A New Synthesis of Alkylidenecyclopropanes by the Julia–Lythgoe-type Olefination Using Sulfones and Sulfoxides

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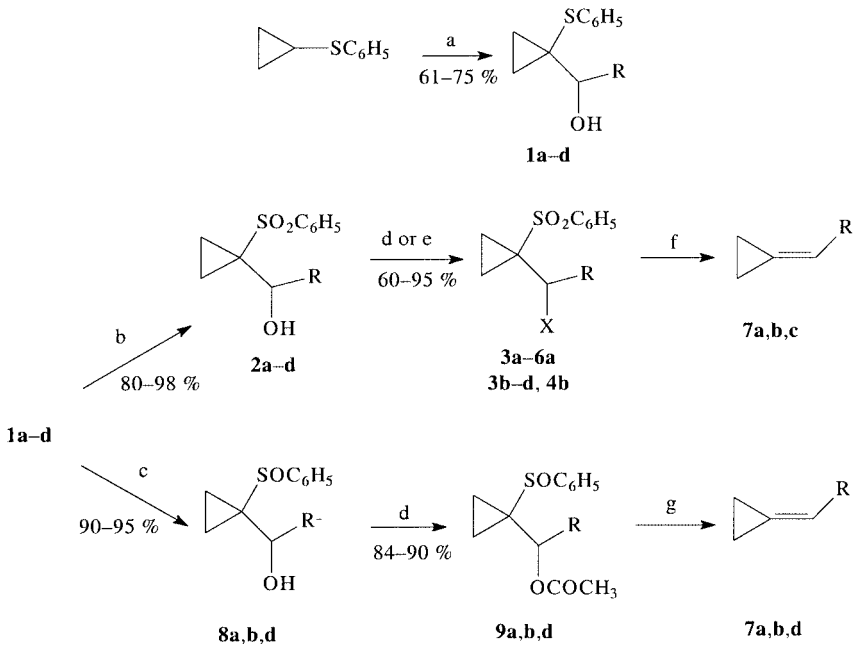
Dedicated to Jacques Salaun, Orsay-Paris, on the occasion of his 65th birthday.

Abstract: The first use of the Julia–Lythgoe-type olefination with cyclopropylsulfones and cyclopropylsulfoxides for the synthesis of alkylidenecyclopropanes is reported.

Key words: olefination, carbocycles, sulfones, sulfoxides, alkylidenecyclopropanes

Methylene and alkylidenecyclopropanes are particularly interesting molecules due to their unique reactivity coming from their high level of strain, that have served as useful building blocks in organic synthesis.[1] They undergo Ni(0)- or Pd(0)-catalyzed reaction with alkenes and alkynes for the synthesis of five-membered rings,[2a,3–7] ring opening with palladium chloride to give π-allyl palladium complexes,[8] 1,3-dipolar cycloaddition[2b,9] and are suitable precursors of cyclobutanones[10–13] and cyclobutanols.[14] More recently they have been used in several transition-metal catalyzed reactions like silaboration,[15] silylcyanation,[16] hydrosilylation,[17] diboration,[18] hydroamination,[19] hydroalkoxylation,[20] and hydrocarbonation.[21] On the other hand, despite their high level of strain they are very often stable and their carbon skeleton can be found in several natural products that display relevant biological properties.[22]

Among the several synthetic strategies reported we are particularly interested in the methods that involve 1,2-elimination from twofold functionally substituted cyclopropane derivatives.[23a–f] As a matter of fact, in continuation of our studies of the chemistry of alkylidenecyclopropanes,[14] we recently reported[24] their synthesis by using the Ramberg–Backlund reaction. Now here we report our successful use of the Julia–Lythgoe-type olefination, both in its sulfone[25] and sulfoxide[26] version for the synthesis of alkylidenecyclopropanes.[27]



Scheme 1 a) *n*-BuLi, THF, RCHO, 0 °C to r.t.; b) MCPBA, CH_2Cl_2, 0 °C; c) MCPBA, CH_2Cl_2, –20 °C; d) Ac_2O, DMAP, CH_2Cl_2, 0 °C to r.t.; e) Different conditions: *n*-BuLi, THF, TsCl, 0 °C to r.t.; BzCl, Et_3N, DMAP, 0 °C to r.t.; $SOCl_2$, CCl_4, reflux; f) Na/Hg 10%, THF–MeOH, –20 °C or Mg, $HgCl_2$ cat., anhyd EtOH, r.t.; g) *n*-BuLi, THF, –78 °C.

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For this purpose, the cyclopropyl carbinols **1a**–**d**, prepared from reaction of the lithium cyclopropylphenyl sulfide[28] with the corresponding aldehydes, were transformed into the corresponding sulfones **2a**–**d** and the sulfoxides **8a**,**b**,**d** by oxidation with MCPBA at different temperatures (Scheme 1).

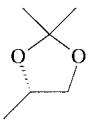
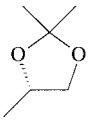
By transformation of their alcoholic function into different X groups (Ac, Ts, Cl, Bz), the cyclopropyl sulfones **2a**–**d** led to the derivatives **3a**–**6a**, **3b**–**d**, **4b**, which were treated with Na/Hg in THF–MeOH at –20 °C or with Mg/$HgCl_2$ (cat.) in anhydrous EtOH at room temperature. Good yields of **7a**,**b**[29] were obtained with the first method (Na/Hg) when the leaving group was the tosylate, and with the second method (Mg/$HgCl_2$) when the leaving group was the chloride. On the other hand **7c**[30] was obtained in low yields (Table 1).

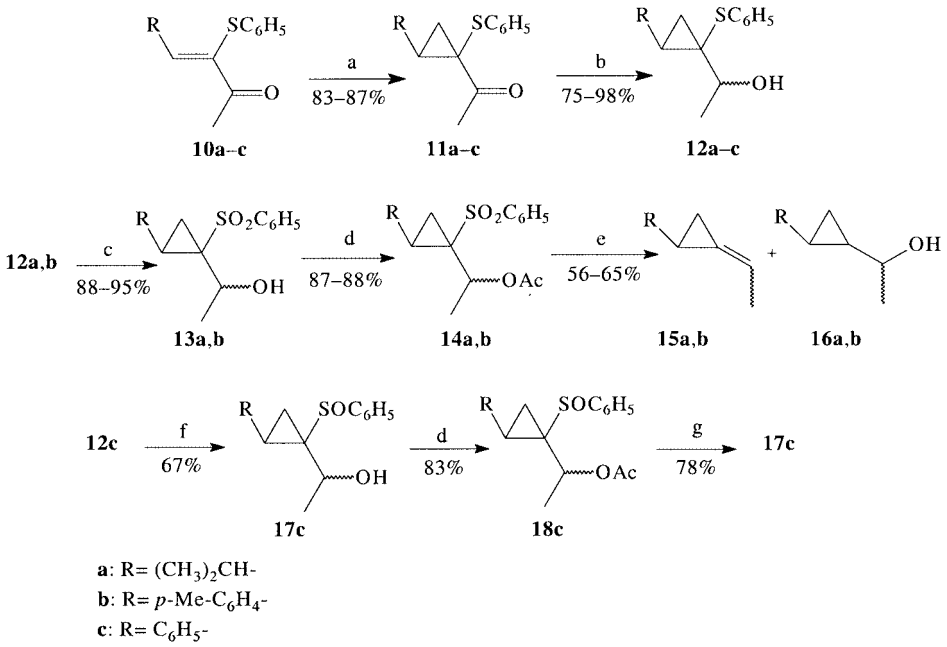
The sulfoxides **8a**,**b**,**d** were transformed into the corresponding acetates **9a**,**b**,**d** that were treated with *n*-BuLi to give reasonable to good yields of **7a**,**b** and **7d**[14] with no traces of side products, coming from simple desulfonylation and deacetylation, which were formed with the other methods (Table 1). By comparing the yields of entries 1, 2, 7, 8, 11 and 12–14 (Table 1) it can be seen that better results were obtained by using the sulfoxide version of the Julia–Lithgoe olefination which, moreover, avoids the use of the polluting sodium amalgam.

Next we checked the possibility of synthesizing alkylidenecyclopropanes carrying a substituent on the cyclopropyl ring. This target was achieved according to the sequence of reactions reported in the Scheme 2. The derivatives **10a**–**c** obtained by Knoevenagel condensation of phenylthioacetone with the corresponding aldehyde, were cyclopropanated as usual with the Corey ylide to give **11a**–**c** that were reduced to the corresponding alcohols **12a**–**c**.

Transformation of **12a**,**b** into the sulfones **13a**,**b** and reaction of these latter derivatives with Ac_2O gave the acetoxy sulfones **14a**,**b** which, after treatment with sodium amalgam, led to the methylcyclopropilidene **15a**,**b** (yields 56% and 65% respectively) as a 60:40 mixture of geometric isomers, accompanied by 20% of **16a**,**b** as a 65:35 and 50:50 *syn*/*anti*-mixture, respectively, which arise from desulfonation and deacetylation reaction. Unexpectedly, the cyclopropylsulfoxide **18c**, obtained by oxidation and acetylation of **12c**, when reacted with *n*-BuLi, gave only the cyclopropylsulfoxide alcohol **17c** through a deacetylation reaction. The reason for this failure is now being investigated as well as the examination of substrates carrying a tertiary leaving group, which, from preliminary experiments, appear to be unreactive under our experimental conditions.

Table 1 Synthesis of Alkylidenecyclopropanes **7a**–**d** from Cyclopropylsulfones **3a**–**6a**, **3b**–**d**, **4b** and Cyclopropylsulfoxides **9a**,**b**,**d**

Entry	Starting Material	R	X	Reagent	Yield (%)
1	**3a**	*p*-Me-C_6H_4	-$OCOCH_3$	Na/Hg	**7a** (53)
2	**3a**	*p*-Me-C_6H_4	-$OCOCH_3$	Mg/$HgCl_2$	**7a** (53)
3	**4a**	*p*-Me-C_6H_4	-$OCOC_6H_4$	Na/Hg	**7a** (35)
4	**5a**	*p*-Me-C_6H_4	-OTs	Na/Hg	**7a** (75)
5	**6a**	*p*-Me-C_6H_4	-Cl	Na/Hg	**7a** (30)
6	**6a**	*p*-Me-C_6H_4	-Cl	Mg/$HgCl_2$	**7a** (95)
7	**3b**	$(CH_2)_9CH_3$	-$OCOCH_3$	Na/Hg	**7b** (50)
8	**3b**	$(CH_2)_9CH_3$	-$OCOCH_3$	Mg/$HgCl_2$	**7b** (48)
9	**4b**	$(CH_2)_9CH_3$	-Cl	Mg/$HgCl_2$	**7b** (89)
10	**3c**	$CH=CH_2$	-$OCOCH_3$	Na/Hg	**7c** (26)
11	**3d**		-$OCOCH_3$	Na/Hg	**7d** (0)
12	**9a**	*p*-Me-C_6H_4	-$OCOCH_3$	*n*-BuLi	**7a** (76)
13	**9b**	$(CH_2)_9CH_3$	-$OCOCH_3$	*n*-BuLi	**7b** (60)
14	**9d**		-$OCOCH_3$	*n*-BuLi	**7d** (42)



Scheme 2 a) Trimethylsulfoxonium iodide, NaH, DMSO, r.t. to 50 °C; b) $LiAlH_4$, THF, –30 °C; c) MCPBA, CH_2Cl_2, 0 °C; d) Ac_2O, DMAP, CH_2Cl_2, 0 °Cr.t.; e) Na/Hg 10%, THF–MeOH, –20 °C; f) MCPBA, CH_2Cl_2, –20 °C; g) *n*-BuLi, THF, –78 °C.

In conclusion we have reported a new method for the synthesis of alkylidenecyclopropanes in moderate to good yields that compares favorably with the already published methods. The easy access to cyclopropanes carrying a sulfur atom makes the method particularly versatile and substituents can be easily introduced on the cyclopropane ring.

Acknowledgment

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(27) **Typical Procedure for the Reductive Elimination of the Sulfones with Na/Hg.**

To a stirred suspension of sodium amalgam (10%, 422 mg, 1.85 mmol) in THF (6 mL) and MeOH (2 mL) at –20 °C, under Argon was added a solution of the appropriate cyclopropylsulfone (0.37 mmol) in THF (2 mL). After 30 min at same temperature the reaction mixture was diluted with Et_2O, washed with brine, dried and concentrated in vacuo. Chromatography with light petroleum-Et_2O, (1:1) yielded the corresponding alkylidenecyclopropanes.

Typical Procedure for the Reductive Elimination of the Sulfones with Mg/$HgCl_2$ cat.

A mixture of the cyclopropylsulfone (0.76 mmol), Mg powder (54.7 mg, 2.28 mmol) and few crystals of $HgCl_2$ in dry EtOH (10 mL) was stirred for 1 h at r.t. The reaction mixture was then poured into cold 0.5 N HCl and extracted with Et_2O. The organic layer was washed with sat. aq $NaHCO_3$, dried (Na_2SO_4), filtered and then concentrated in vacuo to give the crude products which were purified as above.

Typical Procedure for the Reductive Elimination of the Sulfoxides with *n*-BuLi.

To a solution of *n*-BuLi (1.5 M in hexane, 1.6 mL, 2.4 mmol) at –78 °C, under an argon atmosphere, a solution of the cyclopropylsulfoxide (0.6 mmol) in THF (10 mL) was added dropwise with stirring. After stirring for 5 min, the reaction was quenched with sat. aq NH_4Cl and the mixture was extracted with Et_2O. The organic layer, dried and evaporated, gave the corresponding alkylidenecyclopropanes that were purified as above.

All new compounds have been fully characterized by ^1H NMR (300 MHz), ^{13}C NMR (75.4 MHz), IR, GLC mass spectra (70 eV) and elemental analyses.

Selected analytical data for some representative derivatives are reported.

Cyclopropyl carbinol **1d**: A 65:35 mixture of two diastereoisomers. *Minor isomer*. White crystals, mp 58–60 °C. Yield: 21%. $[\alpha]_D^{25}$ +39.30 (*c* 3.89, $CHCl_3$). IR (film): 3400 cm^{-1}.^1H NMR ($CDCl_3$): δ = 0.91–1.30 (m, 4 H), 1.34 (s, 3 H), 1.39 (s, 3 H), 2.62 (br s, 1 H), 3.49 (d, 1 H, *J* = 5.1 Hz), 3.78 (t, 1 H, *J* = 8.1 Hz), 4.04 (dd, 1 H, *J* = 8.1 Hz and 6.6 Hz), 4.43 (q, 1 H, *J* = 6.6 Hz), 7.12–7.46 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ = 11.3, 13.9, 25.2, 26.4, 26.8, 66.8, 73.4, 77.5, 109.1, 125.7, 128.1, 128.7, 136.1. MS: *m/z* (%) = 280 (13) [M^+], 265 (15), 207(10), 191 (13), 178 (14), 149 (13), 101(100), 91(16). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19; S, 11.43. Found: C, 64.41; H, 7.26; S, 11.39. *Major isomer*. Yellow oil. Yield 40%. $[\alpha]_D^{27}$ –25.74 (*c* 4.00, $CHCl_3$). IR (neat): 3430 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.93–1.28 (m, 4 H), 1.31 (s, 3 H), 1.38 (s, 3 H), 2.65 (br s, 1 H), 3.51 (d, 1 H, *J* = 5.7 Hz), 3.91 (dd, 1 H, *J* = 6.3 Hz and *J* = 8.4 Hz), 4.04 (dd, 1 H, *J* = 8.4 Hz and 6.3 Hz), 4.31 (q, 1 H, *J* = 6.3 Hz), 7.12–7.48 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ = 13.3, 13.6, 25.1, 26.1, 27.3, 65.5, 75.0, 78.7, 108.5, 125.6, 128.1, 128.5, 136.0. MS: *m/z* (%) = 280 (14) [M^+], 265 (20), 204 (4), 191(23), 179 (20), 149 (14), 101(100), 91(15). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19; S, 11.43. Found: C, 64.36; H, 7.28; S, 11.34.

Sulfoxide **8d**: (Obtained by oxidation of the minor isomer of **1d**): Colorless oil. Yield 90%. Spectral data refer to a 70:30 mixture of two inseparable diastereoisomers. IR (neat): 1040, 3430 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.98 (s, 3 H), 1.18–1.57 (m, 8 H), 1.22 (s, 3 H), 1.27 (s, 3 H), 1.43 (s, 3 H), 1.84 (s, 2 H), 3.64–4.29 (m, 8 H), 7.51–7.70 (m, 10 H). *Major isomer*: MS: *m/z* (%) = 281 (39) [M^+ – 15], 221 (18), 195 (100), 153 (77), 125 (34), 109 (18), 101(59), 95 (64), 77 (25). *Minor isomer*: MS: *m/z* (%) = 281 (34) [M^+ – 15], 221 (18), 195 (100), 153 (77), 125 (40), 109 (21), 101 (86), 95 (98), 77 (30). Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80; S, 10.82. Found: C, 60.64; H, 6.68; S, 10.61.

Acetate **9d**: Yield 90%. A 70:30 mixture of two inseparable diastereoisomers: IR (neat): 1060, 1740 cm^{-1}. *Major isomer*: ^1H NMR ($CDCl_3$): δ = 1.20–1.36 (m, 4 H), 1.30 (s, 3 H,), 1.34 (s, 3 H), 1.84 (s, 3 H), 3.73 (dd, 1 H, *J* = 6.3 Hz and *J* = 8.7 Hz), 4.07 (dd, 1 H, *J* = 6.3 Hz and *J* = 8.7 Hz), 4.48 (q, 1 H, *J* = 6.3 Hz), 4.85 (d, 1 H, *J* = 6.9 Hz), 7.47–7.70 (m, 5 H). *Minor isomer*: ^1H NMR ($CDCl_3$): δ = 1.20–1.36 (m, 4 H), 1.28, (s, 3 H), 1.32 (s, 3 H), 1.83 (s, 3 H), 3.78 (dd, 1 H, *J* = 6.3 Hz and *J* = 8.7 Hz), 4.02 (dd, 1 H, *J* = 6.3 Hz and *J* = 8.7 Hz), 4.39 (q, 1 H, *J* = 6.3 Hz), 5.03 (d, 1 H, *J* = 6.3 Hz), 7.47–7.70 (m, 5 H). MS (identical for the two isomers): *m/z* (%) = 323 (7) [M^+ – 15], 281 (6), 207 (43), 191 (12), 153 (27), 125 (13), 95 (59), 43 (100). Anal. Calcd for $C_{17}H_{22}O_5S$: C, 60.34; H, 6.55; S, 9.47. Found: C, 60.44; H, 6.78; S, 9.61.

Methylcyclopropilidene **15b**: Colorless oil. Yield 65% Data worked out from the unseparable 60:40 *E*/*Z*-mixture: ^1H NMR ($CDCl_3$): δ = 1.05–1.12 (m, 2 H), 1.63–1.70 (m, 2 H), 1.76–1.80 (m, 3 H, *E*-isomer), 1.84–1.89 (m, 3 H, *Z*-isomer), 2.29 (s, 3 H, *Z*-isomer), 2.30 (s, 3 H, *E*-isomer), 2.52–2.55 (m, 2 H), 5.91–5.95 (m, 2 H), 6.98–7.08 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ = 13.3, 15.0, 16.8, 17.0, 19.2, 19.7, 19.8, 20.9, 21.0, 114.3, 114.5, 126.1, 126.3, 128.9, 129.0, 135.0, 135.1, 139.2, 139.5. MS (identical for the two isomers): *m/z* (%) = 158 (12) [M^+], 143 (100), 128 (65), 115 (25), 91 (7), 77 (12). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.15; H, 8.98.

Compound **16b**: A 50:50 mixture of two *E*-diastereoisomers (*syn* + *anti*). Colorless oil. Yield 20%. IR (neat): 3400 cm^{-1}. *anti*-Diastereoisomer: ^1H NMR ($CDCl_3$): δ = 0.85–0.90 (m, 2 H), 1.24–1.26 (m, 1 H), 1.34 (d, 3 H, *J* = 5.7 Hz), 1.57 (br s, 1 H), 1.75–1.78 (m, 1 H), 2.30 (s, 3 H), 3.36 (q, 1 H, *J* = 5.7 Hz), 6.95–7.08 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ = 13.6, 20.9, 22.7, 30.6, 71.9, 76.6, 125.8, 129.0, 135.2, 139.3. *syn*-Diastereoisomer: ^1H NMR ($CDCl_3$): δ = 0.91–0.98 (m, 2 H), 1.20–1.22 (m, 1 H), 1.32 (d, 3 H, *J* = 5.7 Hz), 1.57 (br s, 1 H), 1.84–1.92 (m, 1 H), 2.30 (s, 3 H), 3.34 (q, 1 H, *J* = 5.7 Hz), 6.95–7.08 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ = 13.1, 20.4, 22.3, 30.6, 71.9, 76.6, 125.7, 129.0, 135.1, 139.4. MS (identical for the two isomers): *m/z* (%) = 176 (5) [M^+], 143 (21), 131 (40), 121 (96), 117 (100), 91 (55), 77 (20). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 8.86.

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