# Synthesis of o- and m-carborane derivatives of [2,2]paracyclophane and abnormal Clemmensen reduction of ketones of the [2,2]paracyclophane and carborane series

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Methods for the synthesis of [2,2] paracyclophane derivatives containing o- and m-carboranyl substituents in position 4, separated from the [2,2] paracyclophane system by one or two C atoms (alcohols and ketones) were developed. The Clemmensen reduction of a number of ketones of the [2,2] paracyclophane and o-carborane series occurs abnormally. The reduction of 1-benzoyl-o-carboranes to the corresponding alcohols by zinc in ethanol in a neutral medium was performed for the first time.

Key words: [2,2] paracyclophane, synthesis, o- and m-carboranyl ketones, Clemmensen reduction.

At present, numerous [2,2]paracyclophane derivatives containing various substituents in the benzene rings are known. The interest in these compounds is due to the fact that they are converted by transport polymerization into thin polymeric coatings with valuable physicochemical characteristics, which depend, to one or another extent, on the substituents attached to the benzene rings.<sup>1</sup> In order to obtain organic polymeric coatings with high contents of boron, in the present study we synthesized a number of [2,2]paracyclophane derivatives having o- and m-carborane substituents in the benzene ring. To ensure that electron-withdrawing bulky 1-oand 1-m-carboranyl groups have no substantial effect on the polymerization of the [2,2]paracyclophane system, we synthesized compounds in which one or two C atoms are located between the benzene ring of [2,2]paracyclophane and the carborane polyhedron.

The first representatives of [2,2] paracyclophanes containing o- and m-carborane substituents were prepared by treatment of accessible<sup>2</sup> [2,2] paracyclophane-4-carbaldehyde (1) with 1-lithio-o- and 1-lithio-m-carboranes 2 and 3 (Scheme 1).

In alcohols 4-6, the paracyclophane and carborane groups are linked with each other through one C atom. These alcohols are of interest because they contain an asymmetrical C atom bound to an OH group and they contain a monosubstituted [2,2]paracyclophane possessing planar chirality. Therefore, alcohols 4-6 have two enantiomeric pairs of diastereomers. The pairs of diastereomers of 4-6 are readily separated by thin layer chromatography on Silufol plates. Diastereomers of alcohol 6, compounds 6a and 6b, were isolated in a pure state by column chromatography.



The reactions of aldehyde 1 with 1,2-dilithio-o- and 1,7-dilithio-m-carboranes smoothly lead to glycols derived from o-carborane (7) and m-carborane (8). These products are high-melting compounds that decompose during melting (Scheme 2).

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Scheme 2





Carborane-substituted [2,2] paracyclophane (9) containing no oxygen atoms in the molecule was prepared by treatment of 4-chloromethyl-[2,2] paracyclophane (10) with 1-lithio-o-carborane (Scheme 3).

Scheme 3



Since the four-step synthesis of compound 10 is complicated, we decided to obtain compounds of type 9, in which the [2,2] paracyclophane and carborane moieties are separated by one or two methylene groups, by the Friedel—Crafts reaction between [2,2] paracyclophane and chlorides of carboranecarboxylic and carboranylacetic acids followed by the Clemmensen reduction of the resulting ketones.

We were not able to accomplish the Friedel—Crafts condensation of carboranecarboxylic acid chlorides with [2,2]paracyclophane; under various conditions, the reaction yielded only resinous products. This result is at variance with the previously reported<sup>3</sup> fact that benzene and its homologs are smoothly acylated with these acid chlorides according to Friedel—Crafts to give the corresponding ketones in high yields. Conversely, chlorides of *o*-carboranylacetic acids 11 and 12 condense with [2,2] paracyclophane in CH<sub>2</sub>Cl<sub>2</sub> at a low temperature to give ketones 13 and 14 in good yields (Scheme 4).



When ketone 14 was subjected to various modifications of Clemmensen reduction with zinc and HCl,<sup>4</sup> the carbonyl group was not reduced to the  $CH_2$  group; instead, the corresponding secondary alcohol 15 was formed (Scheme 5).

Scheme 5



To confirm the structure of alcohol 15, we prepared it also by the reduction of ketone 14 by lithium tetrahydroaluminate. This abnormal reaction pathway observed in the reduction of ketone 14 stimulated us to carry out separately the Clemmensen reduction of ketones of the carborane and [2,2]paracyclophane series that have not been subjected to this reaction previously. We believed that this would reveal the reason for the abnormal reduction of ketone 14.

The Clemmensen reduction of 2-acetyl-1-methyl-ocarborane  $(16)^3$  and 2-benzoyl-1-phenyl-  $(17)^3$  and 2-benzoyl-1-isopropyl-o-carboranes (18) also follows an abnormal pathway and gives only secondary alcohols 19,<sup>5</sup> 20, <sup>5</sup> and 21, respectively (Scheme 6).

Unlike ketones 16--18, 2-methyl-o-carboranylacetone  $(22)^6$  and 2-phenyl-o-carboranylacetone  $(23)^6$ are reduced according to the normal pathway and are converted into 1-methyl-2-propyl-o-carborane  $(24)^7$  and 1-phenyl-2-propyl-o-carborane  $(25)^6$  (Scheme 7).

However, the Clemmensen reduction of 1-phenacyl-o-carborane (26), whose structure is close to those of









ketones 22 and 23, follows the abnormal pathway and yields secondary alcohol 27 (Scheme 8).



1-Phenacylmethyl-o-carborane (28), in which the o-carborane and phenyl groups are separated by three C atoms, undergoes normal Clemmensen reduction to give  $1-(\gamma-phenylpropyl)-o-carborane$  (29) (Scheme 9).





We found that 4-phenylacetyl-[2,2]paracyclophane (30) reacts abnormally under the conditions of the Clemmensen reduction and gives secondary alcohol (31) (Scheme 10).





The abnormal Clemmensen reduction of the [2,2]paracyclophanes and o-carborane ketones studied was somewhat unexpected for us. Although a great number of studies dealing with the use of this reaction have been published, its mechanism has not yet been ultimately established. The intermediate compounds formed in this reaction have not been exactly identified, and the earlier reduction mechanisms that assume the formation of a secondary alcohol as an intermediate compound have now been rejected, because alcohols are not reduced, as a rule, under the reaction conditions. It has been found that the Clemmensen reduction of sterically hindered ketones is sensitive to steric restrictions; this is also typical of heterogeneous processes. For example, ketones containing tert-butyl or neopentyl groups are reduced slowly, and in those cases where steric restrictions are very severe, reduction does not occur at all.

It is believed<sup>8</sup> that the Clemmensen reduction involves four single-electron steps and that the corresponding alkyl chloride is formed intermediately. In the reduction of sterically hindered ketones,  $Ph_3CCOPh$ and  $Me_3CCOPh$ , the corresponding alcohols were obtained in low yields (15 and 13%), along with other reaction products. The authors of the study cited suggested that the reduction of these ketones to alcohols starts with protonation of the ketone by hydrogen chloride, and this is followed by two steps involving single electron transfer (Scheme 11).

## Scheme 11



In our opinion, this mechanism of reduction of ketones is inapplicable to the reduction of 1-acylo-carborane to secondary alcohols for two reasons. First, due to the strong electron-withdrawing effect of the o-carboranyl group, the basicity of these ketones is significantly lower<sup>9</sup> than that of aromatic or alkylaromatic ketones; therefore, their protonation, which is the first step of the proposed reaction mechanism, occurs to only a small extent. Second, using ketones 17 and 18 as examples, we found that in the absence of HCl, they are also reduced by zinc in ethanol to give secondary alcohols 20 and 21 (Scheme 12).

#### Scheme 12



It can be suggested that the ability of 1-acyl-ocarboranes to be reduced by zinc in an alcoholic solution in a neutral medium is due to their low reduction potentials.<sup>9</sup> Therefore, ketone 26 in which the keto group is separated from the carborane nucleus by a methylene bridge and whose reduction potential is higher is not reduced by zinc in ethanol in a neutral medium (Scheme 13).

# Scheme 13 26 + Zn $\xrightarrow{\text{EtOH}}$ HC--CCH<sub>2</sub>CHPh $B_{10}H_{10}$ OH 27

We believe that the reduction of 1-acyl-o-carboranes to secondary alcohols by zinc in a neutral ethanolic medium, like the reduction of aromatic and aliphatic ketones by sodium in ethanol, can occur via zincketyls (Scheme 14).



Scheme 14

Our results on the abnormal Clemmensen reduction of ketones to give secondary alcohols indicate that, in substantiating the reaction mechanism, one should take into account not only the steric features of the structure of the ketone but also its basicity and its reduction potential.

### Experimental

<sup>1</sup>H NMR spectra were obtained using a Bruker WP-200SY instrument in  $(CD_3)_2CO$  with respect to HMDS. IR spectra were recorded on a UR-20 spectrophotometer in KBr pellets. TLC on Silufol plates was used to monitor the course of the reactions and to check the purity of compounds. Amalgamated zinc was obtained from zinc dust according to a known procedure.<sup>4</sup>

(o-Carboranyl)([2,2]paracyclophan-4-yl)methanol (4). [2,2]Paracyclophane-4-carbaldehyde 1 (20 g, 85 mmol) in 100 mL of THF was added at 0 °C to 1-lithio-o-carborane, prepared from o-carborane (14.4 g, 100 mmol) and BuLi (90 mmol, 52.6 mL, 1.77 M) in 150 mL of THF. The mixture was stirred for 4 h at 20 °C, poured into water, acidified with 10% HCl, and extracted with benzene (3×75 mL). The benzene extracts were washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. After the benzene was removed *in vacuo*, the residue was purified on a column with SiO<sub>2</sub> (50×2 cm) using heptane as the eluent to give 29 g (91%) of alcohol 4, m.p. 205-206 °C (benzene-heptane). Found (%): C, 59.84; H, 7.65; B, 28.29.  $C_{19}H_{28}B_{10}O$ . Calculated (%): C, 59.98; H, 7.36; B, 28.44. IR, v/cm<sup>-1</sup>: 3500 (OH); 2600 (BH).

(2-Isopropyl-o-carboranyl)(4-[2,2]paracyclophan-4yl)methanol (5). The reaction between 1-isopropyl-o-carborane (3.72 g, 20 mmol), BuLi (20 mmol), and compound 1 (4.77 g, 20 mmol) in 50 mL THF carried out similarly to that described above gave 7 g (83%) of alcohol 5, m.p. 176–177 °C (benzene-heptane). Found (%): C, 62.70; H, 7.89; B, 25.40.  $C_{22}H_{34}B_{10}O$ . Calculated (%): C, 62.55; H, 8.05; B, 25.59. IR, v/cm<sup>-1</sup>: 3510 (OH); 2598 (BH).

(m-Carboranyl)([2,2]paracyclophan-4-yl)methanol (6) was prepared in a similar way from *m*-carborane (2.4 g, 17 mmol), BuLi (17 mmol), and 1 (3 g) in 40 mL of THF. Yield 4.7 g (93%), m.p. 179 °C (heptane).

**Diastereomer 6a.** M.p. 204–205 °C (heptane). <sup>1</sup>H NMR, 8: 2.75–3.47 (m, 8 H, CH<sub>2</sub>); 3.29 (br.s., 1 H, CH *m*-carborane); 6.22 (d, 1 H, CH–<u>OH</u>, J = 1.6 Hz); 6.46 (d, 1 H, <u>CH</u>–OH, J = 1.6 Hz); 6.53 (s, 2 H, H-15 and H-16); 6.65 (d, 1 H, H-13(12),  $J_{12,13} = 7.4$  Hz); 6.39 (d, 1 H, H-12(13), J = 7.4 Hz); 5.25 (d, 1 H, H-7,  $J_{8,7} = 7.1$  Hz,  $J_{5,7} \le 0.8$  Hz); 6.55 (d, 1 H, H-8,  $J_{7,8} = 7.1$  Hz); 6.45 (s, 1 H, H-5,  $J_{7,5} \le 0.8$  Hz).

**Diastereomer 6b.** M.p. 188–189 °C (heptane). <sup>1</sup>H NMR,  $\delta$ : 2.75–3.47 (m, 8 H, CH<sub>2</sub>); 4.21 (br.s., 1 H, CH *m*-carborane); 6.75 (d, 1 H, CH–<u>OH</u>, J = 3.1 Hz); 6.42 (d, 1 H, <u>CH</u>–OH, J = 3.1 Hz); 6.54 (s, 2 H, H-15 and H-16); 6.61 (d, 1 H, H-13(12),  $J_{12,13} = 7.9$  Hz); 6.39 (d, 1 H, H-12(13),  $J_{13,12} = 7.9$  Hz); 5.54 (d, 1 H, H-7,  $J_{3,7} = 6.7$  Hz,  $J_{5,7} \le 1$  Hz); 6.10 (d, 1 H, H-8,  $J_{7,8} = 6.7$  Hz); 6.47 (s, 1 H, H-5,  $J_{7,5} \le 1.0$  Hz). **1,2-Bis([2,2]paracyclophan-4-yl(hydroxy)methyl)**-*o*-

1,2-Bis([2,2]paracyclophan-4-yl(hydroxy)methyl)-ocarborane (7). A solution of compound 1 (4.7 g, 20 mmol) in 30 mL of ether was added to a solution of 1,2-dilithio-ocarborane, prepared from o-carborane (10 mmol, 1.5 g) and BuLi (20 mmol), in a  $C_6H_6$ —Et<sub>2</sub>O mixture (1 : 1), and the mixture was refluxed for 2 h. The usual workup gave 5.34 g (89%) of compound 7, m.p. 259–261 °C (decomp.) (benzene-heptane). Found (%): C, 70.47; H, 7.20; B. 17.24.  $C_{36}H_{44}B_{10}O_2.$  Calculated (%): C, 70.12; H, 7.14; B, 17.53. IR, v/cm^{-1}: 3515 (OH); 2590 (BH).

1,7-Bis([2,2]paracyclophan-4-yl(hydroxy)methyl)-mcarborane (8) was prepared in a similar way from m-carborane (1.5 g, 10 mmol), BuLi (20 mmol), and compound 1 (4.7 g, 20 mmol). Yield 5.1 g (85%), m.p. 241-243 °C (decomp.) (benzene-heptane). IR, v/cm<sup>-1</sup>: 3510 (OH); 2595 (BH).

1-([2,2]Paracyclophan-4-yimethyl)-o-carborane (9). 4-Chloromethyl[2,2]paracyclophane 10 (25.4 g, 99 mmol) was added at 20 °C to 1-lithio-o-carborane, prepared from o-carborane (15.6 g, 108 mmol) and BuLi (99 mmol), in an ether—benzene mixture. The reaction mixture was refluxed for 3 h in an argon atmosphere until compound 10 completely reacted (TLC); then it was poured into water, the product was extracted with benzene ( $2\times50$  mL), and the benzene extracts were dried with Na<sub>2</sub>SO<sub>4</sub>. After removal of the benzene *in vacuo*, excess o-carborane was sublimed from the residue (100 °C/1 Torr). The remaining material was crystallized from a toluene—heptane mixture to give 31.6 g (88%) of compound 9 as a white solid, m.p. 195–196 °C. Found (%): C, 62.70; H, 8.00; B, 29.43. C<sub>19</sub>H<sub>28</sub>B<sub>10</sub>. Calculated (%): C, 62.63; H, 7.69; B, 29.67.

<sup>1</sup>H NMR, δ: 2.03 (s, 2 H, CH<sub>2</sub>); 2.87–3.37 (m, 8 H, CH<sub>2</sub>); 3.51 (br.s. 1 H, carborane CH).

4-(o-Carboranyl)acetyl[2,2]paracyclophane (13). [2,2]Paracyclophane (3.84 g, 20 mmol) was added at -20 to -10 °C to a mixture of chloride 11 (4.4 g, 20 mmol) and AlCl<sub>3</sub> (2.6 g, 20 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred for 4 h at -10 °C and for 2 h at 20 °C and poured into water; the organic layer was separated, washed with water, and dried with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent *in vacuo* afforded 6.27 g (80%) of compound 13 as a white powder, m.p. 130–131 °C (benzene—heptane). Found (%): C, 60.92; H, 7.06; B, 27.55. C<sub>20</sub>H<sub>28</sub>B<sub>10</sub>O. Calculated (%): C, 61.19; H, 7.19; B, 27.54. IR, v/cm<sup>-1</sup>: 2590 (BH); 1685 (CO).

4-(2-Isopropyl-o-carboranyl)acetyl[2,2]paracyclophane (14). The reaction between chloride 12 (7.9 g, 30 mmol), [2,2]paracyclophane (6.2 g, 30 mmol), and AlCl<sub>3</sub> (4 g, 30 mmol) in 100 mL of  $CH_2Cl_2$  carried out in a similar way gave 11.1 g (85%) of compound 14 as a white solid, m.p. 125-126 °C (benzene-heptane). Found (%): C, 63.99; H, 7.76; B, 24.28.  $C_{23}H_{34}B_{10}O$ . Calculated (%): C, 63.55; H, 7.88; B, 24.87. IR, v/cm<sup>-1</sup>: 2600 (BH); 1676 (CO).

General procedure for the Clemmensen reduction of ketones to alcohols. A ketone (2.3 mmol) was added to a mixture of amalgamated zinc (1.5-2 g), concentrated HCl (4.5 mL), water (2.0 mL), and EtOH or toluene (10 mL), and the mixture was refluxed for 1 h. Then the solution was decanted; in the case of reactions carried out in ethanol, water (10-15 mL) was added, the product was extracted with ether, and the extract was dried with Na<sub>2</sub>SO<sub>4</sub>. For reactions carried out in toluene, the toluene solution was washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. Physicochemical characteristics of the resulting compounds are listed in Table 1.

1-([2,2]Paracyclophan-4-yl)-2-(2-isopropyl-o-carborauyl)ethanol (15). A. By the general procedure, ketone 14 was converted into 1 g of compound 15, m.p. 84-85 °C (benzene-heptane). Found (%): C, 63.45; H, 8.31; B, 24.54. C<sub>23</sub>H<sub>36</sub>B<sub>10</sub>O. Calculated (%): C, 63.30; H, 8.26; B, 24.77. IR, v/cm<sup>-1</sup>: 3620 (OH); 2600 (BH).

**B.** A solution of compound 14 (1.1 g, 2.6 mmol) in 5 mL of anhydrous ether was added at 20 °C in an argon flow to a suspension of LiAlH<sub>4</sub> (0.1 g, 2.6 mmol) in 10 mL of anhydrous ether, and the mixture was stirred for 1 h. Excess LiAlH<sub>4</sub> was quenched by MeOH, and then the reaction mixture was poured into 25 mL of 5% HCl and extracted with ether. The ethereal extracts were washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. Removal of the ether *in vacuo* afforded 1 g (88%) of compound 15.

**2-Benzoyl-1-isopropyl-***o*-carborane (18). A mixture of 1-isopropyl-*o*-carborane-2-carboxylic acid chloride (4.97 g, 20 mmol) and AlCl<sub>3</sub> (2.6 g, 20 mmol) in 30 mL of benzene was refluxed for 1 h (until evolution of HCl ceased) and poured into water; the organic layer was separated, washed with water, and dried with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent *in vacuo* gave 5.1 g (96%) of ketone 18. M.p. 37 °C (hexane).

Table 1. Physicochemical characteristics of the products prepared by the Clemmensen reduction of ketones

Ke- tone	Reaction product	Yield (%)	1 M.p./°C (soivent)	Found Calculated (%)			Molecular formula	IR, v/cm <sup>-1</sup>
				С	Н	В		
16	19	92	153—154					2600 (BH), 2950, 2990, 3010 (Me, CH), 3380 (assoc. OH)
17	20	91	120—121 (hexane)					2605 (BH), 3000 (Ph), 3390 (OH)
18	21	93	142—143 (hexane)	<u>49.44</u> 49.32	<u>8.30</u> 8.22	<u>36.71</u> 36.97	$C_{12}H_{24}B_{10}O$	2600 (BH), 2900, 2930, 3000 (Pr <sup>i</sup> , Ph), 3400 (OH assoc.), 3550 (non-assoc. OH)
22	24	90	50—51 (hexane)	<u>36.17</u> 36.00	<u>9.90</u> 10.00	<u>54.21</u> 54.00	C <sub>6</sub> H <sub>20</sub> B <sub>10</sub>	2600 (BH), 2940, 2990 (Me, CH <sub>2</sub> )
23	25	94	38—39 (hexane)	<u>50.71</u> 50.38	<u>8.61</u> 8.40	<u>41.03</u> 41.22	$C_{11}H_{22}B_{10}$	
26	27	95	261 (C <sub>6</sub> H <sub>6</sub> -heptane)	<u>45.63</u> 45.45	<u>7.70</u> 7.58	<u>40.74</u> 40.91	C <sub>10</sub> H <sub>20</sub> B <sub>10</sub> O	2600 (BH), 3090 (carborane CH), 3400 (OH)
28	29	93	80—81 (hexane)	<u>50.68</u> 50.38	<u>8.51</u> 8.40	<u>41.01</u> 41.22	$C_{11}H_{22}B_{10}$	
30	31	87	153 (THF-pentane)	<u>87.88</u> 87.80	<u>7.29</u> 7.32		C <sub>24</sub> H <sub>24</sub> O	2860, 2940, 3040 (Ph, CH <sub>2</sub> ), 3500 (OH)

Found (%): C, 45.03; H, 8.31; B, 40.72.  $C_{12}H_{22}B_{10}O$ . Calculated (%): C, 45.11; H, 8.27; B, 40.60. IR, v/cm<sup>-1</sup>: 2600 (BH); 1680 (CO).

1-Phenacyl-o-carborane (26) was prepared similarly to compound 18 from o-carboranylacetyl chloride (4.4 g, 20 mmol) and AlCl<sub>3</sub> (2.6 g, 20 mmol) in 30 mL of benzene. The yield of ketone 26 was 4.9 g (93%), m.p. 45-46 °C (hexane). Found (%): C, 45.68; H, 6.71; B, 41.40.  $C_{10}H_{18}B_{10}O$ . Calculated (%): C, 45.80; H, 6.87; B, 41.42. IR, v/cm<sup>-1</sup>: 2600 (BH); 1678 (CO).

1-Phenacyimethyl-o-carborane (28) was prepared similarly to compound 18 from 3-(o-carboranyl)propionyl chloride (4.7 g, 20 mmol) and AlCl<sub>3</sub> (2.6 g, 20 mmol) in 40 mL of benzene. The yield of ketone 28 was 5 g (90%), m.p. 100-101 °C (hexane). Found (%): C, 48.04; H, 7.20; B, 39.09.  $C_{11}H_{20}B_{10}O$ . Calculated (%): C, 47.83; H, 7.25; B, 39.13. IR, v/cm<sup>-1</sup>: 2600 (BH); 1675 (CO).

4-Phenylacetyl-[2,2]paracyclophane (30). A mixture of [2,2]paracyclophane (2.08 g, 10 mmol), phenylacetyl chloride (1.54 g, 10 mmol), and AlCl<sub>3</sub> (1.33 g, 10 mmol) in 40 mL of CH<sub>2</sub>Cl<sub>2</sub> was refluxed for 1 h and poured into water; the organic layer was separated, washed with water, and dried with Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent *in vacuo* gave 3.1 g (94%) of ketone 30, m.p. 84--85 °C (hexane). Found (%): C, 88.38; H, 6.77.  $C_{24}H_{22}O$ . Calculated (%): C, 88.31; H, 6.74. IR, v/cm<sup>-1</sup>: 3040, 2940, 2860 (Ph, CH<sub>2</sub>); 1680 (CO).

Reduction of ketones 17 and 18 to alcohols by zinc in the absence of hydrochloric acid. A mixture of amalgamated zinc (3 g) and ketone 17 or 18 (0.3 g) in 10 mL of EtOH was refluxed for 2 h. The reaction mixture was cooled, and 15 mL of water was added to it. Then the mixture was acidified with 7% HCl and extracted with ether. The extract was washed with

water and dried with  $Na_2SO_4$ . After the solvent was removed in vacuo, alcohols 20 and 21, respectively, were isolated in quantitative yields.

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