



Organic chemistry on surfaces: Direct cyclopropanation by dihalocarbene addition to vinyl terminated self-assembled monolayers (SAMs)

Malgorzata Adamkiewicz, David O'Hagan* and Georg Hähner*

Full Research Paper

Open Access

Address:

EaStCHEM School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

Email:

David O'Hagan* - do1@st-andrews.ac.uk; Georg Hähner* - gh23@st-andrews.ac.uk

* Corresponding author

Keywords:

difluoro-; dichloro-; dibromomethylenecyclopropanes; dihalocarbenes; self-assembled monolayers; surface coating

Beilstein J. Org. Chem. **2014**, *10*, 2897–2902.

doi:10.3762/bjoc.10.307

Received: 11 July 2014

Accepted: 11 November 2014

Published: 05 December 2014

Associate Editor: J. A. Porco Jr.

© 2014 Adamkiewicz et al; licensee Beilstein-Institut.

License and terms: see end of document.

Abstract

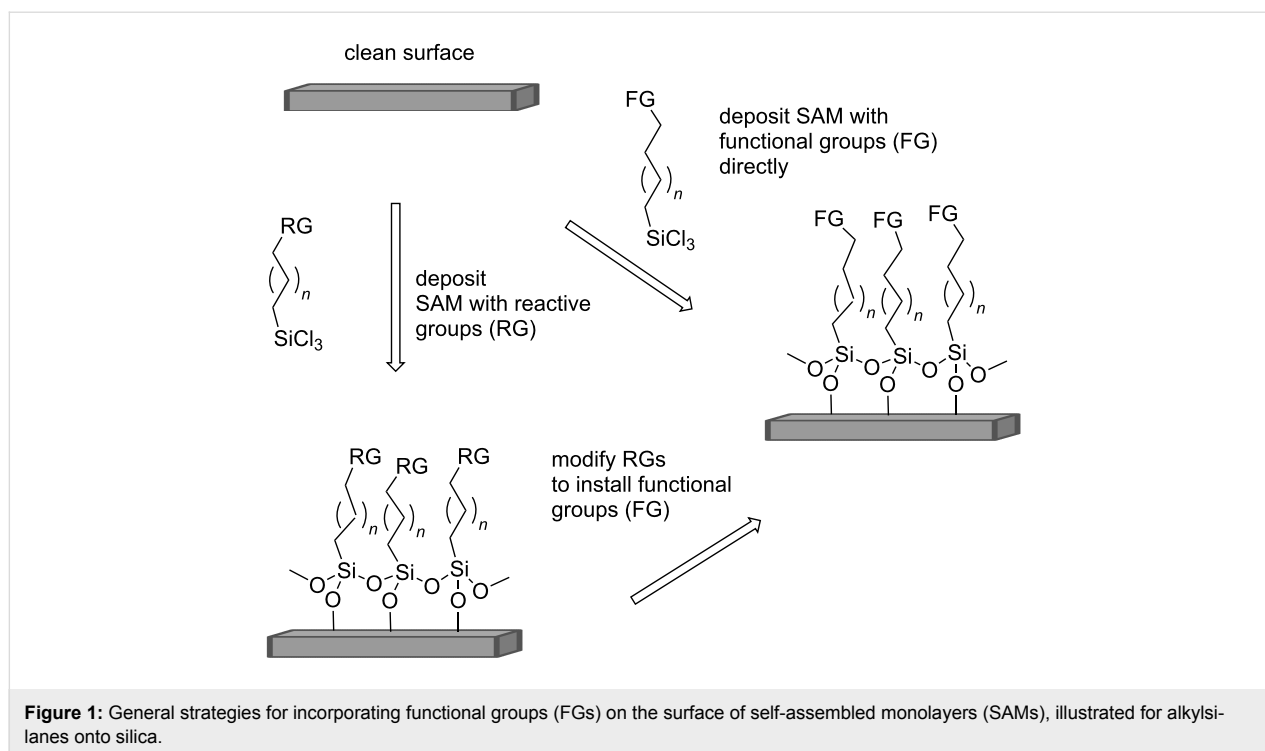
C11-Vinyl-terminated self-assembled monolayers (SAMs) on silica surfaces are successfully modified in C–C bond forming reactions with dihalocarbenes to generate SAMs, terminated with dihalo- (fluoro, chloro, bromo) cyclopropane motifs with about 30% surface coverage.

Introduction

Self-assembled monolayers (SAMs) are increasingly being used as a means of surface modification to alter properties in a tuneable manner [1-3]. The major classes of SAMs are those with adsorbed long chain alkyl thiols on gold surfaces/nanoparticles [4,5], or long chain alkylsilanes on silica surfaces [6,7]. Two general approaches are taken to achieve surface modification as illustrated in Figure 1. The first involves incorporating pre-functionalised alkylsilanes/alkylthiols carrying functional groups (FG) to generate the SAM directly, whereas the second approach involves chemical modification of a pre-assembled monolayer carrying reactive groups (RG), as a means to introduce the SAM carrying the FGs [8]. Both approaches present challenges. In the former the desired functionality (FG) requires to be robust and orthogonal in reactivity to the chemistry

involved in securing the substrate to the organic film (e.g., FG-Alkyl-SiCl₃ and silicon substrate). In the latter chemical modification of the reactive groups of the pre-coated SAM has to be efficient enough such that a reasonable conversion can be obtained, with chemical specificity and lack of surface degradation. In this respect 'click' reactions have become attractive including azide-alkyne cycloadditions [9,10], Diels-Alder reactions [11,12], maleimide-thiol reactions [13], thiol-ene additions [14], and imine/oxime conjugations [15]. In this article we demonstrate that dihalocarbenes can be used to generate dihalocyclopropanes on olefin terminated SAMs.

We recently reported the formation of high quality vinyl-terminated SAMs generated from the vapour phase by adsorption of



octadecyltrichlorosilanes onto silicon wafers [16]. With access to these SAMs it became an objective to explore functional group modification of the vinyl double bond. Carbon–carbon bond formation of vinyl-terminated SAMs has been demonstrated, e.g., through surface modification of radicals generated by C–O bond thermolysis [17] and in a more controlled sense via olefin cross metathesis/enyne metathesis [18] of mixed vinyl and acetylenyl-terminated SAMs followed by Diels–Alder modifications of the resultant dienes [19]. We are not aware however of straightforward carbene additions having been explored with olefin-terminated SAMs. The potential for product cyclopropanes offered a modification of limited steric impact, but if suitably substituted may be used to tune surface properties. Therefore dihalocyclopropanes emerged as an attractive controlled modification particularly as the precursor dihalocarbenes are relatively easily generated [20]. In this context we report dihalocyclopropanation of pre-assembled vinyl-terminated SAMs. Three dihalocarbene modifications were explored involving dibromo- ($:\text{CBr}_2$), dichloro- ($:\text{CCl}_2$) and difluoro- ($:\text{CF}_2$) carbenes [21–23]. The resultant SAMs were analysed by X-ray photoelectron spectroscopy (XPS), contact angle goniometry, ellipsometry, and atomic force microscopy.

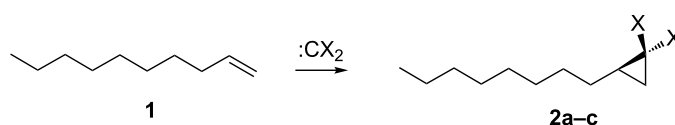
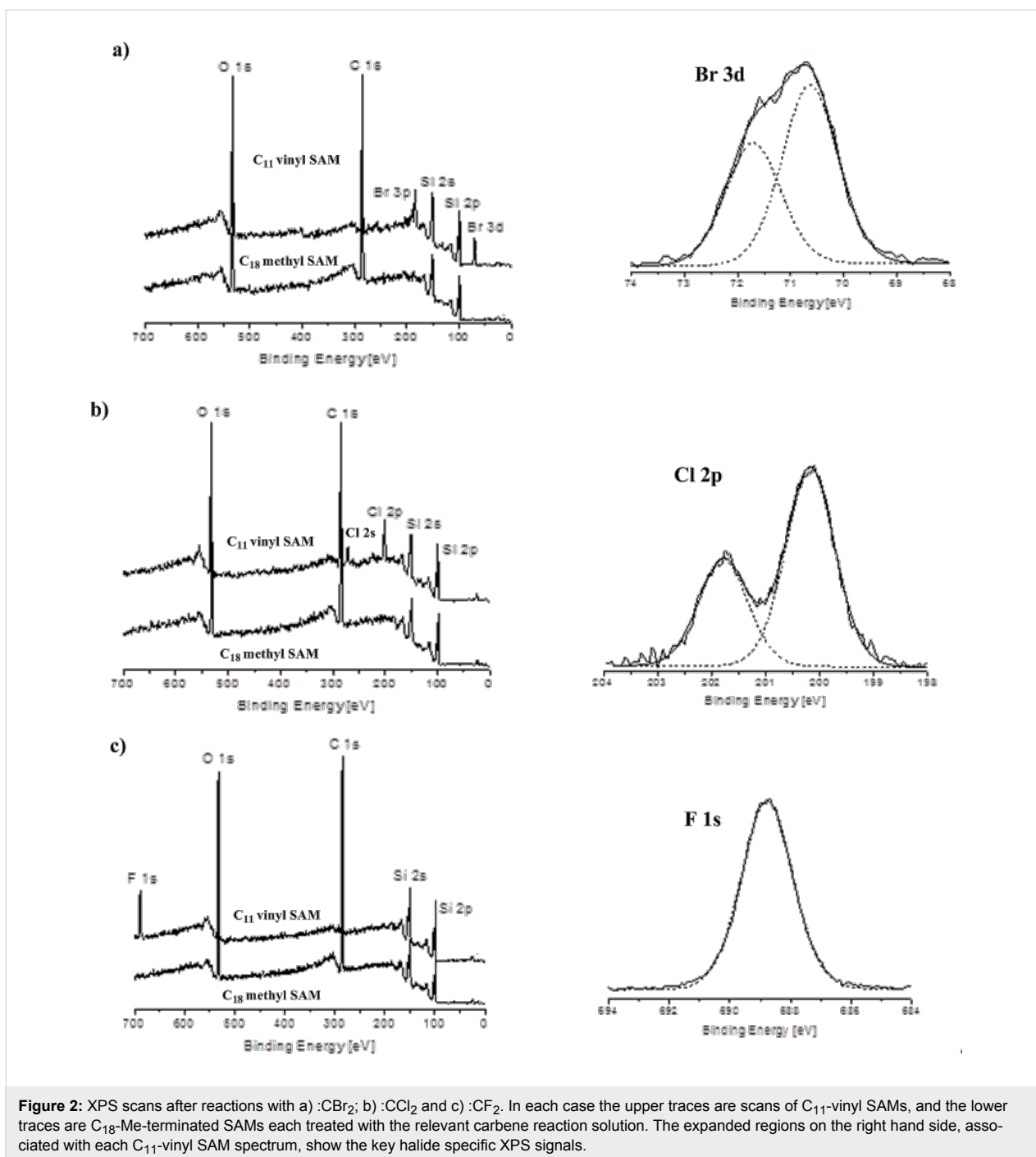
Results and Discussion

After exposure to carbenes the vinyl-terminated SAMs were characterised by XPS, contact angle measurements and ellipsometry (see Supporting Information File 1). With XPS elements such as silicon, carbon and oxygen were expected in

all cases [16]. In each case control reactions were also carried out on the C_{18} -methyl (Me)-terminated SAMs, to ensure that only the vinyl group was responsible for surface reactivity. The resultant XPS analyses are shown for the vinyl-terminated SAMs for each carbene in Figure 2, and directly underneath, the lower traces illustrate the corresponding analyses after exposure of the carbene solutions to the C_{18} -Me-terminated SAMs.

Figure 2a represents a surface after chemical modification with $:\text{CBr}_2$ generated from CHBr_3 . New peaks appeared at binding energies of 71 and 182 eV in all of the samples. These were assigned to Br 3d and Br 3p signals, respectively [24,25]. Figure 2b shows the results obtained from SAMs after modification with $:\text{CCl}_2$ generated from CHCl_3 . New signals at binding energies of 201 and 270 eV were detected. These were assigned to Cl 2p and Cl 2s [26]. Finally Figure 2c represents the surface after chemical modification with $:\text{CF}_2$ generated from TMSCF_3 . A new signal at binding energy of 688.7 eV was detected and assigned to F 1s, consistent with a CF_2 group present on the surface [27].

It was anticipated that *gem*-dibromo-, *gem*-dichloro- and *gem*-difluorocyclopropane-terminated SAMs will be formed, following the usual transformations of these carbenes with double bonds. To add further support to this expectation, model reactions were carried out under each of the reaction conditions with dec-1-ene (**1**, Scheme 1). All of the cyclopropane products **2a–c** were obtained cleanly and in moderate yields (see



a) X = Br, 54%; b) X = Cl, 49%; c) X = F, 48%

Scheme 1: Model reactions of dec-1-ene (**1**) with dihalocarbenes in the liquid phase. a) and b) NaOH, BTEAC, CHX_3 , DCM, 8 h, 25 °C; c) TMSCF_3 , THF, NaI, 3 h, 65 °C.

Supporting Information File 1). The results of the model reactions demonstrate that formation of the dihalocyclopropane rings is a relatively clean process for this long chain terminal vinyl substrate. The absence of any side products gives confidence that only dihalocyclopropanes will be formed in the surface reactions.

Turning to the C₁₁-vinyl-terminated SAMs products. In each case the presence of *gem*-dihalogyclopropane groups on the surface is supported by the ratios of the C 1s signals to the Br 3d, Cl 2p or F 1s signal, respectively. The theoretical and experimental ratios between the carbon and halogen XPS signals are summarised in Table 1. In all cases the ratios are consistent with a modification coverage of ~30%, with a slightly lower conversion rate in case of F, which might be due to its higher electronegativity and an associated higher repulsion between the terminal groups after cyclopropanation. Conversion rates were determined by correcting the experimental C3/(C1 + C2) ratios from Table 1 with a factor of $d/(\lambda(1 - \exp(-d/\lambda)))$, where d is the film thickness (determined with ellipsometry) and λ the mean free path of the electrons. This accounts for the partial attenuation of the C3 XPS carbon signal. The water contact angles (CAs) of Br, Cl and F carbene treated surfaces were recorded and the CA values obtained of 80°, 85° and 104°, respectively, are in good agreement with the literature [28–30]. Notably the fluorinated SAM has the largest contact angle as expected, however, the increase and the final contact angle values are clearly lower than that for a pure CF₃ terminated film (~118–120°) [31], but this is not surprising given that the halogen functional group density is lower.

Finally AFM images were recorded for the three dihalocyclopropane modified surfaces and they are shown in Figure 3a–c. In all cases the images are smooth and defect free. There was no excess of material observed from reagents after washing, and in each case the RMS surface roughness values did not exceeded 150 pm. It is clear that there is no detectable change observed in

Table 1: Assignment of the C 1s XPS signals after treatment of C₁₁-vinyl SAMs with the respective dihalocarbene. Theoretical and experimental ratios of the Br 3d to C 1s, Cl 2p to C 1s and F 1s to C 1s XPS signals of modified C₁₁-vinyl SAMs.

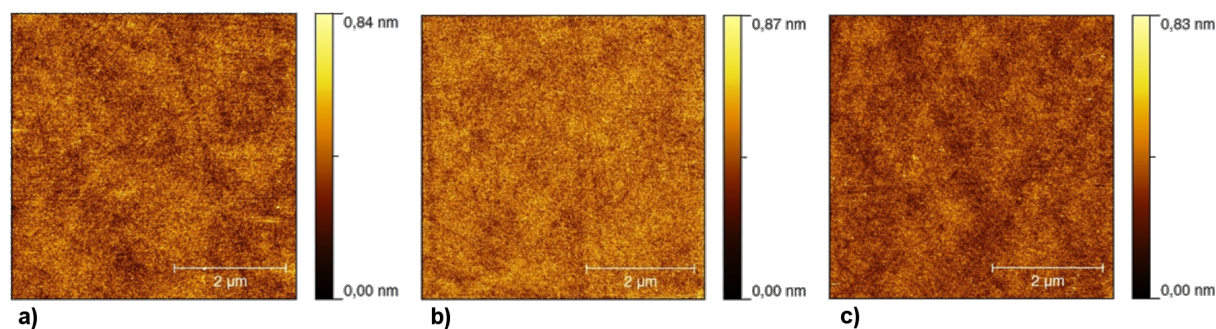
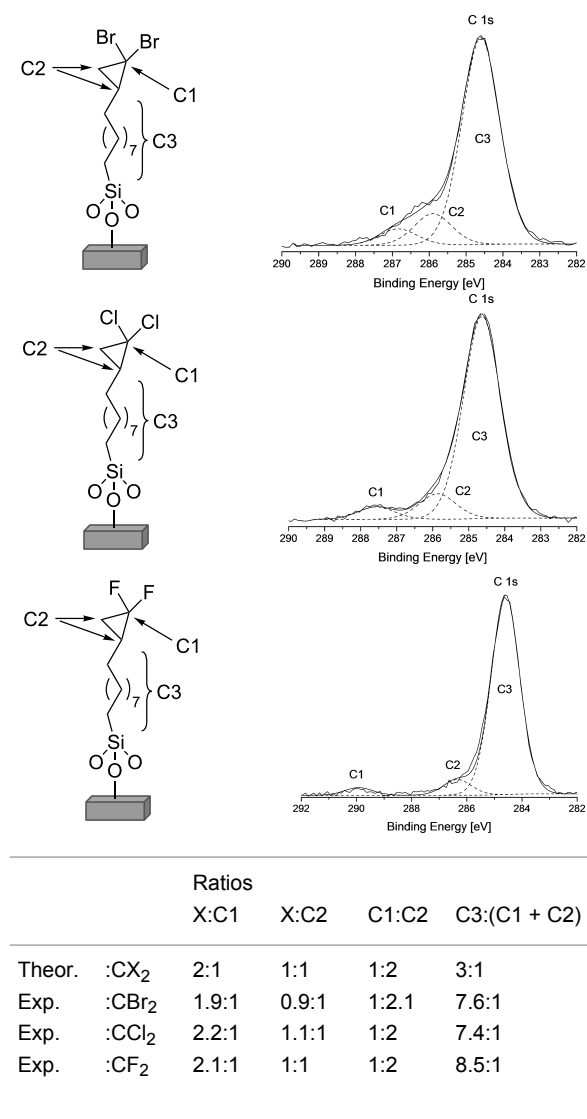


Figure 3: AFM images of 5 μm × 5 μm area of C₁₁-vinyl SAMs modified with a) :CBr₂ carbene, RMS 93 pm; b) :CCl₂ carbene, RMS 101 pm; c) TMSCF₃, RMS 79 pm.

the film after each modification, and that the films are of good integrity.

An alternative approach, also illustrated in Figure 1 is to prepare SAMs using pure samples of pre-halogenated cyclopropyl chains, with deposition directly onto the surface. This presents the obvious challenge of obtaining highly ordered films after direct deposition. The current approach establishes films of good integrity, which then become chemically modified. There is good evidence that this is less straightforward with functionalised surfactants [32].

Conclusion

In summary we have been able to demonstrate that vinyl-terminated SAMs can be chemically modified by a range of dihalocarbenes to generate surfaces carrying the corresponding dihalocyclopropane motifs. The reactions demonstrate that these organic chemical transformations, which have been relatively widely used in solution reactions of olefins, can be extended to surface reactions of SAMs. This opens up prospects too of modifying surfaces in this manner with carbenes carrying more elaborate functional groups, and thus a more dramatic change to the surface properties.

Experimental

Bromoform (CHBr_3), chloroform (CHCl_3) and the Ruppert–Prakash reagent ($\text{CF}_3\text{Si}(\text{CH}_3)_2$) [33,34] were used as the carbene precursors for surface modification, with the resultant carbenes generated in solution. For dibromo- and dichloro-carbene generation a solution of NaOH with CHBr_3 or CHCl_3 was stirred with a solution of benzyltriethylammonium chloride (BTEAC, 0.1 mmol) in dichloromethane for 10 min at 0 °C. Pre-coated silicon wafers (1 cm × 1.5 cm) with C_{11} -vinyl-terminated SAMs, were immersed in the reaction mixture and the liquids were stirred at room temperature for fixed periods of time (see Supporting Information File 1). SAMs on silicon substrates form stable films [6,7], however, they can be vulnerable to chemical degradation particularly in aqueous base [28,35,36]. For this reason the NaOH concentration and reaction time required to be optimised. The reaction temperature

was kept at 25 °C and the phase-transfer catalyst, benzyltriethylammonium chloride (BTEAC) was chosen to generate the $:\text{CX}_2$ carbenes, and minimise exposure of the wafers to the base.

The Ruppert–Prakash reagent (TMSCF_3) was used to prepare the *gem*-difluorocyclopropane-terminated SAMs by generating difluorocarbene, following the procedure of Wang et al. [22] for small molecule transformations. This involved stirring a solution of NaI (0.2 equiv) and TMSCF_3 in THF (2 mL), and then immersing the silicon wafers (1 cm × 1.5 cm) into the reaction mixture at 65 °C for a fixed period of time (see Supporting Information File 1). The experimental set-up for the surface modification with the three different carbenes is shown in Figure 4. Details of the surface analytical techniques used are given in the Supporting Information File 1.

Supporting Information

Supporting Information File 1

Synthesis protocols and additional surface analysis data.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-10-307-S1.pdf>]

Acknowledgements

We thank the Scottish Funding Council for a SPIRIT Studentship (MA) and DO'H thanks the ERC for an Advanced Investigator Grant. Some of the X-ray photoelectron spectra were obtained at the National EPSRC XPS User 's Service (NEXUS) at Newcastle University, UK.

References

- Herzer, N.; Haensch, C.; Hoepfner, S.; Schubert, U. S. *Langmuir* **2010**, *26*, 8358–8365. doi:10.1021/la9047837
- Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103–1170. doi:10.1021/cr0300789
- Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554. doi:10.1021/cr9502357
- Häkkinen, H. *Nat. Chem.* **2012**, *4*, 443–455. doi:10.1038/nchem.1352

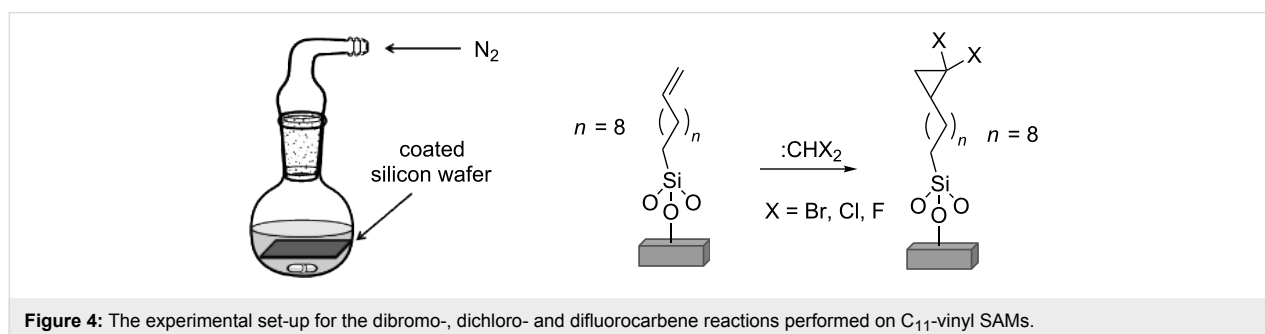


Figure 4: The experimental set-up for the dibromo-, dichloro- and difluorocarbene reactions performed on C_{11} -vinyl SAMs.

5. Vericat, C.; Vela, M. E.; Benitez, G.; Carro, P.; Salvarezza, R. C. *Chem. Soc. Rev.* **2010**, *39*, 1805–1834. doi:10.1039/b907301a
6. Haensch, C.; Hoepfner, S.; Schubert, U. S. *Chem. Soc. Rev.* **2010**, *39*, 2323–2334. doi:10.1039/b920491a
7. Onclin, S.; Ravoo, B. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **2005**, *44*, 6282–6304. doi:10.1002/anie.200500633
8. Nicosia, C.; Huskens, J. *Mater. Horiz.* **2014**, *1*, 32–45. doi:10.1039/c3mh00046j
See for a recent excellent overview see.
9. Orski, S. V.; Poloukhine, A. A.; Arumugam, S.; Mao, L.; Popik, V. V.; Locklin, J. *J. Am. Chem. Soc.* **2010**, *132*, 11024–11026. doi:10.1021/ja105066t
10. Collman, J. P.; Devaraj, N. K.; Chidsey, C. E. D. *Langmuir* **2004**, *20*, 1051–1053. doi:10.1021/la0362977
11. Arumugam, S.; Popik, V. V. *J. Am. Chem. Soc.* **2011**, *133*, 15730–15736. doi:10.1021/ja205652m
12. Yousaf, M. N.; Mrksich, M. *J. Am. Chem. Soc.* **1999**, *121*, 4286–4287. doi:10.1021/ja983529t
13. Houseman, B. T.; Gwalt, E. S.; Mrksich, M. *Langmuir* **2003**, *19*, 1522–1531. doi:10.1021/la0262304
14. Wendeln, C.; Rinnen, S.; Schulz, C.; Arlinghaus, H. F.; Ravoo, B. J. *Langmuir* **2010**, *26*, 15966–15971. doi:10.1021/la102966j
15. Rozkiewicz, D. I.; Kraan, Y.; Werten, M. W. T.; de Wolf, F. A.; Subramaniam, V.; Ravoo, B. J.; Reinhoudt, D. N. *Chem. – Eur. J.* **2006**, *12*, 6290–6297. doi:10.1002/chem.200501554
16. Adamkiewicz, M.; O'Hara, T.; O'Hagan, D.; Hähner, G. *Thin Solid Films* **2012**, *520*, 6719–6723. doi:10.1016/j.tsf.2012.07.054
17. Siegenthaler, K. O.; Schäfer, A.; Studer, A. *J. Am. Chem. Soc.* **2007**, *129*, 5826–5827. doi:10.1021/ja0686716
18. Dutta, S.; Perring, M.; Barrett, S.; Mitchell, M.; Kenis, P. J. A.; Bowden, N. B. *Langmuir* **2006**, *22*, 2146–2155. doi:10.1021/la0532196
19. Lee, J. K.; Shi, Y. S.; Lee, J. S.; Kim, Y.-G.; Jung, Y. H.; Oh, E.; Ko, S.-B.; Jung, H.-j.; Kang, P.-S.; Choi, I. S. *Langmuir* **2005**, *21*, 10311–10315. doi:10.1021/la051680s
20. Makosza, M. *Pure Appl. Chem.* **2000**, *72*, 1399–1403. doi:10.1351/pac200072071399
21. Ziyat, H.; Itto, M. Y. A.; Ali, M. A.; Riahi, A.; Karim, A.; Daran, J.-C. *ARKIVOC* **2006**, *xii*, 152–160. doi:10.3998/ark.5550190.0007.c18
22. Wang, F.; Luo, T.; Hu, J.; Wang, Y.; Krishnan, H. S.; Jog, P. V.; Ganesh, S. K.; Prakash, G. K. S.; Olah, G. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 7153–7157. doi:10.1002/anie.201101691
23. Juliá, S.; Ginebreda, A. *Synthesis* **1977**, 682–683. doi:10.1055/s-1977-24531
24. Balachander, N.; Sukenik, C. N. *Langmuir* **1990**, *6*, 1621–1627. doi:10.1021/la00101a001
25. Cohen, Y. S.; Vilan, A.; Ron, I.; Cahen, D. *J. Phys. Chem. C* **2009**, *113*, 6174–6181. doi:10.1021/jp9006125
26. Chen, J.-K.; Hsieh, C.-Y.; Huang, C.-F.; Li, P.-M.; Kuo, S.-W.; Chang, F.-C. *Macromolecules* **2008**, *41*, 8729–8736. doi:10.1021/ma801127m
27. Ohnishi, S.; Ishida, T.; Yaminsky, V. V.; Christenson, H. K. *Langmuir* **2000**, *16*, 2722–2730. doi:10.1021/la991167c
28. Wasserman, S. R.; Tao, Y. T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074–1087. doi:10.1021/la00088a035
29. Lo, M. K. F.; Gard, M. N.; Goldsmith, B. R.; Garcia-Garibay, M. A.; Monbouquette, H. G. *Langmuir* **2012**, *28*, 16156–16166. doi:10.1021/la302880v
30. Motomatsu, M.; Mizutani, W.; Nie, H.-Y.; Tokumoto, H. *Thin Solid Films* **1996**, *281–282*, 548–551. doi:10.1016/0040-6090(96)08721-4
31. Colorado, R., Jr.; Lee, T. R. *Langmuir* **2003**, *19*, 3288–3296. doi:10.1021/la0263763
32. Fritz, M. C.; Hähner, G.; Spencer, N. D.; Bürl, R.; Vasella, A. *Langmuir* **1996**, *12*, 6074–6082. doi:10.1021/la960623j
33. Prakash, G. K. S.; Yudin, A. *Chem. Rev.* **1997**, *97*, 757–786. doi:10.1021/cr9408991
34. Prakash, G. K. S.; Krishnamurti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393–395. doi:10.1021/ja00183a073
35. Ciampi, S.; Harper, J. B.; Gooding, J. J. *Chem. Soc. Rev.* **2010**, *39*, 2158–2183. doi:10.1039/b923890p
36. Calistri-Yeh, M.; Kramer, E. J.; Sharma, R.; Zhao, W.; Rafailovich, M. H.; Sokolov, J.; Brock, J. D. *Langmuir* **1996**, *12*, 2747–2755. doi:10.1021/la950518u

License and Terms

This is an Open Access article under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/2.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The license is subject to the *Beilstein Journal of Organic Chemistry* terms and conditions: (<http://www.beilstein-journals.org/bjoc>)

The definitive version of this article is the electronic one which can be found at: [doi:10.3762/bjoc.10.307](https://doi.org/10.3762/bjoc.10.307)