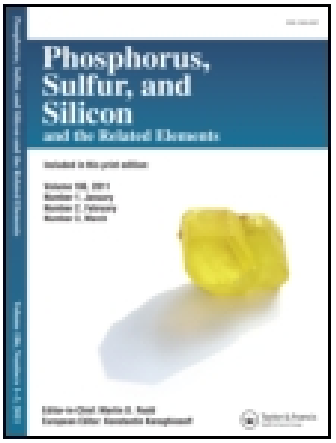

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COMMUNICATION

THE REACTION OF CYCLOPROPANOLS WITH BURGESS REAGENT: A REINVESTIGATION AND CORRECTION

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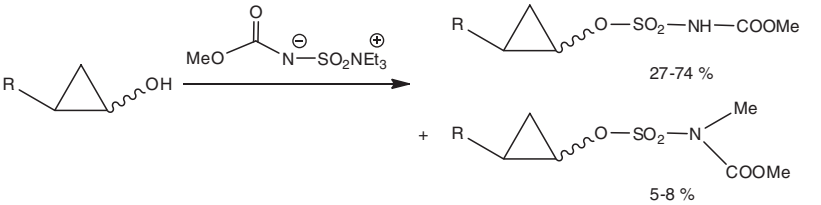
GRAPHICAL ABSTRACT



Abstract *The reaction of cyclopropanols with Burgess reagent yields the unusual sulfamates **8** and their N-methylated derivatives **9**. Unlike a previous study, dicyclopropyl ether formation was not observed. Also, the mechanism of ether formation from a cyclopropanol precursor cannot follow an S_N2 pathway with retention.*

Keywords Alcohols; reaction mechanisms; small ring systems; sulfonamides

INTRODUCTION

Methyl *N*-(triethylammoniumsulfonyl)carbamate (**2**, or, Burgess reagent) opens up a convenient route for the dehydration of secondary or tertiary alcohols to give alkenes, while primary alcohols yield carbamates, but also a variety of other applications have been reported.[1–5] So, when the Clausthal group was looking for a way to achieve dehydration of cyclopropanol **1** with a spiro-attached thioacetal unit, the Burgess reagent was an obvious choice.[6] However, the only product that could be isolated from the complex reaction mixture was not a cyclopropene, but based mainly on the NMR and MS data was assigned ether structure **3**. Moreover, starting from optically active spiro-alcohol (*R*)**-1**, a product with two sets of ^{13}C NMR signals was isolated and assigned the (*R*,*R*)-configuration (Scheme 1). This seemed to indicate an S_N process with retention of configuration, as had been previously discussed in cyclopropane substitution chemistry.[7–9] Both the unusual reaction product and the reaction mechanism called for this, more detailed study of the reaction

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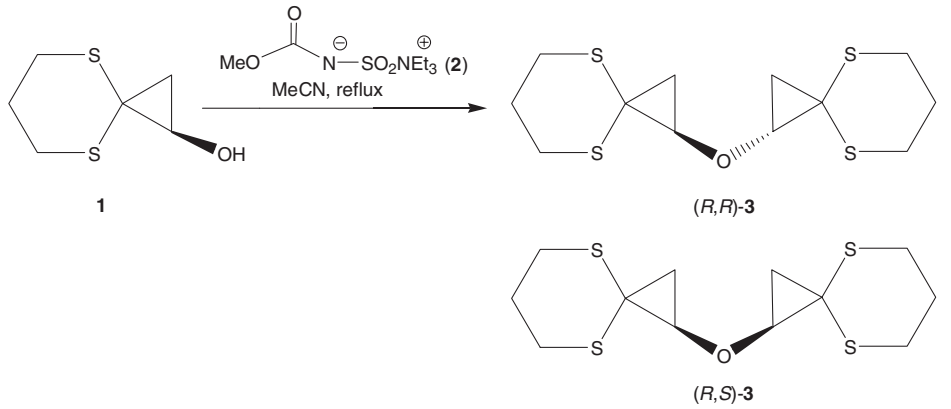
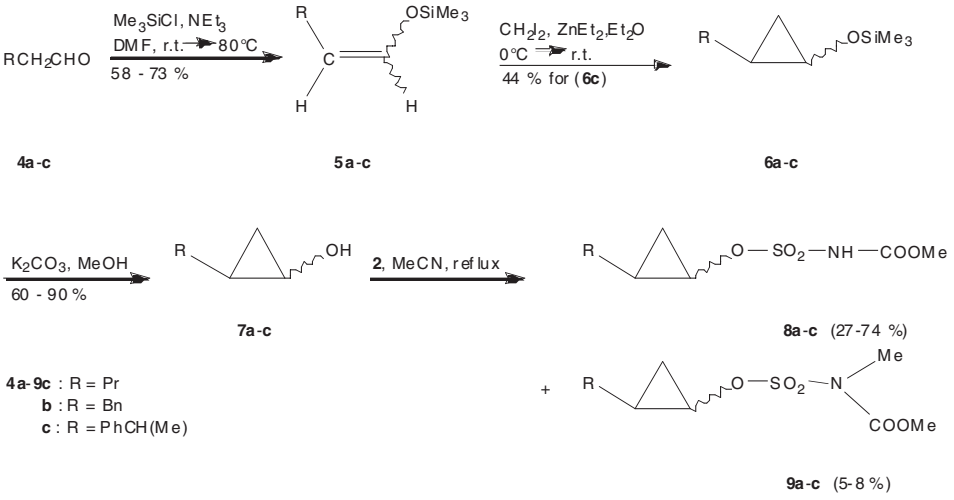


Scheme 1 Reported reaction of cyclopropanols **1** and with Burgess reagent.

of cyclopropanols with Burgess reagent **2**. Here it turned out that the interpretation of the original data cannot be sustained.

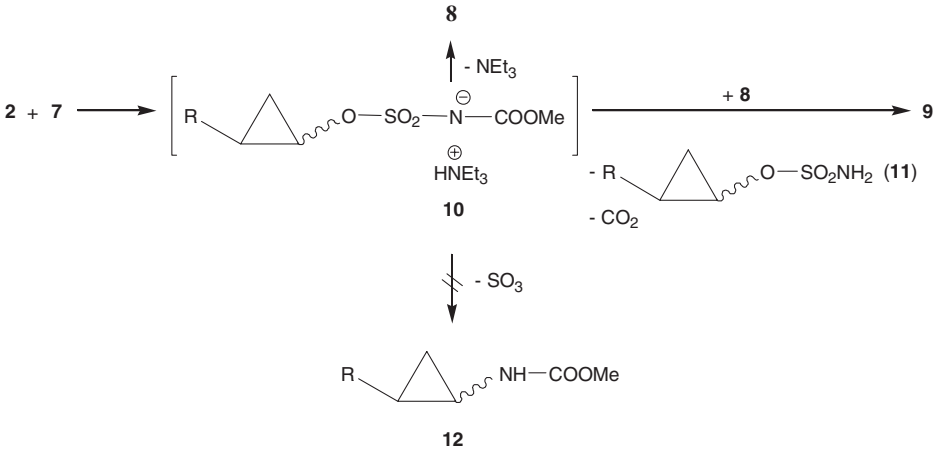
RESULTS AND DISCUSSION

Among the various methods of cyclopropanol synthesis,[10,11] we found the modified Simmons–Smith methylenation of silyl enol ethers with diiodomethane/diethylzinc to be most convenient.[12] Thus, aldehydes **4** are silylated using a conventional protocol[13] to give enol ethers **5a**–**c** as mixtures of the geometrical isomers (*E*/*Z* in comparable amounts). Ethers **5** are then subjected to the joint action of diiodomethane and diethylzinc.[12] The resulting cyclopropyl silyl ethers **6a**,**b** are generated as *cis*/*trans* mixtures, while for **6c**, the presence of an additional stereogenic center gives rise to a complex mixture of four diastereomers. The silyl residue of **6** can easily be removed by methanolic potassium carbonate[14] to give the desired cyclopropanols **7** (Scheme 2).



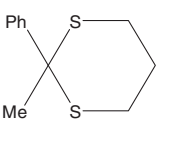
Scheme 2 Synthesis of cyclopropanols **7** and their reaction with Burgess reagent.

Burgess reagent **2** was applied as previously[6] to the diastereomeric mixtures of cyclopropanols **7** (Scheme 2). Column chromatography allowed to isolate *N*-(cyclopropyloxysulfonyl)carbamates (*N*-(methoxycarbonyl)sulfamates) **8** as main products and the *N*-methylated derivatives **9** as major side products. Structure assignment for **8** and **9** is based on the spectroscopic data including HRMS. It appears that a product of type **8** has only rarely been observed in the chemistry of the Burgess reagent, especially when a sterically very hindered hydroxy group was reacted with **2**,[14–16] whereas diols readily give cyclic sulfamates with **2**.[17] Obviously, the reaction between alcohols **7** and the reagent **2** is initiated by the usual S_N attack of the alcoholic hydroxy group at the sulfur of reagent **2** to give sulfamide **10** (Scheme 3). From here, attack of the amide nitrogen on H-2 of the ring to give a cyclopropene, the "normal" Burgess product, is obviously disfavored because of the inherent buildup of ring strain. The alternative, an intramolecular S_N attack on C-1 of the ring to give carbamate **12**,[1–5] is probably suppressed because this would involve a backside attack, which has been seen in cyclopropanes only under specific circumstances.[8,18] In this situation, stabilization of intermediate **10**[19] to product **8** occurs. A competing pathway is methylation of **10** by another molecule of **10** or by the already formed product **8**, though the expected parallel product **11** could not be detected. Prolonged heating does not allow forcing of the formation of cyclopropenes or of carbamates **12**. Rather, formation of methylation product **9** seems to be further encouraged.



Scheme 3 Suggested mechanism for formation of products **8** and **9**.

Even careful chromatography of the product mixture as formed from **2** and **7** did not reveal the formation of dicyclopropyl ethers analogous to **3**. Moreover, other than with **7**, the reaction of cyclopropanol **1** with Burgess reagent **2** had produced a very complex mixture of, except for **3**, unidentified products. This raises the suspicion that the spiro-attached thioacetal unit in **1** interacts with the Burgess reagent. In fact, a model reaction of thioacetal **13** with Burgess reagent **2** under the same reaction conditions as used earlier[6] showed that only 47% of **13** survived this treatment. In the complex product mixture, the main component was dithiepin **14**, while only traces of acetophenone were detected. Normally, the transition from a dithiane to a dithiepin of type **14** requires an exocyclic leaving group in the 2-position of the dithiane[20] or generation of an exocyclic carbene.[21]



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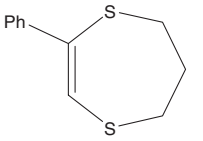

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While the origin of ether **3** remains mysterious, the claimed formation from **1** by an S_N2 pathway with retention has to be revised in any case. Product **3** with (*R*,*R*) configuration would give only one set of NMR signals because of its C_2 axis of symmetry. However, the isolated product showed two sets of NMR signals with comparable intensity, indicating that the (*R*,*S*)-form of **3** is equally present. This speaks against any S_N2 route with a single stereochemical outcome. A possible explanation would be the nonstereoselective addition of alcohol (*R*)-**1** to a cyclopropene intermediate in an EA mechanism.[22] However, as the model reactions of cyclopropanols **7** with reagent **2** give no clue as to cyclopropene formation, this route to **3** remains speculative.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance DPX 200 and Avance 400 instruments in $CDCl_3$ as solvent. Chemical shifts were measured in δ (ppm) and coupling constants J in Hz. TMS ($\delta = 0.00$) or the signal of the solvent ($CDCl_3$: $\delta = 7.26$ ppm) served as internal standard in ^{1}H NMR spectra. The solvent peak ($CDCl_3$ at $\delta = 77.0$ ppm) was used as reference for ^{13}C spectra. For assignment of the number of substituents attached to the specified carbon, each carbon is described as + (primary or tertiary carbon), − (secondary carbon), or 0 (quaternary carbon), as determined by the DEPT-135 method. MS were recorded on a Varian instrument Saturn 2100T or Hewlett-Packard 5989B; high-resolution MS (HRMS) measurements were carried out at the "Institut für Organische Chemie, Leibniz Universität Hannover." LR-ESIMS spectra were recorded on a Hewlett Packard/Agilent instrument LC-MSD Serie 1100 at a dry gas temperature of 300°C, a capillary voltage of 3000 V, and a fragmentor voltage of 0 V. Samples were dissolved in HPLC grade methanol and sprayed directly from methanol. IR spectra were recorded on a Bruker Vektor 22 FT-IR spectrometer. TLC was performed on Merck 60 F254 precoated silica plates, and spots were detected by UV fluorescence quenching or by spraying with a solution of anisaldehyde/sulfuric acid in methanol and subsequent heating. Flash chromatography was performed with silica gel 60 (Merck, 230–400 mesh). Ethyl acetate (EA) and petroleum ether (PE) with the boiling range 60–70°C were used in the separations. All solvents were distilled before use. Silyl ethers **5a** (63%),[12] **b** (75%),[23] and **c** (58%)[24] were obtained as *E*/*Z* mixtures by a general procedure[13] and gave spectroscopic data in accordance with the literature.

Cyclopropanation of Alkenyl Silyl Ethers 5 to Cyclopropyl Silyl Ethers 6

A literature method[12] gave, after aqueous work-up, crude silyl ethers **6a**,**b**, which were desilylated in situ to cyclopropanols **7a**,**b** (vide infra) by the action of K_2CO_3 in MeOH.[14] The desilylation step was not applied to the product from **5c**.

2-(1-Phenylethyl)cyclopropyl Trimethylsilyl Ether (6c)

6c was prepared from **5c** (5.5 g. 24.96 mmol) to give 2.59 g (44%) as a colorless oil. The compound is a mixture of four diastereomers. The cis/trans-forms could at least partially be separated by repeated column chromatography (PE/EA 1:50–> 1:100).

trans-**6c** (isolated major diastereomer): ^{1}H NMR (200 MHz): $\delta = 7.45$–7.21 (m, 5H, Ph), 3.21 (dt, $J = 6.6, 2.8$, 1 H, H-1), 2.07 (dq, $J = 9.6, 7.1$, 1H, PhC*H*), 1.35 (d, $J = 7.1$, 3H, Me), 1.32–1.11 (m, 1H, H-2), 0.85 (ddd, $J = 9.7, 5.8, 2.8$, 1H, H-3a), 0.53 (ddd, $J =$ 6.6, 6.3, 5.8, 1H, H-3b), -0.00 (s, 9H, $SiMe_3$). ^{13}C NMR (50 MHz) $\delta = 146.4$ (o, C-Ar), 128.4, 127.1, 126.1 (+, CH-Ar), 52.0 (+, C-1), 42.4 (+, *C*Me), 27.7 (+, C-2), 20.2 (+, C*Me*), 13.6 (−, C-3), −0.5 (+, $SiMe_3$).

trans-**6c** (isolated minor diastereomer): ^{1}H NMR (200 MHz): $\delta = 7.45$–7.21 (m, 5H, Ph), 3.27 (dt, $J = 6.4, 2.8$, 1 H, H-1), 2.12 (dq, $J = 9.9, 7.0$, 1H, PhC*H*), 1.47 (d, $J = 7.0$, 3 H, Me), 1.32–1.10 (m, 1H, H-2), 0.73 (ddd, $J = 9.7, 5.9, 2.8$, 1H, H-3a), 0.43 (ddd, $J =$ 6.4, 6.1, 5.9, 1H, H-3b), 0.25 (s, 9H, $SiMe_3$). ^{13}C NMR (50 MHz,) $\delta = 146.1$ (o, C-Ar), 128.3, 127.0, 126.0 (+, CH-Ar), 53.0 (+, C-1), 42.4 (+, *C*Me), 26.9 (+, C-2), 21.9 (+, C*Me*), 13.6 (−, C-3), −0.1 (+, $SiMe_3$).

cis-**6c** (isolated major diastereomer): ^{1}H NMR (200 MHz): $\delta = 7.36$–7.07 (m, 5H, Ph), 3.48 (dt, $J = 6.3, 3.4$, 1 H, H-1), 2.53 (dq, $J = 10.2, 7.0$, 1 H, PhC*H*), 1.31 (d, $J = 7.0$, 3 H, Me), 0.94–0.72 (m, 1H, H-2), 0.69 (dt, $J = 9.4, 6.3$, 1 H, H-3a), 0.54 (dt, $J = 9.4, 6.3$, 1H, H-3b), 0.14 (s, 9H, $SiMe_3$). ^{13}C NMR (50 MHz,) $\delta = 148.0$ (o, C-Ar), 128.2, 127.2, 125.7 (+, CH-Ar), 50.8 (+, C-1), 37.7 (+, *C*Me), 23.6 (+, C-2), 22.5 (+, C*Me*), 12.8 (−, C-3), −0.0 (+, $SiMe_3$).

cis-**6c** (isolated minor diastereomer): ^{1}H NMR (200 MHz): $\delta = 7.$ 36–7.07 (m, 5H, Ph), 3.36 (dt, $J = 6.6, 3.4$, 1 H, H-1), 2.63 (dq, $J = 7.0, 3.9$, 1H, PhC*H*), 1.35 (d, $J = 7.0$, 3 H, Me), 0.94–0.72 (m, 1H, H-2), 0.25 (mc, 1 H, H-3a), 0.18–0.08 (m, overlapping, 1 H, H-3b), 0.00 (s, 9H, $SiMe_3$). ^{13}C NMR (50 MHz,) $\delta = 147.7$ (o, C-Ar), 128.1, 127.2, 125.6 (+, CH-Ar), 50.7 (+, C-1), 37.0 (+, *C*Me), 24.5 (+, C-2), 21.8 (+, C*Me*), 12.6 (−, C-3), −0.3 (+, $SiMe_3$).

Cyclopropanols 7

Alcohols **7a**,**b** were obtained by in-situ desilylation.[14] The same procedure allowed conversion of **6c** into **7c**.

2-Propylcyclopropanol (7a). Yield 2.49 g (68%) over two steps from **5a** (5.76 g, 36.4 mmol) as a colorless oil. The spectroscopic data match the literature.[25]

2-Benzylcyclopropanol (7b). Yield 2.19 g (90%) over two steps from **5b** (3.39 g, 16.4 mmol) as a colorless oil: *cis/trans* mixture. The spectroscopic data for *cis*-**7b** match the literature.[26] Data for the *trans* compound: ^{1}H NMR (200 MHz): $\delta = 7.35$–7.15 (m, 5H, Ph), 3.35 (dt, $J = 6.0, 2.7$, 1H, H-1), 2.53 (m, 2H, PhC*H*), 1.9 (broad s, 1H, OH), 1.39–1.15 (m, 1H, H-2), 0.80 (ddd, J = 9.7, 6.0, 2.7, 1H, H-3a), 0.50 ("q", $J = 6.0$, 1H, H-3b). ^{13}C NMR (50 MHz,) $\delta = 141.0$ (o, C-Ar), 128.4, 128.3, 126.0 (+, CH-Ar), 52.6 (+, C-1), 37.3 (+, *C*Ph), 21.5 (+, C-2), 14.6 (−, C-3). IR (NaCl): $\tilde{\nu} = 3421, 3062, 3028, 2926, 1716$.

2-(1-Phenylethyl)cyclopropanol (7c). Yield 463 mg (60%) from *cis*-**6c** (1.12 g, 4.79 mmol) as a colorless oil; diastereomeric mixture, the two *cis*-isomers could be obtained in relatively pure form by repeated column chromatography (PE/EA 8:1). Major *cis*-isomer: ^{1}H NMR (200 MHz): $\delta = 7.38$–7.12 (m, 5H, Ph), 3.67 (ddd, $J = 6.5, 6.3, 3.3$, 1H, H-1), 2.64 (dq, $J = 10.3, 7.0$, 1H, PhC*H*), 1.96 (broad s, 1H, OH), 1.38 (d, $J = 7.0$,

3 H, Me), 0.93 (dddd, J = 10.3, 9.3, 6.5, 6.3, 1H, H-2), 0.67 (dt, J = 9.3, 6.3, 1H, H-3a), 0.28 (dt, J = 6.3, 3.3, 1H, H-3b). ^{13}C NMR (50 MHz,) δ = 147.4 (o, C-Ar), 128.3, 127.1, 125.9 (+, CH-Ar), 50.7 (+, C-1), 37.5 (+, *C*Me), 20.1 (+, C-2), 22.9 (+, C*Me*), 13.1 (−, C-3).

Minor *cis*-isomer: ^{1}H NMR (200 MHz): δ = 7.37–7.12 (m, 5H, Ph), 3.53 (ddd, J = 6.4, 6.1, 3.2, 1H, H-1), 2.64 (dq, J = 10.2, 7.1, 1H, PhC*H*), 1.65 (broad s, 1H, OH), 1.41 (d, J = 7.1 H, Me), 0.99 (dddd, J = 10.2, 9.2, 6.2, 6.1, 1H, H-2), 0.83 (ddd, J = 9.2, 6.4, 5.7, 1H, H-3a), 0.41 (ddd, J = 6.2, 5.7, 3.2, 1H, H-3b). ^{13}C NMR (50 MHz,) δ = 147.5 (o, C-Ar), 128.5, 126.7, 126.0 (+, CH-Ar), 50.4 (+, C-1), 38.1 (+, *C*Me), 25.1 (+, C-2), 22.7 (+, C*Me*), 13.0 (−, C-3).

Typical Procedure for the Reaction of Cyclopropanols 7 with Burgess Reagent 2: Formation of Sulfamates 8a, 9a

Cyclopropanol **7a** (3.8 mmol) and reagent **2** (918 mg, 3.85 mmol) in MeCN (2 mL) were heated to 80°C over 15 min and kept boiling for 1 h. After cooling, water (5 mL) was added to the reaction mixture and the organic products extracted by washing with ether (3 × 10 mL) and CH_2Cl_2 (5 × 10 mL). The combined organic phases were washed with sat. brine (1 × 10 mL) and dried ($MgSO_4$). After filtration, the solvents were carefully evaporated in vacuo. The residue was dissolved in MeOH (20 mL) and stirred with freshly activated Dowex 50 × 8 (1.0 g) at rt. After removal of the ion exchange resin, the concentrated filtrate was subjected to column chromatography (silica) using PE/EA (6:1 –> 1:1) and then CH_2Cl_2/MeOH (10:1).

Methyl *N*-(2-propylcyclopropyloxysulfonyl)carbamate (8a). From **7a** (381 mg, 3.81 mmol) to give 239 mg (27%). Colorless oil. Cis/trans mixture. ^{1}H NMR (200 MHz): δ = 7.95 (broad s, 2H, NH), 4.32 (dt, J = 6.6, 3.0, 1H, H-1, *cis*), 4.00 (dt, J = 6.6, 2.6, 1H, H-1, *trans*), 3.85 (s, 6H, OMe), 1.64–0.80 (m, 18H, H-2, H-3a or H-3b, $CH_2CH_2CH_3$), 0.72–0.53 (m, 2 H-3b or H-3a). ^{13}C NMR (50 MHz): δ = 150.6 (o, *cis*- and *trans*-C = O), 61.9 and 60.9 (+, C-1), 54.1 and 54.0 (+, OMe), 32.8 and 29.2 (−, CH$_2$C-1), 22.4 and 21.5 (−, CH$_2$C-2), 18.1 and 16.3 (+, C-2), 13.8 and 13.7 (+, C*Me*), 11.7 and 11.0 (−, C-3). IR (NaCl): $\tilde{\nu}$ = 3261, 2962, 2957, 2932, 2874, 1758, 1467, 1428, 1381, 1245, 1174.

Methyl *N*-methyl-*N*-(2-propylcyclopropyloxysulfonyl)carbamate (9a). Also from **7a** (381 mg, 3.81 mmol) to give 72 mg (8%). Colorless oil. Cis/trans mixture. ^{1}H NMR (200 MHz): δ = 4.23 (dt, J = 6.6, 3.0, 1H, H-1, *cis*), 3.91 (dt, J = 6.4, 2.4, 1H, H-1, *trans*), 3.87 (s, 6H, OMe), 3.36 (s, 6H, NMe), 1.60–0.84 (m, 18H, H-2, H-3a or H-3b, $CH_2CH_2CH_3$), 0.65–0.53 (m, 2H, H-3b or H-3a).^{13}C NMR (50 MHz): δ = 152.8 and 152.7 (o, C = O), 61.3 and 60.1 (+, C-1), 54.6 and 54.5 (+, OMe), 35.8 and 35.7 (+, NMe), 32.9 and 29.2 (−, CH$_2$C-1), 22.4 and 21.5 (−, CH$_2$Me), 18.1 and 16.3 (+, C-2), 13.8 and 13.7 (+, C*Me*), 11.6 and 10.8 (−, C-3). IR (NaCl): $\tilde{\nu}$ = 3008, 2961, 2957, 2933, 2874, 1746, 1447, 1398, 1293, 1180.

Analogously were prepared:

Methyl *N*-(2-benzylcyclopropyloxysulfonyl)carbamate (8b). From **7b** (523 mg, 3.53 mmol) to give 405 mg (42%). Colorless oil. Cis/trans mixture.^{1}H NMR (400 MHz): δ = 7.35–7.19 (m, 10H, Ph), 4.41 (dt, J = 6.7, 3.2, 1H, H-1, *cis*), 4.09 (m, 1 H, H-1, *trans*), 3.84 (s, 3H, OMe, *cis*), 3.79 (s, 3H, OMe, *trans*), 2.95 (dd, J = 15.0, 6.8, 1H, AB system, PhC*H, cis*), 2.71 (dd, J = 15.0, 7.8, 1H, AB system, PhC*H, cis*), 2.64 (dd, J = 14.9, 7.2, 1H, AB system, PhC*H, trans*), 2.58 (dd, J = 14.9, 7.6, 1H, AB system, PhC*H, trans*), 1.66–1.54 (m, 1H, H-2, *trans*), 1.40–1.20 (m, 2H, H-2 cis, H-3a or H-3b *trans*), 1.07 (dt, J = 9.5, 6.7, 1H, H-3a or H-3b, *cis*), 0.90 (dt, J = 7.3, 3.2, 1H, H-3b or H-3a, *cis*), 0.80

("q", $J = 6.9$, 1H, H-3b or H-3a, *trans*), δ_{NH} not found.^{13}C NMR (50 MHz, *cis*): $\delta = 151.0$ (o, C = O), 140.5 (o, C-Ar), 128.5, 128.3, 126.2 (+, CH-Ar), 60.4 (+, C-1), 54.1 (+, OMe), 33.0 (−, *C*H_2Ph), 17.5 (+, C-2), 11.5 (−, C-3). ^{13}C NMR (50 MHz, *trans*): $\delta = 150.7$ (o, C=O), 139.4 (o, C-Ar), 128.6, 128.4, 126.6 (+, CH-Ar), 61.1 (+, C-1), 54.0 (+, OMe), 36.3 (−, *C*H_2Ph), 19.4 (+, C-2), 11.7 (−, C-3). IR (NaCl): $\tilde{\nu} = 3254$, 3029, 2961, 1761, 1604, 1456, 1383, 1244, 1173, 897. HRMS (ESI): *m/z* calcd. for $C_{12}H_{15}NO_5S$ ([M—H]$^-$) 284.0593, found 284.0595.

Methyl *N*-(2-benzylcyclopropyloxysulfonyl)-*N*-methylcarbamate (9b). Also from **7b** (523 mg, 3.53 mmol) to give 51 mg (5%). Colorless oil. Cis/trans mixture ^{1}H (400 MHz): $\delta = 7.36$–7.15 (m, 10H, Ph), 4.33 (dt, $J = 6.6$, 3.2, 1H, H-1, *cis*), 4.03 (dt, $J = 6.6$, 2.6, 1H, H-1, *trans*), 3.88 (s, 3H, OMe, *cis*), 3.85 (s, 3H, OMe, *trans*), 3.38 (s, 3H, NMe, *cis*), 3.23 (s, 3H, NMe, *trans*), 2.92 (dd, $J = 15.0$, 7.0, 1H, AB system, PhC*H, cis*), 2.72 (dd, $J = 15.0$, 7.6, 1H, AB system, PhC*H, cis*), 2.68 (dd, $J = 14.8$, 6.9, 1H, PhC*H, trans*), 2.57 (dd, $J = 14.8$, 7.3, 1H, PhC*H, trans*), 1.68–0.72 (m, 6H, H-2, H-3a,b). ^{13}C NMR (50 MHz, *cis*): $\delta = 152.8$ (o, C=O), 140.4 (o, C-Ar), 128.5, 128.3, 126.3 (+, CH-Ar), 59.8 (+, C-1), 54.6 (+, OMe), 35.8 (+, NMe), 33.0 (−, *C*H_2Ph), 17.5 (+, C-2), 11.3 (−, C-3). ^{13}C NMR (50 MHz, *trans*): $\delta = 152.7$ (o, C=O), 139.1 (o, C-Ar), 128.6, 128.4, 126.5 (+, CH-Ar), 60.7 (+, C-1), 54.5 (+, OMe), 36.3 (−, *C*H_2Ph), 35.6 (+, NMe), 18.9 (+, C-2), 11.7 (−, C-3). IR (NaCl): $\tilde{\nu} = 3029$, 2969, 1744, 1604, 1497, 1447, 1399, 1294, 1178. HRMS (ESI): *m/z* calcd. for $C_{13}H_{17}NO_5S$ ([M + Na]$^+$) 322.0725, found 322.0721.

Methyl *N*-[2-(1-phenylethyl)cyclopropyloxysulfonyl]carbamate (8c). From *cis*-**7c** (175 mg, 1.08 mmol) to give 240 mg (74%). Colorless oil. Mixture of two diastereomers, one of which could be fully characterized. ^{1}H NMR (200 MHz): $\delta = 7.60$ (broad s, 1H, NH), 7.36–7.17 (m, 5H, Ph), 4.45 (dt, $J = 6.6$, 3.2, 1H, H-1), 3.85 (s, 3H, OMe), 2.57 (dq, $J = 10.5$, 7.0, 1H, H-4), 1.40 (d, $J = 7.0$, 3H, CMe), 1.32–1.14 (m, 1H, H-2), 0.94 (dt, $J = 9.5$, 6.7, 1H, H-3a), 0.78 (dt, $J = 7.5$, 3.2, 1H, H-3b). ^{13}C NMR (50 MHz): $\delta = 151.0$ (o, C=O), 146.0 (o, C-Ar), 128.5, 126.9, 126.3 (+, CH-Ar), 60.9 (+, C-1), 54.1 (+, OMe), 38.2 (−, *C*H_2Ph), 23.1 and 22.2 (+, C-2 and C*C*H_3), 11.3 (−, C-3). HRMS (ESI): *m/z* calcd. for $C_{12}H_{15}NO_5S$ ([M-H]$^-$) 298.0749, found 298.0750.

Methyl *N*-methyl- *N*-[2-(1-phenylethyl)cyclopropyloxysulfonyl]-*N*-methylcarbamate (9c). Also from **7c** (175 mg, 1.08 mmol) to give 12 mg (5%). Colorless oil. Mixture of two diastereomers, one of which could be fully characterized. ^{1}H NMR (200 MHz): $\delta = 7.37$–7.17 (m, 5H, Ph), 4.37 (dt, $J = 6.4$, 3.2, 1H, H-1), 3.91 (s, 3H, OMe), 3.39 (s, 3H, NMe), 2.55 (dq, $J = 10.2$, 6.9, 1H, PhC*H*), 1.40 (d, $J = 6.9$, 3H, CMe), 1.33–1.11 (m, 1H, H-2), 0.90 (ddd, $J = 9.6$, 7.3, 6.4, 1H, H-3a), 0.70 (dt, $J = 7.3$, 3.2, 1H, H-3b). ^{13}C NMR (50 MHz): $\delta = 152.8$ (o, C=O), 145.9 (o, C-Ar), 128.5, 126.9, 126.4 (+, CH-Ar), 60.3 (+, C-1), 54.6 (+, OMe), 35.8 (+, NMe), 38.3 (−, *C*H_2Ph), 23.2 and 22.3 (+, C-2 and C*C*H_3), 11.1 (−, C-3). HRMS (ESI): *m/z* calcd. for $C_{12}H_{15}NO_5S$ ([M + Na]$^+$) 336.0882, found 336.083.

Reaction of Thioacetal 13 with Burgess Reagent 2

Thioacetal **13** (170 mg, 0.81 mmol) and **2** (192.5 mg, 0.81 mmol) were reacted as reported above for the formation of **8a**, **9a**. Column chromatography (silica) gave 80 mg (47%) of **13** and 26 mg (16%) of **14**.[20] Acetophenone was detected in the H NMR spectrum ($\delta_{Me} = 2.61$ in $CDCl_3$) and by addition of a weighed amount of authentic material determined to be formed in 1.2% yield.

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