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REACTIONS OF BENZENE VAPOR-CALCIUM ATOM WITH ORGANIC HALIDES AND CARBONYL COMPOUNDS

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Reactions of benzene vapor-calcium atom with organic halides and carbonyl compounds were examined. Benzene vapor-calcium atom reacted with organic halides (RX) to give phenyl-substituted products (PhR) and reduced products (RH). The reactions of benzene vapor-calcium atom with ketones (RR'CO) or benzaldehyde gave two kinds of alcohol PhRR'COH and RR'CHOH, or Ph_2CHOH and $PhCH_2OH$, respectively

The study of metal vapor reaction has been an active field of research in organometallic chemistry and organic synthesis during recent years.[1] This metal vapor procedure afforded both main group and transition metal compounds which can not be obtained by other methods or which were prepared only in low yields in solution. During the study of calcium atom,[2,3] we found that benzene was activated by the cocondensation of calcium atom with benzene vapor and this benzene vapor-calcium atom was a very useful reagent in organic synthesis. In this paper, we present the reactions of benzene vapor-calcium atom with organic halides and carbonyl compounds.

A typical reaction is as follows.[3] Calcium metal (0.3 g, 7.5 mmol) was vaporized at a temperature of ca. 900 ^{o}C using a filament of tungsten in vacuo (ca. 5×10^{-3} Torr) at a rate of ca. 20 mg min^{-1}. During the vaporization of calcium metal, benzene (8 ml, 90 mmol) was introduced as vapor, into reaction vessel. Benzene vapor-calcium atom condensed on the wall of the reaction vessel which was cooled to 77 K with liquid nitrogen. The initial product of benzene vapor-calcium atom at 77 K was a green solid, probably due to a charge transfer complex.[4] On warming this to 0 ^{o}C, it turned black. The reaction vessel was warmed to 0 ^{o}C and

then excess of organic substrate was introduced as vapor. The reaction vessel was warmed to room temperature and left to stand for 1 h. After removal of the reaction vessel from vacuum line, the reaction mixture was hydrolyzed with water slowly. The organic layer was extracted with ether.

Benzene vapor-calcium atom is very reactive and decomposes very rapidly in an atomosphere. Reactions of benzene vapor-calcium atom with various organic substrates, especially organic halides and carbonyl compounds were examined. These results are summarized in Table 1. Benzene vapor-calcium atom reacted with tolyl halides to give toluene predominantly and methylbiphenyl as the minor product (entries 1-7). The reactions of benzene vapor-calcium atom with alkyl halides or chlorosilanes gave alkylbenzenes and alkanes, or phenylsilanes and hydrosilanes, respectively (entries 8-14). The relative ratios of alkylbenzenes to alkanes and phenylsilanes to hydrosilanes except for ethyl bromide are almost same. The reactions of benzene-d_6 vapor-calcium atom with chlorosilanes gave phenyl-d_5-silanes and deuterosilanes (entries 12, 14). Above 90% of the hydrosilanes contained deuterium in such reactions. Benzene vapor-calcium atom also reacted with carbonyl compounds to give two kinds of alcohol as expected (entries 15-18). The reaction of benzene-d_6 vapor-calcium atom with 2-butanone gave 2-methyl-2-phenyl-d_5-propanol and deuterated 2-butanol (entry 17). About 75% of 2-butanol contained deuterium. With benzaldehyde, benzene vapor-calcium atom gave diphenylmethanol and benzyl alcohol (entries 19, 20). Benzyl alcohol did not contain deuterium from the reaction of benzene-d_6 vapor-calcium atom with benzaldehyde.[5)]

As shown in Table 1, benzene vapor-calcium atom is effective in reducing and phenyl-substituting organic halides and carbonyl compounds.

In general, the yields of products shown in Table 1 are low. The yields of products were based on the amount of consumed calcium metal. Taking into consideration that unreacted calcium metal may be also condensed on the wall of the reaction vessel, the yields of products shown in Table 1 may be underestimated. In fact, the yields of products are high on the base of the amount of consumed benzene.

Benzene vapor-calcium atom mixture by the condensation of calcium atom and then benzene vapor or in the reverse order reacted with organic substrates to give only small amounts of products. Furthermore, the reactions of calcium metal with organic substrates in the reaction vessel were also negligible under these condi-

Table 1. Reactions of Benzene Vapor-Calcium Atom with Organic Halides and Carbonyl Compounds[a)]

Entry	Substrate	Products (Relative ratio)	Yield/%[b)]
	Ar-X	ArC_6H_5/ArH	
1	o-MeC_6H_4F	o-$MeC_6H_4C_6H_5/MeC_6H_5$ (7/93)	10.7
2	m-MeC_6H_4F	m-$MeC_6H_4C_6H_5/MeC_6H_5$ (27/73)	15.3
3	p-MeC_6H_4F	p-$MeC_6H_4C_6H_5/MeC_6H_5$ (6/94)	19.8
4	o-MeC_6H_4Cl	o-$MeC_6H_4C_6H_5/MeC_6H_5$ (0/100)	16.0
5	m-MeC_6H_4Cl	m-$MeC_6H_4C_6H_5/MeC_6H_5$ (10/90)	26.9, 90.0[c)]
6	p-MeC_6H_4Cl	p-$MeC_6H_4C_6H_5/MeC_6H_5$ (6/94)	15.7
7	m-MeC_6H_4Br	m-$MeC_6H_4C_6H_5/MeC_6H_5$ (10/90)	8.1
	R-X	RC_6H_5/RH	
8	EtBr	EtC_6H_5/EtH (100/0)	4.9
9	n-BuBr	n-BuC_6H_5/n-BuH (50/50)	4.0
10	t-BuCl	t-BuC_6H_5/t-BuH (76/24)	21.4
11	Me_3SiCl	$Me_3SiC_6H_5/Me_3SiH$ (43/57)	14.2, 85.0[c)]
12[d)]	Me_3SiCl	$Me_3SiC_6D_5/Me_3SiD$ (45/55)	14.5
13	Et_3SiCl	$Et_3SiC_6H_5/Et_3SiH$ (40/60)	8.0
14[d)]	Et_3SiCl	$Et_3SiC_6D_5/Et_3SiD$ (40/60)	7.0
	RR'CO	$RR'C_6H_5COH/RR'CHOH$	
15	Me_2CO	$Me_2C_6H_5COH/Me_2CHOH$ (75/25)	14.5, 100[c)]
16	MeEtCO	$MeEtC_6H_5COH$/MeEtCHOH (60/40)	18.4, 100[c)]
17[d)]	MeEtCO	$MeEtC_6D_5COH$/MeEtCDOH (60/30)[e)]	17.0
18	Et_2CO	$Et_2C_6H_5COH/Et_2CHOH$ (45/55)	29.3
19	C_6H_5CHO	$(C_6H_5)_2CHOH/C_6H_5CH_2OH$ (23/77)	30.0
20[d)]	C_6H_5CHO	$C_6H_5(C_6D_5)CHOH/C_6H_5CH_2OH$ (20/80)[f)]	25.0

a) Reactions were performed at room temperature for 1 h. b) Yields of products were based on the consumed calcium metal on the assumption that benzene vapor-calcium atom product reacted with organic substrates to give reduced and phenyl-substituted products individually. c) Yields were based on the consumed benzene. d) C_6D_6-calcium atom was used. e) MeEtCHOH was also formed. f) No C_6H_5CHDOH was formed.

tions.

(1) Only benzene vapor-calcium atom product prepared concurrently from benzene vapor and calcium vapor reacts with organic substrates to give reduced and phenyl-substituted products. (2) The color of the initial product of benzene vapor-calcium atom 77 K is green, but the color fades on warming to 0 ^{o}C. (3) The reduction of organic substrates except for benzaldehyde permits deuteration. Judging from above facts, it seems probable that this benzene vapor-calcium atom product is phenylcalcium hydride, a charge transfer complex followed by insertion of C-H bonds of the benzene with calcium atom, or its equilibrium forms. Detailed study on reactions and the structure of benzene vapor-calcium atom is now in progress.

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5) Benzyl alcohol may be formed by proton abstraction from unreacted benzaldehyde with intermediate ketyl generated by the reaction of benzene-d_6 vapor-calcium atom with benzaldehyde.

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