*Journal of Organometallic Chemistry*
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

# ORGANOSILICON COMPOUNDS
# XII. ANHYDRIDE, ACID HALIDE AND CHLOROFORMATE CLEAVAGE OF THE SILICON–CARBON BOND OF 2-SILYLSUBSTITUTED PYRIDINES

FRANK H. PINKERTON AND SHELBY F. THAMES*

*Department of Chemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39401 (U.S.A.)*

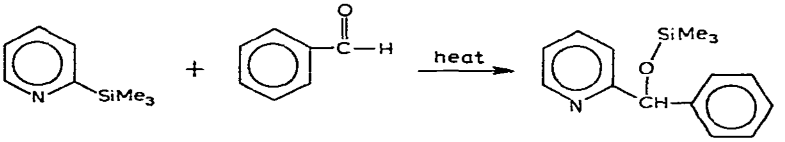
(Received March 11th, 1970)

## SUMMARY

Cleavage of the silicon–carbon bond of 2-(trimethylsilyl)pyridine has been affected by benzoyl chloride, phthalic anhydride, and ethyl chloroformate as well as benzaldehyde to provide a novel pathway to heterocyclic ketones, keto-acids, esters and alcohols. A cyclic four-membered transition state is proposed in which the polarity of both the silicon–aromatic bond and the attacking reagent are stressed.

## INTRODUCTION

Since our discovery[1] that cleavage of the silicon–carbon bond of 2-(trimethylsilyl)pyridine can be affected by benzaldehyde [eqn. (1)], we have extended the scope



(1)

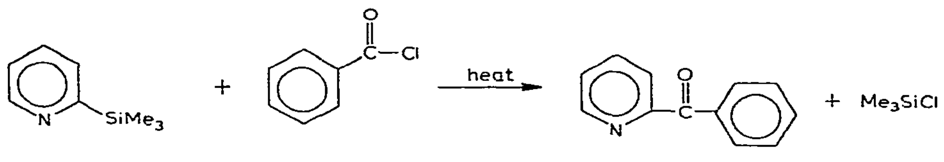
of this cleavage to other neutral reagents in an effort to elucidate factors controlling the reaction mechanism and to provide, as well, a synthetic pathway to various 2-substituted nitrogen heterocycles.

## RESULTS AND DISCUSSION

In this work, benzoyl chloride has been found to produce silicon–carbon cleavage of 2-(trimethylsilyl)pyridine, affording phenyl 2-pyridyl ketone (I) and trimethylchlorosilane [eqn. (2)]. Optimum results were obtained either when a 2:1 excess of the silylpyridine was employed and/or when the trimethylchlorosilane was

---

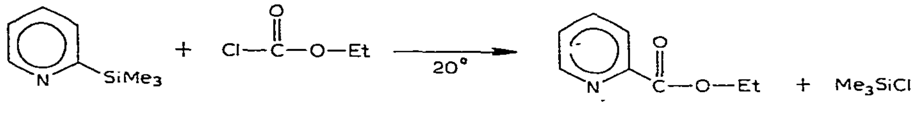
* To whom inquiries should be directed.



(I)

(2)

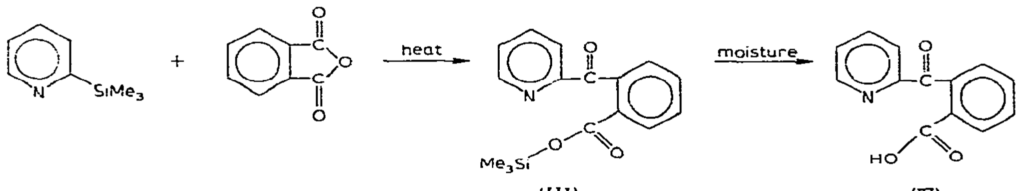
collected as produced under an anhydrous atmosphere. In a similar manner, ethyl chloroformate reacted exothermally with 2-(trimethylsilyl)pyridine to yield ethyl picolinate (II) and trimethylchlorosilane [eqn. (3)].



(II)

(3)

In a procedure similar to that used with benzaldehyde, phthalic anhydride and 2-(trimethylsilyl)pyridine were heated to produce 2-carboxyphenyl 2-pyridyl ketone (IV) [eqn. (4)] after exposure of the reaction mixture to the atmosphere. It is felt that the silyl ester (III) was formed initially and, as a result of the facile nature of the Si–O bond, was cleaved by moisture to (IV). although isolation of this intermediate product was not attempted.



(III) (IV)

(4)

Although cleavage of the silicon–carbon bond of 2-silylpyridines by water and alcohol is well documented[2], we have shown for the first time that certain neutral, non-protic reagents such as benzoyl chloride, ethyl chloroformate and phthalic anhydride may also cause cleavage of this reactive bond. It is suspected that such cleavage reactions proceed through a cyclic 4-member transition state, the formation of which is likely dependent upon the polar nature of both the silicon–aromatic bond and also the attacking reagent. A recent communication with Professor Gilman* describing a similar cleavage of the silicon–perhalophenyl bond by benzaldehyde lends support to this tenet. Furthermore, the dependence of the cleavage on steric features of the silylpyridine and also the attacking reagent has not yet emerged as a major factor in these reactions. Evidence supporting this fact was obtained by the successful cleavages of 2-(diphenylmethylsilyl)pyridine by benzaldehyde and of 2-(trimethylsilyl)pyridine by *o*-chlorobenzaldehyde and 2,6-dichlorobenzaldehyde in yields of 81.5%, 82% and 88.2% respectively.

---

* Personal communication with Professor Henry Gilman, Iowa State University, Ames, Iowa (U.S.A.) *cf.* ref. 3.

We are continuing this investigation to determine the generality of this reaction with respect to the required features of the silicon-substituted aromatic and the attacking reagent as well.

## EXPERIMENTAL

The NMR spectra reported herein were obtained on a Varian A-60D spectrometer in concentrations of approximately 50% by volume and in reference to TMS as an internal standard. The IR spectra reported were obtained on a Perkin–Elmer 257 grating spectrophotometer utilizing KBr pellets.

### *Phenyl 2-pyridyl ketone (I)*

Benzoyl chloride (14.1 g; 0.1 mole) and 2-(trimethylsilyl)pyridine (15.1 g; 0.1 mole) were heated at 100° for 2 h under an atmosphere of dry nitrogen, during which time the trimethylchlorosilane produced was collected. The reaction mixture was then washed with a sodium bicarbonate water solution, extracted with ether, dried over $MgSO_4$ and fractionated to yield 13.4 g (73%) of (I), b.p. 72°/0.02 mm, $n_D^{24}$ 1.6032; 2,4-DNP m.p. 193–195°. Lit.[4] reports b.p. 130°/1–2 mm, $n_D^{20}$ 1.6056; 2,4-DNP m.p. 196.5–197.5°.

### *Ethyl 2-picolinate (II)*

Ethyl chloroformate (10.8 g; 0.1 mole) was added cautiously dropwise with stirring onto 2-(trimethylsilyl)pyridine (30. 2 g; 0.2 mole) at 20° due to the exothermic nature of the reaction. Once the reaction had subsided, the mixture was washed with a bicarbonate water solution, extracted with ether, dried and fractionated to give 8.3 g (55%) of (II), b.p. 48°/0.1 mm, $n_D^{26}$ 1.5100.

### *2-Carboxyphenyl 2-pyridyl ketone (IV)*

The reaction of phthalic anhydride (7 g; 0.047 mole) with 2-(trimethylsilyl)-pyridine (7 g; 0.046 mole) at 100° for 3 h afforded, after exposure to the atmosphere and recrystallization from acetone, 7.5 g (71.5%) of (IV), m.p. 229–232° with decompn. (Found: C, 68.92; H, 3.81. $C_{13}H_9NO_3$ calcd.: C, 68.71; H, 4.00%.)

The NMR spectrum of (IV) in dimethyl sulfoxide exhibited a distorted doublet, representing the 6-pyridyl proton, at $\tau$ 1.44 and multiplets from $\tau$ 1.8 to 2.6 integrating respectively in the correct 1/7 ratio. Difficulty was encountered in locating the acid proton due to internal salt formation; however, the IR spectra of (IV) exhibited no O–H stretch from 2.8 to 3.2 $\mu$, although it did possess medium to strong bands from 3.7 to 4.3 $\mu$ indicative of the pyridyl salt of the acid. Acidification of (IV) with HCl produced the free carboxylic acid and the hydrochloride salt of the pyridyl nitrogen (V). The IR of (V) exhibited broad strong bands from 3.0 to 4.3 $\mu$ indicative of the intense acid dimer stretch coupled with the pyridine salt bands. (Found: C, 60.29; H, 3.81. $C_{13}H_{10}ClNO_3$ calcd.: C, 59.21; H, 3.83%.)

### *2-(Diphenylmethylsilyl)pyridine (VI)*

2-Bromopyridine (15.8 g; 0.1 mole) was added dropwise over a 15 min period to n-butyllithium (62 ml; 1.6 *N*) in 200 ml of anhydrous ether at −70°. After 30 min of stirring at −70°, diphenylmethylchlorosilane (23.3 g; 0.1 mole) was added dropwise within 10 min. The solution was allowed to come to ambient temperature and was refluxed for 30 min, cooled, and the lithium chloride removed by filtration. The filtrate was concentrated *in vacuo* and the residue distilled to yield 14.1 g (51.3%) of (VI), b.p. 128–130°/0.025 mm, $n_D^{30}$ 1.6065. (Found: C, 78.62; H, 6.28; N, 4.92. $C_{18}H_{17}NSi$ calcd.: C, 78.48; H, 6.23; N, 5.09%.)

The NMR spectrum of (VI) in $CCl_4$ exhibited a distorted doublet, representing the 6-pyridyl proton, at $\tau$ 1.47 and integrating for one proton, multiplets from $\tau$ 2.4 to 3.4 integrating for the remaining thirteen aromatic protons, and a singlet at $\tau$ 9.32 integrating for three protons of the methyl group attached to the silicon atom.

*Phenyl-2-pyridylmethyl diphenylmethylsilyl ether (VII)*

2-(Diphenylmethylsilyl)pyridine (12 g; 0.0436 mole) and benzaldehyde (4.6 g; 0.043 mole) were heated at 120° for 5 h to afford after fractionation 13.5 g (81.5%) of (VII), b.p. 163°/0.005 mm, $n_D^{28}$ 1.5967. (Found: C, 78.91; H, 6.17; Si, 7.60. $C_{25}H_{23}NOSi$ calcd.: C, 78.69; H, 6.09; Si, 7.36%.)

The NMR spectrum of (VII) in $CCl_4$ exhibited a distorted doublet, representing the 6-pyridyl proton, at $\tau$ 1.72 and integrating for one proton, multiplets from $\tau$ 2.3 to 3.4 integrating for the remaining eighteen aromatic protons, a singlet at $\tau$ 3.9 integrating for one methine proton, and a singlet at $\tau$ 9.49 integrating for the three protons of the silylmethyl group.

*(2-Chlorophenyl)-2-pyridylmethyl trimethylsilyl ether (VIII)*

2-(Trimethylsilyl)pyridine (10.1 g; 0.067 mole) and *o*-chlorobenzaldehyde (9.4 g; 0.067 mole) were heated at 100° for 4 h to yield after fractionation 16.0 g (82%) of (VIII), b.p. 97°/0.005 mm, $n_D^{26}$ 1.5383. (Found: C, 62.03; H, 6.50; Si, 9.85. $C_{15}H_{18}ClNOSi$ calcd.: C, 61.72; H, 6.23; Si, 9.62%.)

The NMR spectrum of (VIII) in $CCl_4$ exhibited a distorted doublet, representing the 6-pyridyl proton, at $\tau$ 1.59 and integrating for one proton, multiplets from $\tau$ 2.3 to 3.2 integrating for the remaining seven aromatic protons, a singlet at $\tau$ 3.69 integrating for one methine proton, and a singlet at $\tau$ 9.91 integrating for nine protons of the trimethylsilyl group.

The refluxing of (VIII) in 95% ethyl alcohol containing a catalytic amount of dilute hydrochloric acid for 3 h produced quantitative yields of 2-chlorophenyl-2-pyridylmethanol (IX), m.p. 63–65°. Lit.[5] reports m.p. 63–64°.

*(2,6-Dichlorophenyl)-2-pyridylmethyl trimethylsilyl ether (X)*

2-(Trimethylsilyl)pyridine (11 g; 0.073 mole) and 2,6-dichlorobenzaldehyde (12.7 g; 0.073 mole) were heated at 150° for 5 h to yield after recrystallization from hexane, 21.0 g (88.2%) of (X), m.p. 85–87°. (Found: C, 55.32; H, 5.35; N, 4.29. $C_{15}H_{17}Cl_2NOSi$ calcd.: C, 55.20; H, 5.26; N, 4.29%.)

The NMR spectrum of (X) in $CCl_4$ exhibited a distorted doublet, representing the 6-pyridyl proton, at $\tau$ 1.69 and integrating for one proton, multiplets from $\tau$ 2.1 to 3.1 integrating for the remaining six aromatic protons, a singlet at $\tau$ 3.38 integrating for one methine proton, and a singlet at $\tau$ 9.89 integrating for nine protons of the trimethylsilyl group.

Refluxing (X) in 95% ethyl alcohol containing a catalytic amount of dilute hydrochloric acid for 3 h produced quantitative yields of (2,6-dichlorophenyl)-2-

pyridylmethanol (XI), m.p. 79.5–82°. (Found: C, 56.62; H, 3.56. $C_{12}H_9Cl_2NO$ calcd.: C, 56.71; H, 3.58%.)

The NMR spectrum of (XI) in acetone exhibited a distorted doublet, representing the 6-pyridyl proton, $\tau$ 1.49 integrating for one proton, multiplets from $\tau$ 2.05 to 2.95 integrating for the remaining six aromatic protons, a singlet at $\tau$ 3.35 integrating for one methine proton, and a slightly broad singlet at $\tau$ 4.38 integrating for one hydroxyl proton.

## ACKNOWLEDGEMENT

We gratefully acknowledge support of this investigation in part by the Mississippi Research and Development Center and in part by the Paint Research Institute. We also thank Dr. W. H. Daubt of Dow-Corning Corporation for supplying us with generous quantities of silicon reagents.

## REFERENCES

1 F. H. Pinkerton and S. F. Thames, *J. Heterocycl. Chem.*, 6 (1969) 433.
2 D. G. Anderson, M. A. M. Bradney and D. E. Webster, *J. Chem. Soc. B*, (1968) 450.
3 A. F. Webb, D. S. Sethi and H. Gilman, *J. Organometal. Chem.*, 21 (1970) P61.
4 E. H. Huntress and H. C. Walker, *J. Amer. Chem. Soc.*, 70 (1948) 3702.
5 N. Sperber, D. Papa, E. Schwenk and M. Sherlock, *J. Amer. Chem. Soc.*, 71 (1949) 887.