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CYANIDE-ION-CATALYZED REACTION OF PENTAFLUOROPHENYLTRIMETHYLSILANE WITH SUBSTITUTED ACETOPHENONES *

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Summary

Treatment of pentafluorophenyltrimethylsilane (I) with enolizable ketones in the presence of a catalytic amount of potassium cyanide-18-crown-6 complex gave the corresponding trimethylsilyl enol ethers. The same dehydrogenative silylation of highly crowded 2,4,6-trimethylacetophenone with silane I or with Me_3SiCN was extended to the preparation of 1′-(2,4,6-trimethylstyryl)oxytrimethylsilane (XII). On the other hand, potassium cyanide-18-crown-6 complex catalyzed the addition of silane I or Me_3SiCN to the carbonyl group of non-enolizable ketones such as α,α,α-trifluoroacetophenone.

Introduction

Reactions catalyzed by cyanide and fluoride anions have been extensively studied [1,2]. For example, pentafluorophenyltrimethylsilane (I) in the presence of a catalytic amount of potassium cyanide-18-crown-6 complex (II) is well known as an excellent silylating reagent for various enolizable and non-enolizable carbonyl compounds; however, synthetic studies utilizing hindered carbonyl compounds seem to be quite limited [3]. Our interest in this research has prompted us to investigate the possibility of silylating substituted acetophenones. With this aim in mind, we carried out the cyanide-anion-initiated reactions of silane I with substituted acetophenone under comparable conventional conditions (see Experimental).

Results and discussion

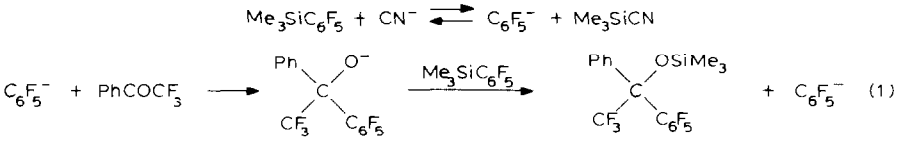
The reaction of enolizable 2,3,4,5,6-pentafluoroacetophenone (III) with an equimolar quantity of silane I in ether in the presence of a catalytic amount of

* Dedicated to Professor Oleg Reutov on the occasion of his 65th birthday on 5 September 1985.

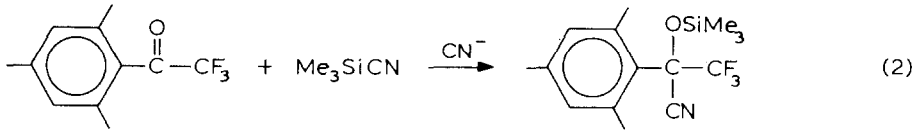
KCN-18-crown-6 complex leads to 1-pentafluorophenyl-1-(trimethylsiloxy)ethylene (IV).

In comparison with the non-fluorinated analogue [3], the reaction of ketone III proceeds slowly (6 months at room temperature). A combination of electronic effects and steric hindrance probably accounts for the reactivity of ketone III [4]. In contrast, the reaction of non-enolizable α,α,α-trifluoroacetophenone (V) with silane I under essentially similar conditions is completed within 10 min to afford the adduct VI. It may be assumed that this reaction occurs with the intermediate formation of $C_6F_5^-$ carbanions according to Scheme 1 (cf. [3]):

SCHEME 1

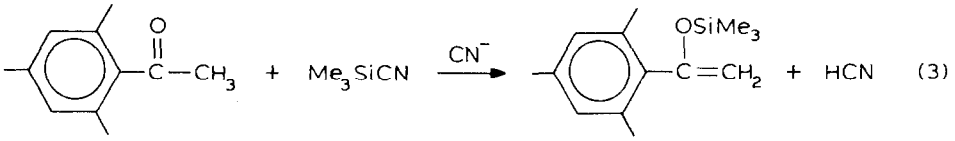


Octafluoroacetophenone, $C_6F_5COCF_3$, fails to react with silane I in the presence of catalyst II even after prolonged reflux in diethyl ether. Our attempts to prepare a similar adduct from highly crowded t-butyl ketone (VII) and silane I in the presence of small amounts of the catalyst were not successful. In contrast, the action of the cyanotrimethylsilane on t-butyl phenyl ketone under comparable experimental conditions gives the expected trimethylsilyl cyanohydrin (VIII) (see also [5]). A similar situation was observed by us in the reactions of silane I and cyanotrimethylsilane with α,α,α-trifluoro-2,4,6-trimethylacetophenone (IX). No reaction was observed when ketone IX was stirred with one equivalent of silane I in diethyl ether at room temperature. However, the reaction with Me_3SiCN under comparable conditions gives adduct X in a high yield.



(IX) (X)

In order to explore further the potential of reagent I, we examined the reaction with sterically crowded 2,4,6-trimethylacetophenone (XI). The present ketone was treated with an equimolar amount of silane I at room temperature in the presence of a catalytic amount of KCN-18-crown-6 complex in diethyl ether. Suprisingly, we observed exclusive formation of the trimethylsilyl enol ether (XII). Moreover, the anion-initiated reaction of Me_3SiCH_2CN (cf. [3]) or Me_3SiCN with ketone XI proceeds analogously. For example:



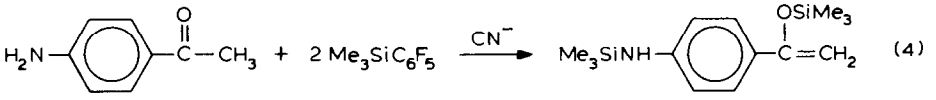
(XI) (XII)

It is known that trimethylcyanosilane is a good reagent for protecting carbonyl groups in organic synthesis [6,7]. The present reaction (eq. 3) is, to our knowledge, the first case in which a sterically hindered ketone fails to form the trimethylsilyl ether of the corresponding cyanohydrin. The mechanism of this reaction is currently being studied. Ketone XI seems to display a steric structure which does not permit the formation of the appropriate *O*-silylated cyanohydrin. On the contrary, ketone XI is characteristic of reactions involving an enolization stage [8].

Some years ago, Fuson et al. reported [9] that ketone XI and other alkyl mesityl ketones react with Grignard reagents in an unusual manner to form halomagnesium enolates. Recently, the kinetics and mechanism of the enolization reactions of some alkyl mesityl ketones (e.g. ketone XI) with Grignard reagents have been discussed [10,11]. The kinetics of the bromination of ketone XI have been measured [12]. The first step of the reaction is postulated to be a fast conversion of the ketoform into the enol form. The rate-determining step may be the reaction of molecular bromine with the enol *.

These observations suggest that the conversion of the keto form into the enol form plays an essential role in the reaction of ketone XI with cyanotrimethylsilane (eq. 3).

In the reaction of *p*-aminoacetophenone (XIII) with silane I, the attack is believed to take place not only at the carbonyl group but also at the NH_2 fragment, the latter being attacked first. The *p*-trimethylsilylaminoacetophenone (XIV) generated in this case was isolated in 85% yield. The structure of product XIV was confirmed by ^{29}Si NMR spectroscopy. Thus, the 1.30 ppm chemical shift is related to the Si–N bond [13].



(XIII) (XIV)

With *m*-aminoacetophenone, the reaction proceeds in a similar way but at a higher rate. The fact that in compound XIII and its *meta*-analogue the amino groups undergo silylation is proved by the cyanide-anion-initiated reaction of diphenylamine with silane I. The yield of diphenyl(trimethylsilyl)amine (XV) is a quantitative one.

Experimental

All reactions were carried out in evacuated, sealed ampoules following the technique described in ref. 14. All experiments were carried out by a standard procedure. Examples for VI and XII are given.

Reaction of trimethylpentafluorophenylsilane with α,α,α-trifluoroacetophenone

A mixture of 4.14 g of $Me_3SiC_6F_5$, 3.01 g of $PhCOCF_3$, 0.13 g of KCN-18-crown-6

* *Note added in proof*. The data concerning the mechanism of acid catalyzed bromination of a hindered 2,4,6-trimethylacetophenone (XI) are reported in more detail in a paper by A.G. Pinkus and R. Gopalan (J. Am. Chem. Soc., 106 (1984) 2630).

The rate of the reaction of bromine with ketone XI was nearly 900 times faster than with the unhindered analogue, acetophenone, under comparable conditions.

complex and 30 ml of acetonitrile was stirred magnetically at ambient temperature for 10 min. The solvent was removed under reduced pressure and the residue was distilled in vacuo to give 6.05 g (84.7%) of 1-phenyl-1-pentafluorophenyl-1-trimethylsiloxy-2,2,2-trifluoroethane (VI), b.p. 83°C/0.5 mmHg; n_D^{20} 1.4637 (Found: C, 49.69; H, 3.66; F, 36.02; Si, 6.34. $C_{17}H_{14}F_8OSi$ calcd.: C, 49.28; H, 3.41; F, 36.68; Si, 6.78%). IR (cm^{-1}): 840, 1250 ($SiMe_3$); 1130–1200 (=CF,CF_3). ^1H NMR (CCl_4) (δ, ppm): 0.003 (s, 9H, $SiMe_3$), 7.34 (s, 5H, C_6H_5).

Reaction of trimethylcyanosilane with 2,4,6-trimethylacetophenone

A mixture of 4.02 g of 2,4,6-$Me_3C_6H_2COMe$, 2.44 g of Me_3SiCN, 0.24 g of KCN-18-crown-6 and 30 ml of THF was stirred magnetically at room temperature for 6.5 months. The reaction mixture was worked up as usual to give 4.02 g (69.6%) of [1′-(2,4,6-trimethylstyryl)oxy] trimethylsilane (XII), b.p. 56°C/0.5 mmHg, n_D^{20} 1.4935. (Found: C, 72.17; H, 9.24; Si, 10.26. $C_{14}H_{22}OSi$ calcd.: C, 71.73; H, 9.16; Si, 11.98%). IR (cm^{-1}); $\nu(Me_3Si)$ 850, 1250; ν(SiOC) 1011; ν(C=C) 1632. ^1H NMR (CCl_4) (δ, ppm): 0.15 (s, 9H, $SiMe_3$), 2.21 (s, 3H, p-CH_3), 2.25 (s, 6H, o-CH_3), 4.05, 4.49 (dd, 2H, =CH_2, ^2J 0.5 Hz), 6.01 (s, 2H, C_6H_2). $\delta(^{29}Si)$ 15.5 ppm.

2-Phenyl-2-trimethylsilyloxy-3,3-dimethylbutyronitrile. The adduct was prepared in 94.6% yield. B.p. 64°C/0.5 mmHg, n_D^{20} 1.4795. (Found: C, 68.98; H, 8.93; N, 5.20; Si, 10.62. $C_{15}H_{23}NOSi$ calcd.: C, 68.91; H, 8.87; N, 5.36; Si, 10.74%). IR (cm^{-1}): $\nu(Me_3Si)$ 850, 890; ν(SiOC) 1135; ν(C≡N) 2230. ^1H NMR (CCl_4) (δ, ppm): 0.13 (s, 9H, $SiMe_3$), 0.98 (s, 9H, Bu^t), 7.33 (m, 5H, C_6H_5). $\delta(^{29}Si)$ 20.64 ppm.

2-(2,4,6-Trimethylphenyl-2-trimethyloxy-3,3,3-trifluoropropionitrile (X). IR (cm^{-1}): $\nu(Me_3Si)$ 840, 1250; $\nu(CF_3)$ 1200. ^1H NMR (CCl_4) (δ, ppm): 0.33 (s, 9H, $SiMe_3$), 2.27 (s, 3H, p-Me), 2.58 (s, 6H, o-Me), 5.39 (s, 2H, C_6H_2); MS m/e 315 (M^+), 246 ($M^+ - CF_3$), 225 ($M^+ - Me_3SiOH$), 147 [$M^+ - F_3CC(OSiMe_3)CN$].

4-N-Trimethylsilylaminoacetophenone

The product was prepared (CH_3CN, 7 h) in 85.5% yield, b.p. 121°C/0.5 mmHg, n_D^{20} 1.5858. (Found: C, 63.52; H, 8.24; N, 6.81; Si, 13.48. $C_{11}H_{17}NOSi$ calcd.: C, 63.72; H, 8.27; N, 6.76; Si, 13.55%). ^1H NMR (CCl_4) (δ, ppm): 0.26 (s, 9H, $SiMe_3$), 2.40 (s, 3H, CH_3), 4.69 (s, 1H, NH), 6.64, 7.71 (dd, 4H, C_6H_4, ^3J 8.06 Hz). $\delta(^{29}Si)$ 1.30 ppm.

1-(4-N-Trimethylsilylaminophenyl)-1-trimethylsiloxyethene

Compound XVI was isolated (CH_3CN, 30 h; or Et_2O, 360 h) in 54.5 and 77.1% yields, respectively, b.p. 102–103°C/0.5 mmHg, n_D^{20} 1.5238. (Found: C, 60.36; H 8.86; N, 4.99; Si, 19.62. $C_{14}H_{25}NOSi_2$ calcd.: C, 60.15; H, 9.02; N, 5.01; Si, 20.10%). IR (cm^{-1}); $\nu(Me_3Si)$ 830, 1250; ν(SiOC) 1020; ν(C=C) 1602; ν(NH) 3390. ^1H NMR (CCl_4) (δ, ppm): 0.24 (s, 18H, $SiMe_3$), 3.34 (s, 1H, NH), 4.13, 4.60 (dd, 2H, =CH_2, ^2J 1.35 Hz), 6.45–7.27 (m, 4H, C_6H_4). $\delta(^{29}Si)$ 16.8 ppm (SiO), 2.35 ppm (SiN).

Diphenylaminotrimethylsilane

A mixture of 2.02 g of Ph_2NH, 2.84 g of $Me_3SiC_6F_5$, 0.02 g of KCN, 0.12 g of 18-crown-6 and 20 ml of THF was stirred magnetically at ambient temperature for 2 h. The solvent was removed under reduced pressure and the residue was recrystallized in hexane to give 2.00 g (70%) of silane XV. M.p. 44–45°C. ^1H NMR ($CDCl_3$) (δ, ppm): 0.25 (s, 9H, $SiMe_3$), 6.84–7.33 (m, 10H, $2 \times C_6H_5$), $\delta(^{29}Si)$ 6.1 ppm.

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