditions.

The formation of allene **5** can be rationalized by trapping the expected cyclopropene **4a** with 1,3-diphenylisobenzofuran (→**11**), elimination of HCl (→**12**), isomerization **12** → **13**, and *Wolff* rearrangement [23] (*Scheme 3*). Another mechanism would consist in a ring-opening of cyclopropene **4a** to the vinylcarbenes **9a,b** which may be intercepted by 1,3-diphenylisobenzofuran in a [1 + 4] cycloaddition (→**14**); hydro,chloro-elimination would then give **5**. This mechanism seems, however, less likely, as there are only a few examples of intermolecular [1 + 4] cycloadditions of carbenes to dienes described in the literature [24]. Vinylcarbenes, generated from diazo compounds with $Rh_2(OAc)_4$, react with furans generally by (formal) [3 + 4] cycloaddition [25].

Scheme 3

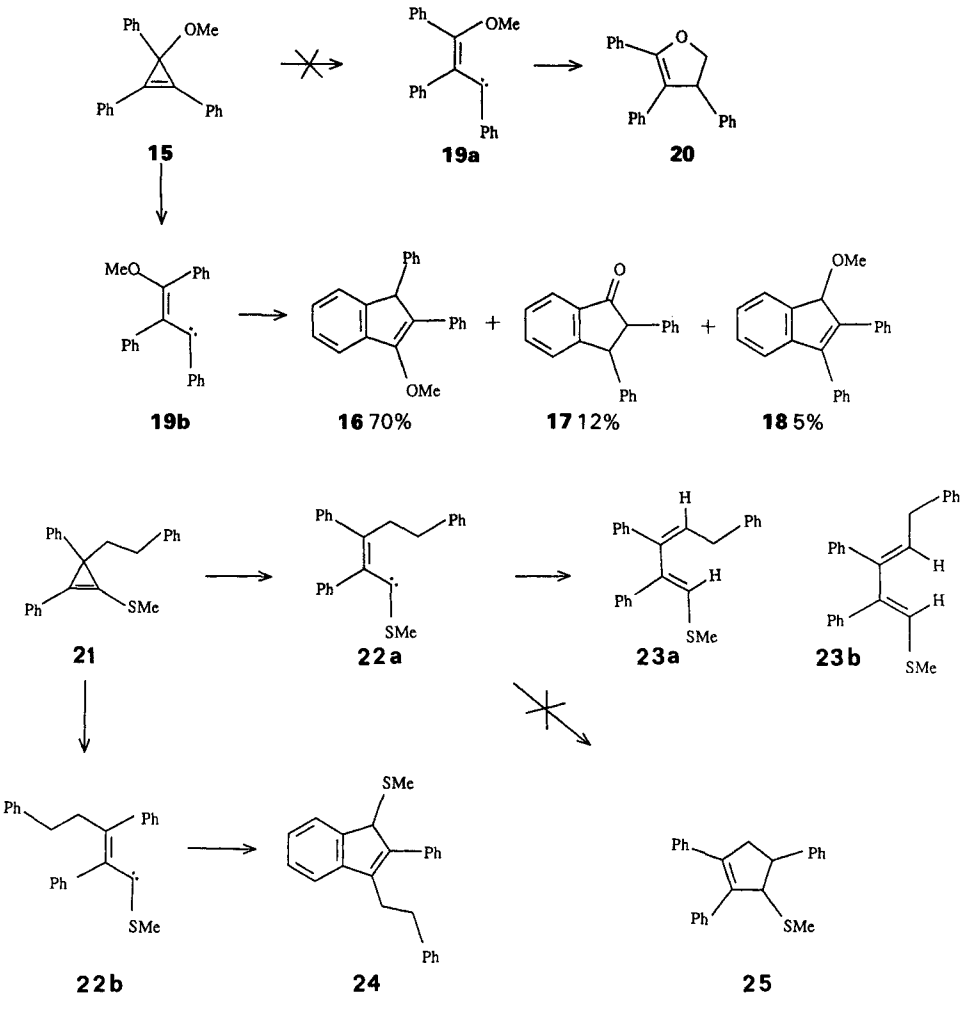


4a **11** **12** **13**

9 **14** **5**

So far, only a few vinylcarbenes derived from cyclopropenes have been trapped by intramolecular insertion reactions [26]. Moreover, these reactions often were mechanistically poorly analyzed. In order to gain more insight into these processes, we have investigated the thermal rearrangements of two relatively stable Ph-substituted cyclopropenes **15** and **21** (*Scheme 4*). The pyrolysis of **15** [27] at 250° during 10 min afforded 3-methoxy-1,2-diphenyl-1*H*-indene (**16**; 70%), 2,3-dihydro-2,3-diphenyl-1*H*-inden-1-one (**17**; 12%), and 1-methoxy-2,3-diphenyl-1*H*-indene (**18**; 5%) [28], all products derived from vinylcarbene **19b**, but no products originating from the thermodynamically

Scheme 4

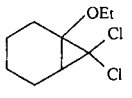


less stable isomeric **19a**, where the Ph groups are oriented *cis* to each other and where insertion into the MeO group would give dihydrofuran **20**. In contrast, pyrolysis (80°, benzene, 90 min) of the MeS-substituted cyclopropene **21**, prepared from diphenylcyclopropenone by analogy to a procedure developed by *Yoshida et al.* [29] [30], afforded products derived from both expected isomeric vinylcarbenes **22a** and **22b**, namely 1-(methylthio)-2-phenyl-3-(2-phenylethyl)-1*H*-indene (**24**; 58%) and the two stereoisomeric 1-(methylthio)-2,3,5-triphenylpenta-1,3-dienes (**23a,b**; 21%; (3*Z*)/(3*E*) 3:2). In this case, the carbene with the appropriate configuration for the formation of a cyclopentene is indeed formed, but it prefers [1,4]-H migration to give dienes **23** rather than CH insertion to give **25**. The formation of dienes from MeS-substituted cyclopropenes has been observed previously [29].

The different temperatures required to effect rearrangement of **15** and **21** are remarkable. While **21** rearranges at 80°, **15** has to be heated at 230°, which corresponds to the temperature at which tetraphenylcyclopropene rearranges. Other authors [30] [31] have noted that the presence of a MeS substituent at C(1) of the cyclopropene greatly facilitates carbene formation, while substitution by MeS or Ph [26] at C(3) has no effect. This is consistent with the observation, that 1-chlorocyclopropenes rearrange to chlorovinyl carbenes at room or sub-room temperatures [5], while their counterparts lacking the carbene-stabilizing Cl-substituent do not ring open at low temperature. Note, however, that 3-chlorocyclopropenes do not rearrange to vinylcarbenes under mild conditions.

In view of the known preference of Rh^{II} complexed carbenes for CH insertions [32], the thermocatalytic rearrangements of **15** and **21** in the presence of $[Rh_2(PFB)_4]$ (PFB = perfluorobutyrate) were also investigated, but without success. Reaction of **15** (60°, benzene, 6% of catalyst) gave exclusively 1,2,3-triphenylprop-2-enone, which probably results from triphenylcyclopropenium ion, while **21** was recovered unchanged after exposure to 4% of $[Rh_2(PFB)_4]$ (0°, toluene).

Reaction of the bicyclic dichlorocyclopropanes **26** and **27** is expected to afford the cyclopropenes **28** and **29**. Their ring opening can only lead to chlorovinyl carbenes, which have the proper orientation for intramolecular insertion. Nevertheless, no furans were formed. Typically, adduct **26** [33] gave 2-chlorocyclohept-2-en-1-one when elimination was carried out under the usual conditions. At elevated temperature (*t*-BuOK, C_6H_6, crown ether, 65°), 2-methylphenetol (= 1-ethoxy-2-methylbenzene) was formed in 58%



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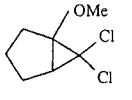

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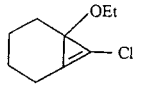

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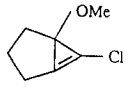

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yield. Similarly, **27** [34] partly decomposed during purification to anisol (distillation) or 2-chlorocyclohex-2-en-1-one (chromatography on silica gel). When **27** was synthesized at low temperature and under strongly basic conditions ($CHCl_3$, *t*-BuOK) [35], mixtures of chlorocyclohexenone and anisol resulted [36]. The mechanism of these reactions has not been investigated, but *Path B* provides a plausible interpretation. The primary rearrangement products must undergo prototropic shifts in order to achieve aromatization [37], and this would also apply to mechanisms involving cyclopropene-vinylcarbene rearrangements [4] or 1/hydro,4/chloro-eliminations [38]. No experiments were carried out to distinguish between these mechanisms. The observation that the carbene adduct of 1-ethoxy-3,3,6,6-tetramethylcyclopentene [39] ring opens *in situ* to a chlorocyclopentenone [36] indicates that the pathway *via* 1/4-elimination is unlikely, since this compound cannot enter the reaction owing to the lack of protons α to the cyclopropane ring.

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Experimental Part

General. See [40].

*1,1-Dichloro-*r*-2-methoxy-2,3-*c*-diphenylcyclopropane* (**1a**). To MeONa (0.371 g, 6.86 mmol) in dry Et_2O (7 ml) was added α-methoxy-*trans*-stilbene [10] (0.217 g, 1.03 mmol) and, dropwise at −15°, ethyl trichloroacetate (1.30 g, 6.79 mmol) in Et_2O. After 90 min at −15°, the mixture was stirred overnight at 4°. It was then decomposed at r.t. by addition of H_2O and worked up. Purification by column chromatography (silica gel, CH_2Cl_2/petroleum ether 3:1) yielded 0.285 g (95%) of **1a** as viscous oil. An anal. sample was further purified by prep. TLC (petroleum ether/CH_2Cl_2 1:1). M.p. 38–40°. When column chromatography was carried out slowly, partial decomposition to *(Z)-2-chloro-1,3-diphenylprop-2-en-1-one* (**2**) occurred.

Data of **1a**: IR (liq.): 3060*m*, 3030*m*, 3000*m*, 2960*m*, 2940*m*, 2900*w*, 2830*m*, 1600*m*, 1500*s*, 1450*s*, 1380*m*, 1240*s*, 1200*m*, 1080*s*, 1060*s*, 1030*m*, 1000*w*, 980*m*, 955*m*, 920*m*, 870*m*, 760*s*, 700*s*. ^{1}H-NMR: 3.20 (br. *s*, 4 H); 7.35–7.75 (*m*, 10 H). MS: no 292 (M^+, $C_{16}H_{14}Cl_2O$); 257, 259 (20); 242, 244 (32); 207 (34); 179 (7); 105 (100); 77 (60); 57 (13). HR-MS: 257.0718 (calc. (^{35}Cl) 257.0733), 259.0703 (calc. (^{37}Cl) 259.0704).

Data of **2** [12]: IR ($CHCl_3$): 3060*m*, 3030*w*, 1665*s*, 1600*s*, 1575*m*, 1490*m*, 1450*s*, 1390*m*, 1320*m*, 1290*s*, 1250*s*, 1210*m*, 1180*m*, 1160*w*, 1085*s*, 1070*s*, 1025*m*, 1000*m*, 925*m*, 860*s*, 820*m*, 785*m*, 755*s*, 710*s*, 690*s*. ^{1}H-NMR: 7.32–7.64 (*m*, 7 H); 7.76–8.06 (*m*, 4 H). MS: 242, 244 (34, 3:1 M^+, $C_{15}H_{11}ClO$); 207 (63); 178 (13); 129 (15); 105 (100); 77 (96); 51 (81).

1,3-Diphenylprop-2-yn-1-one (**3**). To *t*-BuOK (82.5 mg, 0.735 mmol) and dicyclohexano[18]crown-6 (20 mg) in dry THF (5 ml) cooled to −50° was added dropwise **1a** (104 mg, 0.35 mmol) in THF (5 ml). After 45 min of stirring at −50°, the temp. was slowly raised to r.t. After addition of H_2O, the mixture was worked up as usual. The crude product was purified by prep. TLC (petroleum ether/CH_2Cl_2 1:1): 31.6 mg (43%) of **3** (liq.) [11]. IR (liq.): 3080*w*, 3060*m*, 3030*w*, 2200*s*, 1640*s*, 1600*s*, 1580*s*, 1490*s*, 1450*s*, 1320*s*, 1285*s*, 1240*m*, 1210*s*, 1170*s*, 1160*m*, 1090*w*, 1070*m*, 1030*s*, 1010*s*, 995*s*, 930*w*, 920*w*, 840*w*, 810*m*, 790*m*. ^{1}H-NMR: 7.36–7.74 (*m*, 8 H); 8.19–8.27 (*m*, 2 H). MS: 206 (76, M^+), 178 (95), 129 (100).

1,1-Dichloro-2-methoxy-2-phenylcyclopropane (**1b**). Ethyl trichloroacetate (37.7 g, 0.197 mmol) in dry Et_2O was added dropwise to MeONa (10.64 g, 0.197 mmol) and α-methoxystyrene [13] (4.0 g, 29.81 mmol) in Et_2O (50 ml) with cooling (ice/NaCl). After 2 h of stirring, the temp. was raised to 4° and stirring continued overnight. The mixture was decomposed by addition of H_2O and worked up. The crude product was filtered through a silica-gel column (petroleum ether/CH_2Cl_2 3:1), washed with hexane, and recrystallized from hexane: 3.85 g (59%) of **1b**. M.p. 67–68°. IR ($CHCl_3$): 3090*w*, 3060*w*, 3030*w*, 3010*m*, 2960*m*, 2940*m*, 2900*w*, 2830*m*, 1600*s*, 1495*m*, 1460*m*, 1450*s*, 1440*m*, 1415*m*, 1315*m*, 1290*w*, 1235*s*, 1180*w*, 1155*w*, 1105*s*, 1080*s*, 1070*s*, 1040*m*, 1020*m*, 1000*s*, 970*w*, 930*w*, 850*m*, 700*s*, 675*m*, 650*w*. ^{1}H-NMR: 1.85 (*AB*, ^2J = 8.5, 1 H); 2.06 (*AB*, ^2J = 8.5, 1 H); 3.26 (*s*, 3 H); 7.36–7.50 (*m*, 1 H). ^{13}C-NMR: 30.09 (*t*); 55.33 (*s*); 64.03 (*q*); 70.48 (*s*); 128.35 (*d*); 128.92 (*d*); 129.27 (*d*); 133.90 (*d*). MS: 216, 218 (19, M^+); 215, 217 (41); 181, 183 (49); 149 (23); 146 (21); 137 (12); 115 (15); 105 (49); 77 (65); 69 (100); 57 (49). Anal. calc. for $C_{10}H_{10}Cl_2O$: C 55.33, H 4.64, Cl 32.66; found: C 55.32, H 4.55, Cl 32.77.

Hydro,Chloro-Elimination of **1b**: *1,3-Epoxy-2,3-dihydro-2-(2-methoxy-2-phenylethenylidene)-1,3-diphenyl-1*H*-indene* (**5**). To a soln. of *t*-BuOK (0.262 g, 2.33 mmol), dicyclohexano[18]crown-6 (50 mg), and 1,3-diphenylisobenzofuran (0.400 g, 1.53 mmol) in THF (5 ml) was added **1b** (0.334 g, 1.53 mmol) in THF (5 ml) at −40° dropwise. After 80 min at −40°, the temp. was allowed to reach r.t. H_2O was added and the mixture worked up. After purification by flash chromatography (silica gel, petroleum ether/$CHCl_3$ 1:1), **5** was obtained (0.206 g, 33%) as a mixture of two stereoisomers (orange amorphous solid), separable by prep. TLC (alox neutral, CCl_4). IR ($CHCl_3$): 3060*w*, 3020*w*, 2040*m*, 1660*m*, 1600*w*, 1490*m*, 1450*m*, 1320*m*, 1290*s*, 1260*m*, 1235*s*, 1180*w*, 1140*m*, 1100*w*, 1075*w*, 1025*w*, 940*w*, 700*s*, 690*s*, 650*s*. ^{1}H-NMR: 3.83 (*s*, 3 H); 7.1–7.7 (*m*, 1 H); 7.4–7.7 (*m*, 8 H). ^{13}C-NMR: 197.9 (*s*); 156.96 (*s*); 108.73 (*s*); 57.94 (*q*); 141.2–134.1 (*s*, 6 C); 132.5–126.3 (series of *d*, not attributable). MS: 414 (79, M^+), 413 (92), 399 (41), 383 (33), 294 (43), 265 (25), 191 (7), 105 (100), 77 (47). HR-MS: 414.1599 ($C_{30}H_{22}O_2$, calc. 414.1619).

Hydro,Chloro-Elimination of **1c**: *Prop-2-ynal* tert-*Butyl Ethyl Acetal* (**7**). To *t*-BuOK (0.481 g, 4.3 mmol) and 20 mg of dicyclohexano[18]crown-6 (20 mg) in dry THF (10 ml) was added at −50° **1c** [14] [15] (0.367 g, 2.3 mmol) in THF (2 ml). After 30 min stirring at −50°, the mixture was allowed to reach r.t. and worked up. The crude product was distilled to afford 0.125 g of **7** (35%). B.p. 45–60°/8–15 Torr ([16]: 48–50°/10 Torr). IR (liq.): 3290*w* (br.), 2980*s*, 2930*m*, 2120*w*, 1390*w*, 1370*m*, 1340*w*, 1260*w*, 1230*w*, 1190*m*, 1120*m*, 1090*m*, 1040*s*, 1025*s*, 1005*m*. ^{1}H-NMR: 1.23 (*t*, ^3J = 7, 3 H); 1.30 (*s*, 9 H); 2.50 (*d*, ^4J = 2, 1 H); 3.70 (*qAB*, ^2J = 10, ^3J = 7, 2 H); 5.48 (*d*, ^4J = 2, 1 H). MS: no 156 (M^+, $C_9H_{16}O$), 83 (56), 57 (100).

Synthesis of **1d**. *Ethoxy(trimethylsilyl)acetylene* [17]. To ethoxyacetylene (techn.; 40% in hexane; 24 ml, 102 mmol) in dry Et_2O (250 ml) under Ar at 0° was added MeLi (1.6M in Et_2O; 67 ml, 107 mmol). After stirring at

0° for 30 min, freshly distilled Me_3SiCl (13.2 ml, 104 mmol) was added and the soln. stirred overnight at r.t. After filtration, the precipitate was extracted with Et_2O. The Et_2O was evaporated and the product dissolved in pentane and filtered. After evaporation, the crude product was distilled to furnish ethoxy(trimethylsilyl)acetylene (8.86 g, 61%). B.p. 57–60°/42 Torr. IR (liq.): 2960, 2180, 1250, 860–830. ^{1}H-NMR: 0.09 (*s*, 9 H); 1.2 (*t*, ^3J = 7, 3 H); 4.1 (*q*, ^3J = 7, 2 H).

(Z)-1-Ethoxy-2-(trimethylsilyl)ethene. Ethoxy(trimethylsilyl)acetylene (62.3 mmol) was hydrogenated in presence of 10% $Pd/BaSO_4$ (0.9 g) and quinoline [18] (0.25 g; IR monitoring: disappearance of the peak at 2180 cm^{-1}). After 9 h, the catalyst was filtered and washed with pentane. After evaporation, the crude product was purified by distillation: 7.60 g (85%). B.p. 60°/72 Torr. IR (liq.): 2980*s*, 2960*s*, 2900*m*, 2880*m*, 1610*s*, 1480*w*, 1445*w*, 1395*m*, 1350*w*, 1300*m*, 1245*s*, 1225*s*, 1150*w*, 1100*s*, 1075*m*, 1015*w*, 990*w*, 895*m*, 860*s*, 835*s*, 760*s*, 720*w*, 690*m*, 635*m*. ^{1}H-NMR: 0.08 (*s*, 9 H); 1.22 (*t*, ^3J = 7, 3 H); 3.77 (*q*, ^3J = 7, 2 H); 4.17 (*d*, ^3J = 8.3, 1 H); 6.55 (*d*, ^3J = 8.3, 1 H). ^{13}C-NMR: 0.27 (*q*); 15.22 (*q*); 67.36 (*t*); 100.42 (*d*); 157.93 (*d*). MS: 144 (13, M^+, $C_7H_{16}OSi$), 129 (22), 103 (100), 99 (24), 75 (50), 59 (18).

1,1-Dichloro-2-ethoxy-3-(trimethylsilyl)cyclopropane (**1d**). To (*Z*)-1-ethoxy-2-(trimethylsilyl)ethene (7.10 g, 49.2 mmol) in $CHCl_3$ (17.9 g, 150 mmol) in dry Et_2O (20 ml) was added at −78° *t*-BuOK (11.3 g, 100 mmol) in small portions. After stirring for 30 min, the temp. was raised to r.t. and stirring continued overnight. After addition of H_2O followed by usual workup, the volatiles were distilled off (40°/30 Torr), and the residue was filtered on a silica-gel column (hexane) to yield 4.68 g (42%) of **1d** as colorless oil. The product decomposed partially to 2-chloro-3-(trimethylsilyl)prop-2-enal during the filtration procedure. IR (liq.): 3000*w*, 2980*s*, 2920*m*, 2900*m*, 1490*w*, 1455*w*, 1415*m*, 1380*m*, 1350*s*, 1300*w*, 1250*s*, 1225*s*, 1160*s*, 1120*s*, 1080*s*, 1050*s*, 1020*s*, 960*s*, 890*s*, 850*s*, 810*s*, 760*m*, 700*m*, 670*m*. ^{1}H-NMR: 0.166 (*s*, 9 H); 0.905 (*d*, ^3J = 9, 1 H); 1.23 (*t*, ^3J = 7, 3 H); 3.65 (*d*, ^3J = 9, 1 H); 3.68 (*qAB*, ^3J = 7, ^2J = 12, 2 H). ^{13}C-NMR: 0.08 (*q*); 14.89 (*q*); 28.92 (*d*); 63.97 (*s*); 66.40 (*d*); 66.77 (*t*). MS: no 226 (M^+, $C_8H_{16}Cl_2OSi$), 197, 199 (11), 147, 149 (10), 93 (22), 83 (58), 73 (100).

Chloro,Trimethylsilyl-Elimination of **1d**: *1a-Chloro-2,7-epoxy-1-ethoxy-1a,2,7,7a-tetrahydro-2,7-diphenyl-1*H*-cyclopropa[*b*]naphthalene* (**8**). To Bu_4NF (1M in THF; 1.5 ml, 1.5 mmol) and 1,3-diphenylisobenzofuran (0.178 g, 0.66 mmol) in dry THF (10 ml) was added slowly at −22° **1d** (0.147 g, 0.645 mmol) in THF (3 ml). After 30 min of stirring at −22°, the soln. was allowed to reach r.t. The solvent was evaporated, H_2O added, and the mixture extracted with $CHCl_3$. After workup, the mixture was purified by prep. TLC (CH_2Cl_2). The product was washed wit EtOH, then with pentane to yield 0.074 g (30%) of **8**. M.p. 102.5–103.5°. IR ($CHCl_3$): 3080*w*, 3040*w*, 2980*m*, 2960*w*, 2930*w*, 2900*w*, 2880*w*, 1600*w*, 1500*w*, 1460*s*, 1450*s*, 1380*s*, 1360*m*, 1340*s*, 1310*s*, 1270*w*, 1260*w*, 1180*m*, 1120*m*, 1060*m*, 1040*m*, 1020*m*, 1010*m*, 990*s*, 870*w*, 830*w*, 790*w*. ^{1}H-NMR: 1.30 (*t*, ^3J = 7, 3 H); 2.07 (*d*, ^3J = 1.6, 1 H); 3.84 (*m*, 2 H); 4.38 (*d*, ^3J = 1.6, 1 H); 7.05–7.95 (*m*, 14 H). ^{13}C-NMR: 15.08 (*q*); 38.13 (*d*); 55.36 (*s*); 66.92 (*t*); 67.68 (*d*); 88.78 (*s*); 90.91 (*s*); 119.68 (*d*); 122.13 (*d*); 126.73 (*d*); 127.15 (*d*); 127.69 (*d*); 128.58 (*d*); 128.92 (*d*); 129.17 (*d*); 133.37 (*s*); 135.24 (*s*); 146.97 (*s*); 148.78 (*s*). MS: 388 (weak, M^+), 353 (100), 270 (22), 105 (69), 77 (40). Anal. calc. for $C_{25}H_{21}ClO_2$: C 77.21, H 5.44, Cl 9.12; found: C 77.00, H 5.36, Cl 8.95.

Thermal Rearrangement of 3-Methoxy-1,2,3-triphenylcyclopropene [19] (**15**). For 15 min, **15** [18] (0.144 g, 0.48 mmol) was heated in a wood metal bath to 250°. Prep. TLC (SiO_2, hexane/$CHCl_3$ 2:1) gave *3-methoxy-1,2-diphenyl-1*H*-indene* (**16**; 100 mg, 70%) and **17**/**18**. The latter was further separated by prep. TLC (alox, hexane/Et_2O 4:1): *2,3-dihydro-2,3-diphenyl-1*H*-inden-1-one* (**17**; 16.7 mg, 12%) and *1-methoxy-2,3-diphenyl-1*H*-indene* (**18**; 6.7 mg, 5%).

Data of **16**: M.p. 102–103°. IR ($CHCl_3$): 3060*m*, 3000*m*, 2940*m*, 2840*w*, 1600*s*, 1490*s*, 1470*m*, 1450*m*, 1440*m*, 1350*s*, 1325*m*, 1310*m*, 1280*w*, 1190*w*, 1140*w*, 980*m*, 910*w*, 710*m*, 695*s*. ^{1}H-NMR: 3.98 (*s*, 3 H); 4.90 (*s*, 1 H); 7.10–7.34 (*m*, 11 H); 7.47–7.51 (*m*, 1 H); 7.57–7.63 (*m*, 2 H). ^{13}C-NMR: 53.8 (*q*); 59.3 (*d*); 118.7 (*d*); 124.0 (*d*); 126.1 (*d*); 126.4 (*d*); 126.6 (*d*); 126.8 (*d*); 127.1 (*s*); 127.8 (*d*); 128.0 (*d*); 128.1 (*d*); 128.6 (*d*); 134.4 (*s*); 139.5 (*s*); 140.2 (*s*); 146.6 (*s*). MS: 298 (100, M^+, $C_{12}H_{18}O$), 283 (36), 265 (22), 255 (33), 178 (39), 119 (48), 77 (83), 56 (86).

Data of **17**: Red crystals. M.p. 153–154°. IR ($CHCl_3$): 1710 (C=O). ^{1}H-NMR: 7.15–7.20 (*m*, 1 H); 7.24–7.34 (*m*, 6 H); 7.86–7.46 (*m*, 6 H); 7.58–7.62 (*m*, 1 H). MS: 282 (100, M^+, $C_{21}H_{14}O$), 265 (15), 252 (59), 176 (15), 149 (25), 126 (52), 113 (33).

Data of **18**: Pale yellow crystals. M.p. 132–133°. ^{1}H-NMR: 3.04 (*s*, 3 H); 5.72 (*s*, 1 H); 7.18–7.48 (*m*, 13 H); 7.60–7.64 (*m*, 1 H). MS: 298 (100, M^+, $C_{22}H_{18}O$), 283 (57), 255 (54), 239 (55), 221 (41), 205 (28), 178 (55), 132 (69), 113 (90), 77 (51).

1-(Methylthio)-2,3-diphenyl-3-(2-phenylethyl)cyclopropene (**21**). To a suspension of (methylthio)diphenylcyclopropenium bromide [29] (0.311 g, 0.98 mmol) in dry benzene (10 ml) was added, at 8° in 3 min, a soln. of (2-phenylethyl)magnesium bromide (prepared from 5 mmol of Mg and 5.0 mmol of 1-bromo-2-phenylethane) in THF (5.0 ml). After stirring for 10 min, ice was added and Et_2O. After usual workup, the crude product was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 3:1): 0.106 g (32%) of **21**. Colorless oil. IR ($CHCl_3$):

3120*w*, 3065*w*, 3030*w*, 3015*m*, 2960*m*, 2930*m*, 2060*w*, 1785*m*, 1600*w*, 1495*m*, 1455*w*, 1450*m*, 1625*m*, 1220*w*, 1110*w*, 1080*w*, 750*s*, 700*s*. ^{1}H-NMR: 2.64 (*s*, 3 H); 2.70–2.88 (*m*, 4 H); 7.30–7.60 (*m*, 15 H). ^{13}C-NMR: 17.0 (*q*); 34.0 (*t*); 37.0 (*t*); 115.1 (*s*); 117.0 (*s*); 125.65 (*d*); 125.73 (*d*); 126.6 (*d*); 127.4 (*d*); 128.0 (*d*); 128.3 (*d*); 128.4 (*d*); 128.5 (*d*); 128.6 (*s*); 128.7 (*d*); 128.8 (*d*); 129.3 (*d*); 142.6 (*s*); 146.0 (*s*). MS: 342 (1, $M^{+\cdot}$, $C_{24}H_{22}S$), 295 (1), 251 (5), 238 (2), 217 (4), 203 (23), 191 (7), 167 (2), 149 (7), 115 (5), 91 (100), 71 (18), 57 (35).

Thermolysis of **21**. A soln. of **21** (40.4 mg) was heated in benzene (30 ml) at 80° for 90 min. The solvent was evaporated and the crude product purified by column chromatography (SiO_2, hexane/toluene 2:1): 23.6 mg (58%) of **24** and 8.6 mg (21%) of **23a**/**23b**.

*1-(Methylthio)-2-phenyl-3-(2-phenylethyl)-1*H*-indene* (**24**): IR ($CHCl_3$): 3068*m*, 3032*m*, 3012*m*, 2952*w*, 2920*m*, 2860*w*, 1603*m*, 1494*m*, 1465*m*, 1456*m*, 1441*m*, 1421*m*, 1226*w*, 1153*w*, 1029*w*, 965*m*, 912*m*, 747*m*, 735*m*, 729*m*, 723*m*, 700*s*. ^{1}H-NMR: 1.42 (*s*, 3 H); 3.04 (br. *s*, 4 H); 4.76 (*s*, 1 H); 7.20–7.54 (*m*, 13 H); 7.70 (*d*, ^3J = 7, 1 H). MS: 342 (19, $M^{+\cdot}$, $C_{24}H_{22}S$), 295 (5), 251 (31), 238 (13), 217 (21), 203 (66), 191 (25), 165 (3), 91 (100), 65 (22).

1-(Methylthio)-2,3,5-triphenylpenta-1,3-dienes: **23a** [41]: ^{1}H-NMR: 2.32 (*s*, 3 H); 3.65 (*d*, ^3J = 7.5, 2H); 6.26 (*s*, 1 H); 6.32 (*t*, ^3J = 7.5, 1 H); 7.04–7.54 (*m*, 15 H).

23b: IR ($CHCl_3$): 3080*m*, 3060*m*, 3030*m*, 3010*s*, 2957*m*, 2926*m*, 1600*m*, 1490*s*, 1453*m*, 1441*m*, 1262*s*, 1224*m*, 1218*m*, 1100*m*, 1074*m*, 1029*s*, 1012*s*, 909*m*. ^{1}H-NMR: 2.12 (*s*, 3 H); 3.23 (*d*, ^3J = 7.5, 2 H); 5.46 (*t*, ^3J = 7.5, 1 H); 5.75 (*s*, 1 H); 7.04–7.54 (*m*, 15 H). MS: 342 (10, $M^{+\cdot}$, $C_{24}H_{22}S$), 327 (16), 295 (5), 251 (6), 215 (16), 203 (22), 191 (14), 178 (7), 165 (7), 134 (4), 108 (26), 91 (100), 77 (10), 65 (14).

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