Base-catalysed Aralkylations of Trimethylvinylsilane[1]

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Summary Dispersed sodium and potassium catalyse the side-chain addition of alkylarenes to trimethylvinylsilane; in the case of potassium, cyclic compounds are also produced.

ALKYLAROMATIC compounds with at least one hydrogen atom at the α-carbon of the alkyl group add to olefins in the presence of a base as catalyst. Such a reaction seems to be quite general in the case of ethylene,[2] conjugated dienes,[3] and styrenes.[2,3] In order to broaden the scope of this reaction, trimethylvinylsilane (TVS) was used in the present study as the olefin moiety and was treated with 4-methylpyridine, toluene, and 1-methylnaphthalene as the alkylarenes. Sodium and potassium dispersed with or without a promoter were used as catalysts.

The general procedure used consisted of dispersing a catalytic amount of the alkali metal in 0·1 mole of freshly distilled methylaromatic compound. The dispersion was made at either 25° (expts. 1 and 2, in Table) or 110—120° (expts. 3—6) using a three-necked flask provided with a high-speed stirrer. Usually, 3—6 hr. were required for the production of an active catalyst, as indicated by the dark-brown coloration of the solution. Trimethylvinylsilane reacted with pyridine at 55°, at atmospheric pressure, in a slow stream of nitrogen. The reactions with toluene and 1-methylnaphthalene took place at 150—170° in an autoclave of 50 ml. capacity, provided with an agitator. The reaction was quenched with ethyl alcohol after 12—15 hr. The reaction products were first analysed by g.l.c. and then distilled, purified on a preparative g.l.c. column, and their structures determined by means of n.m.r.

The reaction catalysed with sodium consisted only of the addition of the side-chain carbanion to the vinyl group:

$$\mathrm{ArCH_2^-} \xrightarrow{\text{TVS}} \mathrm{ArCH_2{\cdot}CH_2{\cdot}\overset{-}{C}HSiMe_3} \xrightarrow{\text{ArMe}} \mathrm{Ar[CH_2]_3SiMe_3 + ArCH_2^-}$$

The structures of 1-aryl-3-trimethylsilylpropanes are unequivocally confirmed by the n.m.r. spectra. The presence of 2-aryl-1-trimethylsilylpropane was not observed. The mono-addition product was never obtained without the

Reaction of trimethylvinylsilane (TVS) with methylaromatic and methylheterocyclic compounds (ArMe)

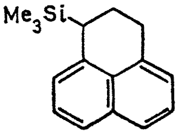
Expt. no.	Ar-	Catalyst (g.atom $\times 10^3$)	Promoter, ml.	Moles TVS/ArMe	Reaction temp. °	ArMe Conversion %	Mono-adduct[a] %	Di-adduct[b] %	Other %
1	γ-NC_5H_4-	Na (0·5)	0	1·0	55[c]	58	43	49	8
2	γ-NC_5H_4-	K (1·0)	0	1·0	55[c]	41	33	60	7
3	Ph-	Na (5·0)	0·35[d]	0·5	155	30	78	16	6
4	Ph-	K (5·0)	0·35[e]	0·5	170	37	66	18	16
5	α-$C_{10}H_7$-	Na (5·0)	0·35[d]	0·5	155	35	85	12	3
6	α-$C_{10}H_7$-	K (5·0)	0·35[e]	1·0	150	47	11	16	43[f] + 40

[a] $Ar[CH_2]_3SiMe_3$. [b] $ArCH(CH_2CH_2SiMe_3)_2$. [c] At atmospheric pressure. [d] *m*-Chlorotoluene. [e] *o*-Chlorotoluene. [f] Compound (1)

concomitant formation of the di-adduct, because the mono-adduct is more reactive than the starting material:

$$\mathrm{ArCH_2{\cdot}CH_2{\cdot}CH_2SiMe_3} \xrightarrow[\mathrm{TVS}]{\mathrm{B^-}} \mathrm{ArCH(CH_2{\cdot}CH_2SiMe_3)_2}$$

The potassium-catalysed reaction of 4-methylpyridine also resulted in the formation of related products. However, the reaction of toluene and 1-methylnaphthalene with potassium as catalyst was more complex. The major product from expt. 6 corresponded to 1,2-dihydro-1-trimethylsilylphenalene (**1**):



(1)

A similar cyclisation was observed in the reaction of 1-methylnaphthalene with ethylene in the presence of potassium.[5]

The conversion of the aromatic compounds depends only on the amount of TVS used. If two moles of TVS are present the starting material can be completely converted into the di-adduct. The base-catalysed addition of alkylaromatic and alkylheterocyclic compounds to vinylsilanes seems to be a convenient method for the preparation of aralkylsilyl compounds in high yields.

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[1] See also H. Pines and S. V. Kannan, preceding communication.

[2] For literature references see H. Pines and L. A. Schaap, *Adv. Catalysis*, 1960, **12**, 110.

[3] H. Pines and J. Oszczapowicz, *J. Org. Chem.*, 1967, **32**, 3183.

[4] H. Pines and N. E. Sartoris, *J. Org. Chem.*, 1969, **34**, 2113.

[5] B. Stipanovic and H. Pines, *J. Org. Chem.*, 1969, **34**, 2106.