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THE SYNTHESIS OF ALKENES FROM CARBONYL COMPOUNDS AND CARBANIONS ALPHA TO SILICON, II: 1,2-ALKADIENES[1].

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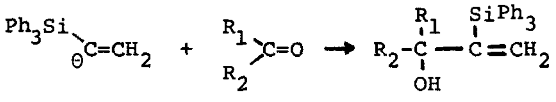
The synthesis of alkenes from carbonyl compounds and carbanions alpha to silicon has been reported by Peterson[2] and by us[1]. The reaction has gained increasing acceptance[3] and was found to be particularly useful in the preparation of hetero-substituted alkenes[4-7]. We wish to report our studies in extending this reaction to the synthesis of 1,2-alkadienes.

We found that the lithium salt of the carbanion I (equation 1), generated by metal-halogen exchange of α-bromovinyltriphenylsilane with n-butyl lithium[8,9] reacted very readily with a number of aldehydes and ketones to give the alcohols (IIIa-d) in good yields (50-80%).



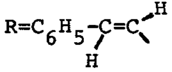
I II III

equation 1

a. $R_1=C_6H_5$, $R_2=H$

b. $R_1=R_2=C_6H_5-$

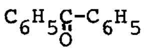
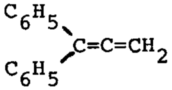
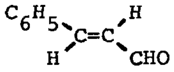
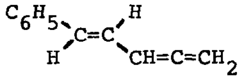
c. $R_1=H$, $R_2=n-C_{10}H_{21}-$

d. $R_1=H$, 

$R=C_6H_5-C(H)=C(H)-$

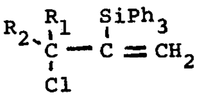
In view of the propensity of β-functionalized organosilicon compound to undergo elimination to give alkene[10,11], we were surprised to find that the alcohols (IIIa-d) were exceptionally resistent to elimination under conventional reaction conditions. For example, IIIa was recovered unchanged on treatment with either dilute sulfuric acid[12] or sodium hydride[2], which are conditions normally employed to effect elimination of silanol from β-hydroxysilane. Reaction of IIIa with either acetic acid/sodium acetate[13], or acetic in 60 ml anhydrous ether at -24°, equal mole of n-butyl lithium was added slowly and stirred for 1-1/2 h. Equal mole of undecanal was added and the reaction mixture was stirred at -24° for one hour. The stirring was continued at room temperature overnight. The reaction mixture was poured into 50 ml 10% HCl, and the organic phase was extracted, dried and evaporated to give the crude product IIIc. The crude alcohol was dissolved in 25 ml carbon tetrachloride and 50% excess thionyl chloride was added. The reaction was stirred for 2 h and then evaporated to give the crude chloride Vc. The crude chloride was dissolved in DMSO (25 ml per gram Et_4NF) and Et_4NF was added (20% excess). The mixture was stirred for 2 h at room temperature. The reaction mixture was partitioned between ether and water. The ether phase was dried and evaporated to give the crude product which was distilled to give 1,2-tridecadiene, b.p. 63-64°/0.1 mm (yield 44% based on undecanal). Similar yields were realized for other terminal allenes (Table I)

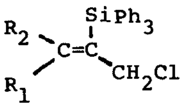
Table I. Preparation of 1,2-Alkadienes

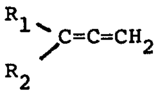
Starting Material			Product Allene	Isolated Yield %	b.p.
IIa.	C_6H_5CHO	VIa.	$C_6H_5CH=C=CH_2$	59	83-85°/24 mm[b]
IIb.	 $C_6H_5\underset{O}{\overset{}{C}}-C_6H_5$	VIb.		45[a]	100°/0.025 mm[c]
IIc.	$CH_3(CH_2)_9CHO$	VIc.	$CH_3(CH_2)_9CH=C=CH_2$	44	63-64°/0.1 mm[d]
IId.		VId.		35	70-75/0.075 mm[e]

a. Purified by preparative layer chromatography on silica gel.
b. L. Skatteböl, Tetrahedron Letters, 167 (1961).
c. L. Skatteböl, Acta Chem. Scand. 17, 1683 (1963).
d. Ir. (neat) cm^{-1}: 1960 (C=C=C); 850 ($C=C=C\langle^{H}_{H}$).
Nmr. (neat) δ: 0.8-1.6 (m, 19H), 1.6-2.0 (m, 2H), 4.4 (m, 2H), 4.9 (m, 1H).
Ms: $\frac{m}{e}$ = 180 (M^+).
e. Ir. (neat) cm^{-1}: 1960 (C=C=C); 860 ($C=C=C\langle^{H}_{H}$)
Nmr (CCl_4) δ: 4.9 (d, 2H), 5.7-6.8 (m, 3H), 7.3 (m, 5H)
Ms: $\frac{m}{e}$ = 142 (M^+)

anhydride/pyridine, or acetyl chloride gave in quantitative yield the corresponding acetate. The acetate of IIIa gave no evidence of allene formation on treatment with dilute acid or on heating to 200°. The trifluoroacetate of IIIa, obtained from the reaction of IIIa with trifluoroacetic anhydride and pyridine, was similarly resistent to elimination. Reaction of IIIa with thionyl chloride in carbon tetrachloride gave the chloride IVa in quantitative yield. Again, no evidence of allene formation was found when IVa was subjected to either alcoholic silver nitrate[14] or heating to 175°. On the other hand, IVa, when dissolved in a polar solvent such as dimethyl sulfoxide (DMSO), rearranged readily to the allylic isomer Va[15]. Reaction of IIIb-d with thionyl chloride gave only the rearranged chloride Vb-d.


IV


V


VI

Recently it was reported that potassium fluoride (KF) in DMSO caused facile elimination of β-chlorovinylsilane[16]. We were therefore gratified to find that when the chloride (IVa or Va) was stirred with slight excess of potassium fluoride in DMSO at room temperature, phenylallene (VIa) was formed in quantitative yield. The reaction was however slow (reaction time: ∿10 hrs) possibly due to the slight solubility of KF in DMSO. The reaction can be facilitated by the use of either tetraethyl or tetramethylammonium fluoride instead. Acetonitrile was found to be a suitable solvent as well. The other product isolated from the reaction mixture on work-up was identified to be triphenylsilanol. It is undoubtedly derived from triphenylfluorosilane during the hydrolytic work-up[17].

The sequence of operations constitute therefore a synthesis of terminal allenes from the corresponding carbonyl compounds. The convenience of the procedures is enhanced by carrying out the preparation without purification of the intermediate compounds.

A typical experiment can be illustrated by the preparation of 1,2-tridecadiene. To a solution of 8.8 g (0.024 m) of α-bromovinyltriphenylsilane

The advantages of the present synthetic method appear to be: (1) the starting carbonyl compounds are in general readily available, (2) because of the mild conditions in the allene generation step, the allenes produced were free of contamination by the isomeric acetylenes, (3) double bond elsewhere in the molecule is not affected, (e.g. IId → VId)

We are continuing our effort to extend this reaction to the synthesis of non-terminal allenes and other systems.

References and Notes

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