

## Catalytic Activity of Tetracyanoethylene in the Reactions of Aldehydes, Ketones and Acetals with Silylated Nucleophiles

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Tetracyanoethylene catalyses the reactions of aldehydes, ketones and acetals with silylated carbon- and hydrogen-nucleophiles to promote carbon-carbon bond formation and reduction under neutral conditions.

In recent years, a variety of efficient catalysts or promoters have been developed to induce carbon-carbon bond-forming reactions and the reduction of aldehydes, ketones, and acetals with silylated nucleophiles.<sup>1</sup> Because most of these catalysts have high acidity and are moisture sensitive, the development of new efficient catalysts which can be easily prepared, handled, and used under mild conditions is still of interest. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), a representative one-electron oxidant, has been reported to catalyse the deprotection of acetals,<sup>2a</sup> the tetrahydropyranulation of alcohols,<sup>2b</sup> and the novel *O*- and *C*-glycosidation of glycols.<sup>3</sup> In the context, we recently reported that a catalytic amount of tetracyanoethylene (TCNE), a representative  $\pi$ -acid and one-electron acceptor,<sup>4</sup> accelerates substrate-specific rearrangement, acetonidation, and alkanolysis of epoxides.<sup>5</sup> Here we disclose that in the presence of a catalytic amount of TCNE, silylated nucleophiles such as trimethylsilyl cyanide (TMS-CN), allyltrimethylsilane (TSM-allyl), aryl methyl ketones TMS-enol ethers and triethylsilane (TES-H) reacted smoothly with aldehydes, ketones, or acetals to afford the corresponding adducts or substitution products in high yields under mild and neutral conditions.

Decanal when heated under reflux with TMS-CN (1.5 equiv.) in MeCN in the presence of a catalytic amount of TCNE (0.2 equiv.) gave the corresponding cyanohydrin† (87%) after acidic hydrolysis. Similarly, benzaldehyde, octan-2-one, and acetophenone, also reacted with TMS-CN to give the corresponding cyanohydrins in good to high yield. Unexpectedly, TCNE was a poor catalyst for the reaction of these carbonyl compounds with other silylated nucleophiles (TMS-allyl and acetophenone TMS-enol ether), except for the reaction of benzaldehyde with acetophenone TMS-enol ether to give carbon-carbon bond formation (Table 1). In turn, attention was focused on the reactivities of acetals with silylated nucleophiles.

† All compounds were purified by silica gel chromatography or distillation and characterized by spectroscopic means or identification with authentic compounds prepared.

Dimethyl acetals derived from benzaldehyde, (*E*)-cinnamaldehyde, (*E*)-hex-2-enal, decanal and octan-2-one when treated with TMS-CN, TMS-allyl, aryl methyl ketone TMS-enol ethers, and TES-H in the presence of a catalytic amount of TCNE afforded the corresponding substitution products in good yields (see Table 2).

Although mechanisms for the TCNE-catalysed reaction of carbonyl compounds and their acetals described here are still unclear, activation of the C=O and C-O bond of carbonyl and acetal group for attack of silylated nucleophiles is presumed to be initiated by the single-electron transfer (SET)<sup>3</sup> or coordination to the electron-deficient double bond of TCNE from the carbonyl and acetal oxygen.

In addition to the previously reported isomerization, acetonidation and alkanolysis of epoxides,<sup>5</sup> the high efficiency of TCNE in the coupling reactions between silylated nucleophiles and carbonyl compounds and acetals demonstrated that a  $\pi$ -acid, TCNE, seems to promise much as a versatile and mild catalyst for Lewis acid-promoted reactions.

### Experimental

**General Procedure for the Reaction of Aldehydes or Ketones with Silylated Nucleophiles.**—Decanal (58.1 mg, 0.372 mmol) and TMS-CN (55 mg, 0.558 mmol) were added to a solution of TCNE (9.5 mg, 0.074 mmol) in MeCN (2 cm<sup>3</sup>) under an argon atmosphere, and the mixture was stirred at the reflux temperature for 1 h. 3% HCl was added to the reaction mixture which was then extracted with ether. The crude product thus obtained was purified by silica gel column chromatography (AcOEt-hexane, 1:6) to give 2-hydroxyundecanenitrile (59.0 mg, 87%) as a colourless oil (Table 1; entry 1).

**General Procedure for the Reaction of Acetals with Silylated Nucleophiles.**—Benzaldehyde dimethyl acetal (100 mg, 0.657 mmol) and TMS-CN (98 mg, 0.986 mmol) were added to a solution of TCNE (16.8 mg, 0.131 mmol) in MeCN (2 cm<sup>3</sup>)

**Table 1** The reaction of aldehydes or ketones with silylated nucleophiles catalysed by TCNE

RR'CO 1				RR'C(OH)Nu 2a-d (a-d as in formula 1)	
a R = H, R' = Me(CH <sub>2</sub> ) <sub>8</sub>		TCNE (0.2 equiv), TMS-Nu (1.5 equiv) → 3% HCl			
b R = H, R' = Ph		MeCN, reflux			
c R = Me, R' = Me(CH <sub>2</sub> ) <sub>5</sub>					
d R = Me, R' = Ph					
Entry	Aldehyde/ketone 1	TMS-Nu	Time (T/h)	Product 2	Yield (%)
1	1a	TMS-CN	1	2a, Nu = CN	87
2	1b	TMS-CN	3	2b, Nu = CN	93
3	1b	TMS-CH <sub>2</sub> CH=CH <sub>2</sub>	4	2b, Nu = CH <sub>2</sub> CH=CH <sub>2</sub>	10 <sup>a</sup>
4	1b	TMS-O-C(Ph)=CH <sub>2</sub>	4	2b, Nu = CH <sub>2</sub> COPh	97
5	1c	TMS-CN	2	2c, Nu = CN	87 <sup>b</sup>
6	1d	TMS-CN	2	2d, Nu = CN	74 <sup>b</sup>

<sup>a</sup> The starting material was recovered in 80% yields. <sup>b</sup> The corresponding TMS ether of the cyanohydrin was isolated.

**Table 2** The reaction of acetals with silylated nucleophiles catalysed by TCNE

$RR'C(OMe)_2$   
**3**  
**a** R = H, R' = Ph  
**b** R = H, R' = PhCH=CH  
**c** R = H, R' = Me(CH<sub>2</sub>)<sub>2</sub>CH=CH  
**d** R = H, R' = Me(CH<sub>2</sub>)<sub>8</sub>  
**e** R = Me, R' = Me(CH<sub>2</sub>)<sub>5</sub>

$\xrightarrow[\text{MeCN, reflux}]{\text{TCNE (0.2 equiv), TMS-Nu (1.5 equiv)}}$

$RR'C(OMe)Nu$   
**4a-d**  
 (a-d as in formula 3)

Entry	Acetal	TMS-Nu	Time (T/h)	Product	Yield (%)
1	<b>3a</b>	TMS-CN	5	Nu = CN	72
2	<b>3a</b>	TMS-CH <sub>2</sub> CH=CH <sub>2</sub>	1	Nu = CH <sub>2</sub> CH=CH <sub>2</sub>	68
3	<b>3a</b>	TMS-O-C(Ph)=CH <sub>2</sub>	1	Nu = CH <sub>2</sub> C(O)Ph	83
4	<b>3a</b>	TMS-O-C(2-Furyl)=CH <sub>2</sub>	1	Nu = CH <sub>2</sub> C(O)2-Furyl	94
5	<b>3a</b>	Et <sub>3</sub> SiH	3	Nu = H	46 <sup>a,b</sup>
6	<b>3b</b>	TMS-CN	1	Nu = CN	80
7	<b>3b</b>	TMS-O-C(Ph)=CH <sub>2</sub>	1	Nu = CH <sub>2</sub> C(O)Ph	79
8	<b>3b</b>	TMS-O-C(2-Furyl)=CH <sub>2</sub>	1	Nu = CH <sub>2</sub> C(O)2-Furyl	93
9	<b>3b</b>	Et <sub>3</sub> SiH	5	Nu = H	70 <sup>a</sup>
10	<b>3c</b>	TMS-CN	1	Nu = CN	66
11	<b>3c</b>	TMS-O-C(Ph)=CH <sub>2</sub>	2	Nu = CH <sub>2</sub> C(O)Ph	75
12	<b>3c</b>	TMS-O-(2-Furyl)=CH <sub>2</sub>	1	Nu = CH <sub>2</sub> C(O)2-Furyl	85
13	<b>3d</b>	TMS-CN	5	Nu = CN	87
14	<b>3d</b>	TMS-CH <sub>2</sub> CH=CH <sub>2</sub>	5	Nu = CH <sub>2</sub> CH=CH <sub>2</sub>	66
15	<b>3e</b>	TMS-CN	2	Nu = CN	63
16	<b>3e</b>	TMS-O-C(Ph)=CH <sub>2</sub>	1	Nu = CH <sub>2</sub> C(O)Ph	53

<sup>a</sup> TCNE (0.3 equiv.) and Et<sub>3</sub>SiH (4 equiv.) were used in this reaction. <sup>b</sup> Considerable loss of product occurred during work-up because of its low boiling point; the yield indicated stands for a tentative isolated yield.

under argon atmosphere, and the mixture was stirred at the reflux temperature for 5 h. The reaction mixture was extracted with ether. The crude product thus obtained was purified by silica gel column chromatography (EtOAc-hexane, 1:50) to give 2-methoxy-2-phenylethanenitrile (69.9 mg, 72%) as a colourless oil (Table 2; entry 1).

## References

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