Pergamon

SCIENCE @ DIRECT®

Tetrahedron Letters 44 (2003) 8001–8003

TETRAHEDRON
LETTERS

Allylgallation of cyclopropenes. Crystal structure of a novel cyclopropylgallium compound prepared by allylgallation of hydroxy-bearing cyclopropene

Shuki Araki,[a,*] Takashi Tanaka,[a] Tsunehisa Hirashita[a] and Jun-ichiro Setsune[b]

[a] *Omohi College, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

[b] *Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan*

Received 22 July 2003; revised 22 August 2003; accepted 22 August 2003

Abstract—Allylgallation of cyclopropenes with allylgallium sesquibromide has been investigated; a novel cyclopropylgallium compound was isolated via allylgallation of hydroxy-bearing cyclopropene, and its structure was fully characterized by X-ray crystallography.

Contrary to the increasing importance of indium in organic synthesis,[1] gallium, a member of the same group 13 elements, has hitherto received relatively little attention.[2] Very recently, a convenient method for the preparation of allylgallium sesquibromide was disclosed, and it was shown that this organogallium compound is as reactive as the corresponding allylindium reagent for allylation of carbonyl compounds and terminal alkynes.[3] Unlike non-activated carbon–carbon double bonds, cyclopropene double bonds undergo smooth carbometallation reactions. We recently reported that allylindium sesquihalides react with cyclopropenes to give allylindation products regio- and stereoselectively depending on the substituents on cyclopropenes and, in favourable cases, cyclopropylindium products can be isolated.[4] We have investigated similar reactions with allylgallium sesquibromide and found that the allylgallation reactions proceed equally with high selectivity, but the structure of the resulting cyclopropylgallium product is distinct from the corresponding cyclopropylindium compound.

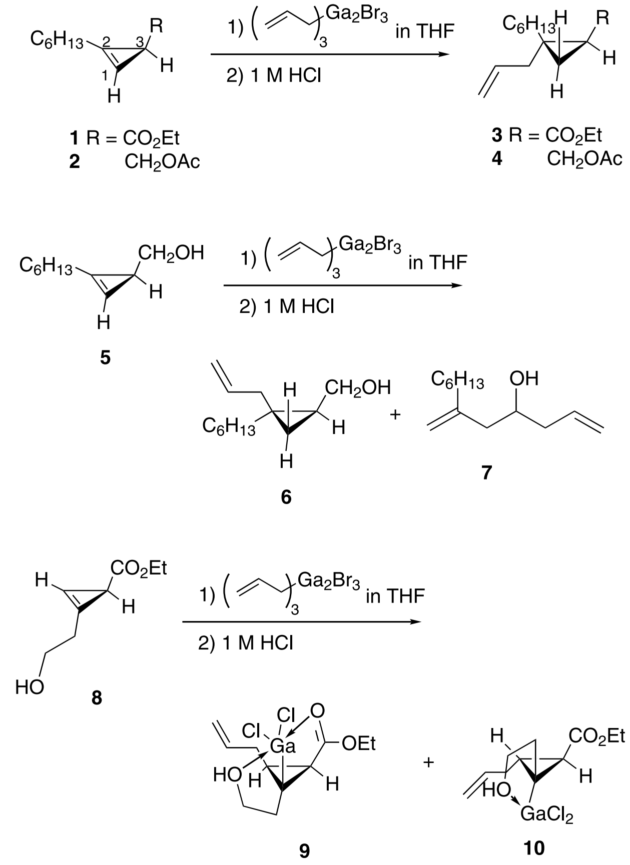
The reactions of cyclopropenes and allylgallium sesquibromide were carried out in THF. The results are summarized in Scheme 1. Cyclopropenes **1** and **2** gave good yields of the allylgallation products **3** and **4**, where complete regio- and stereoselectivity were attained. The allylgallium reagent added from the *trans*-face, avoiding the steric repulsion by the substituent at the C^3 carbon. 3-Hydroxymethylcyclopropene **5**, in turn, exerted *cis*-selectivity owing to the chelation with the hydroxyl group, though a considerable amount of the ring-opened product **7** was formed. The compound **7** is considered to be formed by the allylation of 3-hexyl-3-butenal, which is derived via the Ga(III)-catalysed isomerization of **5**. These features are similar to those of the allylindation of cyclopropenes with allylindium sesquihalides;[4] however, the stereoselectivity with the allylgallium reagent is higher than that with the allylindium reagent (Table 1).

The reaction of (2-hydroxyethyl)cyclopropene **8** gave two products **9** and **10**. The former product **9** was obtained as colorless crystals after recrystallization from a chloroform–hexane mixture, and its *cis*-allylgallated structure was unambiguously determined by X-ray crystallography. The latter compound **10** is unstable and, therefore, could not be purified completely. Nevertheless, the spectral data suggest that this compound is another cyclopropylgallium, a *trans*-allylgallation product. The structure of **10** was deduced by the fact that the protolysis of **10** furnished *trans*-allylcyclopropane **11**. From allylindation of **8**, cyclopropylindium **12** akin to **9** was isolated; however, the *trans*-allylindation product corresponding to **10** was not isolated owing to rapid hydrolysis during an aqueous work-up.[4]

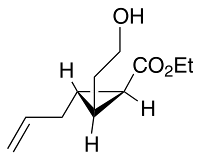
Keywords: allylation; carbometallation; cyclopropanes; cyclopropenes; gallium and compounds.

* Corresponding author.

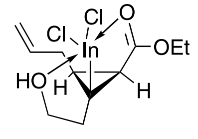
0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2003.08.121



Scheme 1. Allylgallation of cyclopropenes.



11



12

Cyclopropylgallium **9** crystallizes in the monoclinic $P2(1)/c$ with four molecules in the unit cell.[5] The compound is monomeric and both alcoholic (O(1)) and carbonyl oxygen atoms (O(2)) are coordinated to the gallium atom resulting in a coordination number of five. The geometry at the gallium center is best described as a distorted trigonal bipyramid, in which the O(1) and O(2) atoms represent the axial ligands and the C(1)GaCl(1)Cl(2) moiety serves as the trigonal plane (Fig. 1). The angle between the axial oxygens is 161.82(9)°. The axial–Ga–equatorial angles range from 80.69(10)° for O(2)–Ga–C(1) to 101.87(8)° for O(1)–Ga–Cl(2), and the equatorial angles from 109.15(4)° for Cl(1)–Ga–Cl(2) to 129.18(10)° for C(1)–Ga–Cl(2). The cyclopropyl C(1)–Ga bond distance is 1.944(3) Å. The carbonyl Ga–O(2) distance (2.355(2) Å) is considerably larger than the alcoholic Ga–O(1) distance (2.124(3) Å), whereas the difference in the two Cl–Ga bond distances (2.1847(9) Å and 2.1670(9) Å) is small. The alcoholic hydrogen is intermolecularly hydrogen bonded to the carbonyl oxygen. It is intriguing to compare the structure of **9** with the corresponding cyclopropylindium **12**. Compound **12** bears the same ligands as **9**, but adopts a chlorine-bridged dimeric structure in the crystalline state and the geometry at the indium centre is distorted octahedral with a coordination number of six.

We are now investigating how these structural differences between the cyclopropylgallium **9** and -indium compounds **12** reflect on their reaction behaviour.

Typical experimental procedure: Allylgallium sesquibromide was prepared[3a] by mixing gallium powder (0.11 g, 1.5 mmol), indium powder (9.0 mg, 0.075 mmol) and allyl bromide (0.20 mL, 2.3 mmol) in THF (2.0 mL) at 10°C for 2 h. Cyclopropene **8** (0.16 g, 1.0 mmol) was added and the mixture was stirred at room temperature for 24 h. The reaction was quenched with hydrochloric acid (1 M, 5.0 mL) and the products were extracted quickly with ether. The extracts were washed with brine and concentrated. Column chromatography (SiO_2, EtOAc–hexane gradient) gave **9** (90 mg, 27%) and **10** (126 mg, 37% yield).

Compound **9**. Colourless crystals; mp 123.5–125.5°C (from $CHCl_3$–hexane); IR (KBr): $\nu = 3445$, 2990, 2935, 1622, 1418, 1376, 1350, 1290, 1260, 1228, 1084, 1008, 924, 852 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$): δ 1.23–1.38 (m, 1H, CH_2), 1.34 (t, $J = 7.2$ Hz, 3H, Me), 1.57 (q, $J = 7.8$ Hz, 1H, CH_2), 2.08–2.47 (m, 3H, CH_2 and CH), 2.22 (d, $J = 8.6$ Hz, 1H, CH), 3.42 (br s, 1H, OH), 3.71 (m, 1H, CH_2), 4.14 (m, 1H, CH_2), 4.38 (q, $J = 7.2$ Hz, 2H, CH_2), 5.03 (dd, $J = 10.4$, 1.8 Hz, 1H, CH), 5.10 (dd,

Table 1. Allylgallation and allylindation of cyclopropenes

Cyclopropene	Allylmetal	Conditions	Products			
			Cyclopropane (*cis*:*trans*)	Yield (%)	Others	Yield (%)
1	$(allyl)_3Ga_2Br_3$	reflux, 6 h	**3** (0:100)	57		
1	$(allyl)_3In_2I_3$	reflux, 3 h	**3** (26:74)	63		
2	$(allyl)_3Ga_2Br_3$	rt, 24 h	**4** (0:100)	55		
2	$(allyl)_3In_2I_3$	rt, 4 h	**4** (0:100)	66		
5	$(allyl)_3Ga_2Br_3$	rt, 2 h	**6** (100:0)	47	**7**	12
5	$(allyl)_3In_2I_3$	rt, 3 h	**6** (93:7)	95		
8	$(allyl)_3Ga_2Br_3$	rt, 24 h	**9** (100:0)	27	**10**	37
8	$(allyl)_3In_2I_3$	rt, 5 h	**12** (100:0)	36	**11**	13

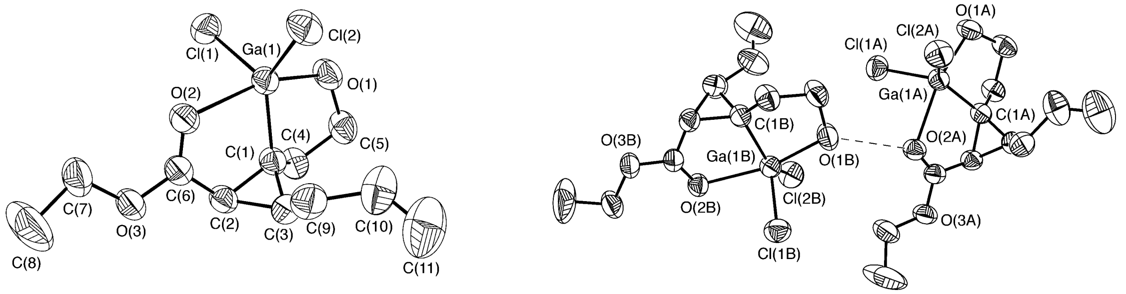


Figure 1. Molecular structure of **9**. Selected bond angles (°) and lengths (Å): C(1)–Ga–O(1) 82.05(11), C(1)–Ga–Cl(2) 129.18(10), O(1)–Ga–Cl(2) 101.87(8), C(1)–Ga–Cl(1) 121.09(9), O(1)–Ga–Cl(1) 94.82(8), Cl(2)–Ga–Cl(1) 109.15(4), C(1)–Ga–O(2) 80.69(10), O(1)–Ga–O(2) 161.82(9), Cl(2)–Ga–O(2) 93.47(6), Cl(1)–Ga–O(2) 89.21(6), C(1)–Ga 1.944(3), Cl(1)–Ga 2.1847(9), Cl(2)–Ga 2.1670(9), Ga–O(1) 2.124(3), Ga–O(2) 2.355(2), O(1)–O(2)* 2.878(3).

$J=17.2$, 1.8 Hz, 1H, CH), 5.83 (ddt, $J=17.2$, 10.4, 6.6 Hz, 1H, CH); ^{13}C NMR (50 MHz; $CDCl_3$): δ 14.1, 26.2 (C-Ga), 27.2, 32.0, 35.1, 35.2, 62.5, 64.6, 115.6, 136.4, 180.9; MS (SIMS): $m/z=871$ (7%), 869 (13, M_3H^+-4Cl), 867 (12), 605 (9), 604 (5), 603 (12, M_2H^+-2Cl), 601 (8), 571 (7), 570 (12), 569 (56), 567 (89, M_2H^+-3Cl), 565 (51), 305 (24), 304 (12), 302 (14), 301 (100, M^+H-HCl). Anal. calcd for $C_{11}H_{17}Cl_2GaO_3$ (337.87): C, 39.10; H, 5.07. Found: C, 39.15; H, 5.10%.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 10640518) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1. (a) Cintas, P. *Synlett* **1995**, 1087; (b) Li, C.-J. *Tetrahedron* **1996**, *52*, 5643; (c) Marshall, J. A. *Chemtracts-Org. Chem.* **1997**, *10*, 481; (d) Coldhaam, I. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1343; (e) Li, C.-J.; Chan, T.-H. *Tetrahedron* **1999**, *55*, 11149; (f) Chauhan, K. K.; Frost, C. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3015; (g) Ranu, B. C. *Eur. J. Org. Chem.* **2000**, *55*, 2347; (h) Babu, G.; Perumal, P. T. *Aldrichim. Acta* **2000**, *33*, 16; (i) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163; (j) Podlech, J.; Maier, T. C. *Synthesis* **2003**, 633.
2. (a) Araki, S.; Ito, H.; Butsugan, Y. *Appl. Organomet. Chem.* **1988**, *2*, 475; (b) Han, Y.; Huang, Y.-Z. *Tetrahedron Lett.* **1994**, *35*, 9433; (c) Zhang, X.-L.; Han, Y.; Tao, W.-T.; Huang, Y.-Z. *J. Chem. Soc., Perkin Trans. 1* **1995**, 189; (d) Yamaguchi, M.; Sotokawa, T.; Hirama, M. *Chem. Commun.* **1997**, 743; (e) Usugi, S.-i.; Yorimitsu, H.; Oshima, K. *Tetrahedron Lett.* **2001**, *42*, 4535.
3. (a) Takai, K.; Ikawa, Y. *Org. Lett.* **2002**, *4*, 1727; (b) Takai, K.; Ikawa, Y.; Ishii, K.; Kumanda, M. *Chem. Lett.* **2002**, 172.
4. (a) Araki, S.; Nakano, H.; Subburaj, K.; Hirashita, T.; Shibutani, K.; Yamamura, H.; Kawai, M.; Butsugan, Y. *Tetrahedron Lett.* **1998**, *39*, 6327; (b) Araki, S.; Shiraki, F.; Tanaka, T.; Nakano, H.; Subburaj, K.; Hirashita, T.; Yamamura, H.; Kawai, K. *Chem. Eur. J.* **2001**, *7*, 2784.
5. Crystal data for **9**: $C_{11}H_{17}Cl_2GaO_3$, M = 337.87, monoclinic, space group $P2(1)/c$, $a=9.1288(10)$, $b=11.3392(13)$, $c=14.5356(16)$ Å, $\alpha=90$, $\beta=96.141(2)$, $\gamma=90°$, $V=1496.0(3)$ Å^3, $Z=4$, $D_{\text{calcd}}=1.500$ Mg/m^3, μ(Mo Kα) = 2.190 mm^{-1}, $T=294(2)$ K, crystal size 0.4×0.1×0.1 mm. A total of 2953 unique reflections ($R_{\text{int}}=0.0325$) were collected ($4.5<2\theta<54.1°$) and 203 parameters were refined after structure solution by direct methods (SHELXTL). $R_1=0.036$, $wR_2=0.099$ for 2411 reflections with $I>2\sigma(I)$ and $R_1=0.047$, $wR_2=0.107$ for all data. GOF on $F^2=1.100$. The methyl hydrogens (H8A, H8B, H8C) of the ester group and the terminal methylene hydrogens (H11A, H11B) of the vinyl group were included at standard positions (C–H = 0.96 and 0.93 Å, respectively), but not refined. The other 12 hydrogen atoms and all the non-hydrogen atoms were located in the difference Fourier maps and fully refined. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 213537. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).