Notes

A Simple C-Allylation of Boron-Carbon Clusters via a New Type of Stabilized Carbonucleophiles

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One area of interests concerns the carboranes or boron-carbon cage molecules, upon which a large part of the recent research in the boron field has centered. A significant aspect of carborane chemistry is its considerable overlap with organic, organometallic and transition metal coordination chemistry.[1]

Carboranes are of great interest for BNCT (Boron Neutron Capture Therapy) because of high content of boron.[2] A number of carborane derivatives with different functional groups including polyol, nucleoside and other substituents were synthesized for this purpose.[3]

We were the first to synthesize a new type of stabilized carbonucleophiles due to the strong electron-withdrawing effect of carboranyl group.[4] Especially in order to test the ability of carboranylacetic esters to form stabilized carbanions, the palladium catalyzed C-allylation of carbonucleophiles was carried out under neutral conditions using allylic carbonates.[5]

In this paper, the authers wish to report the palladium-catalyzed reaction of carbonucleophiles containing a carboranyl group as shown in Scheme 1.

Palladium-catalyzed C-allylation of *o*-carboranyl acetic esters was investigated under the neutral conditions. These compounds could be converted to C-allylated compounds in good to excellent yields in the presence of catalytic amounts of $Pd(dba)_2$ and a phosphorous ligand at room temperature in THF under nitrogen.

Experimental

Reagents and Instruments. Melting points were checked by using a Yamato Model MP-21 and were uncorrected. FT-IR spectra were recorded on a Mattson Galaxy 6030E FT-IR spectrophotometer. Mass spectra were determined on a Shimadzu QP-1000 spectrometer at 70 eV by the electron impact (EI) method. ^1H NMR spectra were obtained at 60 MHz on a Varian EM 360 or at 300 MHz on a Bruker AM 300 spectrometer. All chemical shifts were measured relative to TMS ($\delta=0.00$). ^{13}C NMR spectra were obtained at 75.5 MHz on a Bruker AM 300 spectrometer with $CDCl_3$ as solvent and internal standard ($\delta=77.0$). Analytical thin-layer chromatography (TLC) was performed using Merck silica gel 60 F_{254}. Preparative thin-layer chromatography was prepared using Merck silica gel 60 HF_{254}, calcium sulfate and water (weight ratio=10 : 1 : 30) on 20×20 cm^2 glass plate. Column chromatography was performed using Merck silica gel 60 (70-230 mesh). Elemental analyses were performed by a Carlo Erba 1108 Elemental analyzer.

Employed 1,2-dicarba-*closo*-dodecaboranes were received from the Institute of Organoelement Compounds in Russia and identified by ^1H NMR, FT-IR, and GC-MS spectrometers before use. Dibenzylideneacetone,[6] ethyl cinnamyl carbonate,[7] and ethyl allyl carbonate,[7] and bis(dibenzylideneacetone)palladium(0)[8] were prepared according to the method described in literatures.

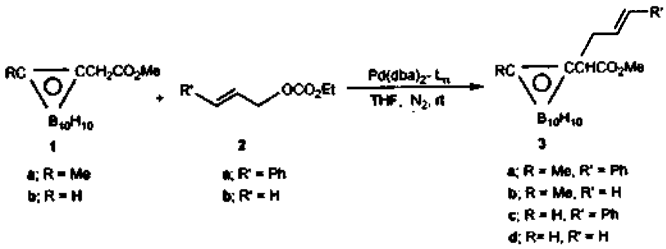
Preparation of Methyl 2-(2-methyl-*o*-carboran-1-yl)-acetate. To a solution of sodium metal (0.46 g, 20 mmol) and iron nitrate nonahydrate (0.20 g, 0.5 mmol) in liq. NH_3 (200 mL) at −45 ℃ was added 1-methyl-*o*-carborane (3.16 g, 20 mmol) in dry diethyl ether (20 mL) dropwise over 10 minutes. The reaction mixture was allowed to stir for 15 minutes, and then added sodium bromoacetate (3.3 g, 20 mmol). The mixture was allowed to stir for 20 minutes in an ice bath. After the ice bath was removed, the reaction mixture was allowed to stir for 1 h, then quenched with water (100 mL), transferred to a separatory funnel, and extracted with diethyl ether. The aqueous layer was acidified by the concentrated hydrochloric acid (100 mL) to pH 4-5, then extracted with diethyl ether. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated *in vacuo*. The carboxylic acid was converted directly into ester by Fisher esterification. The crude white solid was purified by recrystallization with hexane (3.78 g, 82%). Methyl 2-(*o*-carboran-1-yl)acetate could also be synthesized as described method above.

Methyl 2-(2-methyl-*o*-carboran-1-yl)acetate. Colorless oil; MS m/z 230 (M^+); IR (KBr) 2590 (B-H), 1747 (CO) cm^{-1}; ^1H NMR (CCl_4) δ 2.10 (s, 3H, $\underline{CH_3}C$-C), 3.13 (s, 2H, $\underline{CH_2}CO_2$), 3.73 (s, 3H, $CO_2\underline{CH_3}$).

Methyl 2-(*o*-carboran-1-yl)acetate. White crystal; mp 38-39 ℃; MS m/z 216 (M^+); IR (KBr) 2592 (B-H), 1745 (CO) cm^{-1}; ^1H NMR (CCl_4) δ 3.20 (s, 2H, $\underline{CH_2}CO_2$), 3.73 (s, 3H, $CO_2\underline{CH_3}$), 4.31 (br, 1H, $\underline{HC}$-C).

Preparation of Methyl 2-(2-methyl-*o*-carboran-1-yl)-2-cinnamylacetate Catalyzed by $Pd(dba)_2$ and DPPE. A mixture of ethyl cinnamyl carbonate (0.21 g, 1 mmol), methyl 2-(2-methyl-*o*-carboran-1-yl)acetate (0.21 g, 1 mmol), $Pd(dba)_2$ (0.03 g, 5 mol%), 1,2-bis(diphenylphosphino)ethane (DPPE) (0.04 g, 10 mol%) and dry THF(5 mL) was stirred under atmospheric nitrogen at room temperature for 5 h. After addition of water the mixture was extracted with diethyl ether. The organic layer was dried over magnesium sulfate. After the solvent was removed, methyl 2-(2-methyl-*o*-carboran-1-yl)-2-cinnamylacetate was isolated by column chromatography (0.268 g, 77%).

Methyl-2-(-2-methyl-*o*-carboran-1-yl)-2-allyl acetate(0.233 g, 86%), methyl 2-(*o*-carboran-1-yl)-2-cinnamyl acetate(0.205 g, 80%) and methyl 2-(*o*-carboran-1-yl)-2-allyl acetate could be



Scheme 1.

also synthesized as described method above (0.293 g, 88 %).

Methyl 2-(2-methyl-*o*-carboran-1-yl)-2-cinnamylacetate (3a). White crystal; mp 78-79 ℃; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3H), 2.71 (m, 2H), 3.12 (dd, 1H), 3.69 (s, H), 5.93 (ddd, 2H), 6.47 (d, 1H), 7.24 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 23.4, 37.4, 49.8, 52.4, 76.3, 77.7, 123.9, 126.3, 127.8, 128.6, 134.3, 136.6, 169.6; MS m/z 306 (M^+); IR (KBr) 2598-2608 (B-H), 1734 (CO) cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_3$: C, 52.00; H, 7.56. Found: C, 51.82; H, 7.70.

Methyl 2-(2-methyl-*o*-carboran-1-yl)-2-allylacetate (3b). White crystal; mp 50 ℃; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3H), 2.57 (m, 2H), 3.04 (dd, 1H), 3.70 (s, 3H), 5.11 (dd, 2H), 5.58 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 23.4, 38.0, 49.4, 52.3, 76.3, 76.6, 119.2, 132.8, 169.5; MS m/z 270 (M^+); IR (KBr) 2588-2598 (B-H), 1748 (CO) cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_3$: C, 39.98; H, 8.20. Found: C, 40.02; H, 8.24.

Methyl 2-(*o*-carboran-1-yl)-2-cinnamylacetate (3c). White crystal; mp 56 ℃; ^{1}H NMR ($CDCl_3$) δ 2.63 (m, 2H), 3.32 (dd, 1H), 3.67 (s, H), 4.01 (br, 1H), 5.92 (ddd, 1H), 6.43 (d, 1H), 7.25 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 37.2, 51.3, 52.5, 59.2, 73.0, 123.7, 126.2, 127.8, 128.6, 134.1, 136.4, 170.5; MS m/z 332(M^+); IR(KBr) 2588-2598 (B-H), 1740 (CO) cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_3$: C, 50.58; H, 7.28. Found: C, 50.61; H, 7.30.

Methyl 2-(*o*-carboran-1-yl)-2-allylacetate (3d). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.46 (m, 2H), 3.25 (dd, 1H), 3.71 (s, 3H), 3.98 (br, 1H), 5.51 (dd, 2H), 5.55 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 37.9, 51.1, 52.4, 59.2, 73.0, 119.1, 132.7, 170.4; MS m/z 256 (M^+); IR (KBr) 2588-2598 (B-H), 1742 (CO) cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_3$: C, 37.48; H, 7.86. Found: C, 37.73; H, 8.04.

Results and Discussion

Treatment of *o*-carboranyl acetic ester (**1a**: R=Me, **1b**: R=H) with ethyl allylic carbonate (**2a**: R'=Ph, **2b**: R'=H), and $Pd(dba)_2$-phosphine complex as a catalyst in THF at room temperature under the nitrogen atmosphere for 2-5 h gave the corresponding mono C-allylated products **3** in good to excellent yields (Scheme 1).

The palladium-catalyzed C-alkylation reaction of *o*-carboranylacetic ester with the corresponding carbonates under neutral condition was very sensitive to the CH-acidity of carbonucleophiles. Yields of products were affected significantly by reaction conditions.

Table 1 shows the ligand dependence of the yield of C-allylation. As shown in Table 1, it was found that the ligand had a critical effect in the reaction. $Pd(dba)_2$-1,2-bis(diphenylphosphino)ethane(DPPE) and $Pd(dba)_2$-bis(diphenylphosphino)methane(DPPM) complexes were found to be the best catalysts among bis(dibenzylideneacetone)palladium-phosphorous complexes employed (Exp. Nos. 1, 2, 5, 6, 15 and 16).[9] $Pd(dba)_2$-1,3-bis(diphenylphosphino)propane(DPPP), $Pd(dba)_2$-PPh_3 and $Pd(dba)_2$-PBu_3 had some catalytic activity (Exp. Nos. 7-10, 17-18), but their catalytic actyivities were inferior to those of $Pd(dba)_2$-1,2-bis(diphenylphosphino)ethane(DPPE) and $Pd(dba)_2$-bis(diphenylphosphino)-methane (DPPM).

Table 1. Ligand Effect on the Reaction of *o*-Carboranyl Acetic Esters with Ethyl Cinnamyl or Ethyl Allyl Carbonate Catalyzed by Palladium[a]

Exp. no.	1	2	Cat.	Product	Yield (%)[b]
1	**1b**	**2a**	$Pd(dba)_2$+2DPPE	**3c**	80
2	**1a**	**2a**	$Pd(dba)_2$+2DPPE	**3a**	77
3	**1b**	**2a**	$Pd(dba)_2$	**3c**	0
4	**1a**	**2a**	$Pd(dba)_2$	**3a**	0
5	**1b**	**2a**	$Pd(dba)_2$+2DPPM	**3c**	75
6	**1a**	**2a**	$Pd(dba)_2$+2DPPM	**3a**	78
7	**1b**	**2a**	$Pd(dba)_2$+4PPh_3	**3c**	74
8	**1a**	**2a**	$Pd(dba)_2$+4PPh_3	**3a**	68
9	**1b**	**2a**	$Pd(dba)_2$+4PBu_3	**3c**	62
10	**1a**	**2a**	$Pd(dba)_2$+4PBu_3	**3a**	59
11	**1b**	**2a**	$Pd(dba)_2$+4PhCN	**3c**	trace
12	**1a**	**2a**	$Pd(dba)_2$+4PhCN	**3a**	trace
13	**1b**	**2a**	$Pd(dba)_2$+4$P(OEt)_3$	**3c**	0
14	**1a**	**2a**	$Pd(dba)_2$+4$P(OEt)_3$	**3a**	0
15	**1b**	**2b**	$Pd(dba)_2$+2DPPE	**3d**	88
16	**1a**	**2b**	$Pd(dba)_2$+2DPPE	**3b**	86
17	**1b**	**2a**	$Pd(dba)_2$+2DPPP	**3c**	68
18	**1a**	**2a**	$Pd(dba)_2$+2DPPP	**3a**	65

[a]All reactions were carried out with *o*-carboranyl acetic esters (1 mmol), ethyl allylic carbonate (1 mmol), $Pd(dba)_2$ (0.029 g, 5 mol %), and ligand in THF (3 mL) at room temperature for 5 h under nitrogen. [b]Isolated yield.

However, when other ligands such as PhCN and $P(OEt)_3$ were used, the catalytic activity was reduced drastically (Exp. Nos. 11-14). In addition, $Pd(dba)_2$-$P(OEt)_3$ system was not active (Exp. Nos. 13, 14). In the cases of ligand such as benzonitrile or triethyl phosphite, all the substrates were recovered quantitatively. $Pd(dba)_2$ without phosphorous ligand did not show any catalytic activity (Exp. Nos. 3, 4). This fact suggests that $Pd(dba)_2$ was immediately dissociated to metallic palladium and dibenzylideneacetone in solution. Accordingly, remarkable ligand effect was observed and 1,2-bis(diphenylphosphino)ethane(DPPE) and bis(diphenylphosphino)methane (DPPM) seem to be the best ligands for the C-allylation.

The mechanism of C-allylation was proposed by several authors.[10,11] Oxidative addition of Pd(0)-phosphine complex to ethyl allylic carbonates gives the π-allylpalladium carbonate, which undergoes decarboxylation to form π-allylpalladium ethoxide. The ethoxide anion formed *in situ* then abstracts active hydrogen from an active methylene in carboranylacetic ester to generate a carbanion. The *in situ* forma-

tion of the carbanion in this way explains why the allylation reaction with allylic carbonates can be carried out without addition of bases. Nucleophilic attack of carbanion on π-allylpalladium gives the allylated product, with regeneration of Pd(0)-phosphine.

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A Novel Cation Radical Induced Oxidation of Hydrazonitriles

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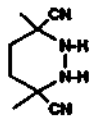
Much attention has been focused on the oxidation of hydrazonitriles [N,N'-dicyanoalkylhydrazines], which are among the most important intermediates for synthesizing azonitriles. Azonitriles are widely used as a source of radicals and biradicals.[1] In particular 1,1'-azobiscyclohexanecarbonitrile (ACN, 9) and 2,2'-azobis-1-isobutyronitrile (AIBN, **10**) are useful as polymerization initiators and blowing agents for thermoplastics.[2]

We now present an account of a new cation radical induced oxidation of one cyclic and two acyclic hydrazonitriles; namely 3,6-dicyano-3,6-dimethylpiperidazine (**1**), 1,2-di-1-(1-cyano)cyclohexylhydrazine (**2**), and 1,2-di-2-(2-cyano)propylhydrazine (**3**).



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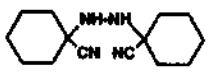

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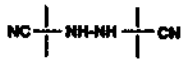

3

The reaction of **1** with thianthreniumyl perchlorate ($Th^{+\cdot}ClO_4^-$) was carried out in both the absence and presence of 2,6-di-tert-butyl-4-methylpyridine (DTBMP). The reaction took 1 day without DTBMP, but was completed within 5 minutes in the presence of DTBMP. Results are given in Table 1. Instead of the cyclic azoalkane, 3,6-dicyano-3,6-dimethyl-1,2-diazacyclohexene (**6**), the coupled product, trans-1,2-dicyano-1,2-dimethylcyclobutane (**7**) and the cleavage product, methacrylonitrile (**8**) were obtained with nitrogen evolution. There are two ways in which product formation can be visualized, although mechanistic detail for establishing the sequence of steps has not been validated. One of the possible routes is (a) in Scheme 1, which shows that $Th^{+\cdot}$ bonds at the nitrogen atom of **1** and that the intermediate (**4**) thus formed is oxidized by a second molecule of $Th^{+\cdot}$, giving intermediate **5**. The other [route (b)] is a net electron

Table 1. Products (%) of Reaction of Thianthrene Cation Radical with Hydrazonitriles in MeCN at Room Temperature[a]

Run	Hydrazonitrile[c]	Products (%)[b]					
		7	8	9	10	Th	ThO
1[c]	DCDMP	49	25			76	6
2[d]	DCDMP	49	26			95	3
3	DCCH			81		79	2
4	DCPH				92	92	3

[a] Oxidation was carried out by adding acetonitrile by syringe to a stirred, septum-capped round-bottomed flask containing the solids, 1.00 mmol of $Th^{+\cdot}ClO_4^-$ and 0.50 mmol of hydrazonitrile, under argon until the color of $Th^{+\cdot}$ was discharged. Stirring was continued for 24 h. Water was then added, the solution was neutralized with $NaHCO_3$ and extracted repeatedly with CH_2Cl_2. [b] Second entry in each run. Products were identified and quantified by GC, using the method of "standard addition" of authentic samples,[22] and by ^1H NMR and GC/MS. GC analysis employed a 2 m×1/8 in. 10% OV-101/Chrom W packed column programmed from 50° to 250 °C at 10 deg/min. The hydrazonitriles and the four products were prepared by standard procedures as referenced and had satisfactory GC/ MS, NMR, and other data. [c] After 24 h stirring, the color of $Th^{+\cdot}$ was dispelled. [d] DTBMP (1.5 mmol) was placed in the flask with the $Th^{+\cdot}ClO_4^-$ and 1 before solvent was added (the mole ratio used was 3 : 2 : 1). The color of $Th^{+\cdot}$ was discharged completely within 5 minutes.