A Simple Procedure for the Preparation of 1-Alkylindenes

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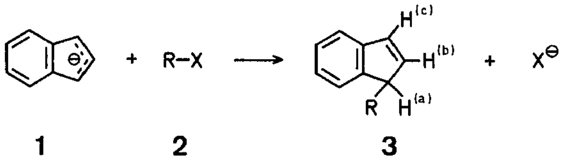
1-Alkylindenes (**3**) have usually been prepared by methods involving several steps[1,2,3]. Attempts to synthesize 1-alkylindenes (**3**) via alkylation of the indenyl anion (**1**) have met with limited success due to the base-catalyzed isomerization of the 1-alkylindene first formed to the 3-alkyl derivative. Thus, treatment of indenyllithium with methyl iodide afforded a mixture of 1- (50%) and 3-methylindene (40%)[4]; on the other hand, carboxylation of indenyllithium at −40° in ether, followed by rapid acidification, did give the expected 1-carboxylic acid[5]. Similarly, deuteration of indenyllithium gave a good yield of 1-deuteroindene[6].

We report here that 1-alkylindenes (**3**) are easily prepared through the reaction of indenyllithium ($1 \cdots Li^{\oplus}$) with an alkyl halide (**2**) in ether at room temperature[7] using an inverse addition technique. The results obtained with some representative systems are given in the Table; note that even *t*-butyl chloride gives the corresponding 1-alkylindene in fair yield.



1 **2** **3**

Table. Yields of 1-Alkylindenes (**3**) from the Alkylation of Indenyllithium ($1 \cdots Li^{\oplus}$) with Alkyl Halides (**2**) or Dimethyl Sulfate

Alkylating Agent **2**	Ratio Alkylating Agent/Indenyl-Li	Reaction Time[a] (hr)	Yield of **3** (%)[b]
$(CH_3)_2SO_4$	1.0	None	74
C_2H_5—Br	4.0	0.5	80
n-C_3H_7—Cl	4.0	48	66
n-C_4H_9—Cl	4.0	48	56
n-C_6H_{13}—Br	3.0	24	90[c]
i-C_3H_7—Cl	4.0	72	49
t-C_4H_9—Cl	5.0	96	37[d]

[a] Time between the addition of the alkylating agent and work-up.

[b] Isolated yield.

[c] New compound: $C_{15}H_{20}$ calc. C 90.0 H 10.0
found 89.7 10.0

^{1}N-N.M.R.: $\delta = 7.4$–7.0 (m, 4H), 6.72 (q, $J_{ac} = 1.80$, $J_{bc} = 5.50$, H_c), 6.45 (q, $J_{ab} = 1{,}80$, H_b), 3.6–3.2 (m, H_a), 1.8–0.6 ppm (m, 13H).

[d] New compound: $C_{13}H_{16}$ calc. C 90.7 H 9.3
found 90.3 9.3

^{1}H-N.M.R.: $\delta = 7.4$–7.0 (m, 4H), 6.72 (q, $J_{ac} = 1.85$, $J_{bc} = 5.75$, H_c), 6.42 (q, $J_{ab} = 1.85$, H_b), 3.20 (t, H_a), 0.98 ppm (s, 9 H).

The identity and purity of the compounds prepared were checked by ^{1}H-N.M.R. spectrometry and G.L.C. analysis. Samples of the 1-alkylindenes were isomerized under basic conditions to the corresponding 3-alkylindenes which were used as reference substances for these analyses.

Alkylation of Indenyllithium; General Procedure:

A solution of indene (58 g, 0.5 mol) in dry ether (400 ml) is placed in a 1000-ml three-necked flask equipped with a condenser, gas-inlet tube, dropping funnel, and magnetic stirrer. To this solution is slowly added, with stirring under a nitrogen atmosphere, a 1.67 *M* solution (300 ml, 0.5 mol) of butyllithium in hexane. After the addition, stirring is continued for 10 min at room temperature. The solution is transferred to a 1000-ml dropping funnel and then added to a vigorously stirred solution of the alkylating agent in dry ether (under nitrogen). After standing for a suitable period of time (see Table), water (300 ml) is added with efficient stirring. The ether layer is separated, washed with water (300 ml), and dried with magnesium sulfate. The ether is evaporated using a rotary evaporator. Final purification is achieved by fractional distillation through a helix-filled column of 7–8 theoretical plates.

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