1.1 and 11.1 Hz, 1 H), 2.65 (t, J = 6.9 Hz, 2 H), 2.09 (q, J = 6.8 Hz, 2 H), 1.88 (quint, J = 6.9 Hz, 2 H), 1.18 (s, 6 H).

16: IR (neat, cm^{-1}) 3010, 2940, 2860, 1650, 1450, 1420, 1380, 1200, 1150, 880, 770, 690, 640; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.30–6.24 (dt, J = 4.48 and 12.5 Hz, 1 H), 5.97–5.92 (dt, J = 2.0 and 12.5 Hz, 1 H), 2.39–2.20 (m, 2 H), 2.15–1.95 (m, 2 H), 1.80–1.70 (m, 2 H), 1.70–1.50 (m, 6 H), 1.48–1.30 (m, 2 H); mass spectrum, m/z (M^+) calcd 164.1201, obsd 164.1185.

17: IR (neat, cm^{-1}) 3020, 2960, 2860, 1705, 1470, 1450, 1440, 1355, 680; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.70–5.60 (m, 1 H), 5.52 (d, J = 11.2 Hz, 1 H), 2.65 (t, J = 6.5 Hz, 2 H), 2.25–2.08 (m, 4 H), 1.90 (quint, J = 6.5 Hz, 2 H), 1.78–1.50 (m, 6 H); mass spectrum, m/z (M^+) calcd 164.1201, obsd 164.1217.

25: IR (neat, cm^{-1}) 2960, 2940, 2870, 1670, 1625, 1475, 1465, 1455, 1385, 1365, 1310, 1260, 1255, 1100, 1075, 890, 850, 835, 775, 670; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.73 (d, J = 0.93 Hz, 1 H), 3.52–3.39 (m, 1 H), 2.34 (ddt, J = 1.32, 4.85, and 13.62 Hz, 1 H), 2.02–1.93 (m, 1 H), 1.85–1.40 (m, 7 H), 1.27 (tq, J = 4.39 and 13.31 Hz, 1 H), 1.10 (s, 3 H), 1.08 (s, 3 H), 1.03 (s, 3 H), 0.86 (s, 9 H), 0.02 (s, 3 H), 0.00 (s, 3 H); mass spectrum, m/z ($M^+ - C_4H_9$) calcd 279.1780, obsd 279.1803.

26: IR (neat, cm^{-1}) 2970, 2940, 2860, 1712, 1670, 1475, 1380, 1365, 1260, 1250, 1100, 1085, 1030, 1010, 970, 960, 940, 860, 775, 670, 640; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.10 (d, J = 1.52 Hz, 1 H), 3.35 (dd, J = 4.71 and 10.92 Hz, 1 H), 2.68–2.44 (m, 2 H), 2.34–2.22 (m, 1 H), 1.94–1.48 (m, 7 H), 1.25 (s, 3 H), 1.18 (s, 3 H), 1.00 (s, 3 H), 0.86 (s, 9 H), 0.02 (s, 3 H), 0.00 (s, 3 H); mass spectrum, m/z ($M^+ - C_4H_9$) calcd 279.1780, obsd 279.1780.

29: IR (neat, cm^{-1}) 3010, 2960, 2930, 2860, 1660, 1615, 1465, 1455, 1390, 1360, 1250, 1075, 1005, 960, 940, 910, 880, 830, 770; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.79 (s, 1 H), 5.78–5.70 (m, 1 H), 5.60–5.52 (m, 1 H), 3.54 (d, J = 5.8 Hz, 1 H), 3.18 (dt, J = 5.7 and 13.2 Hz, 1 H), 2.85–2.72 (br d, J = 16.0 Hz, 1 H), 2.62–2.51 (dq, J = 4 and 17 Hz, 1 H), 2.40–2.29 (dd, J = 7.7 and 16.7 Hz, 1 H), 2.10–1.85 (m, 5 H), 1.75–1.60 (m, 2 H), 1.30–1.26 (dd, J = 6.7 and 14.6 Hz, 1 H), 1.05 (s, 3 H), 1.01 (s, 3 H), 0.93 (d, J = 7.3 Hz, 3 H), 0.91 (s, 9 H), 0.024 (s, 3 H), 0.018 (s, 3 H); mass spectrum, m/z ($M^+ - C_4H_9$) calcd 331.2093, obsd 331.2080.

30: IR (neat, cm^{-1}) 2960, 2940, 2860, 1660, 1610, 1470, 1450, 1250, 1090, 1005, 950, 905, 850, 835, 770; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.97 (s, 1 H), 3.27 (d, J = 4.26 Hz, 1 H), 3.08–2.94 (dt, J = 6.3 and 13.3 Hz, 1 H), 2.20–1.45 (m, 12 H), 1.20–1.10 (dd, J = 6.25 and 14.6 Hz, 1 H), 1.06 (s, 3 H), 1.03 (s, 3 H), 0.95 (d, J = 7 Hz, 3 H), 0.90 (s, 9 H), –0.02 (s, 6 H); mass spectrum, m/z ($M^+ - C_4H_9$) calcd 413.1470, obsd 413.1466.

34: IR (neat, cm^{-1}) 3080, 2975, 2935, 2900, 2875, 1680, 1650, 1475, 1455, 1400, 1387, 1360, 1223, 1042, 1020, 840; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.94–5.90 (m, 1 H), 4.67–4.63 (m, 2 H), 2.39–2.12 (m, 3 H), 1.85 (q, J = 1.62 Hz, 3 H), 1.68 (t, J = 0.88 Hz, 3 H), 1.77–1.52 (m, 2 H), 1.17 (s, 3 H), 1.05 (s, 3 H); mass spectrum, m/z (M^+) calcd 192.1514, obsd 192.1517.

35: IR (neat, cm^{-1}) 3095, 3030, 2980, 2950, 2875, 1715, 1685, 1650, 1455, 1378, 1365, 1275, 1095, 890; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.45 (dt, J = 1.30 and 7.61 Hz, 1 H), 4.73–4.71 (m, 2 H), 2.82–2.63 (m, 2 H), 2.53–2.42 (m, 1 H), 2.14–1.92 (m, 2 H), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.12 (s, 3 H), 1.11 (s, 3 H); mass spectrum, m/z (M^+) calcd 192.1514, obsd 192.1523.

38: IR (neat, cm^{-1}) 3080, 2960, 2875, 1675, 1650, 1450, 1375, 1220, 1060, 1025, 930, 890; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.05–5.98 (m, 1 H), 4.75–4.65 (m, 2 H), 2.38–2.25 (m, 4 H), 1.97–1.36 (m, 9 H), 1.88 (t, J = 1.60 Hz, 3 H), 1.70 (t, J = 0.97 Hz, 3 H); mass spectrum, m/z (M^+) calcd 218.1671, obsd 218.1660.

39: IR (neat, cm^{-1}) 3098, 3030, 2970, 2950, 2880, 1710, 1650, 1455, 1445, 1380, 1330, 1275, 1220, 1135, 1070, 1030, 890, 840; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.46 (dt, J = 1.29 and 7.48 Hz, 1 H), 4.75–4.72 (m, 2 H), 2.71 (dd, J = 8.46 and 13.15 Hz, 2 H), 2.53 (dd, J = 11.82 and 13.95 Hz, 1 H), 2.24–1.95 (m, 4 H), 1.88–1.55 (m, 6 H), 1.76 (s, 3 H), 1.71 (s, 3 H); mass spectrum, m/z (M^+) calcd 218.1671, obsd 218.1671.

Acknowledgment. This work was supported by PHS Grant GM 30827. A preliminary experiment by Dr. T. J. Nitz and laboratory assistance by Michael E. O'Brien are gratefully acknowledged.

Investigation of the Formation of Methyl 2-Cyano-2-[(trimethylsilyl)oxy]-4-oxopentanoate from Methyl 2,4-Dioxopentanoate. A Clarification of the Pathway for the Reaction of Trimethylsilyl Cyanide with Enolized β-Diketones

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Received June 13, 1985

The possible reaction pathways for the reaction of methyl 2,4-dioxopentanoate (1) with trimethylsilyl cyanide, with and without catalysts present, have been investigated by monitoring these reactions by ^1H NMR. While all reactions of 1 with Me_3SiCN, whether catalyzed or uncatalyzed, involve the initial formation of the silyl enol ether **5**, it is not an intermediate in the formation of the cyanohydrin **3** from the reaction of 1 with Me_3SiCN alone or in the presence of ^-CN. Evidence is presented which indicates that the silyl enol ether **5** and HCN are in equilibrium with 1 and Me_3SiCN and that it is the keto tautomer **1a**, containing a very reactive α-keto ester group, which reacts with Me_3SiCN to produce **3** (Scheme III). The existence of the equilibrium **5** + HCN ⇌ 1 + Me_3SiCN is demonstrated by isolation of the cyclic silyl enol ether cyanohydrin **9** when the silyl enol ether **5** is allowed to react with $Me_2Si(CN)_2$. Evidence that trialkylsilyl cyanides react with the keto tautomer of 1, and the exclusion of other possible reaction pathways, is obtained on reaction of 1 with *t*-$BuMe_2SiCN$ to give the *tert*-butyldimethylsilyl enol ether **10** and the unprotected cyanohydrin **11**. The reaction of 2,4-pentanedione (**4**) with Me_3SiCN, with and without the presence of catalysts, was reinvestigated and the mechanism is shown, in contrast with the earlier proposals,[5,6] to be consistent with the mechanistic ideas presented here for the reaction of 1 with Me_3SiCN.

Previously we reported[1] that treatment of 1 at room temperature with 1 equiv of trimethylsilyl cyanide (Me_3SiCN) and a catalytic amount of zinc iodide[2,3] gave a 1:1 mixture of the trimethylsilyl-protected cyanohydrin enol ether **2** and starting material and that by increasing

(1) Foley, L. H. *Synth. Commun.* **1984**, *14*, 1291.

(2) Evans, D. A.; Truesdale, L. K.; Carroll, G. L. *J. Chem. Soc., Chem. Commun.* **1973**, 55.

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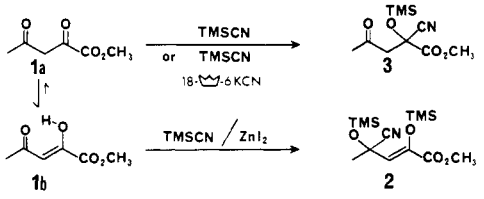
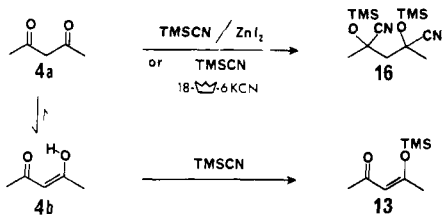
the amount of Me_3SiCN to 2 equiv the complete conversion of 1 into 2 was observed. A route to the cyanohydrin



3 was based on the premise that only the α-keto carbonyl carbon of 1 should be sufficiently electrophilic to react with Me_3SiCN without a catalyst. Indeed when 1 was treated with Me_3SiCN alone the sole product was the cyanohydrin 3. Interestingly 3 was also the product of a very rapid reaction of 1 with Me_3SiCN in the presence of the KCN·18-crown-6 complex as a catalyst.[1]

Methyl 2,4-dioxopentanoate (1) on reaction with Me_3SiCN alone or Me_3SiCN in the presence of the KCN·18-crown-6 complex gave only 3, none of the trimethylsilyl cyanohydrin enol ether 2 could be detected, while reaction of 1 with Me_3SiCN in the presence of zinc iodide afforded only 2 with no detectable amounts of 3. Each reaction is thus mutually exclusive!

Earlier Gostevskii et al.[5,6] had reported that 2,4-pentanedione (4) on reaction with Me_3SiCN alone gave the silyl enol ether 13, while the reaction of 4 with Me_3SiCN



in the presence of zinc iodide or the KCN·18-crown-6 complex afforded only the dicyanohydrin 16. On the basis of these results the authors proposed that 4 reacted with Me_3SiCN in its enol form, while with Me_3SiCN in the presence of catalysts 4 reacted via its keto tautomer.

Thus Me_3SiCN also appeared to show selectivity in its reaction with 2,4-pentanedione (4); however, there was clearly a discrepancy concerning the tautomeric forms in which 1 and 4 appeared to be reacting with Me_3SiCN. For example, the formation of only 3 on the reaction of methyl 2,4-dioxopentanoate (1) with Me_3SiCN (alone) would suggest that 1 was reacting as the keto tautomer, while the isolation of the silyl enol ether 13 from the reaction of Me_3SiCN with 2,4-pentanedione (4) suggested that this β-diketo compound was reacting via the enol form. This discrepancy was also apparent on analysis of the products of the reactions of 1 and 4 with Me_3SiCN in the presence of either zinc iodide or the KCN·18-crown-6 complex as the catalysts.

It must be noted that the mechanistic proposals of the Russian workers and our preceding comments concerning these reactions are questionable since they are based only on the products actually isolated and not on the observation of any intermediates in these reactions. The lack of a sound basis for these proposals and the fact that the β-dicarbonyl compounds 1 and 4 are highly enolized and that Me_3SiCN is known to silylate enols and alcohols

Chart I

	H3	H5	CO_2CH_3	$SiMe_2R$
1b	6.40	2.27	3.93	
2	5.92	1.73	3.80	0.27 & 0.32
5	6.26	2.37	3.87	0.30
3	3.27	2.20	3.89	0.25
	3.37	1.75	3.93	0.25
9	6.05	1.77	3.86	0.39 & 0.48
10	6.31	2.37	3.85	0.98(tBu), 0.25
11	3.42	2.23	3.97	

readily at room temperature[4] led us to an investigation of these reactions. The consideration of other reaction pathways became of even more interest when it was found that the first products formed in reactions of either 1 or 4 with Me_3SiCN, whether catalyzed or not, was the corresponding silyl enol ethers, 5[1] and 13.

Three reaction pathways leading from 1 to 3 have been considered: (1) the addition of HCN to the α,β-unsaturated carbonyl system of 5 to afford 3 directly; (2) a 1,5-shift of the silyl group in 5 to give the α-keto ester 6 which reacts further to give 3; (3) an equilibrium between the silyl enol ether 5 and starting material; the keto tautomer, 1a, of the starting material would then react with Me_3SiCN to yield 3.

The results of investigations which allow the distinction between these reaction pathways, using ^1H NMR to identify intermediates in the reactions of 1 with various alkylsilyl cyanides, are now presented.

Results and Discussion

The Me_3SiCN reactions were run neat at room temperature to allow the detection of intermediates in these reactions by analysis of the ^1H NMR spectra of aliquots removed at various times. In all reactions aliquots were removed and catalysts were added without opening the reaction flasks so that no loss of HCN occurred. As shown in Charts I and II, for each reaction the products and possible intermediates have at least one characteristic proton resonance (H-3) which is sufficiently removed from the other resonances to make ^1H NMR a useful method for following these reactions.

A. Reactions of Methyl 2,4-Dioxopentanoate (1) with Me_3SiCN. The reaction 1 with Me_3SiCN, with or without the presence of a Lewis acid or KCN·18-crown-6, resulted in the rapid formation of the silyl enol ether 5 and HCN, as evidenced by the complete disappearance in the ^1H NMR spectrum of the peak at δ 6.40 for the vinyl proton of 1 and the appearance of a new peak at δ 6.26 for

(3) Groutas, W. C.; Felker, D. *Synthesis* **1980**, 861.
(4) Evans, D. A.; Hoffman, J. M.; Truesdale, L. K. *J. Am. Chem. Soc.* **1973**, *95*, 5822.
(5) Gostevskii, B. A.; Kruglaya, O. A.; Albanov, A. I.; Vyazankin, N. S. *J. Gen. Chem. USSR (Engl. Transl.)* **1981**, *51*, 676.
(6) Gostevskii, B. A.; Kruglaya, O. A.; Albanov, A. I.; Vyazankin, N. S. *J. Organomet. Chem.* **1980**, *187*, 157.

Chart II

		H1	H3	H5	$SiMe_3$
4		2.03	5.57	2.03	
		2.23	3.60	2.23	
13	Z	2.13	5.30	2.13	0.30
	E	2.27	5.63	2.13	0.27
14	(major)	1.75	4.48	1.87	0.27
	(minor)	1.75	4.80	2.00	0.30
15		1.67	2.87	2.23	0.25
16		1.67& 1.72	2.03& 2.23	1.67& 1.72	0.30& 0.26

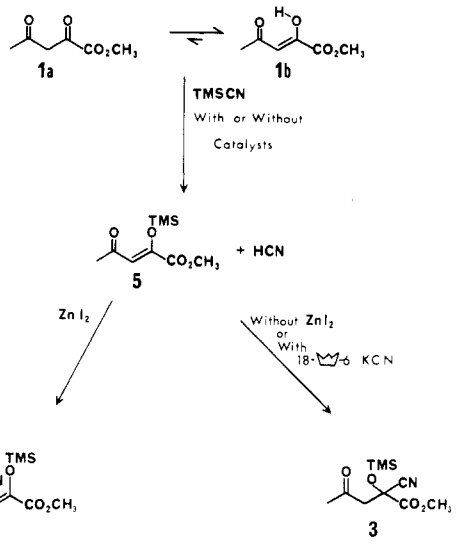
the vinyl proton of **5**. In the presence of zinc iodide the silyl enol ether **5** reacted further to give **2**; the mechanism of this reaction is discussed later.

1. **Reaction of 1 with Me_3SiCN (Neat) or in the Presence of KCN·18-Crown-6.** The reaction of **1** with Me_3SiCN alone resulted initially in the formation of **5** and HCN. On monitoring the reaction by ^1H NMR the peak corresponding to the vinyl hydrogen of **5** was observed, over several days, to disappear slowly as the peak at δ 3.27 for the methylene protons of **3** appeared. On the other hand the reaction of **1** with Me_3SiCN in the presence of the KCN·18-crown-6 complex to give **3** was extremely fast at room temperature. Only by running this reaction at 0 °C was it possible to observe, by ^1H NMR, the formation of the silyl enol ether **5** and again see the disappearance of **5** as **3** was formed. When distilled **5** (no HCN present) was treated with Me_3SiCN in the presence of KCN·18-crown-6 the reaction took the same course, again giving **3**, but this reaction was considerably slower, requiring over 24 h for completion. However, if **1** was allowed to react with Me_3SiCN alone to give **5** and HCN and then the KCN·18-crown-6 complex was introduced the formation of **3** was again rapid, indicating a catalytic effect of HCN on this reaction. Thus it initially appeared that the silyl enol ether **5** might be an intermediate in both the uncatalyzed and KCN·18-crown-6 catalyzed reactions. These observations are summarized in Scheme I

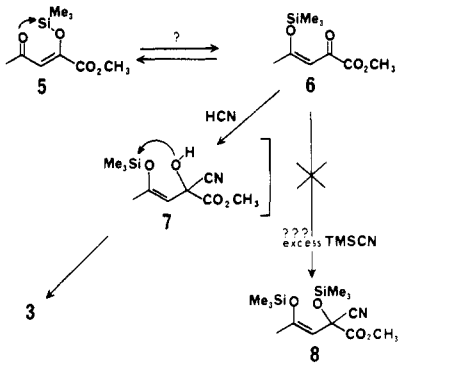
a. Possible Reaction Pathways. There are two pathways involving the silyl enol ether **5** as an intermediate which can be considered as an explanation for the formation of **3** on reaction of **1** with neat Me_3SiCN. One mechanism would involve the 1,4-addition of HCN to the unsaturated ketone system of the silyl enol ether **5**. Such a mechanism is unattractive on electronic grounds since it would require the unfavorable generation of a positive charge on a carbon adjacent to a carbonyl carbon, even though in this case such an effect is mitigated by the silyloxy substituent. It is important to note in this regard that 2,4-pentanedione (**4**) on reaction with Me_3SiCN gives only the silyl enol ether **13** (Scheme VI). Even after extended reaction times **13** does not undergo a 1,4-addition of HCN, even though this molecule does not suffer from the unfavorable electronic effect described above for the silyl enol ether **5**.

The Michael addition of cyanide ion to the α,β-unsaturated enone system of **5** might explain the observed production of **3** on reaction of **1** with Me_3SiCN in the presence of KCN·18-crown-6. However, it should be noted that the reaction of α,β-unsaturated ketones with Me_3SiCN in the presence of the KCN·18-crown-6 catalyst resulted in 1,2-addition and not 1,4-addition. Therefore this explanation is also unlikely for the KCN·18-crown-6 catalyzed reaction.

Scheme I



Scheme II

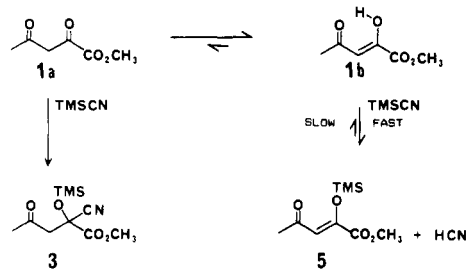


A second pathway considered (Scheme II) would involve an initial intramolecular 1,5-shift of the trimethylsilyl group in **5** to give the α-keto ester **6**. The α-keto group of **6** would be expected to undergo a rapid reaction with HCN to give **7**, which after a second intramolecular silyl shift, would then afford **3**. Such intramolecular 1,5-silyl shifts are well-known in enolized β-diketones.[7]

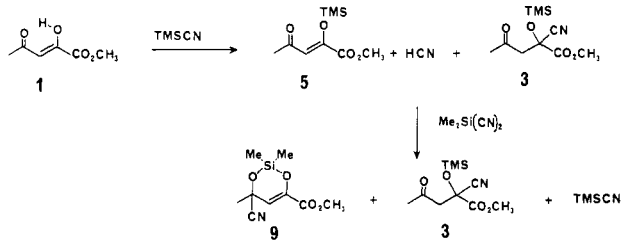
If the α-keto ester derivative **6** is an intermediate in the formation of **3**, it would be expected that reaction of **1** with a large excess of Me_3SiCN would allow the interception of **6** as the trimethylsilyl-protected cyanohydrin enol ether **8**. In fact, when this reaction is carried out the only product observed is the trimethylsilyl enol ether **5** with no evidence for the formation of **8**. Thus this initially very appealing explanation has no experimental support. It should be noted at this point that the silyl enol ether **5** appears to be a single isomer from analysis of its ^{13}C and ^1H NMR spectra. We have been unable to detect any 1,5-silyl shift[7] in this silyl enol ether up to 50 °C. The absence of such a silyl shift might indicate that **5** exists as the *E* isomer and not as the *Z* isomer shown in structure **5**. However, the product of a 1,5-silyl shift, the silyl enol ether **6**, lacks the extended conjugation present in **5** and

(7) Pinnavaia, T. J.; McClarin, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 3012 and references cited therein.

Scheme III



Scheme IV

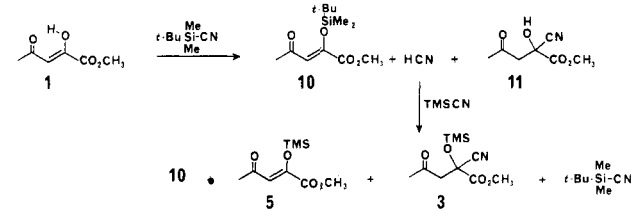


therefore should be less stable than the observed silyl enol ether **5**. On the basis of ^{1}H NMR NOE experiments (irradiation of the methyl protons of the ester group resulted in an enhancement of the signal for the vinyl hydrogen) we have assigned **5** the *Z* configuration as shown. It therefore appears that the failure to observe a 1,5-silyl shift reflects the greater stability of the enol **5** and is not due to the configuration of the double bond.

A third possible explanation for the transformation of **1** into **3**, involves the reversible formation of the silyl enol ether **5** (Scheme III). If such an equilibrium pertains then this equilibrium mixture will contain not only the silyl enol ether **5** and the enol **1b** but also small amounts of the keto tautomer **1a**. It would then be the minor component of this equilibrium, the keto tautomer **1a**, which represents the reactive species undergoing reaction with Me_3SiCN to give the trimethylsilyl-protected cyanohydrin **3**. Indeed if the α-keto ester **1** is allowed to react with Me_3SiCN to give a mixture of the silyl enol ether **5**, HCN, and cyanohydrin **3** and then to this mixture is added $Me_2Si(CN)_2$,[8] the formation of the cyclic silyl enol ether cyanohydrin **9**, the trimethylsilyl protected cyanohydrin **3**, and Me_3SiCN are observed (Scheme IV). The ratio of **5** to **3** before the addition of $Me_2Si(CN)_2$ is identical with the ratio of the products **9** and **3** at the end of the reaction. The fact that this ratio does not change over time indicates that the formation of the cyanohydrin **3** is not, or is only slowly, reversible. The replacement of the trimethylsilyl group in **5** by the dimethylsilyl group, with formation of the cyclic derivative **9**, demonstrates that the silyl enol ether **5** is in equilibrium with the starting material **1**.

A final and convincing experiment which supports the mechanistic proposal outlined in Scheme III involved the reaction of **1** with *t*-BuSiMe$_2$CN[9] to afford the silyl enol ether **10** and the unprotected cyanohydrin **11** (Scheme V). The formation of only the unprotected cyanohydrin **11** clearly shows that this reaction is proceeding via the keto tautomer **1a**. Reaction of the mixture of **10** and **11** with excess Me_3SiCN gave the silyl enol ethers **10** and **5**, the

Scheme V



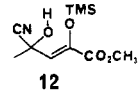
trimethylsilyl-protected cyanohydrin **3**, and *t*-BuSiMe$_2$CN. Had the reaction occurred by the addition of HCN to the silyl enol ether **10** a *tert*-butyldimethylsilyl-protected cyanohydrin would have been formed and not, as observed, the unprotected cyanohydrin **11**.

The reaction pathway which is outlined in Scheme III is also consistent with the formation of only the silyl enol ether **5**, and no **8**, when **1** was allowed to react with excess Me_3SiCN. In the presence of large excesses of Me_3SiCN the equilibrium is driven largely to the side of the silyl enol ether **5** and will contain none of the starting material **1**. Since it is the keto tautomer of **1** which is required for the formation of the cyanohydrin **3** with 1 equiv of Me_3SiCN, with excess Me_3SiCN the formation of only the silyl enol ether **5** is the expected and observed result.

The reaction of **1** with *t*-BuSiMe$_2$CN in the presence of the KCN·18-crown-6 complex also gave the silyl enol ether **10** and the cyanohydrin **11**. This result supports the mechanism (as outlined in Scheme III) involving an equilibrium between the silyl enol ether **5** and starting keto ester **1**, with the keto tautomer **1a** being the reactive species in this reaction as well. Further support for this suggestion is found in the observation that treatment of **1** with excess Me_3SiCN in the presence of the KCN·18-crown-6 complex gave none of the cyanohydrin **3** but rather afforded the silyl enol ether **5** and the silyl enol ether cyanohydrin **2**. Again with excess Me_3SiCN the equilibrium lies on the side of the silyl enol ether **5**; this result indicates that the keto tautomer of **1** is required for formation of **3** from reaction of **1** with Me_3SiCN in the presence of KCN·18-crown-6.

2. The Reaction Pathway of the Zinc Iodide Catalyzed Reaction of 1 with Me_3SiCN. On reaction of **1** with 1 equiv of Me_3SiCN in the presence of zinc iodide, the initially formed silyl enol ether **5** and HCN reacted further to give a mixture of **2** and starting material. Additional evidence for the intermediacy of **5** in this reaction was obtained by allowing **1** to react with Me_3SiCN (1 equiv) in the absence of a Lewis acid, verifying by ^{1}H NMR the formation of the silyl enol ether **5** and HCN, and then introducing zinc iodide into the closed system. Once again a 1:1 mixture of **2** and starting material was obtained.

The mechanism of this reaction appears to be straightforward, involving the zinc iodide catalyzed cyanohydrin formation from ketones.[2,3] When 1 equiv of Me_3SiCN is used the remaining keto group in **5** reacts with HCN to afford the cyanohydrin **12**. The cyanohydrin **12**



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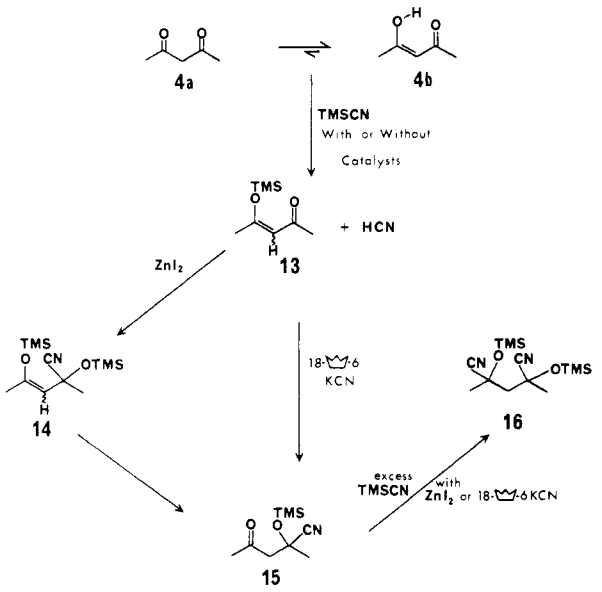
is then converted into the trimethylsilyl-protected cyanohydrin **2** by an intermolecular transfer of the trimethylsilyl group[10] from **5**, giving the starting material **1** and product **2**.

(8) Ryu, I.; Murai, S.; Horiike, T.; Shinonaga, A.; Sonoda, N. *Synthesis* **1978**, 154. These authors have reported the use of this reagent in reactions with enolizable β-diketones.[11]

(9) Two recent preparations of *tert*-butyldimethylsilyl cyanide have appeared: Baker, D. C.; Putt, S. R.; Showalter, H. D. H. *J. Heterocycl. Chem.* **1983**, *20*, 629. (The procedure is in a footnote of the preceding as a private communication from D. A. Evans and is an easy and reliable method.) Hwu, J. R.; Lazar, J. G.; Corless, P. F. *Synthesis* **1984**, 1020.

(10) The intermolecular transfers of trialkylsilyl groups from trialkylsilyl enol ethers are well-known, see, for example: Veysoglu, T.; Mitscher, L. A. *Tetrahedron Lett.* **1981**, *22*, 1299, 1303.

Scheme VI



B. Reinvestigation of the Reaction of 2,4-Pentanedione (4) with Me_3SiCN, with and without Catalysts. The results of our reinvestigation of the reaction of Me_3SiCN with **4**, as outlined in Scheme VI, are consistent with the above mechanistic proposals. Monitoring these reactions by ^1H NMR demonstrated that the first product formed when **4** is allowed to react with Me_3SiCN, with or without a catalyst present, is a trimethylsilyl enol ether, in this case **13**. As noted by the Russian authors[5] and confirmed by us, this silyl enol ether undergoes no further reaction at room temperature in the absence of a catalyst.

The apparent discrepancies between our results and those of the Russian workers are easily explained. Presumably an equilibrium also exists between the silyl enol ether **13** and starting material, analogous to the equilibrium observed between **5** and **1**. However, unlike the silyl enol ether **5**, where this equilibrium includes a molecule containing an α-keto ester functionality, with **13** this equilibrium does not contain a keto tautomer with a carbonyl carbon having sufficient electrophilicity to react further with either Me_3SiCN or HCN in the absence of catalysts. Therefore with Me_3SiCN alone **4** gives only the silyl enol ether **13**, whereas in the presence of zinc iodide or KCN·18-crown-6 the silyl enol ether **13** reacts further to yield the observed products.

In the presence of zinc iodide the silyl enol ether **13** is converted into the bis(trimethylsilyl)-protected enol ether cyanohydrin **14**. After 1 h at room temperature **14** is the major compound present, the silyl enol ethers **13** now being present in minor amounts. At a reaction time of 3 h, in addition to signals assigned to **13** (trace) and **14**, a new peak is observed at δ 2.87 for the monocyanohydrin **15**. As the peaks assigned to **14** decrease in intensity this peak continues to grow, and at the end of 24 h the conversion to the cyanohydrin **15** is complete. If instead of 1 equiv of Me_3SiCN, 2 equiv is used, the same progression of intermediates is observed (**13** → **14** → **15**), but **15** now reacts further with the second equivalent of Me_3SiCN to afford the dicyanohydrin **16**. Monitoring this reaction by ^1H NMR showed that the signals which come from **16** are not observed until the methylene signal for **15** at δ 2.87 is present, indicating that **15** may be an intermediate in the formation of **16**. There is no evidence to support the proposal of Gostevskii et al.[5] that **16** is the result of HCN addition to **14**.

The reaction of **4** with 1 equiv of Me_3SiCN in the presence of KCN·18-crown-6 again involves the initial formation of the silyl enol ether **13**. At no time during this reaction was the silyl enol ether cyanohydrin **14** observed, but rather as the enol ether **13** disappeared, only peaks corresponding to the cyanohydrin **15** were observed. Thus the silyl enol ether **14**, which had been proposed as an intermediate in this reaction by the Russian workers,[5] could not be detected in even trace amounts during this reaction. It appears that this reaction once again involves the equilibrium of the silyl enol ether with starting material and that the product is the result of cyanide ion catalyzed addition of Me_3SiCN to the keto carbonyl of **4**.

Conclusions

The mechanistic proposals presented here, which are supported by the detection of intermediates in these reactions by analysis of ^1H NMR spectra, are consistent for both the reactions of Me_3SiCN with 2,4-pentanedione (**4**) and methyl 2,4-dioxopentanoate (**1**), with and without the presence of catalysts. These results indicate that silyl enol ethers are the first products formed in an equilibrium reaction when enolizable β-diketones are allowed to react with Me_3SiCN, whether in the presence or absence of catalysts. The formation of the trimethylsilyl-protected cyanohydrin **3** from the reactions of **1** with neat Me_3SiCN or Me_3SiCN with KCN·18-crown-6 demonstrates that further reactions may occur if the starting material present in that equilibrium contains a highly electrophilic carbonyl center. In addition it should be noted that the mechanisms proposed in this work agree with an earlier suggestion made by Murai et al.,[11] but without supporting experimental evidence, for the cyanosilylation of β-diketones with $Me_2Si(CN)_2$.

It is interesting that the KCN·18-crown-6 catalyzed and zinc iodide catalyzed reactions of **1** with Me_3SiCN *do not* give the same product. To our knowledge this is the first time that such a result has been reported; this finding suggests that some caution should be exercised in the interchangeable use of these two catalysts, since they may not always lead to the same product.

Experimental Section

General. All reactions with Me_3SiCN were carried out without solvent, under nitrogen, and in flasks dried overnight at 130 °C and sealed with a rubber septum. In all cases where Me_3SiCN was used it was added to the reactants throught the septum by syringe. Monitoring of the reactions was carried out by 60-MHz ^1H NMR of a $CDCl_3$ solution of aliquots removed by syringe at various time intervals. *Extreme care* must be taken during the addition of Me_3SiCN or t-$BuMe_2SiCN$ and in the subsequent handling of all the silyl cyanide reactions due to the toxicity of these reagents and also because HCN is produced in these reactions.

The ^1H NMR spectra were run in $CDCl_3$ at 60 MHz on a Varian EM360A instrument. The NOE experiment was carried out on a JEOL FX90Q instrument.

Methyl 2-(Trimethylsiloxy)-4-oxo-2-pentenoate (5). Me_3SiCN (1.4 mL, 1.1 g, 0.011 mol) was added at room temperature to the dioxopentanoate **1**[12] (1.6 g, 0.0111 mol) in a dry flask under a dry nitrogen atmosphere. After the mixture was stirred at ambient temperature for 40 min the pure silyl enol ether **5** (2.2 g, 92%) was obtained by distillation using a short-path apparatus: bp 46–49 °C (0.2 mm); IR (neat) 1745, 1700 (w), 1675, 1625, 1255, 1240 (sh), 850 cm^{-1}; mass spectrum, m/z 201 ($M^+ - CH_3$); 157 ($M^+ - CO_2CH_3$). Anal. Calcd for $C_9H_{16}O_4Si$: C, 49.97;

(11) Ryu, I.; Murai, S.; Shinonaga, A.; Horiike, T.; Sonoda, N. *J. Org. Chem.* **1978**, *43*, 780.

(12) Methyl 2,4-dioxopentanoate is available from Aldrich Chemical Co.

H, 7.46. Found: C, 49.88; H, 7.77.

3-Carbomethoxy-5-cyano-5-methyl-2,6-dioxa-1-silacyclohex-3-ene (9). In a dry flask under nitrogen was placed dimethyldicyanosilane[8] (0.51 g, 4.64 mmol) and the flask cooled in a dry ice–acetone bath while methyl 2,4-dioxopentanoate (1) (0.66 g, 4.58 mmol) in dry $CHCl_3$ (3 mL) was added. Stirring in the cold bath was continued for 15 min, and then the bath was removed and the reaction solution allowed to come to room temperature. After the reaction had stirred at room temperature for 45 min the analysis of a ^1H NMR spectrum of an aliquot showed the reaction to be complete. The removal of the HCN under vacuum followed by distillation using a Kugelrohr apparatus afforded 0.91 g of pure **9** (87%) which solidified at room temperature: bp 130 °C (0.2 mm); IR (Nujol) 1755, 1740, 1645, 1280, 1265, 1205, 1160, 1010, 910, 850, 815 cm^{-1}; IR ($CHCl_3$) 1740, 1640 cm^{-1}; mass spectrum, m/z 227 (M^+), 212 ($M^+ - CH_3$); 168 ($M^+ - CO_2CH_3$).

4-Cyano-4-(trimethylsiloxy)-2-pentanone (15). In a dry flask under nitrogen was placed ZnI_2 (catalytic amount) and 2,4-pentanedione (4) (1.0 g, 0.01 mol). To this mixture was added Me_3SiCN (1.35 mL, 1.05 g, 0.011 mol) by syringe through a rubber septum. The resulting mixture was stirred at ambient temperature for 6 h, after which time ^1H NMR indicated the desired product was present together with some starting material. The reaction solution was distilled by using a short-path distillation apparatus to give 1.2 g (60%) of pure **15**: bp 110–112 °C (16 mm); IR (neat) 1730, 1375, 1270, 1140, 1135, 1040, 855 cm^{-1}; mass spectrum, m/z 184 ($M^+ - CH_3$). Anal. Calcd for $C_9H_{17}NO_2Si$: C, 54.23; H, 8.60; N, 7.03. Found: C, 54.65; H, 8.70; N, 7.43.

Reaction of 1 with Excess Me_3SiCN. Into a dry flask, under nitrogen, was placed **1** (0.3 g, 2.1 mmol), and then Me_3SiCN (0.96 mL, 0.75 g, 7.5 mmol) was added. Analysis of the NMR spectrum of an aliquot removed after the mixture was stirred at room temperature for 48 h showed about 75% of the silyl enol ether **5** and 25% of the silyl enol ether cyanohydrin **2**. Analysis of a ^1H NMR spectrum taken of an aliquot removed from the reaction solution after it had stirred at room temperature for 12 days showed the ratio of **5** to **2** to be approximately 1:1. No resonances assignable to **3** could be detected.

Reaction of 1 with Me_3SiCN Followed by the Addition of $Me_2Si(CN)_2$. In a dry flask, under nitrogen, was placed the keto ester **1** (0.22 g, 1.53 mmol) followed by Me_3SiCN (0.21 mL, 0.16 g, 1.65 mmol). The NMR of an aliquot removed at 2.5 h showed a ratio of silyl enol ether **5** to cyanohydrin **3** of 67:33. To this reaction solution was then added $Me_2Si(CN)_2$ (0.16 g, 1.45 mmol), and stirring at room temperature was continued. Removal of an aliquot at 0.5 h showed, by NMR analysis, the presence of the cyclic enol ether **9**, and the cyanohydrin **3** in a ratio of approximately 64:36. The NMR spectra taken of aliquots removed from the reaction at 23 h and 3 days indicated that this ratio was unchanged within experimental error.

Reaction of 1 with t-$BuMe_2SiCN$ Followed by Me_3SiCN. In a dry flask under nitrogen was placed the ester **1** (0.1 g, 0.69 mmol) and t-$BuMe_2SiCN$ (0.1 g, 0.71 mmol), and the flask was warmed gently to melt this solid mixture; usually warming in a 50 °C bath for several hours was required to initiate the reaction. When the warm bath could be removed without the reaction mixture totally solidifying, the reaction could be stirred at room temperature and monitored by ^1H NMR. At 22 h the NMR spectrum indicated the presence of the silyl enol ether **10** and the unprotected cyanohydrin **11** in a ratio of 68:32. To this reaction solution was then added Me_3SiCN (0.15 mL, 1.18 mmol). The ^1H NMR of an aliquot after 2.5 h at room temperature showed the two silyl enol ethers **10** and **5** (1:1) and the silyl-protected cyanohydrin **3**, the overall ratio of the silyl enol ethers to **3** was 70:30, and while eventually the silyl enol ether **10** was all converted to **5**, the ratio of silyl enol ether to **3** remained constant (70:30) for 2 days. In all spectra taken after Me_3SiCN was added the peak at δ 1.03 for the t-Bu group of t-$BuMe_2SiCN$ increased as the peak associated with the t-Bu group of the t-$BuMe_2SiO$ substituent of **10** at δ 0.98 decreased.

Reaction of 1 with t-$BuMe_2SiCN$ Followed by Me_3SiCN and KCN·18-Crown-6. The reaction was carried out as outlined above to give a ratio of **10** to **3** of 70:30. To this reaction solution were then added Me_3SiCN (0.15 mL, 1.18 mmol) and KCN·18-crown-6 (a few crystals). The ^1H NMR taken after the reaction had stirred at room temperature for 2.5 h showed only the silyl enol ether **5** and the trimethylsilyl-protected cyanohydrin **3**, in a ratio of 70:30. Once again the resonance at δ 0.98 for the t-Bu group of **10** disappeared and a resonance at δ 1.03 for the t-Bu group of t-$BuMe_2SiCN$ was observed to increase.

Acknowledgment. I thank K. S. Gallagher for carrying out the NOE experiments. Partial support of this work by the University of New Hampshire Chemistry Department and University of New Hampshire Sea Grant Program is gratefully acknowledged.[13] The partial support from the UNH Sea Grant Program was funded by the Office of Sea Grant, National Oceanic and Atmospheric Administration, U.S. Department of Commerce, through Grant NA-81-AA-D-00035 to the University of New Hampshire.

(13) This is contribution UNH MP-JR-SG-85-11 from the University of New Hampshire Sea Grant Program.