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Preliminary communication

SILATRANE AS A REDUCING AGENT

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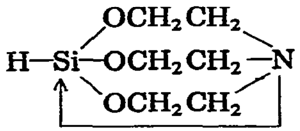
Summary

Silatrane has been shown to have potential as a reducing agent for some organic compounds, including halides, carbonyl compounds, and azoxybenzene.

Frye, Vince, and Finzel noted that 3,7,10-trimethylsilatrane readily generates hydrogen when treated with hydrogen chloride or bromide in chloroform, indicating that this derivative, and thus probably the parent silatrane (I), are more powerful hydride-ion donors than simple organosilicon hydrides [1]. This suggested to us that silatrane might have potential as a reducing agent, and the preliminary study described below confirms this.



(I)

The results in Table 1 show that silatrane, usually in refluxing xylene, reduces benzyl bromide, benzoyl chloride, azoxybenzene, and some carbonyl compounds. (Presumably in this last case addition to the carbonyl bond occurs, the alcohol being formed by the subsequent hydrolysis.) With mesityl oxide, for which higher temperatures were used to increase the rate, the olefinic bond was not reduced. Nitrobenzene also reacts in refluxing xylene, though rather slowly, to give a mixture of products, including azobenzene.

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TABLE 1

REDUCTION OF ORGANIC COMPOUNDS BY SILATRANE I [a]

Substrate (mmole)	I (mmole)	Solvent (ml)	Temp. (°C)	Time (h)	Product (yield %) [b]
$PhCH_2Br$ (1.0)	1.0	Xylene (75)	Reflux	44	PhMe (35)
PhCOCl (1.0)	2.0	Xylene (250)	Reflux	48	PhCHO (57); $PhCH_2OH$ (37) [c,d]
MeCOMe (0.25)	0.5	PhH (30)	140	48	Me_2CHOH (46) [e,f]
$Me_2C{=}CHCOMe$ (2.0)	8.0	$(EtOCH_2CH_2)_2O$ (250)	Reflux	22	$Me_2C{=}CHCH(OH)Me$ (70)
p-HOC_6H_4CHO (0.5)	2.0	Xylene (250)	Reflux	72	p-$HOC_6H_4CH_2OH$ (32)
$PhN(^{+}{-}O^{-}){=}NPh$ (0.5)	2.0	Xylene (250)	Reflux	62	$PhN{=}NPh$ (28); PhNHNHPh (7) [g]

[a] The silatrane was made as described by Zelchan and Voronkov [2]. Unless otherwise indicated, the reaction mixture was refluxed under nitrogen. Except in the case of $PhCH_2Br$, the mixture was treated with dil. aq. HCl or NH_4Cl, and the product(s) extracted into ether or (for azobenzene) benzene. [b] Except where indicated, yields refer to isolated product or its derivative. [c] Yields determined by GLC with the aid of authentic samples. [d] Benzaldehyde was isolated in 37% yield. From interaction of (I) (20 mmole) and PhCOCl (10 mmole) in benzene (30 ml) for 48 h at 100° (ampoule), benzaldehyde was isolated as its 2,4-dinitrophenylhydrazone in 66% yield, GLC indicated that ca. 10% of $PhCH_2OH$ was also formed. [e] Yield of 2,4-dinitrophenylhydrazone. [f] Reaction carried out in sealed ampoule. [g] Products isolated by TLC on silica gel with 3:1 cyclohexane/benzene as solvent.

While long reaction times at rather high temperatures were necessary, and yields were not very good, it should be noted that fairly dilute solutions of the reagents were used, and that no attempt was made to optimize the conditions. Thus the results suffice to convince us that we should undertake a systematic study of the reducing properties of silatrane and its derivatives.

Acknowledgments

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