

Polymer-Supported Dicyanoketene Acetal as a π -Acid Catalyst: Monothioacetalization and Carbon–Carbon Bond Formation of Acetals

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Polymeric dicyanoketene acetals (DCKA) were synthesized by copolymerization of styrene and divinylbenzene or ethylene glycol dimethacrylate. These novel polymers could be used successfully as recyclable π -acid catalysts in monothioacetalization or carbon–carbon bond forming reaction of acetals.

Key words polymeric dicyanoketene acetal; π -acid; recyclable catalyst; monothioacetalization; carbon–carbon bond formation

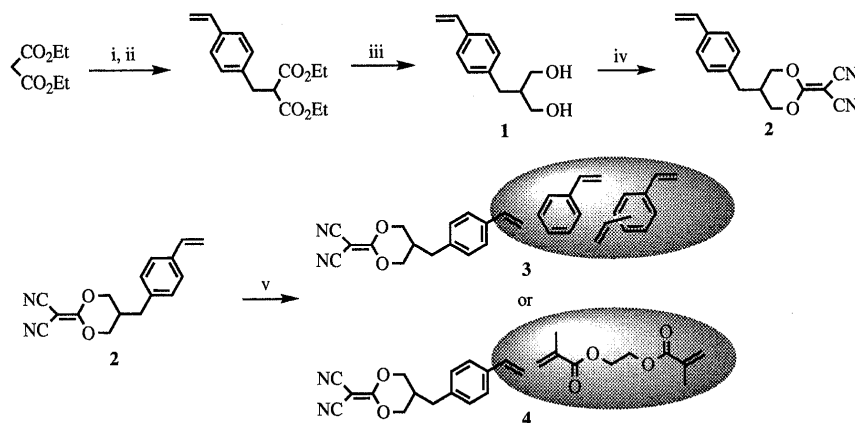
Since Merrifield's solid phase synthesis of peptides,^{1a)} polymer-supported catalysts, reagents, and substrates have attracted much attention for many years due to their inherent advantages in synthetic chemistry: simplification of reaction procedures including easy separation of products, application to automation systems leading to combinatorial chemistry, and recycling of catalysts and reagents.^{1b)}

Useful polymer-supported acid catalysts are classified into several types from the viewpoint of their elements of intrinsic acidity: 1) Lewis acids incorporated coordinately in inorganic and organic polymer matrix such as zeolites,^{2a)} clays,^{2b)} silica,^{2c)} and resins,^{2d)} 2) Lewis acidic metals introduced covalently in organic^{3a)} and mixed organic-inorganic polymer matrix,^{3b)} 3) polymeric protonic (Brønsted) acids such as proton-exchanged zeolites^{4a)} and clays,^{4b)} and protonated ion-exchange resins including hydrochloric,^{4c)} sulfonic,^{4d)} and carboxylic acid,^{4e)} and 4) organic cation species bound to a polystyrene resin.⁵⁾

In the course of our investigation on the π -acid property of tetracyanoethylene (TCNE)⁶⁾ we have found that certain capto-dative olefins, dicyanoketene acetals (DCKA), in which two geminal cyano groups are substituted with alkoxy groups, work well as a promoter in alcoholysis of epoxides,^{7a)}

tetrahydropyranylation of alcohols,^{7b)} and monothioacetalization of acetals.^{7c)} During modification of the structure of DCKA aiming at novel catalytic activities, we have designed polymer-supported dicyanoketene acetals, which are accessible by polymerization of styrene derivatives bearing dicyanoketene acetal moiety. We recently reported in preliminary communications that a polymer-supported DCKA, a new type of solid acid catalyst which does not belong to the above classification, catalyzes monothioacetalization^{8a)} and carbon–carbon bond formation^{8b)} of acetals under unhydrous conditions, and deprotects acetals and silyl ethers in aqueous media.^{8c)} We herein provide full details of monothioacetalization and carbon–carbon bond formation of acetals under mild reaction conditions using a polymer-supported DCKA.

The preparation of polymeric DCKAs (**3** and **4**) is shown in Chart 1. Condensation of diethyl malonate with an equivalent mole of 4-chloromethyl styrene in the presence of NaH gave an inseparable mixture (18:5) of monoalkylated malonate and dialkylated malonate as a by-product. This mixture was reduced with LiAlH₄ to provide a diol derivative (**1**) after chromatographic separation in 46% overall yield in two steps. Condensation of the diol (**1**) with 1.3 mole equivalent of TCNE in the presence of a catalytic amount of Et₂NH⁹⁾ in



i: 1.1 eq NaH, DMF, r.t., 1 h; ii: 0.3 eq NaI, 1.0 eq 4-chloromethyl styrene, 50 °C, 2 h; iii: 3.0 eq LiAlH₄, Et₂O, reflux, 2 h (46% for 2 steps); iv: 0.2 eq Et₂NH, 1.3 eq TCNE, THF, r.t., 2 h (67%); v: (synthesis of **3**), 0.05 eq. AIBN, 1.0 eq divinylbenzene, toluene, 100 °C, 22 h (49%); (synthesis of **4**), 0.05 eq AIBN, 1.0 eq EGDMA, toluene, 100 °C, 2 h (80%).

Chart 1

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Table 1. Solvent Effect and the Reusing of **3** and **4** in the Monothioacetalization of **5**

$\text{Ph}-\text{C}(\text{OMe})_2$ (5, 50 mg) $\xrightarrow[\text{3 h}]{\text{polymeric DCKA (3 or 4) (50 mg), PhSH (1.5 eq)}}$ $\text{Ph}-\text{C}(\text{OMe})(\text{SPh})$ (6)

Entry	Solvent	Polymeric DCKA	$T/^\circ\text{C}$	Yield (%)		
				1st	2nd	3rd
1	CH_3CN	3	60	21	25	—
2	CH_3CN	4	60	83	88	87
3	CH_2Cl_2	4	Reflux	10	—	—
4	Et_2O	4	Reflux	32	—	—
5	Benzene	4	60	29	—	—
6	Toluene	4	60	35	—	—
7	DMSO	4	60	42	—	—
8	DMF	4	60	61	58	60

THF produced a monomeric styrene derivative (**2**) in 67% yield, which was ascertained to have the catalytic activities in the reaction of benzaldehyde dimethyl acetal (**5**) with thiophenol (1.5 eq) in acetonitrile at 60°C for 3 h to give the corresponding monothioacetal (**6**) in 87% yield. Copolymerization of **2** with one equivalent mole of each of styrene and divinylbenzene as cross-linking agents using a catalytic amount of AIBN as a radical initiator¹⁰ produced in 49% yield a polymer-supported DCKA (**3**) as a white powder; this was estimated to be composed of an approximate ratio 2:2:1 of **2**, styrene, and divinylbenzene from elemental analysis (2.30 mmol/g for loaded DCKA). Another DCKA (**4**) was obtained with an equivalent mole of ethylene glycol dimethacrylate (EGDMA) as a cross-linking agent according to Dhai's method¹¹ in 95% yield as a white powder, which was estimated to be composed of an approximate ratio 2:1 of **2** and EGDMA from elemental analysis (2.74 mmol/g for loaded DCKA).

The polymeric DCKAs (**3** and **4**) were evaluated as catalysts in monothioacetalization of benzaldehyde dimethyl acetal (**5**) with thiophenol. The polymer (**3** or **4**) (50 mg) was added to a solution of the dimethyl acetal (**5**) (50 mg, 0.33 mmol) and thiophenol (PhSH) (0.50 mmol) in a solvent (1.0 ml). The mixture was stirred at 60°C and the reaction was monitored by TLC. The reaction displayed a noticeable solvent dependence as listed in Table 1. Although the polymeric DCKA (**3**) showed little catalytic activity, the other one (**4**) accelerated remarkably the monothioacetalization reaction in acetonitrile, which was the solvent of choice for providing a high yield (83%) of a monothioacetal (**6**) (entries 1 and 2). Solvents, CH_2Cl_2 , Et_2O , C_6H_6 , $\text{CH}_3\text{C}_6\text{H}_5$, and DMSO were poor to sluggish and DMF was moderate for the reaction (entries 3—8). The product could be easily isolated by filtration of the catalyst followed by the usual workup. After washing the recovered polymer successively with water and ethyl acetate followed by drying at room temperature in vacuo for 4 h, the catalysts (**3** and **4**) could be reused without loss of the activities (entries 1, 2, and 8).

Next, efficiency of the catalyst (**4**) was investigated in the monothioacetalization¹² of several aliphatic acetals including α,β -unsaturated acetals (**10**—**12**), and mixed acetals such as methoxymethyl (MOM) (**13**), tetrahydropyranyl (THP) (**14**), and tetrahydrofuranyl (THF) ethers (**15**) using PhSH as well as phenylthiotrimethylsilane (TMS-SPh) as a nucleophile,

and the results are summarized in Table 2. Typical dimethyl acetals of decyl aldehyde (**7**), 2-octanone (**8**), and cyclohexanone (**9**) smoothly underwent substitution reactions under the conditions at 60°C within two days to give the corresponding monothioacetals (**16**), (**17**), and (**18**), respectively, although the ketone acetals (**8**, **9**) reacted more rapidly than that of the aldehyde (**7**) (entries 3, 4, 5, 7, and 9). α,β -unsaturated dimethyl acetals of *trans*-cinnamaldehyde (**10**), *trans*-2-hexenal (**11**), and 3-methyl-2-butenal (**12**) gave inseparable complex mixtures, even if the reaction was carried out at room temperature or DMF was used as a solvent (entries 10—16). Unexpectedly, no reaction was observed with dodecyl MOM ether (**13**) (entries 17 and 18). Mixed acetals, THP (**14**) and THF ethers (**15**) derived from *n*-pentanol, underwent regioselective thiolysis depending on the amount of the catalyst and the reaction time, especially when TMS-SPh was used as a nucleophile to afford selectively endo- (**20** and **22**) or exo-cyclic C—O bond cleaved products (**19** and **21**) (entry 19—23). The fact that a smaller amount of the catalyst and shorter period of reaction time led to the linear monothioacetals (**20**) selectively (entry 20) indicated that the endocyclic C—O bond of the THP ether (**14**) appears to be cleaved more rapidly than the exocyclic one, leading initially to **20** which is transformed to cyclic monothioacetal (**19**) with elimination of *n*-pentanol under the reaction conditions. Thus, the intermediate linear monothioacetal (**20**) was subjected to the reaction conditions for 20 h to produce 71% yield of the cyclic monothioacetal (**19**) (Chart 2).

Encouraged by the results of monothioacetalization, we were intrigued by the substitution reaction of aldehydes and acetals¹³ with carbon nucleophiles catalyzed by the polymeric DCKA (**4**). As a preliminary examination, catalytic activity of dicyanoketene ethylene acetal (DCKEA) (**23**) in the carbon-carbon bond forming reaction of aldehydes and ketones was investigated. Thus, benzaldehyde (**24**) when heated under reflux with TMS-CN (A) (1.5 eq) in acetonitrile in the presence of a catalytic amount of DCKEA (**23**) (0.2 eq) gave the corresponding cyanohydrin derivative (**25**) in 63% yield after acidic hydrolysis (Table 3, entry 1). Similarly, *p*-anisaldehyde (**26**), *p*-chlorobenzaldehyde (**28**) and heptanal (**30**) also reacted with TMS-CN (A) to give the corresponding cyanohydrins (**27**, **29** and **31**) in high yields under the same conditions (Table 3, entries 4—6). The methyl ketones acetophenone (**32**) and 2-octanone (**34**), however, gave low yields of the corresponding TMS ether of the cyanohydrins (**33** and **35**) in the reaction with TMS-CN (A) under the same conditions (Table 3, entries 9 and 10). Furthermore, DCKEA (**23**) was found to be a poor catalyst for the reaction of these carbonyl compounds with other silylated nucleophiles (allyltrimethylsilane (TMS-allyl) (B) and acetophenone enol TMS ether (C)) (Table 3, entries 2, 3, 7, 8, 11 and 12).

In turn, attention was focused on the reactivities of acetals with silylated nucleophiles. As shown in Table 4, *p*-anisaldehyde dimethyl acetal (**36**) (0.27 mmol) when heated under reflux for 2 h with TMS-CN (A) (1.5 eq) in acetonitrile in the presence of a catalytic amount of DCKEA (**23**) (0.2 eq) gave the corresponding cyanohydrin derivative (**37**) in 92% yield after workup (entry 1). The finding of the high catalytic activity of a monomeric DCKA (**2**) having styrene moiety to give 98% yield of **37** with 98% recovery of the catalyst (**2**) in

Table 2. Monothioacetalization of Acetals Catalyzed by 4

R OMe OMe 50 mg polymeric DCKA (4) (50mg), Nucleophile (1.5 eq) CH₃CN, 60 °C R OMe SPh					
Entry	Substrate	Nucleophile	Time (h)	Product/Yield (%)	
1	n-C₉H₁₉ OMe OMe 7	PhSH	6	n-C₉H₁₉ OMe SPh 16	73 ^{a)}
2		PhSH	20		75
3		TMS-SPh	7		50 ^{b)}
4		TMS-SPh	20		61
5		TMS-SPh	40		86
6	n-C₆H₁₃ OMe OMe 8	PhSH	2	n-C₆H₁₃ OMe SPh 17	64
7		TMS-SPh	5		69
8	OMe OMe 9	PhSH	6	OMe SPh 18	29
9		TMS-SPh	7		80
10	Ph OMe OMe 10	PhSH	2	Mixture	
11		TMS-SPh	20	Mixture	
12		TMS-SPh ^{c)}	27	Mixture	
13	OMe OMe 11	PhSH	20	Mixture	
14		TMS-SPh ^{d)}	20	Mixture	
15		TMS-SPh ^{c)}	27	No reaction	
16	OMe OMe 12	PhSH	2	Mixture	
17	n-C₁₂H₂₅-O OMe 13	PhSH	31	No reaction	
18		TMS-SPh	31	No reaction	
19	O O-n-C₅H₁₁ 14	PhSH	12	O SPh 19	73
20		TMS-SPh	19		6 ^{e)}
21		TMS-SPh	40		48 ^{f)}
				HO PhS O-n-C₅H₁₁ 20	35
22	O O-n-C₅H₁₁ 15	PhSH	12	O SPh 21	86
23		TMS-SPh	40		75
				HO PhS O-n-C₅H₁₁ 22	18

a) 14% of the starting material was recovered. b) 40% of the starting material was recovered. c) The reaction was carried out at room temperature. d) DMF was used as a solvent. e) 31% of the starting material was recovered. f) 21% of the starting material was recovered.

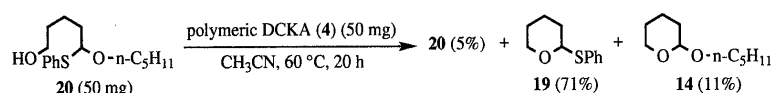


Chart 2

the same reaction prompted us to use the polymeric DCKA (4) as a catalyst in a substitution reaction of 36 with TMS-CN (A) (entry 2). Thus, a mixture of the polymeric DCKA (4) (50 mg), the dimethyl acetal (36) (50 mg, 0.27 mmol), and TMS-CN (A) (0.41 mmol) was refluxed for 2 h in acetonitrile (3 ml). Isolation by the usual workup after filtration of the catalyst (4) gave almost quantitatively the cyanohydrin derivative (37). After washing the recovered polymeric DCKA (4) successively with water and ethyl acetate followed by drying at room temperature *in vacuo* for 4 h, the catalyst (4) could be reused without loss of the activity (entry 3).

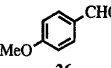
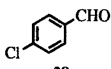
As shown in Table 5, the dimethyl acetals (36, 5 and 44) derived from aryl aldehydes, *p*-anisaldehyde, benzaldehyde and 2-furaldehyde, when treated with TMS-CN (A), TMS-allyl (B), and aryl methyl ketone enol TMS ethers (C and D) in the presence of the polymeric DCKA (4) afforded the corresponding substitution products (37–39, 40–43, 45–47)

in good yields except for allyl-substituted products (entries 1–12). The dimethyl acetals (10 and 11) derived from an α,β -unsaturated aldehyde, *trans*-cinnamaldehyde and *trans*-2-hexenal, when treated with silylated nucleophiles under the same conditions gave the corresponding substitution products (48–54) in good yields except for allyl-substituted product (49) (entries 13–19). Saturated acetals including aldehyde and ketone acetals appear less reactive than α,β -unsaturated ones under the present conditions. Thus, the reaction of decanal and 2-octanone dimethyl acetals (7 and 9) with acetophenone and 2-acetyl furan enol TMS ethers (C and D) proceeded sluggishly to give respectively low yields or no trace of the corresponding aldol methyl ethers (entries 22, 23, 25 and 26), although the reaction with TMS-CN (A) provided moderate to excellent yields of the corresponding substitution products (55 and 58) (entries 20 and 24).

As shown in Table 6, mixed acetals, THP (61) and THF

Table 3. The Reaction of Aldehydes and Ketones with Silylated Nucleophiles Catalyzed by **23**

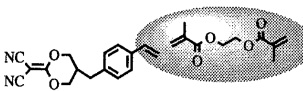
$$\begin{array}{c}
 \text{R}^1-\text{C}(=\text{O})-\text{R}^2 \xrightarrow[\text{CH}_3\text{CN, reflux}]{\begin{array}{c} 0.2 \text{ eq DCKEA (23)} \\ \text{NC} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{NC} \quad \text{O} \end{array}} \xrightarrow[3\% \text{ HCl}]{1.5 \text{ eq TMS-Nu}} \text{R}^1-\text{C}(\text{OH})(\text{Nu})-\text{R}^2
 \end{array}$$

Entry	Substrate	TMS-Nu	Time (h)	Product	Yield (%)
1		TMS-CN (A)	3	25 Nu=CN	63
2	24		10	No reaction	
3			10	No reaction	
4	26	A	2	27 Nu=CN	Quant.
5		A	21	29 Nu=CN	90
6		A	2	31 Nu=CN	96
7	30	B	10	No reaction	
8	30	C	10	No reaction	
9		A	21	33 Nu=CN	10 ^{a)}
10		A	5	35 Nu=CN	34 ^{b)}
11	34	B	10	No reaction	
12	34	C	10	No reaction	

a) The corresponding TMS ether of the cyanohydrine was isolated as a product and 72% of the substrate (**28**) was recovered. b) The corresponding TMS ether of the cyanohydrine was isolated as a product and 27% of the substrate (**30**) was recovered.

Table 4. The Reaction of **36** with TMS-CN (A) Catalyzed by DCKAs

$$\text{36 (50mg)} \xrightarrow[\text{CH}_3\text{CN, reflux, 2h}]{\text{Catalyst, 1.5 eq TMS-CN (A)}} \text{37}$$

Entry	Catalyst	Yield (%) of 37
1	 DCKEA (23) (0.2 eq)	92
2	 Monomeric DCKA (2) (0.2 eq)	98 (Catalyst recovery; 98%)
3	 Polymeric DCKA (4) (50 mg)	1st 99 2nd quant. 3rd quant.

ethers (**63**) derived from *n*-octanol, underwent carbon-carbon bond formation reaction in the presence of the catalyst. The reactions proceeded, however, without regioselectivity to give low yields of the ring-opening products (**62** and **64**), although the other probable products, 2-cyanotetrahydropyran¹⁴⁾ and 2-cyanotetrahydrofuran¹⁵⁾ corresponding to the produced *n*-octanol (**65**) could not be isolated by the usual workup because of their low boiling points. In contrast to the thiolysis, the ring-opening product (**62**) did not undergo any change under the same reaction conditions, and was recov-

ered quantitatively.

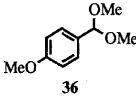
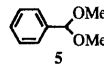
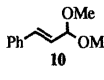
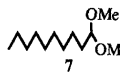
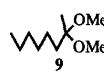
In conclusion, a novel polymer-supported DCKA (**4**) reported herein was found to be an unprecedented and recyclable polymeric π -acid and to successfully promote mild monothioacetalization and carbon-carbon bond formation of acetals.

Experimental

Melting points (Mps) were measured with a Yanagimoto micromelting point apparatus and are uncorrected. IR absorption spectra were recorded on a JASCO IRA-1 spectrometer and a Perkin Elmer Spectrum One. ¹H-NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) and a JEOL JNM-EX-400 (400 MHz) spectrometer with SiMe₄ as an internal standard; *J* values are given in Hz. Mass spectra (MS) and high-resolution MS (HRMS) were recorded on a JEOL JMS-D300 or a JEOL JMS-SX102A spectrometer. Products were purified by silica gel chromatography or preparative TLC. Acetonitrile was distilled from CaH₂ and stored over molecular sieves.

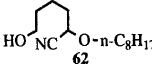
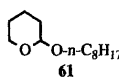
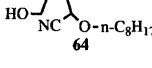
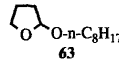
2-(4-Vinylbenzyl)-1,3-propanediol (1) A suspension of NaH (60%, 2.2 g, 55 mmol) in DMF (30 ml) was added to a solution of diethyl malonate (7.6 ml, 50 mmol) in DMF (20 ml) at 0 °C under argon atmosphere, and the mixture was stirred at room temperature for 1 h. A solution of 4-vinylbenzyl chloride (7.1 ml, 50 mmol) and NaI (1.5 g, 10 mmol) in DMF (50 ml) was added, and the mixture was stirred at 50 °C for 2 h. After cooling to room temperature, water was added, and the reaction mixture was extracted with AcOEt. The crude product thus obtained was purified by silica gel chromatography (AcOEt-hexane, 1 : 10) to give a mixture (18 : 5) of a monoalkylated product and a dialkylated one as a by-product. A solution of this mixture in ether (80 ml) was added to a suspension of LiAlH₄ in ether (20 ml), and the mixture was refluxed for 2 h. After cooling to room temperature, 2 M-HCl was added and filtered, and the reaction mixture was extracted with AcOEt. The crude product thus obtained was purified by silica gel chromatography (AcOEt-hexane, 1 : 1 to 1 : 0) to give **1** (4.4 g, 46% for 2 steps) as a colorless oil. IR (neat) cm⁻¹: 3260, 2900, 1610 (C=C), 1380, 1030, 920, 850. ¹H-NMR (CDCl₃) δ : 2.02–2.09 (3H, m+br), 2.62 (2H, d, *J*=7.8 Hz), 3.66, 3.68 (2H, each d, *J*=10.5 Hz), 3.80, 3.81 (2H, each d, *J*=10.7 Hz), 5.21 (1H, d, *J*=10.7 Hz), 5.71 (1H, d, *J*=17.6 Hz), 6.69 (1H, dd, *J*=17.6, 10.7 Hz), 7.15 (2H, d, *J*=7.8 Hz), 7.34 (2H, d, *J*=7.8 Hz).

Table 5. The Reaction of Acetals with Silylated Nucleophiles Catalyzed by **4**

$\text{R}-\begin{array}{c} \text{OMe} \\ \\ \text{OMe} \end{array} \xrightarrow[\text{CH}_3\text{CN, reflux}]{\text{polymeric DCKA (4) (50mg), 1.5 eq. TMS-Nu}} \text{R}-\begin{array}{c} \text{OMe} \\ \\ \text{Nu} \end{array}$					
Entry	Substrate	TMS-Nu	Time (h)	Product	Yield (%)
1		TMS-CN (A)	2	37 Nu=CN	99
2		 (B)	2	No reaction	
3		 (C)	6	38 Nu=CH ₂ COPh	96
4		 (D)	5	39 Nu=CH ₂ CO-2-Furyl	74
5		A	2	40 Nu=CN	95
6		B	24	41 Nu=CH ₂ CH=CH ₂	Trace
7		C	6.5	42 Nu=CH ₂ COPh	Quant.
8		D	21	43 Nu=CH ₂ CO-2-Furyl	63
9		A	3	45 Nu=CN	85
10		B	24	No reaction	
11		C	16	46 Nu=CH ₂ COPh	75
12		D	21	47 Nu=CH ₂ CO-2-Furyl	59
13		A	1.5	48 Nu=CN	94
14		B	24	49 Nu=CH ₂ CH=CH ₂	12 ^{a)}
15		C	16	50 Nu=CH ₂ COPh	98
16		D	21	51 Nu=CH ₂ CO-2-Furyl	95
17		A	1.5	52 Nu=CN	80
18		C	6	53 Nu=CH ₂ COPh	92
19		D	21	54 Nu=CH ₂ CO-2-Furyl	87
20		A	2	55 Nu=CN	96
21		B	24	56 Nu=CH ₂ CH=CH ₂	16 ^{a)}
22		C	16	57 Nu=CH ₂ COPh	38 ^{b)}
23		D	17	No reaction	
24		A	3	58 Nu=CN	63
25		C	6	59 Nu=CH ₂ COPh	44
26		D	21	60 Nu=CH ₂ CO-2-Furyl	15

a) A considerable extent of the aldehyde was obtained. b) 37% of the substrate (**7**) was recovered.

Table 6. The Reaction of Mixed Acetals with TMS-CN (A)

$\begin{array}{c} \text{Cyclohexyl-O-n-C}_8\text{H}_{17} \\ \text{61 (50 mg)} \\ \text{or} \\ \text{Cyclopentyl-O-n-C}_8\text{H}_{17} \\ \text{63 (50 mg)} \end{array} \xrightarrow[\text{CH}_3\text{CN, reflux}]{\text{Catalyst, 1.5 eq TMS-CN (A)}} \begin{array}{c} \text{HO-NC-Cyclohexyl-O-n-C}_8\text{H}_{17} \\ \text{62} \\ \text{or} \\ \text{HO-NC-Cyclopentyl-O-n-C}_8\text{H}_{17} \\ \text{64} \end{array} + \begin{array}{c} \text{61} \\ \text{or} \\ \text{63} \end{array} + \text{n-C}_8\text{H}_{17}\text{OH} \text{ (65)}$					
Entry	Substrate	Catalyst	Time (h)	Product/Yield (%)	
					
1		Polymeric DCKA (4) (50 mg)	3	11	22
2		Polymeric DCKA (4) (50 mg)	21	38	29
3		DCKEA (23) (0.2 eq)	21	24	35
					
4		Polymeric DCKA (4) (50 mg)	21	31	32
5		DCKEA (23) (0.2 eq)	21	26	43

HRMS (EI) m/z : 192.1147 (Calcd for $C_{12}H_{16}O_2$: 192.1150).

5-(4'-Vinylbenzyl)-2-dicyanomethylidene-1,3-dioxane (2) A solution of **1** (4.4 g, 23 mmol) in THF (40 ml) was added to TCNE (3.8 g, 30 mmol) in THF (20 ml) under argon atmosphere. Et_2NH (0.5 ml, 4.6 mmol) was added, and the mixture was stirred at room temperature for 4 h. The reaction mixture was extracted with AcOEt. The crude product thus obtained was purified by recrystallization (AcOEt-hexane) to give **2** (4.1 g, 67%) as a slightly yellow prism. mp 166 °C. IR ($CHCl_3$) cm^{-1} : 2235 (CN), 1570 (C=C), 1480, 1280, 1170, 905. 1H -NMR ($CDCl_3$) δ : 2.67 (1H, m), 2.75 (2H, d, $J=7.3$ Hz), 4.25, 4.28 (2H, each d, $J=10.7$ Hz), 4.56, 4.57 (2H, each d, $J=11.0$ Hz), 5.28 (1H, d, $J=11.2$ Hz), 5.76 (1H, d, $J=17.6$ Hz), 6.70 (1H, dd, $J=17.6, 10.8$ Hz), 7.11 (2H, d, $J=8.3$ Hz), 7.40 (2H, d, $J=7.8$ Hz). *Anal.* Calcd for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.12; H, 5.33; N, 10.62.

Polymeric DCKA (3) A solution of AIBN (3.1 mg, 0.019 mmol) in toluene (6.2 ml) was added to the mixture of **2** (100 mg, 0.376 mmol), styrene (43.1 μ l, 0.376 mmol) and divinylbenzene (55%, 96.8 μ l, 0.376 mmol), and the reaction mixture was stirred at 100 °C for 22 h. After cooling to room temperature, the reaction mixture was added to MeOH (80 ml), and filtered. The solid product thus obtained was dried *in vacuo* at 40 °C for 4 h to give **3** (80.2 mg, ca. 49%) as a white powder. This polymeric DCKA (**3**) was estimated to be composed of a 2 : 2 : 1 ratio of **2** and styrene and divinylbenzene from elemental analysis (2.30 mmol/g for loaded DCKA). IR (KBr) cm^{-1} : 3513, 3022, 2926, 2228 (CN), 1754, 1684, 1567 (C=C), 1513, 1490, 1443, 1291, 1240, 1181, 1089, 962, 909, 842, 707, 543. *Anal.* Found: C, 76.09; H, 6.19; N, 6.73.

Polymeric DCKA (4) A solution of AIBN (92.5 mg, 0.563 mmol) in toluene (185 ml) was added to the mixture of **2** (3.0 g, 11 mmol) and EGDMA (2.1 ml, 11 mmol), and the reaction mixture was stirred at 100 °C for 2 h. After cooling to room temperature, the reaction mixture was added to MeOH (1.5 l), and filtered. The solid product thus obtained was dried *in vacuo* at 40 °C for 4 h to give **4** (3.9 g, ca. 95%) as a white powder. This polymeric DCKA (**4**) was estimated to be composed of a 2 : 1 ratio of **2** and EGDMA from elemental analysis (2.74 mmol/g for loaded DCKA). IR (KBr) cm^{-1} : 3156, 2944, 2228 (CN), 1726 (C=O), 1563 (C=C), 1492, 1445, 1396, 1292, 1242, 1182, 1131, 962, 909, 712, 543. *Anal.* Found: C, 65.55; H, 5.67; N, 7.28.

General Procedure for the Reactions of Acetals with Thiophenol Catalyzed by the Polymeric DCKA (4) Benzaldehyde dimethylacetal (**5**) (50.7 mg, 0.333 mmol) and thiophenol (51.3 μ l, 0.500 mmol) were added to a suspension of polymeric DCKA (**4**) (50.0 mg) in acetonitrile (1 ml) under argon atmosphere, and the mixture was stirred at 60 °C for 3 h. After filtration of catalyst, the crude product was purified by preparative TLC (AcOEt-hexane, 1 : 10) to give methoxy(phenylthio)methyl benzene (**6**) (63.5 mg, 83%) as a slightly yellow oil. After washing the recovered polymer (**4**) successively with water and ethyl acetate followed by drying at room temperature *in vacuo* for 4 h, the catalyst (**4**) could be reused without loss of the activities (2nd. recycle; 67.6 mg, 88%, 3rd recycle; 67.1 mg, 87%).

Compounds (**6**, **17**, **18**, **19**, **21**)^{12d)}, (**16**, **20**, **22**)^{7c)} were identified by comparison of their spectroscopic behavior with those described in the references. The yields and reaction conditions of other products are shown in Table 2.

General Procedure for the Reactions of Aldehydes and Ketones with Silylated Nucleophiles Catalyzed by DCKEA (23) *p*-Anisaldehyde (**26**) (50.0 mg, 0.367 mmol) and TMS-CN (**A**) (54.8 μ l, 0.551 mmol) were added to a solution of DCKEA (**23**) (10.0 mg, 0.073 mmol) in acetonitrile (3 ml) under argon atmosphere, and the mixture was refluxed for 2 h. Hydrochloric acid (3%) was added to the reaction mixture which was then extracted with ether. After workup, the crude product was purified by silica gel column chromatography (AcOEt-hexane, 1 : 2) to give 2-hydroxy-2-(4-methoxyphenyl)-ethanenitrile (**27**) (59.9 mg, quant.) as a colorless oil.

Compounds (**25**, **27**, **31**, **33**)¹⁶⁾, **29**¹⁷⁾, **35**¹⁸⁾ were identified by comparison of their spectroscopic behavior with those described in the references.

General Procedure for the Reactions of Acetals with Silylated Nucleophiles Catalyzed by DCKEA (23) *p*-Anisaldehyde dimethylacetal (**36**) (50.0 mg, 0.274 mmol) and TMS-CN (**A**) (54.8 μ l, 0.411 mmol) were added to a solution of DCKEA (**23**) (7.5 mg, 0.055 mmol) in acetonitrile (3 ml) under argon atmosphere, and the mixture was refluxed for 2 h. Water was added to the reaction mixture which was then extracted with ether. After workup, the crude product was purified by silica gel column chromatography (AcOEt-hexane, 1 : 2) to give 2-methoxy-2-(4-methoxyphenyl)-ethanenitrile (**37**) (44.9 mg, 92%) as a slightly yellow oil.

General Procedure for the Reactions of Acetals with Silylated Nucleophiles Catalyzed by the Polymeric DCKA (4) *p*-Anisaldehyde dimethyl-

acetal (**36**) (50.0 mg, 0.274 mmol) and TMS-CN (**A**) (54.8 μ l, 0.411 mmol) were added to a suspension of polymeric DCKA (**4**) (50.0 mg) in acetonitrile (3 ml) under argon atmosphere, and the mixture was refluxed for 2 h. After filtration of catalyst (**4**), the crude product was purified by silica gel column chromatography (AcOEt-hexane, 1 : 4) to give 2-methoxy-2-(4-methoxyphenyl)-ethanenitrile (**37**) (48.1 mg, 99%) as a slightly yellow oil. After washing the recovered polymer (**4**) successively with water and ethyl acetate followed by drying at room temperature *in vacuo* for 4 h, the catalyst (**4**) could be reused without loss of the activities (2nd recycle; 48.6 mg, quant., 3rd recycle; 48.6 mg, quant.).

Compounds (**37**, **38**, **42**, **52**, **55**)^{13e)} (**39**, **40**, **43**, **45**, **46**, **47**, **50**, **51**, **53**, **54**, **56**, **57**, **59**)^{6d)} (**48**, **49**)¹⁶⁾ (**58**)¹⁸⁾ were identified by comparison of their spectroscopic behavior with those described in the references. The yields and reaction conditions of other products are shown in Table 5.

1-(2-Furyl)-3-methoxy-3-methyloctane-1-one (60) Slightly yellow oil; IR ($CHCl_3$) cm^{-1} : 2950, 2870, 1665 (C=O), 1570 (C=C), 1470, 1390, 1360, 1280, 1160, 1070, 1010, 900, 880, 830. 1H -NMR ($CDCl_3$) δ : 0.87 (3H, t, $J=7.3$ Hz), 1.27 (13H, m), 1.68 (2H, m), 3.21 (3H, s), 6.54 (1H, dd, $J=3.4, 1.5$ Hz), 7.19 (1H, d, $J=3.4$ Hz), 7.59 (1H, s). HRMS (FAB) m/z : 253.1809 (Calcd for $C_{15}H_{24}O_3$: 253.1803).

1'-Cyano-5'-hydroxy-pentyl Octyl Ether (62) Colorless oil; IR ($CHCl_3$) cm^{-1} : 3340 (OH), 2900, 1460, 1330, 1100. 1H -NMR ($CDCl_3$) δ : 0.88 (3H, t, $J=6.6$ Hz), 1.27 (11H, brs), 1.61 (6H, m), 1.88 (2H, q, $J=6.8$ Hz), 3.43 (1H, dt, $J=6.4$ Hz), 3.68 (2H, t, $J=5.9$ Hz), 3.76 (1H, dt, $J=6.4$ Hz), 4.11 (1H, t, $J=6.6$ Hz). HRMS (FAB) m/z : 242.2115 (Calcd for $C_{14}H_{27}NO_2$: 242.2120).

1'-Cyano-4'-hydroxy-butyl Octyl Ether (64) Colorless oil; IR ($CHCl_3$) cm^{-1} : 3420 (OH), 2880, 1440, 1330, 1100. 1H -NMR ($CDCl_3$) δ : 0.88 (3H, t, $J=6.6$ Hz), 1.28 (10H, brs), 1.59—1.81 (5H, m), 1.97 (2H, q, $J=6.8$ Hz), 3.45 (1H, dt, $J=6.6$ Hz), 3.70 (2H, t, $J=6.1$ Hz), 3.76 (1H, dt, $J=6.6$ Hz), 4.19 (1H, t, $J=6.3$ Hz). HRMS (FAB) m/z : 228.1973 (Calcd for $C_{13}H_{25}NO_2$: 228.1963).

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