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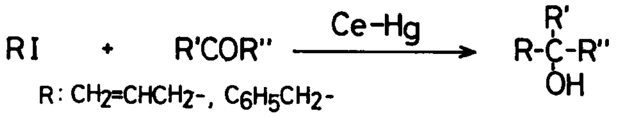
THE REACTION OF ALLYL IODIDE WITH KETONES IN THE PRESENCE OF CERIUM AMALGAM. AN EFFICIENT METHOD FOR THE PREPARATION OF HOMOALLYLIC ALCOHOLS

Tsuneo Imamoto*, Yasuo Hatanaka, Yoshinori Tawarayama, and Masataka Yokoyama
Department of Chemistry, Faculty of Science, Chiba University,
Yayoi-cho, Chiba City 260, Japan

Summary: Allyl iodide reacts in situ with cerium amalgam to generate allyl cerium iodide, which in turn reacts with ketones to yield homoallylic alcohols in good yields.

Among lanthanide elements, cerium metal is commercially available and may be much cheaper than others, but its synthetic utility seems to be limited since it has less reactivity toward alkyl or aryl halides than other lanthanides such as ytterbium and samarium.1) We examined the activation of cerium metal with the object of its synthetic use. After various screenings, it was found that cerium amalgam reacted readily with allyl iodide in the coexistence of a ketone to yield a homoallylic alcohol in good yield.



$$RI + R'COR'' \xrightarrow{Ce\text{-}Hg} R\text{-}\overset{R'}{\underset{OH}{C}}\text{-}R''$$

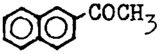
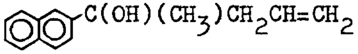
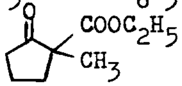
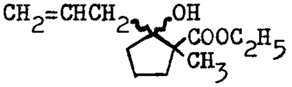
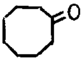
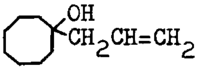
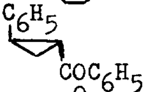
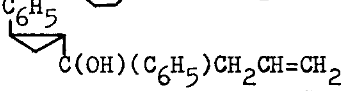
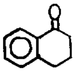
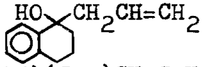
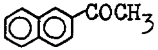
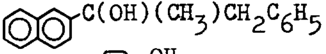
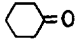
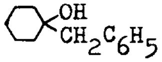
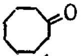
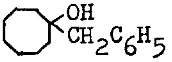
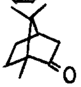
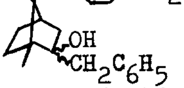
R: $CH_2{=}CHCH_2$-, $C_6H_5CH_2$-

A typical experimental procedure is as follows: cerium ingots (280 mg) were cut to small pieces (ca. 1 mm^3) and treated with a solution of mercuric chloride (250 mg) in ethanol (2 ml) for 2 min. The cerium amalgam was washed with ethanol several times under nitrogen and dried in vacuo.2) To this activated cerium was added a mixture of allyl iodide (338 mg, 2mmol) and p-bromoacetophenone (199 mg, 1 mmol) in dry tetrahydrofuran (3 ml) under nitrogen at 0°C. After stirring at 0°C for 5 h and then at room temperature for 1 h, the reaction was quenched with a saturated aqueous ammonium chloride solution, and the usual work-up afforded 4-(p-bromophenyl)-4-hydroxy-1-pentene (229 mg, 95%).3)

In a similar manner, various ketones were converted into the corresponding homoallylic alcohols.4,5) Next, we tried similar reactions using benzyl iodide. In every case, the reaction proceeded smoothly and the corresponding alcohols were isolated in satisfactory yields.

One of the characteristics of this method is that the procedure is one-step; the reaction proceeds in coexistence of ketones giving allylic alcohols. Another noteworthy fact is that the reaction is chemoselective; ketones react smoothly, while other functional groups such as ester, nitlile , and aryl bromide are

Table 1. One-step Synthesis of Homoallylic Alcohols Using Cerium Amalgam.

Allyl iodide or benzyl iodide	Ketone	Conditions	Product[a)]	Yield (%)
$CH_2=CHCH_2I$	p-$BrC_6H_4COCH_3$	0° C(5h), r.t.(1h)	p-$BrC_6H_4C(OH)(CH_3)CH_2CH=CH_2$	95
"	p-$NCC_6H_4COCH_3$	0°C(5h), r.t.(1h)	p-$NCC_6H_4C(OH)(CH_3)CH_2CH=CH_2$	80
"		0°C(3h), r.t.(1h)		84
"	$C_6H_5CH=CHCOC_6H_5$	0° C(2h)	$C_6H_5CH=CHC(OH)(C_6H_5)CH_2CH=CH_2$	70
"		0°C(3h)		81
"	$C_6H_5COCH_3$	0° C(5h), r.t.(1h)	$C_6H_5C(OH)(CH_3)CH_2CH=CH_2$	60
"		0°C(2h), r.t.(1h)		58
"		0°C(4h), r.t.(1h)		77
"		0°C(3h), r.t.(1h)		48
$C_6H_5CH_2I$	p-$BrC_6H_4COCH_3$	0°C(2h), r.t.(16h)	p-$BrC_6H_4C(OH)(CH_3)CH_2C_6H_5$	85
"	$C_6H_5CH=CHCOC_6H_5$	0°C(4h)	$C_6H_5CH=CHC(OH)(C_6H_5)CH_2C_6H_5$ $C_6H_5CH(CH_2C_6H_5)CH_2COC_6H_5$	45 43
"	$C_6H_5COCH_3$	0°C(3h), r.t.(15h)	$C_6H_5C(OH)(CH_3)CH_2C_6H_5$	84
"		0°C(1h), r.t.(3h)		85
"		0°C(4h)		59
"		0°C(5h), r.t.(12h)		94
"		0°C(5h), r.t.(12h)		40
"	p-$BrC_6H_4COCH_2Br$	0°C(3h)	p-$BrC_6H_4C(OH)(CH_3)CH_2C_6H_5$	72

a) All the products gave satisfactory IR and NMR spectra.

tolerant under the conditions.

From these data, it may be concluded that this reaction using activated cerium provides an efficient method for the preparation of homoallylic alcohols.

References and Notes

1) D. F. Evans, G. V. Fazakerley, and R. F. Phillips, J. Chem. Soc. (A), 1931 (1971). 2) Cerium amalgam thus prepared burned immediately on contact with air. 3) The same reaction was carried out by using cerium without pretreatment with mercuric chloride. In this case long induction period was required and the yield of the product was low (52%). 4) Attempted reactions with substituted benzaldehydes accompanied the Tishchenko reaction giving the corresponding benzyl benzoates in moderate yields. 5) Allylations of carbonyl compounds via Sn and Si derivatives have been reported; T. Mukaiyama, T. Harada, and S. Shoda, Chem. Lett. 1507 (1980); H. Yatagai, Y. Yamamoto, and K. Maruyama, J. Am. Chem. Soc., 102, 4548 (1980) and references cited therein.

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