Tetrahedron Letters No.22, pp. 1755-1756, 1969. Pergamon Press. Printed in Great Britain.

SILYL RADICALS IV
HOMOLYTIC AROMATIC SILYLATIONS WITH HYDROSILANES

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(Received in Japan 13 March 1969; received in UK for publication 31 March 1969)

There is a substantial body of evidence for addition of hydrosilanes to carbon-carbon double and triple bonds involving free silyl radicals (1). However, no work has been reported to date on the reaction of aromatic compounds with hydrosilanes leading to homolytic aromatic silylations (2).

We now report that such a homolytic aromatic substitution is a general reaction of free silyl radicals derived from hydrosilanes by the reaction with peroxide in aromatic solvents.

When a benzene solution of an equimolar mixture of triethylsilane and di-t-butyl peroxide (DTBP) was heated in a sealed tube under nitrogen at 135° for 20 h, triethylphenylsilane was obtained in 16.3% yield. Similarly, the following phenylsilanes were prepared by the reaction with DTBP in benzene at 135° from the corresponding hydrosilanes (compound and % yield given): $PhSiMe_2$-n-Pr, 29.5; $PhSiMe_2SiMe_3$, 19.2; $PhSiMe_2SiMe_2SiMe_3$, 15.0.

Reaction of pentamethyldisilane with toluene was examined more throughly. The products were isolated by preparative glc and identified by ir, uv, and nmr spectra and elemental analysis. Some of the products were prepared by alternative and unequivocal route for comparison. Amounts of the products were determined by glc, the results being listed in TABLE 1.

Formation of every possible termination products between pentamethyldisilanyl and benzyl radicals indicates clearly that the process should be homolytic.

TABLE 1

Reaction of Pentamethyldisilane with Toluene in the Presence of DTBP at 135°

Compound	Run 1 m mole	Run 1 % Yield[a]	Run 2 m mole	Run 2 % Yield[a]
Starting Materials				
Me_5Si_2H	5.108		1.576	
DTBP	5.164		1.653	
$PhCH_3$	8.249		2.540	
Products				
$PhCH_3$ (recovered)	4.717		1.664	
o-$CH_3C_6H_4Si_2Me_5$	0.115	3.26	0.0263	3.00
m-$CH_3C_6H_4Si_2Me_5$	0.277	7.84	0.0637	7.27
p-$CH_3C_6H_4Si_2Me_5$	0.145	4.11	0.0319	3.64
$PhCH_2Si_2Me_5$	0.266	7.53	0.0588	6.71
$(PhCH_2)_2$	0.141	7.98	0.0411	9.38
$PhCH(Si_2Me_5)OC(CH_3)_3$	0.236	6.68	0.0462	5.27
$Me(SiMe_2)_4Me$	0.333		0.0748	
$Me_5Si_2OC(CH_3)_3$	1.06		0.239	
$(CH_3)_3COH$	3.13		1.801	
CH_3COCH_3	trace		trace	

a Based on the amount of consumed toluene.

Rather high meta/para isomer ratio should be noteworthy. Partial rate factors were determined by two independent runs of competitive experiments; k_o/k = 0.40, 0.39, k_m/k = 0.96, 0.94, and k_p/k = 1.00, 1.02. It is interesting to note that these values resemble quite closely to those of cyclohexyl radicals (3), but details will be discussed in a future publication.

REFERENCES

1 F. W. Stacey and J. F. Harris, Jr., Org. Reactions, 13. 91 (1963).

2 C. Eaborn, R. A. Jackson, and R. Pearce, Chem. Commun., 920 (1967).

3 J. R. Shelton and C. W. Uzelmeier, J. Amer. Chem. Soc., 88, 5222 (1966).