Synthesis of compounds of the triallylmethane series based on reactions of triallylborane and derivatives of carbonic acid

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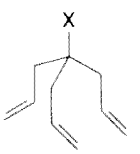
An original method was developed for the synthesis of functional derivatives of triallylmethane $(CH_2{=}CH{-}CH_2)_3C{-}X$ (X = OH, NH_2, or SCOPh) based on reactions of triallylborane with the corresponding derivatives of carbonic acid (ethylene carbonate, diethylcyanamide, and *O,S*-dimethyldithio carbonate) at 110—120 °C.

Key words: allylboronation, triallylborane, derivatives of carbonic acid, triallylmethane derivatives.

Triallylborane is a valuable compound in synthesis because of its ability to add to organic compounds with multiple bonds (allylboronation).[1] Deboronation of the products of addition of triallylborane to carbonyl compounds, their sulfur and nitrogen analogs, acids, esters, nitriles,[1] and aromatic nitrogen heterocycles[2] with the use of mono-, di-, and triethanolamines and an aqueous solution of alkali or sodium carbonate yields homoallyl alcohols, amines, thiols,[1] and α-mono- and α,α′-diallylated nitrogen heterocycles.[2]

Esters, organic acids,[3,4] and nitriles[5,6] undergo reductive diallylation under the action of triallylborane (20—120 °C) to form (after deboronation) diallylcarbinols and diallylmethylamines, respectively. Apparently, the reactions with acids and esters proceed through the addition of the boron-allyl fragment at the double C=O bond followed by β-elimination, which leads to repeat formation of the double bond and its allylboronation, for example, according to Scheme 1.

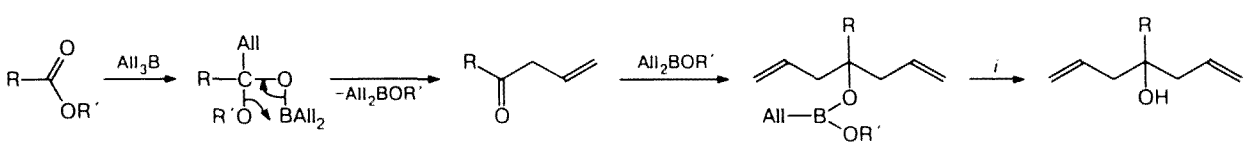
In this work, we studied reactions of triallylborane with derivatives of carbonic acid for the purpose of obtaining hydroxy (**1**), amino (**2**), and thiol (**3**) derivatives of triallylmethane, which are promising starting compounds in the synthesis of carbocyclic, heterocyclic, and cage compounds.



1: X = OH
2: X = NH_2
3: X = SH

Previously, triallylcarbinol **1** was prepared by reactions of ethyl chloroformate with allyl iodide and zinc (the yield was 40%)[7] or with allylmagnesium halides (yields were 66—68%)[8,9] and by reactions of allylzinc bromide (the yield was 51%)[10] or allylmagnesium bromide (the yield was 70%)[11] and diethyl carbonate. When allylmagnesium bromide was treated with CO_2, carbinol **1** formed in low yield (15%).[12] In addition, carbinol **1** was obtained by reactions of CO_2 with various organometallic complexes containing an allyl group as a ligand: All_4U (the yield was 90%),[13] All_4Zr,[14] and η^3-$AllCp_2Ti$ (yields were 30—50%).[15] Triallylcarbinol was obtained also by dehydrohalogenation of 4-hydroxy-4-(2-chloropropyl)hepta-1,6-diene[16] with PhNa (62%) or PhK (94%). It is interesting to note that the reaction of triallylborane with ethyl orthoformate followed by oxidation of the reaction product with alkaline H_2O_2 produced compound **1** in a yield of 51%.[17]

Scheme 1



All = C_3H_5
i. Deboronation

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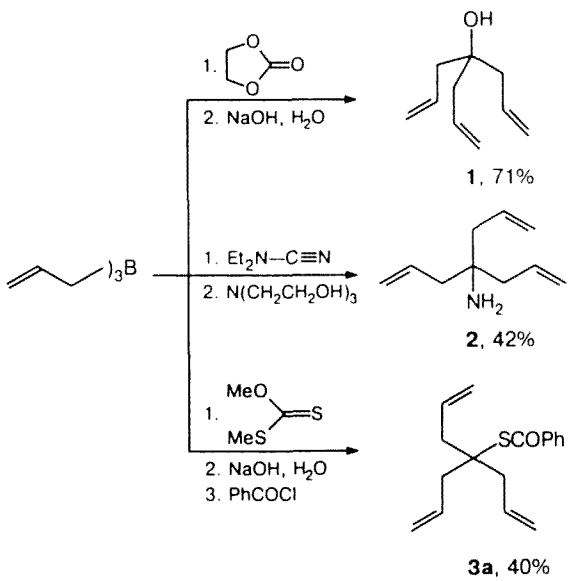
Triallylmethylamine **2** was obtained by reactions of allyl cyanide[18] or dimethyl *N*-tosylimino carbonate[19] with allylmagnesium bromide in yields of 46 and 48 %, respectively. Previously, thiol **3** and its derivatives were unknown.

We used commercial ethylene carbonate and diethylcyanamide and *O,S*-dimethyl dithiocarbonate, which is readily available from the corresponding xanthate,[20] as the starting compounds in the synthesis of carbinol **1**, amine **2**, and thiol **3** based on triallylborane (Scheme 2).

Scheme 2

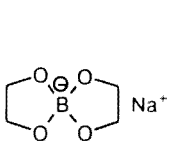


All reactions were carried out by adding the derivative of carbonic acid to 2—2.5 equivalents of triallylborane at 100—120 °C. The reactions were accompanied by substantial heat evolution. Then the reaction mixture was kept at 110—120 °C for 1—2 h.

When compound **1** was synthesized, standard decomposition of the reaction mixture with aqueous alkali was carried out. In this case, the organic layer was completely freed from the ethylene glycol that formed, which bonded to boron to form an *ate*-complex (**4**).

After distillation, the yield of compound **1** was 71%.

When amine **2** was prepared, the reaction mixture was treated with triethanolamine, and the amine that formed was refluxed *in vacuo* (11 Torr). Apparently, its moderate yield (42%) was a consequence of side processes, for example, dimerization of the monoallylboronation product to form a stable compound (**5**).



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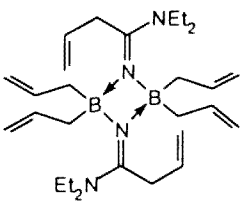

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Increasing the reaction time and treating the reaction mixture with an aqueous NaOH solution did not increase the yield of compound **2**.

Products of the reaction of triallylborane with *O,S*-dimethyl dithiocarbonate were deboronated with an aqueous NaOH solution. Then the reaction mixture was treated with benzoyl chloride with the aim of obtaining the benzoyl derivative of thiol **3a**. After distillation, the yield was 40%. In one experiment (without treatment with benzoyl chloride), we succeeded in isolating thiol **3** in a yield of 50%. However, we failed to reproduce this experiment because of the high tendency of thiol **3** to polymerize (apparently, intermolecular addition of the SH group at double bonds proceeds readily).

We failed to obtain triallylmethanethiol by the reaction of triallylborane with CS_2. This reaction does not proceed even at 135 °C.

We believe that reductive triallylation of dialkyl carbonates, cyanamides, and xanthates proceeds analogously to diallylation of acids and esters (as successive allylboronation and β-elimination). The probable mechanism of the reaction of triallylborane with dimethyl xanthate is presented in Scheme 3.

After the preparation of compounds **1**—**3a**, we decided to obtain triallylmethane, which is a parent compound of this series. For this purpose, we carried out the following transformations.

Scheme 3

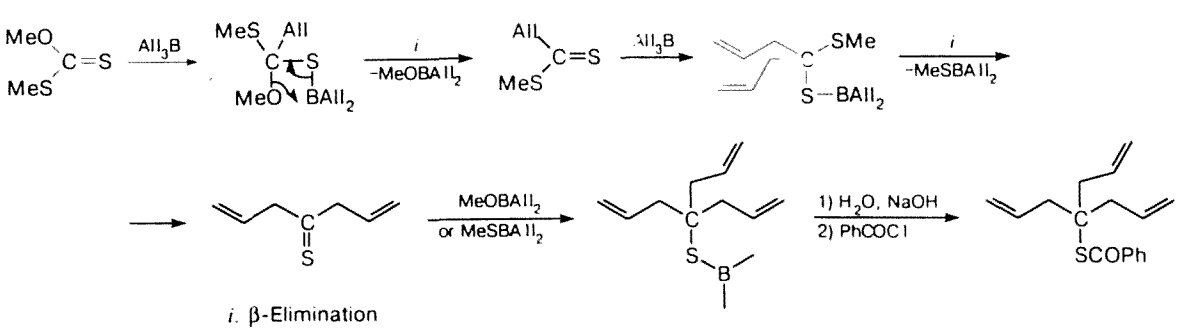
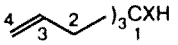
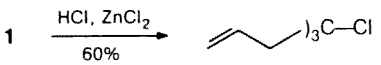


Table 1. Physicochemical data and the characteristics of the NMR spectra of compounds **1**, **2**, **3a**, and **6**



Compound	B.p./°C (*p*/Torr)	n_D^{20}	^{1}H NMR, δ (CDCl$_3$/TMS)				^{1}H NMR, δ (CDCl$_3$)			
			H—C(2)	H—C(3)	H—C(4)	H—X	C(1)	C(2)	C(3)	C(4)
1	85—88(19)	1.4705	2.25 d	5.77—5.97 m	5.15 m	2.09 d	72.80	43.32	133.4	118.19
2	67—68(11)	1.4723	2.13 d	5.75—5.96 m	5.14 m	1.09 br.s	53.17	44.29	133.71	118.09
3a	147—149(1)	1.5641	2.70 d	5.80—6.00 m	5.12 m		57.40	40.02	133.02	118.57
6	90—91(26)	1.4726	2.43 d	5.78—5.99 m	5.12 m		73.91	45.33	133.08	118.97

Triallylmethyl chloride **6** was synthesized by treating triallylcarbinol **1** with the Lucas reagent (concentrated HCl + $ZnCl_2$).[21] However, in attempting to reduce **6** to triallylmethane with the lithium salt of 9-butyl-9-ethyl-9-boratabicyclo[3.3.1]nonane,[22] we obtained a mixture of two compounds (in a ratio of ~1 : 1, GLC), which we failed to separate by distillation.



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Physicochemical properties and the data of the ^{1}H and ^{13}C NMR spectra of the compounds obtained are given in Table 1.

Experimental

All reactions were carried out under an atmosphere of dry argon. The NMR spectra were recorded on a Bruker AC-200P instrument. The IR spectrum was obtained on a Perkin-Elmer 577 instrument in a thin film (KBr). The mass spectrum (EI) was measured on a Kratos MS-30 instrument with direct introduction of the sample into the ion source. *O,S*-Dimethyl dithiocarbonate was prepared by the reaction of potassium methylxanthate[23] with dimethyl sulfate.[20]

4-Allylhepta-1,6-dien-4-ol (1). Molten (m.p. 38 °C) ethylene carbonate (6.18 g, 70.2 mmol) was added dropwise with stirring to triallylborane (18.81 g, 140.4 mmol) at 110 °C at such a rate that the temperature in the flask was kept at 110—120 °C. The reaction mixture was stirred at this temperature for 1 h. Then, ether (10 mL), methanol (1 mL), and a 5 *N* NaOH solution (39 mL, 194 mmol) were added successively to the reaction mixture with cooling (5—15 °C). The mixture was stirred at 20 °C for 1 h. Then the organic layer was separated. The aqueous layer was extracted with ether (3×10 mL). The combined organic etxracts were washed with distilled water and a saturated aqueous NaCl solution and dried with K_2CO_3. The ether was distilled off *in vacuo*. The residue was refluxed, and compound **1** was obtained in a yield of 7.81 g (70%), b.p. 85—88 °C (19 Torr), *cf.* Refs. 8, 11, 16, and 19.

4-Allyl-4-aminohepta-1,6-diene (2). Diethylcyanamide (2.78 g, 28.4 mmol) was added dropwise with stirring to triallylborane (7.89 g, 58.9 mmol) heated to 110—120 °C. The reaction mixture was kept at 110—120 °C for 1 h. Then the reaction mixture was cooled to 5 °C, and methanol (1 mL) was added. The mixture was stirred at 20 °C for 0.5 h. Then the reaction mixture was placed in an apparatus for distillation *in vacuo*. Triethanolamine (11.2 mL, 85.1 mmol) was added with shaking, and the mixture was heated to 100 °C for 0.5 h. Then product **2** was distilled by heating *in vacuo* (11 Torr), b.p. 51—67 °C (11 Torr). Repeated distillation gave amine **2** in a yield of 1.82 g (42%), b.p. 67—68 °C (11 Torr), *cf.* Ref. 19.

4-Allyl-4-benzoylthiohepta-1,6-diene (3a). *O,S*-dimethyl dithiocarbonate (1.99 g, 16.28 mmol) was added with stirring to triallylborane (5.49 g, 40.96 mmol) at 104—114 °C for 15 min. The reaction mixture was kept at 105—115 °C for 2 h. Then a 2 *N* NaOH solution (80 mL, 160 mmol) was added carefully at 5—15 °C (methanethiol and propylene were eliminated). The reaction mixture was stirred at ~20 °C for 1 h. Then PhCOCl (2 mL, 17.34 mmol) was added, and the mixture was stirred for 1 h 45 min. Then a 4.72 *N* NaOH solution (33 mL, 156 mmol) was added. The mixture was stirred for 1 h 50 min, and then PhCOCl (2 mL, 17.34 mmol) was added. The mixture was stirred for 1 h, and ether (12 mL) was added. The organic layer was separated. The aqueous layer was extracted with ether (4×15 mL). The combined organic extracts were washed with distilled water (2×15 mL) and a saturated NaCl solution (1×15 mL) and dried with $MgSO_4$. The ether was removed *in vacuo*. The residue was refluxed, and thiobenzoate **3a** was obtained in a yield of 1.79 g (40%), b.p. 147—149 °C (1 Torr). Found (%): C, 74.94; H, 7.40; S, 11.26. $C_{17}H_{20}OS$. Calculated (%): C, 74.96; H, 7.40; S, 11.77. ^{1}H NMR ($CDCl_3$, δ): 2.70 (d, 6 H, CH_2); 5.12 (m, 6 H, CH_2=); 5.90 (m, 3 H, —CH=); 7.45 (m, 3 H_{arom}); 7.93 (m, 2 H_{arom}). ^{13}C NMR ($CDCl_3$, δ): 40.02 (CH_2); 57.40 ($C_{quatern.}$); 118.57 (CH_2=); 126.81, 128.25, 132.82 (Ph); 133.02 (—CH=); 137.95 (Ph); 191.89 (C=O). IR (KBr) ν/cm^{-1}: 3075, 3005, 2977, 2910, 1655 (C=O), 1638 sh. (CH=CH_2), 1595, 1580, 1445, 1313, 1266, 1205, 1176, 998, 910, 775, 692, 650. Mass spectrum (EI, 70 eV), m/z (I_{rel} (%)): 231 $[M-C_3H_5]^+$ (33), 167 $[M-PhCO]^+$ (40), 135 $[M-PhCOS]^+$ (25), 105 $[PhCO]^+$ (100), 77 $[Ph]^+$ (50).

4-Allyl-4-chlorohepta-1,6-diene (6). Carbinol **1** (3.86 g, 25.36 mmol) was added with intense stirring to a solution of $ZnCl_2$ (8.59 g, 63.03 mmol) in an 11 *N* HCl solution (5.20 mL) at 0—5 °C for 20 min. Then the reaction mixture was stirred at this temperature for 10 min and then at 20 °C for 1 h. The mixture was extracted with benzene. The organic layer was twice washed with distilled water and a saturated $NaHCO_3$ solution and dried with $MgSO_4$. The solvent was distilled *in vacuo*. The residue was refluxed, and chloride **6** was obtained in a yield of 2.67 g (61%), b.p. 90—91 °C (26 Torr), *cf.* Ref. 21.

Reduction of 4-allyl-4-chlorohepta-1,6-diene with lithium 9-butyl-9-ethyl-9-boratabicyclo[3.3.1]nonane. A solution of 2.09 *M* BuLi (10.33 mL) in *n*-hexane (21.59 mmol) was added with stirring to a solution of 9-ethyl-9-borabicyclo[3.3.1]nonane (3.69 g, 24.59 mmol) in *n*-hexane (25 mL) at 2—5 °C. The reaction mixture was stirred at 20 °C for 30 min, and chloride **6** (2.43 g, 14.25 mmol) was added to the reaction mixture at 2—5 °C. Then the mixture was heated carefully to ~20 °C and stirred for 12 h. The product was distilled *in vacuo* with heating of the reaction mixture to 60 °C. A 3 *N* NaOH solution (1.5 mL) and a 7.35 *M* H_2O_2 solution (2 mL) were added with stirring to the distillate at 20 °C, and the mixture was stirred for 2 h. Then the mixture was extracted with hexane (3×10 mL). The solvent was removed under atmospheric pressure. Distillation of the residue *in vacuo* gave a mixture of two compounds (1.37 g) in a ratio of ~1 : 1 (GLC), b.p. 54—61 °C (20 Torr).

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