[Contribution from the Department of Chemistry, The University of Buffalo]

# STUDIES IN SILICO-ORGANIC COMPOUNDS. XXIX. THE PREPARATION AND PROPERTIES OF CERTAIN SILA-KETONES

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## DISCUSSION

In 1948, Newman and Smith (1) reported the preparation of ketones in high yields by the interaction of Grignard reagents and acid anhydrides at −70°. Four years later, Hauser and Hance (2) described the preparation of trimethylsilylacetone and of 1-trimethylsilyl-1-phenylacetone by the interaction of trimethylsilylmethylmagnesium bromide and of trimethylsilylphenylmethylmagnesium bromide, respectively, with acetic anhydride:

$$\text{I.}\quad (CH_3)_3SiCH(C_6H_5)MgBr + (CH_3CO)_2O \rightarrow CH_3COOMgBr + (CH_3)_3SiCH(C_6H_5)COCH_3$$

In this work, use was made of the method of Grüttner and Cauer (3, 4) in the preparation of several secondary sila-alcohols. These alcohols have now been oxidized by the Oppenauer method (5–7)

$$\text{II.}\quad p\text{-}(C_2H_5)_3SiC_6H_4CH(OH)CH_3 + CH_3COCH_3 \xrightleftharpoons{Al(OC_4H_9\text{-}tert)_3} p\text{-}(C_2H_5)_3SiC_6H_4COCH_3 + CH_3CH(OH)CH_3$$

In this manner there have been prepared *p*-triethylsilylphenyl methyl ketone, *p*-triethylsilylphenyl ethyl ketone, *p*-triethylsilylphenyl *n*-propyl ketone, *p*-triethylsilylphenyl isopropyl ketone and *p*-triethylsilylphenyl phenyl ketone in respective percentage yields of 41.8, 22.8, 33.3, 48.0, and 59.5.

*p*-Trimethylsilylphenylphenylcarbinol was oxidized to the corresponding ketone by the Oppenauer method, yield 22.8 %.

In the second method of approach to the problem of ketone formation, *p*-triethylsilylphenylmagnesium bromide was added to acetic anhydride. *p*-Triethylsilylphenyl methyl ketone was obtained in 38 % yield. Similarly, using the proper acid anhydrides, *p*-triethylsilylphenyl ethyl ketone, *p*-triethylsilylphenyl *n*-propyl ketone, and *p*-triethylsilylphenyl phenyl ketone were prepared in respective percentage yields of 19.0, 30.0, and 24.0. Corresponding ketones were prepared from the interaction of *p*-trimethylsilylphenylmagnesium bromide and acetic anhydride (39.0 % yield), propionic anhydride (44.0 %), *n*-butyric anhydride (31.0 %), and benzoic anhydride (33.0 %).

## EXPERIMENTAL PART

*p-Trimethylsilylphenyl methyl ketone.* In a 500-cc., three-necked flask equipped with a mercury-sealed stirrer, dropping-funnel, and reflux condenser, 0.15 mole of *p*-trimethylsilylphenylmagnesium bromide was added slowly, in 50 cc. of dry ethyl ether, to 14 cc. (0.15 mole) of acetic anhydride in 130 cc. of dry ethyl ether, at −70°, with stirring. The sys-

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TABLE I

PHYSICAL PROPERTIES OF THE KETONES $p$-$R'_3SiC_6H_4COR$

| R′ | R | b.p., °C. | mm. | $n_D^{25}$ | $d_4^{25}$ | Method |
|---|---|---|---|---|---|---|
| $CH_3$ | $CH_3$ | 89.0 | 1.0 | 1.5145 | 0.9704 | Anhydride |
| $CH_3$ | $C_2H_5$ | 107.5–108.0 | 1.0 | 1.5120 | .9590 | Anhydride |
| $CH_3$ | $n$-$C_3H_7$ | 116.0–117.0 | 1.0 | 1.5084 | .9544 | Anhydride |
| $CH_3$ | $C_6H_5$ | 158.0 | 3.0 | 1.5575 | 1.0370 | Anhydride |
| $CH_3$ | $C_6H_5$ | 156.0 | 3.0 | 1.5581 | 1.0329 | Oppenauer |
| $C_2H_5$ | $CH_3$ | 121.0–122.0 | 1.0 | 1.5159 | .9576 | Oppenauer |
| $C_2H_5$ | $CH_3$ | 125.0–126.0 | 1.0 | 1.5185 | .9572 | Anhydride |
| $C_2H_5$ | $C_2H_5$ | 133 | 1.0 | 1.5150 | .9533 | Anhydride |
| $C_2H_5$ | $C_2H_5$ | 177.0 | 10.0 | 1.5131 | .9498 | Oppenauer |
| $C_2H_5$ | $n$-$C_3H_7$ | 187.0–189.0 | 10.0 | 1.5100 | .9375 | Oppenauer |
| $C_2H_5$ | $n$-$C_3H_7$ | 150.5 | 1.5 | 1.5128 | .9454 | Anhydride |
| $C_2H_5$ | iso-$C_3H_7$ | 136.0–136.5 | 1.0 | 1.5070 | .9415 | Oppenauer |
| $C_2H_5$ | $C_6H_5$ | 184.0 | 2.0 | 1.5633 | 1.0183 | Oppenauer |
| $C_2H_5$ | $C_6H_5$ | 178.0 | 1.5 | 1.5631 | 1.0196 | Anhydride |

tem was stirred at that temperature for an hour, then treated with acidulated ice water. The ether layer, after separation, was washed several times with water then dried over calcium chloride overnight. The filtered ether layer was distilled yielding $p$-trimethylsilylphenyl methyl ketone, 9.5 g., b.p. 89.0° (1 mm.), $n_D^{25}$ 1.5145, $d_4^{25}$ 0.9704, 39% yield.

*Anal.* Calc'd for $C_{11}H_{16}OSi$: Si, 14.61; M.R., 59.21.
Found: Si, 14.38, 14.52, 14.53; M.R., 59.72.

*2,4-Dinitrophenylhydrazone,* m.p. 199.0–199.5°.

*Anal.* Calc'd for $C_{17}H_{20}N_4O_4Si$: Si, 7.52; N, 15.05.
Found: Si, 7.36, 7.46: N, 15.00, 14.79.

*p-Trimethylsilylphenyl ethyl ketone.* In manner similar to the above, 0.16 mole of $p$-trimethylsilylphenylmagnesium bromide reacted with 0.16 mole of propionic anhydride giving $p$-trimethylsilylphenyl ethyl ketone, 14.0 g., b.p. 107.5–108.0° (1 mm.), $n_D^{25}$ 1.5120, $d_4^{25}$ 0.9590, yield 44%.

*Anal.* Calc'd for $C_{12}H_{18}OSi$: Si, 13.60; M.R., 63.64.
Found: Si, 13.33, 13.30; M.R., 64.55.

*2,4-Dinitrophenylhydrazone,* m.p. 190.0–191.5°.

*Anal.* Calc'd for $C_{18}H_{22}N_4O_4Si$: Si, 7.30; N, 14.51.
Found: Si, 7.36, 7.33; N, 14.50, 14.40.

*p-Trimethylsilylphenyl n-propyl ketone.* At −70°, 0.158 mole of $p$-trimethylsilylphenylmagnesium bromide was reacted with 0.16 mole of $n$-butyric anhydride in 180 cc. of dry ethyl ether. $p$-Trimethylsilylphenyl $n$-propyl ketone was isolated, 11.0 g., b.p. 116–117° (1 mm.), $n_D^{25}$ 1.5084, $d_4^{25}$ 0.9544, yield 31%.

*Anal.* Calc'd for $C_{13}H_{20}OSi$: Si, 12.73; M.R., 68.47.
Found: Si, 12.51, 12.61; M.R., 68.87.

*2,4-Dinitrophenylhydrazone,* m.p. 178.5°.

*Anal.* Calc'd for $C_{19}H_{24}N_4O_4Si$: Si, 6.95; N, 14.00.
Found: Si, 6.93; 6.84; N, 13.75, 13.80.

*p-Trimethylsilylphenyl phenyl ketone.* In a 2-liter flask equipped with a reflux condenser, 20 g. (0.078 mole) of $p$-trimethylsilylphenylphenylcarbinol was refluxed for 12 hours with 1200 cc. of dry acetone, 400 cc. of dry benzene, and 20 g. of aluminum *tert*-butoxide. After refluxing, the system was treated with two portions, 100 cc. each, of 20% sulfuric acid and the benzene layer, separated from the aqueous layer, was washed several times with distilled water. The benzene layer then was dried over calcium chloride, overnight. The filtered benzene solution was distilled yielding *p*-trimethylsilylphenyl phenyl ketone, 4.5 g., b.p. 156.0° (3 mm.), $n_D^{25}$ 1.5581, $d_4^{25}$ 1.0329, yield 22.8%.

*Anal.* Calc'd for $C_{16}H_{18}OSi$: Si, 11.03; M.R., 78.82.
Found: Si, 10.85, 10.92; M.R., 79.42.

*2,4-Dinitrophenylhydrazone,* m.p. 172–173°.

*Anal.* Calc'd for $C_{22}H_{22}N_4O_4Si$: Si, 6.46; N, 12.90.
Found: Si, 6.30, 6.36; N, 13.00, 12.92.

As described above, 0.18 mole of *p*-trimethylsilylphenylmagnesium bromide reacted with 0.2 mole of benzoic anhydride, all in 190 cc. of dry ethyl ether, with the formation of *p*-trimethylsilylphenyl phenyl ketone, 15.0 g., b.p. 158° (3 mm.), $n_D^{25}$ 1.5575, $d_4^{25}$ 1.0370, yield 33%.

*Anal.* Found Si, 11.08, 10.98; M.R., 79.05; Mol. Wt., 257.0; (Calc'd Mol. Wt.), 254.4.

*2,4-Dinitrophenylhydrazone,* m.p. 173°.

*Anal.* Found: Si, 6.40, 6.45.

*p-Triethylsilylphenyl methyl ketone.* A 16-hour reflux of 13.5 g. (0.058 mole) of *p*-triethylsilylphenylmethylcarbinol with 700 cc. of dry acetone, 200 cc. of dry benzene, and 10 g. of aluminum *tert*-butoxide produced *p*-triethylsilylphenyl methyl ketone, isolated in the benzene layer after treatment as described above, 5.6 g., b.p. 121–122° (1 mm. $n_D^{25}$ 1.5159, $d_4^{25}$ 0.9576, yield 41.8%.

*Anal.* Calc'd for $C_{14}H_{22}OSi$: Si, 11.97; M.R., 73.10.
Found: Si, 11.90, 11.92; M.R., 73.82.

*2,4-Dinitrophenylhydrazone,* m.p. 187°.

*Anal.* Calc'd for $C_{20}H_{26}N_4O_4Si$: Si, 6.77; N, 13.51; Mol. Wt., 414.6.
Found: Si, 6.85, 6.76; N, 13.60, 13.58; Mol. Wt., 420.0.

*p*-Triethylsilylphenylmagnesium bromide (0.1 mole) was allowed to react with 9.3 cc. (0.1 mole) of acetic anhydride in 130 cc. of dry ethyl ether at −70° with stirring. Stirring was continued for one hour after addition. The system then was treated with ice water, the ether layer was separated, washed several times with water, and dried overnight over calcium chloride. *p*-Triethylsilylphenyl methyl ketone was obtained on distillation, 8 g., b.p. 125–126° (1 mm.), $n_D^{25}$ 1.5185, $d_4^{25}$ 0.9572, yield 38%.

*Anal.* Found: Si, 12.18, 12.28; M.R., 74.30.

*2,4-Dinitrophenylhydrazone,* m.p. 187°.

*Anal.* Found: Si, 6.75, 6.76; N, 13.68, 13.40.

*p-Triethylsilylphenyl ethyl ketone.* A mixture of 17.6 g. (0.07 mole) of *p*-triethylsilylphenylethylcarbinol, 700 cc. of dry acetone, 250 cc. of dry benzene, and 10 g. of aluminum *tert*-butoxide was kept at reflux temperature for 12 hours, then treated as above with isolation of *p*-triethylsilylphenyl ethyl ketone, 4.0 g., b.p. 177.0–177.1° (10 mm.), $n_D^{25}$ 1.5131, $d_4^{25}$ 0.9498, yield 22.8%.

*Anal.* Calc'd for $C_{15}H_{24}OSi$; Si, 11.29; M.R., 77.73.
Found: Si, 11.10, 11.19; M.R., 78.55.

*2,4-Dinitrophenylhydrazone,* m.p. 135–136°.

*Anal.* Calc'd for $C_{21}H_{29}N_4O_4Si$: Si, 6.55; N, 13.08; Mol. Wt., 428.6.
Found: Si, 6.64, 6.59; N, 13.23, 13.10; Mol. Wt., 429.6.

*p*-Triethylsilylphenylmagnesium bromide (0.082 mole) in 50 cc. of dry ethyl ether was slowly added to propionic anhydride (12.85 cc., 0.1 mole) in 100 cc. of dry ethyl ether at −70° with stirring. The system was treated as above, yielding *p*-triethylsilylphenyl ethyl ketone, 3.6 g., b.p. 133° (1 mm.), $n_D^{25}$ 1.5150, $d_4^{25}$ 0.9533, yield 19%.

*Anal.* Found: Si, 11.40, 11.38; M.R., 78.60.

*2,4-Dinitrophenylhydrazone,* m.p. 136°.

*Anal.* Found: Si, 6.60, 6.58.

*p-Triethylsilylphenyl n-propyl ketone.* *p*-Triethylsilylphenyl-*n*-propylcarbinol (17.0 g., 0.065 mole), 400 cc. of dry acetone, 250 cc. of dry benzene, and 10 g. of aluminum *tert*-butoxide were allowed to react as described above, with formation of *p*-triethylsilylphenyl *n*-propyl ketone, 5.0 g., b.p. 187–189° (10 mm.), $n_D^{25}$ 1.5100, $d_4^{25}$ 0.9375, yield 30%.

*Anal.* Calc'd for $C_{16}H_{26}OSi$: Si, 10.70; M.R., 82.36.
Found: Si, 10.49, 10.52; M.R., 83.64.

*2,4-Dinitrophenylhydrazone*, m.p. 103–104°.

*Anal.* Calc'd for $C_{22}H_{30}N_4O_4Si$: Si, 6.34; N, 12.69.
Found: Si, 6.45, 6.43; N, 12.65, 12.60.

*p*-Triethylsilylphenylmagnesium bromide (0.096 mole) in 60 cc. of dry ethyl ether was allowed to react with 15.9 cc. of *n*-butyric anhydride (0.1 mole) in 100 cc. of dry ethyl ether at −70° with formation of *p*-triethylsilylphenyl n-propyl ketone, 8.5 g., b.p. 150.5°, (1.5 mm.), $n_D^{25}$ 1.5128, $d_4^{25}$ 0.9454, yield 33.3%.

*Anal.* Found: Si, 10.90, 10.92; M.R., 83.17; Mol. Wt., 258.

*2,4-Dinitrophenylhydrazone*, m.p. 104°.

*Anal.* Found: Si, 6.40, 6.36.

*p-Triethylsilylphenyl isopropyl ketone. p*-Triethylsilylphenylisopropylcarbinol (21.5 g., 0.082 mole) was mixed with 750 cc. of dry acetone, 250 cc. of dry benzene, and 10 g. of aluminum *tert*-butoxide, then refluxed for 16 hours. Distillation of the washed and dried benzene layer gave *p*-triethylsilylphenyl isopropyl ketone, 12.2 g., b.p. 136.0–136.5° (1 mm.), $n_D^{25}$ 1.5070, $d_4^{25}$ 0.9415, yield 48%.

*Anal.* Calc'd for $C_{16}H_{26}OSi$: Si, 10.70; M.R., 82.36.
Found: Si, 10.65, 10.61; M.R., 82.96.

*2,4-Dinitrophenylhydrazone*, m.p. 149.5°.

*Anal.* Calc'd for $C_{22}H_{30}N_4O_4Si$: Si, 6.34; N, 13.69; Mol. Wt., 442.6.
Found: Si, 6.50, 6.47; N, 12.48, 12.49; Mol. Wt., 444.9.

*p-Triethylsilylphenyl phenyl ketone.* Refluxing for 20 hours a mixture of 16 g. (0.053 mole) of *p*-triethylsilylphenylphenylcarbinol, 750 cc. of dry acetone, 250 cc. of dry benzene, and 10 g. of aluminum *tert*-butoxide gave *p*-triethylsilylphenyl phenyl ketone, 9.5 g., b.p. 184° (2 mm.), $n_D^{25}$ 1.5633, $d_4^{25}$ 1.0183, yield 59.5%.

*Anal.* Calc'd for $C_{19}H_{15}OSi$: Si, 9.47; M.R., 92.71; Mol. Wt., 296.4.
Found: Si, 9.49, 9.52; M.R., 94.56; Mol. Wt., 297.6.

*2,4-Dinitrophenylhydrazone*, m.p. 211°.

*Anal.* Calc'd for $C_{25}H_{28}N_4O_4Si$: Si, 5.89; N, 11.72.
Found: Si, 5.90, 5.78; N, 11.63, 11.70.

The reaction between *p*-triethylsilylphenylmagnesium bromide (0.08 mole) in 50 cc. of dry ethyl ether and 22.6 g. of benzoic anhydride) (0.1 mole) in 200 cc. of dry ethyl ether at −70° gave *p*-triethylsilylphenyl phenyl ketone, 6.5 g., b.p. 178° (1.5 mm.), $n_D^{25}$ 1.5631, $d_4^{25}$ 1.0196, yield 24%.

*Anal.* Found: Si, 9.59, 9.59; M.R., 94.42.

*2,4-Dinitrophenylhydrazone*, m.p. 211–212°.

*Anal.* Found: Si, 5.85, 5.87.

*Grignard reagents.* The preparation of these reagents has already been described in a previous contribution (4).

*Other reagents.* Silicon compounds, acid anhydrides, and acetone were purchased from reliable sources and were found to have satisfactory physical constants. Aluminum *tert*-butoxide was prepared in accordance with a method already in the literature (9).

*Silicon determinations* were carried out as before (4).

*Nitrogen determinations.* A sample weighing between 0.04 g. and 0.05 g. contained in a 100-cc. Kjeldahl flask was treated with 3 cc. of a hydriodic and hypophosphorous acid solution (prepared by mixing 90 cc. of 50% hydriodic acid and 10 cc. of 50% hypophosphorous acid) and was heated gently until most of the liquid had volatilized. Several additions of 2-cc. portions of water with repeated heatings were necessary to remove the white fumes completely. After cooling, 5 cc. of water and 5 cc. of concentrated sulfuric acid were added. Also, 0.5 g. of potassium sulfate and a selenium pellet were added. The mixture was heated again until it had become colorless. After cooling, 10 cc. of water was added until solution was complete. The system was transferred to the Kjeldahl distillation apparatus and 15 cc. of 50% sodium hydroxide solution was added. The steam-distilled ammonia was collected in a receiver containing 50 cc. of 0.01 *N* hydrochloric acid and the latter back titrated with 0.01 *N* sodium hydroxide, using Methyl Red indicator.

## SUMMARY

1. By the Oppenauer method, six chosen secondary sila-alcohols have been converted to the corresponding ketones; *p*-trimethylsilylphenyl phenyl ketone and five ketones of the general formula *p*-$(C_2H_5)_3SiC_6H_4COR$ where "R" is methyl, ethyl, *n*-propyl, isopropyl, and phenyl.

2. By the interaction of the proper Grignard reagent and a chosen acid anhydride, eight sila-ketones have been prepared, of the types *p*-$(CH_3)_3SiC_6H_4COR$ and *p*-$(C_2H_5)_3SiC_6H_4COR$ where "R" is methyl, ethyl, *n*-propyl, and phenyl. Yields were somewhat lower than those obtained by the Oppenauer method.

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