Reaction of Cyclic Aminals with Isocyanates

Giovanni Parrinello*,[1a] and Rolf Mülhaupt[1b]

Plastics Research Center, Ciba-Geigy AG, 1701 Fribourg, Switzerland

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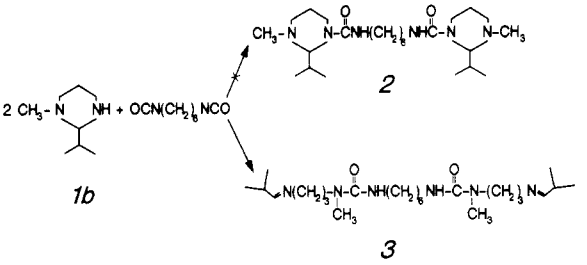
The reaction of cyclic aminals with isocyanates gave two different products depending on the substituents and the ring size of the heterocycle. Six-membered aminal rings (hexahydropyrimidines) that contain electron-donating substituents in the 2-position reacted with isocyanates to provide urea imines via a ring-opening mechanism, whereas those containing electron-withdrawing substituents gave the corresponding urea aminals or a mixture of both products. Five-membered aminal rings (imidazolidines) reacted with isocyanates to provide a mixture of urea imines and urea aminals. The product composition was dependent on the substituents in the 2- and N-position and on the type of isocyanate. Two different mechanisms were proposed to account for the formation of the two types of products.

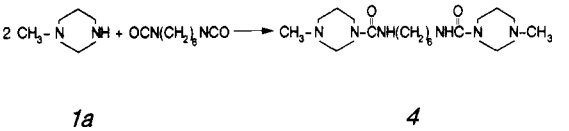
The reaction of amines with isocyanates is the key step in the preparation of a great variety of urea compounds[2] and plays an important role in the polyurethane chemistry.[3] The presence of urea linkages in diamine-extended polyurethanes facilitates phase separation of the hard segments in comparison to diol-extended polyurethanes, providing enhanced mechanical properties such as resilience, toughness, stiffness, and stress relaxation.[4] Because of their reactivity, diamines are used as cross-linking agents for isocyanate-terminated or blocked urethane prepolymers in two-component coatings, sealants, and adhesives.[3b] In one-component polyurethane systems it is desirable to use latent amines that are stable in the presence of isocyanates but initiate cure upon hydrolysis. One approach to meet this objective is based on moisture-sensitive amine precursors such as imines[5] or heterocycles such as oxazolidines[6] and cyclic aminals,[7] which release amino alcohols or diamines in the presence of moisture.

In the course of some studies involving the preparation of polyurethanes containing cyclic aminals as moisture-sensitive amine precursors, we found that the reaction of hexahydropyrimidine **1b** with hexamethylene diisocyanate did not provide the urea aminal **2** as reported (Scheme I).[7a] Instead, the urea imine **3** was obtained in quantitative yield (Scheme I). The structure of compound **3** was confirmed by ^{1}H NMR (C*H*=N at δ 7.58), ^{13}C NMR (*C*H=N at δ 169.6), and IR ($\nu_{C=N}$ 1668 cm^{-1}). However, when the reaction was carried out with use of the heterocycle **1a**, which does not contain substituents in the 2-position, the expected addition product **4** was obtained quantitatively (Scheme II). The cyclic structure of **4** was confirmed by ^{1}H NMR (NC*H*$_2$N at δ 3.89) and ^{13}C NMR (N*C*H$_2$N at δ 67.3).

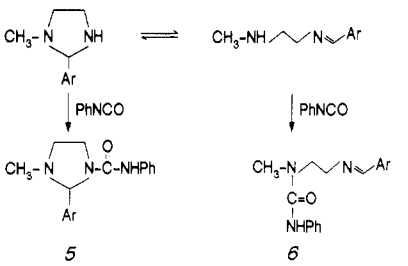
Scheme I



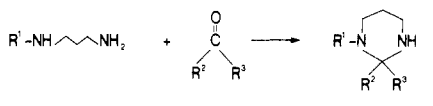
Scheme II



Scheme III



Scheme IV



a: $R^1 = CH_3$; $R^2 = R^3 = H$
b: $R^1 = CH_3$; $R^2 = H$; $R^3 = CH(CH_3)_2$
c: $R^1 = CH_3$; $R^2 = H$; $R^3 = C_6H_5$
d: $R^1 = CH_3$; $R^2 = H$; $R^3 = p\text{-}O_2N\text{-}C_6H_4$
e: $R^1 = CH_3$; $R^2 - R^3 = -(CH_2)_5-$
f: $R^1 = CH_2CH_2OH$; $R^2 = R^3 = H$
g: $R^1 = R^2 = H$; $R^3 = CH(CH_3)_2$

Recently the existance of a ring–chain tautomerism was proposed to account for the formation of the two products **5** and **6** when some imidazolidines reacted with phenyl isocyanate (Scheme III).[8] Accordingly, the urea aldimine

(1) (a) Current address: ICI Europa Limited, Everslaan 45, B-3078 Kortenberg, Belgium. (b) Current address: Institut für Makromolekulare Chemie, Stefan-Meier-Str. 31, D-7800 Freiburg i.Br., West Germany.

(2) (a) Richter, R.; Ulrich, H. In *The Chemistry of Cyanates and their Thio Derivatives*, Part 2; Patai, S., Ed.; John Wiley and Sons, 1977; p 619. (b) Stachell, D. P. N.; Stachell, R. S. *Chem. Soc. Rev.* **1975**, *4*, 231.

(3) (a) Herman, M. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. *Encyclopedia of Polymer Science and Engineering*, Vol. 13; John Wiley and Sons: New York, 1988; pp 212–303. (b) Wood, G. *The ICI Polyurethane Book*; ICI-Polyurethane and Wiley and Sons: 1987. (c) Saunders, J. H.; Frisch, K. C. *Polyurethanes: Chemistry and Technology*, Parts I and II; Interscience Publishers; New York, London, 1963.

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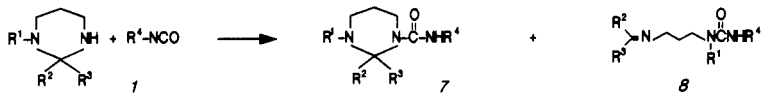
(6) (a) Naples, G. U.S. patent 4,381,388, 1983. (b) Emmons, W. D. U.S. Patent 3,743,626, 1973.

(7) (a) Hajek, M.; Wagner, K.; Uerdingen, W.; Wellner, W. U.S. Patent 4,404,379, 1983. (b) Zengel, H.-G.; Wallrabenstein, M.; Brodowski, W. U.S. Patent 4,289,869, 1981.

(8) Witek, S.; Bielawska, A.; Bielawski, J. *Heterocycles* **1980**, *14*, 1313.

0022-3263/90/1955-1772$02.50/0

Table I. Reaction of Hexahydropyrimidines with Isocyanates[a]



	aminal 1				yield	product composition (%)[b]		
	R^1	R^2	R^3	R^4	(%)		7	8
a	CH_3	H	H	Bu	95	A	100	
a	CH_3	H	H	Ph	91	B	100	
b	CH_3	H	$CH(CH_3)_2$	Bu	97	C		100
b	CH_3	H	$CH(CH_3)_2$	Ph	96	D		100
c	CH_3	H	C_6H_5	Bu	83	E	27	73
c	CH_3	H	C_6H_5	Ph	95	F	22	78
d	CH_3	H	p-$O_2NC_6H_4$	Bu	96	G	36	64
d	CH_3	H	p-$O_2NC_6H_4$	Ph	97	H	40	60
e	CH_3		-$(CH_2)_5$-	Bu	94	I		100
e	CH_3		-$(CH_2)_5$-	Ph	93	J		100
f	CH_2CH_2OH	H	H	Bu	94	K	100	
f	CH_2CH_2OH	H	H	Ph	93	L	100	
g	H	H	$CH(CH_3)_2$	Bu	87	M	100	
g	H	H	$CH(CH_3)_2$	Ph	94	N	100	

[a] Carried out in toluene at room temperature. [b] Determined by ^1H NMR (see Experimental Section).

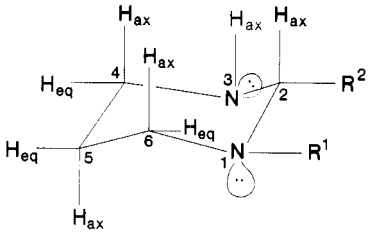


Figure 1.

6 would be derived from the corresponding open-chain tautomer. Ring-opening reactions of cyclic aminals in the presence of isocyanates to produce urea imines have not been reported in the literature.

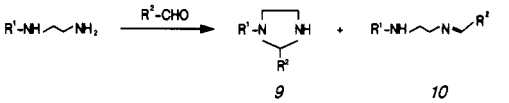
This paper describes the reaction of a variety of five- and six-membered ring aminals with aliphatic and aromatic isocyanates in order to determine the influence of the substituents and the ring size of the heterocycle on the reaction product compositions.

Results and Discussion

Hexahydropyrimidines. A series of hexahydropyrimidines was synthesized by reaction of equimolar amounts of a 1,3-diamine with the corresponding aldehyde or ketone according to the standard procedure (Scheme IV).[7a,9] These products were obtained in high purity and their ^1H NMR, ^{13}C NMR, and IR spectra showed no evidence of the ring–chain tautomerism that has been reported for hexahydropyrimidines containing bulky substituents in the 2- and/or in the N-positions.[10]

Characterization by ^1H NMR revealed that these cyclic aminals prefer at room temperature a chair conformation with the lone pair on N-1 in the axial position and the lone pair on the N-3 in the equatorial position (Figure 1). This is consistent with previous reports on similar compounds.[11] The spectra of such compounds show different chemical shifts for the two axial protons on the C-4 and C-6 and for the two protons on C-5 due to the presence of the lone pair on N-1 in the axial position. For example, the spectrum of compound **1c** ($R^1 = CH_3$, $R^2 = H$, $R^3 = C_6H_5$) shows a triplet of doublets for 4-H_{ax} at δ 2.75 and the corresponding peak for 6-H_{ax} at δ 2.30, which is shielded by the axial lone pair on N-1. Similarly, the equatorial proton on C-5 (a doublet of multiplets at δ 1.62) appears at a lower chemical shift than its geminal proton (a quartet of triplets at δ 1.93), which is deshielded by the 1,3-diaxial interaction with the lone pair on N-1. The preference of an equatorial position for the lone pair on N-3 has been established.[11,12]

Table II. Reaction Products of 1,2-Diamines with Aldehydes



product(s) 9 + 10	R^1	R^2	product composition (%)[a] 9	10
a	CH_3	$CH(CH_3)_2$	100	
b	CH_3	p-$O_2NC_6H_4$	100	
c	CH_3	$C(CH_3)_3$	78	22
d	C_6H_5	$CH(CH_3)_2$	70[b]	30[b]

[a] Determined by ^1H NMR (see Experimental Section). [b] These values are consistent with those reported in the literature.[13]

These observations suggest that the reaction of cyclic aminals with electrophyles should involve preferentially the attack of the lone pair on N-3, which is less hindered than the more nucleophilic lone pair on N-1. These aminals were allowed to react with isocyanates at room temperature to obtain the corresponding urea aminals **7** and/or urea imines **8** (Table I). The course of the reaction was highly dependent on the substituent in the 2-position. Unsubstituted aminals **1a** and **1f** reacted with the isocyanates by direct addition of the secondary amino group, whereas compounds **1b** and **1e**, which contain alkyl substituents in the 2-position, gave the corresponding urea imines exclusively. Compounds containing aromatic substituents in the 2-position (**1c** and **1d**) reacted via both the direct and the ring-opening mechanisms. This indicates that the reaction is controlled by electronic effects. Mechanistically, it can be speculated that the ring-opening reaction that is favored by electron-donating substituents

(9) Reibsomer, J. L.; Morey, G. H. *J. Org. Chem.* **1950**, *15*, 245.
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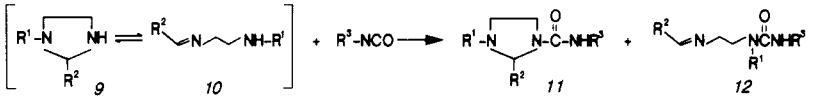
(12) Booth, H.; Lemieux, R. V. *Can. J. Chem.* **1971**, *49*, 777.

Table III. Reaction of Imidazolidines with Isocyanates[a]



	aminal 9(+ 10)						product composition (%)[b]		
			tautom. composition (%)[b]			yield			
	R^1	R^2	9	10	R^3	(%)		11	12
a	CH_3	$CH(CH_3)_2$	100		Bu	90	A	80	20
a	CH_3	$CH(CH_3)_2$	100		Ph	82	B	80	20
b	CH_3	p-$O_2NC_6H_4$	100		Bu	95	C	57	43
b	CH_3	p-$O_2NC_6H_4$	100		Ph	89	D	77	23
c	CH_3	$C(CH_3)_3$	78	22	Bu	88	E	29	71
c	CH_3	$C(CH_3)_3$	78	22	Ph	82	F	66	34
d	C_6H_5	$CH(CH_3)_2$	70	30	Bu	86	G	100	
d	C_6H_5	$CH(CH_3)_2$	70	30	Ph	98	H	100	

[a] Carried out in toluene at room temperature. [b] Determined by ^1H NMR (see Experimental Section).

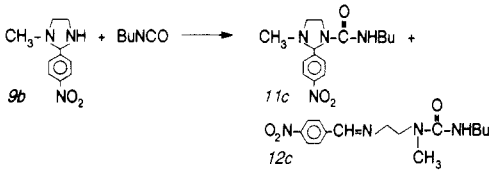
proceeds via the attack of the lone pair of the tertiary nitrogen on the isocyanate. Electron-withdrawing substituents that decrease the nucleophilicity of the tertiary nitrogen favor the addition of the secondary amino group to the isocyanate. The product composition of the reaction of **1c** with isocyanates was not influenced by the presence of acidic or basic catalysts such as dibutyltin dilaurate and 1,4-diazabicyclo[2.2.2]octane (DABCO) nor by the use of different solvents such as toluene, diethyl ether, and dimethylformamide. No solvent or catalyst effects were observed in the reaction of aminal **9b** with isocyanates that gave the ring-opening products exclusively.

The assumption that the presence of a tertiary nitrogen plays a key role in the ring-opening mechanism was confirmed by the reaction of isocyanates with aminal **1g**. This reaction gave the direct addition exclusively due to the absence of a tertiary nitrogen.

Imidazolidines. The imidazolidines shown in Table II were obtained by reaction of the corresponding 1,2-diamines with the appropriate aldehyde. Characterization by ^1H NMR, ^{13}C NMR, and IR spectroscopy revealed that aminals **9c** and **9d** exhibited ring–chain tautomerism. The existance of such tautomerism for a number of substituted imidazolidines has been reported in the literature.[8,13] However, compounds **9a** and **9b** only existed in the cyclic form since no spectral evidence for the open tautomer was observed.

These cyclic aminals were allowed to react with isocyanates at room temperature to obtain the corresponding urea aminals **11** and urea imines **12** (Table III). The product composition was highly dependent on the 2-substituent and, in some cases, on the type of isocyanate. Aminal **9a** reacted with butyl isocyanate and phenyl isocyanate to give the corresponding urea aminals preferentially. The corresponding urea imines also were obtained as minor products (20%) probably via the ring-opening mechanism described above for the six-membered ring analogue. Reaction of aminal **9b** with phenyl isocyanate proceeded preferentially via the direct addition mechanism, whereas with the less reactive butyl isocyanate the ring-opening mechanism became almost equally favored.

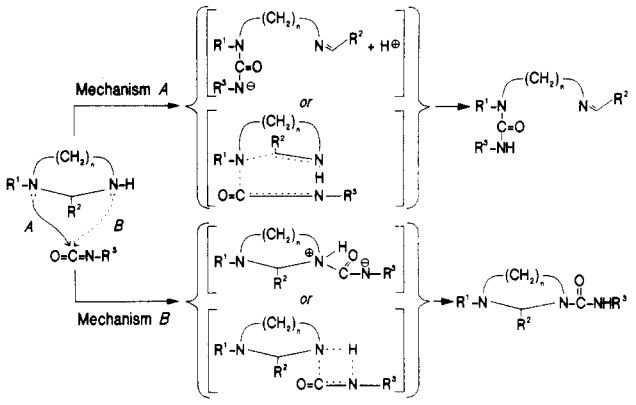
Table IV. Effect of Solvent and Catalyst on the Reaction of Aminal 9b with Butyl Isocyanate[a]



		product composition (%)[b]	
solvent	catalyst	11c	12c
toluene	none	57	43
dimethylformamide	none	46	54
toluene	DABCO[c]	76	24
toluene	DBTDL[d]	64	36

[a] Carried out at room temperature. [b] Determined by ^1H NMR (see Experimental Section). [c] DABCO: 1,4-diazobicyclo[2.2.2]octane. [d] DBTDL: dibutyltin dilaurate.

Scheme V



This dependence of the different reactivity of the isocyanate on the product composition was more accentuated in the case of aminal **9c**. In this case, however, the formation of urea imine may be due to the existence of the tautomeric equilibrium rather than to the ring-opening mechanism. The reaction of **9d** with both aromatic and aliphatic isocyanates gave the corresponding urea aminals exclusively. In this case the reactivity of the open-chain tautomer has decreased due to the presence of an N-phenyl substituent and consequently the tautomeric equilibrium shifted toward the more reactive cyclic structure.

(13) Chapuis, C.; Gauvreau, A.; Klaebe, A.; Lattes, A.; Perie, J. J. *Bull. Soc. Chim. Fr.* **1973**, 977.
(14) Cook, M. J.; Jones, R. A. Y.; Katritzky, A. R.; Moreno Manas, M.; Richards, A. C.; Sparrow, A. J.; Trepanier, D. L. *J. Chem. Soc., Perkin Trans. II* **1973**, 325.
(15) *Beilsteins Handbuch der Organischen Chemie*, E III/IV, Vol. 23, p 13.

Table V. Physical Characteristics of Cyclic Aminals

aminal	bp or mp, °C	elem. anal. calcd	elem. anal. found	^{1}H NMR (δ)[b]	^{13}C NMR (δ)
1a	bp 140 (lit.[14] 138–139)	C, 59.96 H, 12.08 N, 27.97	59.97 12.11 27.93	(100 MHz) 3.30 (s, 2 H), 2.79 (t, J = 6, 2 H), 2.53 (t, J = 6, 2 H), 2.15 (s, 3 H), 1.63 (p, J = 6, 2 H)	70.3, 54.2, 43.4, 41.7, 26.2
1b	bp_{70} 91 (lit.[7a] bp_{15} 68–75)	C, 67.49 H, 12.65 N, 19.68	67.45 12.62 19.66	(360 MHz) 3.02 (dm, J = 12, 1 H_{eq}), 2.88 (dm, J = 12, 1 H_{eq}), 2.54 (d, J = 3, 1 H), 2.52 (td, J_{gem} = 12, J_{vic} = 3, 1 H_{ax}), 2.25 (td, J_{gem} = 12, J_{vic} = 3, 1 H_{ax}), 2.08 (s, 3 H), 1.95 (qt, J_{gem} = 12, J_{vic} = 3, 1 H_{ax}), 1.61 (m, 1 H), 1.38 (dm, J = 12, 1 H_{eq}), 0.95 (d, J = 6, 3 H), 0.88 (d, J = 6, 3 H)	83.1, 56.8, 45.8, 40.6, 28.4, 27.2, 19.6, 14.7
1c	bp_{50} 130	C, 74.96 H, 9.15 N, 15.89	74.87 8.98 15.90	(300 MHz) 7.47–7.26 (m, 5 H), 3.67 (s, 1 H), 3.17 (dm, J_{gem} = 11, 1 H_{eq}), 3.12 (dm, J_{gem} = 11, 1 H_{eq}), 2.75 (td, J_{gem} = 11, J_{vic} = 3, 1 H_{ax}), 2.30 (td, J_{gem} = 11, J_{vic} = 3, 1 H_{ax}), 1.94 (s, 3 H), 1.92 (qt, J_{gem} = 11, J_{vic} = 3, 1 H_{ax}), 1.62 (dm, J_{gem} = 11, 1 H_{eq})	141.7, 127.9, 127.5, 126.7, 83.0, 55.7, 45.1, 42.2, 26.8
1d	mp 90–91 (recryst from hexane)	C, 59.71 H, 6.83 N, 18.99	59.68 6.78 18.97	(300 MHz) 8.21 (d, J = 9, 2 H), 7.62 (d, J = 9, 2 H), 3.82 (s, 1 H), 3.21 (dm, J_{gem} = 11, 1 H_{eq}), 3.16 (dm, J_{gem} = 11, 1 H_{eq}), 2.76 (td, J_{gem} = 11, J_{vic} = 4, 1 H_{ax}), 2.35 (td, J_{gem} = 11, J_{vic} = 4, 1 H_{ax}), 1.94 (s, 3 H), 1.91 (qt, J_{gem} = 11, J_{vic} = 4, 1 H_{ax}), 1.65 (dm, J_{gem} = 11, 1 H_{eq})	148.9, 147.3, 128.0, 123.4, 82.0, 55.6, 45.2, 42.3, 26.9
1e	bp_{70} 112	C, 71.42 H, 11.89 N, 16.65	71.29 11.92 16.76	(100 MHz) 2.92–2.64 (m, 10 H), 2.33 (s, 3 H), 1.67–1.56 (m, 6 H)	69.2, 48.3, 38.5, 37.1, 29.7, 25.8 25.4, 21.4
1f	$bp_{0.01}$ 65 (lit.[15] bp_{17} 137–140); mp 30–32	C, 55.38 H, 10.77 N, 21.54	55.28 10.70 21.52	(100 MHz) 3.60 (t, J = 5, 2 H), 3.47 (s, 2 H), 2.85 (t, J = 6, 2 H), 2.61 (t, J = 6, 2 H), 2.46 (t, J = 5, 2 H), 1.61 (p, J = 6, 2 H)	69.4, 57.9, 56.8, 52.7, 44.7, 26.5
1g	bp_{50} 65	C, 65.57 H, 12.58 N, 21.85	65.60 12.49 21.90	(100 MHz) 3.25–3.12 (m, 3 H), 2.94–2.66 (m, 2 H), 1.69–1.30 (m, 5 H), 0.95 (d, J = 6, 6 H)	75.6, 45.1, 32.5, 26.9, 17.1
9a	bp_{50} 54	C, 65.57 H, 12.58 N, 21.85	65.56 12.46 21.80	(100 MHz) 3.19–2.85 (m, 4 H), 2.45–2.19 (m, 1 H), 2.32 (s, 3 H), 1.94–1.70 (m, 2 H), 1.12 (d, J = 6, 3 H), 0.90 (d, J = 6, 3 H)	85.2, 55.6, 43.3, 38.9, 28.7, 19.0, 14.4
9b	mp 41 (lit.[8] 39–40)	C, 57.96 H, 6.33 N, 20.28	57.86 6.32 20.34	(100 MHz) 8.21 (d, J = 9, 2 H), 7.67 (d, J = 9, 2 H), 4.07 (s, 1 H), 3.45–3.07 (m, 2 H), 2.60–2.48 (m, 2 H), 2.26 (s, 3 H)	148.3, 147.8, 128.6, 123.8, 83.6, 55.7, 44.9, 38.8
9c + 10c	bp_{70} 56	C, 67.55 H, 12.76 N, 19.69	67.50 12.68 19.67	**9c**: (100 MHz) 3.10 (s, 1 H),[a] 3.10–2.73 (m, 4 H), 2.44 (s, 3 H), 0.92 (s, 9 H) **10c**: 7.57 (t, J = 1, 1 H),[a] 3.50 (td, J = 6, J = 1, 2 H), 5.59–2.37 (m, 2 H), 2.44 (s, 3 H), 1.06 (s, 9 H)	**9c**: 90.6, 60.4, 51.6, 36.0, 35.7, 26.6 **10c**: 172.8, 57.6, 44.9, 44.7, 35.7, 25.7
9d + 10d	bp_{50} 148	C, 75.74 H, 9.53 N, 14.72	75.68 9.56 14.65	**9d**: (100 MHz) 7.32–7.00 (m, 2 H), 6.80–6.50 (m, 3 H), 4.38 (d, J = 4, 1 H),[a] 3.59–3.05 (m, 4 H), 2.20–1.93 (m, 1 H), 1.06 (d, J = 4, 3 H), 0.99 (d, J = 4, 3 H) **10d**: 7.51 (dt, J = 5, J = 1, 1 H),[a] 7.32–7.00 (m, 2 H), 6.80–6.50 (m, 3 H), 3.59–3.05 (m, 4 H), 2.50–2.27 (m, 1 H), 0.85 (d, J = 7, 6 H)	**9d**: 146.8, 128.7, 115.8, 112.5, 78.9, 49.3, 45.3, 30.8, 19.0, 15.7 **10d**: 171.0, 147.8, 128.8, 116.8, 112.7, 59.4, 43.9, 33.7, 18.9

[a] The integration of these two peaks was used to calculate the tautomeric composition (see Table II). [b] J values are in hertz.

Table VI. Characteristics of the Reaction Products of Cyclic Aminals with Isocyanates

product	elem. anal. calcd	elem. anal. found	^{1}H NMR (δ, 100 MHz)[g]	^{13}C NMR (δ)
3[a]	C, 63.68 H, 10.69 N, 18.57	63.62 10.71 18.54	7.58 (d, J = 5, 2 H), 5.96 (br t, 2 H), 3.41–3.26 (m, 8 H), 3.13 (t, J = 4, 4 H), 2.88 (s, 6 H), 2.41 (qd, J = 8, J = 5, 2 H), 1.71 (p, J = 6, 4 H), 1.45–1.26 (m, 8 H), 1.06 (d, J = 8, 12 H)	169.6, 158.6, 56.5, 45.8, 40.5, 33.8, 33.7, 30.3, 29.3, 26.5, 19.0
4[a]	C, 58.67 H, 9.85 N, 22.80	58.62 10.01 22.84	4.76 (br, t, 2 H), 3.89 (s, 4 H), 3.37 (t, J =, 4 H), 3.24–3.12 (m, 4 H), 2.59 (t, J = 6, 4 H), 2.26 (s, 6 H), 1.65 (p, J = 6, 4 H), 1.49–1.18 (m, 8 H)	157.1, 67.3, 54.3, 43.3, 41.6, 40.0, 29.7, 25.7, 23.5
7A[a]	C, 60.27 H, 10.62 N, 21.08	60.22 10.72 21.01	5.14 (br, t, 1 H), 3.91 (s, 2 H), 3.38 (t, J = 6, 2 H), 3.30–3.10 (m, 2 H), 2.59 (t, J = 6, 2 H), 2.25 (s, 3 H), 1.64 (p, J = 6, 2 H), 1.48–1.14 (m, 4 H), 0.91 (t, J = 6, 3 H)	157.2, 67.5, 54.3, 43.4, 41.7, 40.2, 31.9, 23.4, 19.7, 13.4
7B[b]	C, 65.73 H, 7.81 N, 19.16	65.69 7.74 19.08	7.43–7.20 (m, 3 H), 7.17–6.99 (m, 2 H), 6.75 (br s, 1 H), 3.98 (s, 2 H), 3.47 (t, J = 6, 2 H), 2.63 (t, J = 6, 2 H), 2.29 (s, 3 H), 1.69 (p, J = 6, 2 H)	155.0, 138.9, 128.6, 122.8, 119.9, 67.9, 54.5, 44.1, 41.8, 23.7
8C[a]	C, 64.69 H, 11.28 N, 17.41	64.72 11.27 17.50	7.58 (dt, J = 6, J = 1, 1 H), 5.93 (br t, 1 H), 3.42–3.26 (m, 4 H), 3.15 (t, J = 6, 2 H), 2.89 (s, 3 H), 2.41 (qd, J = 8, J = 5, 1 H), 1.71 (p, J = 6, 2 H), 1.47–1.24 (m, 4 H), 1.16 (d, J = 8, 6 H), 0.83 (t, J = 6, 3 H)	169.3, 159.0, 56.4, 45.6, 40.3, 33.6, 33.5, 32.3, 29.1, 19.8, 18.8, 13.5
8D[a]	C, 68.93 H, 8.87 N, 16.08	68.84 8.79 16.07	8.77 (br s, 1 H), 7.58 (dt, J = 5, J = 1, 1 H), 7.41–7.21 (m, 3 H), 7.02–6.90 (m, 2 H), 3.48 (t, J = 6, 2 H), 3.42 (t, J = 6, 2 H), 2.95 (s, 3 H), 2.54–2.29 (m, 1 H), 1.73 (p, J = 6, 2 H), 1.10 (d, J = 7, 6 H)	171.1, 157.3, 140.4, 128.6, 122.4, 120.4, 56.0, 46.0, 34.2, 33.9, 29.5, 19.4
7E + 8E	C, 69.78 H, 9.15 N, 15.26	69.70 9.15 15.29	**7E**: 7.75–7.61 (m, 2 H), 7.44–7.21 (m, 3 H), 5.90 (s, 1 H), 5.15 (br t, 1 H), 3.92–3.88 (m, 1 H_{eq}), 3.86–3.81 (m, 1 H_{eq}), 3.20–2.80 (m, 4 H), 2.66 (s, 3 H),[c] 1.68–1.12 (m, 6 H), 0.90 (t, J = 6, 3 H) **8E**: 8.30 (s, 1 H), 7.75–7.61 (m, 2 H), 7.44–7.21 (m, 3 H), 5.83 (br t, 1 H), 3.61 (t, J = 6, 2 H), 3.41 (t, J = 6, 2 H), 3.15 (t, J = 6, 2 H), 2.91 (s, 3 H),[c] 1.84 (p, J = 6, 2 H), 1.58–1.22 (m, 4 H), 0.83 (t, J = 6, 3 H)	**7E**: 158.2, 138.5, 128.1, 126.8, 126.6, 73.0, 56.8, 45.4, 40.7, 38.7, 32.2, 29.4, 18.4, 13.7 **8E**: 160.9, 158.7, 135.4, 130.4, 128.2, 127.6, 126.9, 56.9, 45.8, 40.4, 33.6, 32.3, 29.3, 19.9, 13.6
7F + 8F	C, 71.19 H, 7.17 N, 14.23	71.24 7.17 14.19	**7F**: 7.83–6.84 (m, 10 H), 6.49 (br s, 1 H), 5.95 (s, 1 H),[c] 4.98–4.05 (m, 1 H_{eq}), 4.01–3.90 (m, 1 H_{eq}), 3.10 (td, J_{gem} = 13, J_{vic} = 3, 1 H_{ax}), 2.70 (s, 3 H), 2.33 (td, J_{gem} = 13, J_{vic} = 3, 1 H_{ax}), 2.05–1.85 (m, 1 H_{ax}), 1.18 (dm, J = 13, 1 H_{ax}) **8F**: 8.55 (s, 1 H), 8.39 (s, 1 H),[c] 7.83–6.84 (m, 10 H), 3.74 (t, J = 6, 2 H), 3.61 (t, J = 6, 2 H), 3.02 (s, 3 H), 1.90 (p, J = 6, 2 H)	**7F**: 155.9, 139.5, 138.2, 128.7, 127.9, 126.9, 126.8, 122.2, 119.9, 73.5, 56.0, 45.4, 40.7, 27.2 **8F**: 161.7, 156.6, 139.8, 135.0, 130.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.0, 121.9, 120.1, 56.3, 45.8, 33.7, 29.4
7G + 8G	C, 59.98 H, 7.55 N, 17.49	59.92 7.52 17.47	**7G**: 8.18 (d, J = 9, 2 H), 7.62 (d, J = 9, 2 H),[c] 6.20 (s, 1 H), 5.24 (br s, 1 H), 3.98–3.78 (m, 1 H_{eq}), 3.76–3.70 (m, 1 H_{eq}), 3.25–3.10 (m, 4 H), 3.18–3.07 (m, 1 H_{ax}), 3.10–2.80 (m, 1 H_{ax}), 2.69 (s, 3 H), 1.64–1.12 (m, 6 H), 0.94 (t, J = 6, 3 H) **8G**: 8.43 (s, 1 H), 8.27 (d, J = 9, 2 H), 7.91 (d, J = 9, 2 H),[c] 5.24 (br t, 1 H), 3.71 (t, J = 6, 2 H), 3.44 (t, J = 6, 2 H), 3.15 (t, J = 6, 2 H), 2.93 (s, 3 H), 1.92 (p, J = 6, 2 H), 1.62–1.23 (m, 4 H), 0.86 (t, J = 6, 3 H)	**7G**: 157.9, 148.3, 147.0, 127.9, 123.0, 72.2, 57.7, 45.5, 40.6, 40.4, 32.0, 29.1, 19.8 13.5 **8G**: 158.7, 158.2, 146.5, 141.0, 128.2, 123.2, 57.7, 45.8, 40.3, 33.6, 32.1, 28.9, 19.7, 13.5
7H + 8H	C, 63.52 H, 5.92 N, 16.46	63.60 5.94 16.39	**7H**: 8.21 (d, J = 9, 2 H), 7.65 (d, J = 9, 2 H), 7.47–6.89 (m, 5 H), 6.61 (s, 1 H), 6.13 (s, 1 H),[c] 3.92–3.79 (m, 1 H_{eq}), 3.78–3.70 (m, 1 H_{eq}), 3.13 (td, J_{gem} = 13, J_{vic} = 3, 1 H_{ax}), 2.88 (td, J_{gem} = 13, J_{vic} = 3, 1 H_{ax}), 2.73 (s, 3 H), 2.08–1.84 (m, 1 H_{ax}), 1.17 (dm, J_{gem} = 13, 1 H_{eq}) **8H**: 8.46 (s, 1 H),[c] 8.23 (d, J = 9, 2 H), 7.86 (d, J = 9, 2 H), 7.69 (s, 1 H), 7.47–6.89 (m, 5 H), 3.80 (t, J = 6, 2 H), 3.59 (t, J = 6, 2 H), 3.03 (s, 3 H), 1.96 (p, J = 6, 2 H)	**7H**: 155.8, 148.6, 146.8, 139.4, 128.2, 128.1, 123.3, 122.4, 120.2, 72.7, 57.5, 45.6, 40.8, 29.0 **8H**: 159.4, 156.0, 146.7, 140.7, 139.5, 128.6, 128.1, 123.5, 122.1, 119.8, 57.5, 46.0, 33.9, 29.1
8I[a]	C, 67.37 H, 10.93 N, 15.71	67.25 11.01 15.74	5.91 (br t, 1 H), 3.56–3.18 (m, 6 H), 2.89 (s, 3 H), 2.39–2.21 (m, 4 H), 1.81–1.15 (m, 12 H), 0.90 (t, J = 6, 3 H)	173.0, 158.9, 45.5, 45.1, 40.0, 39.4, 33.4, 32.0, 28.8, 28.2, 27.2, 26.8, 25.4, 19.6, 13.3

8J[a]	C, 71.04 H, 8.77 N, 14.62	70.95 8.80 14.70	7.98 (br s, 1 H), 7.49–7.13 (m, 3 H), 7.02–6.85 (m, 2 H), 3.54–3.35 (m, 4 H), 2.89 (s, 3 H), 2.46–2.26 (m, 2 H), 1.95–1.56 (m, 10 H)	173.4, 156.5, 140.0, 127.6, 121.2, 119.4, 45.1, 44.0, 39.4, 33.0, 28.2, 28.0, 26.8, 26.2, 25.0
7K[a]	C, 57.64 H, 10.04 N, 18.34	57.70 10.08 18.31	5.27 (br t, 1 H), 4.13 (s, 2 H), 3.69 (t, J = 5, 2 H), 3.43 (t, J = 6, 2 H), 3.29–3.10 (m, 2 H), 2.78 (t, J = 6, 2 H), 2.61 (t, J = 5, 2 H), 1.64 (p, J = 6, 2 H), 1.46–1.15 (m, 4 H), 0.91 (t, J = 6, 3 H)	157.6, 65.1, 58.9, 53.9, 52.5, 43.5, 39.9, 31.5, 22.5, 19.3, 13.1
7L[a]	C, 62.63 H, 7.68 N, 16.85	62.58 7.67 16.83	7.71 (br s, 1 H), 7.39–7.13 (m, 3 H), 7.01–6.90 (m, 2 H), 4.23 (s, 2 H), 3.71 (t, J = 5, 2 H), 3.53 (t, J = 6, 2 H), 2.79 (t, J = 6, 2 H), 2.61 (t, J = 5, 2 H), 1.61 (p, J = 6, 2 H)	155.6, 139.2, 128.2, 122.3, 119.9, 65.5, 60.2, 53.4, 53.1, 44.1, 22.6
7M[d]	C, 62.54 H, 10.50 N, 17.16	62.54 10.46 17.21	(250 MHz), 5.67 (br s, 2 H), 5.41 (d, J = 4, 1 H), 3.91 (m, 1 H), 3.85 (m, 1 H), 3.26–3.12 (m, 6 H), 2.51–2.41 (m, 1 H), 1.65–1.26 (m, 10 H), 0.94–0.88 (m, 12 H)	158.4, 68.5, 40.6, 38.6, 32.1, 26.6, 24.6, 20.0, 18.4, 13.8
7N[e]	C, 68.83 H, 7.15 N, 15.29	68.78 7.16 15.33	(250 MHz, DMSO-d_6) 8.67 (br s, 2 H), 7.44 (d, J = 3, 4 H), 7.24 (t, J = 3, 4 H), 6.94 (t, J = 3, 2 H), 5.95 (d, J = 4, 1 H), 4.07 (m, 1 H), 4.01 (m, 1 H), 3.33–3.22 (m, 2 H), 2.64–2.55 (m, 1 H), 1.58 (m, 2 H), 0.91 (d, J = 3, 6 H)	(DMSO-d_6) 155.0, 140.4, 128.4, 121.9, 119.7, 67.3, 38.5, 26.3, 24.9, 18.2
11A + 12A	C, 63.40 H, 11.08 N, 18.48	63.42 11.02 18.47	**11A**: 4.27 (br t, 1 H), 4.10 (d, J = 6, 1 H),[c] 3.54–3.41 (m, 1 H), 3.32–3.01 (m, 3 H), 3.25–3.05 (m, 2 H), 2.32 (s, 3 H), 1.92–1.62 (m, 1 H), 1.52–1.27 (m, 4 H), 0.89 (d, J = 7, 3 H), 0.87 (d, J = 7, 3 H), 0.83 (t, J = 6, 3 H) **12A**: 7.52 (d, J = 4, 1 H),[c] 5.35 (br t, 1 H), 3.25–3.05 (m, 2 H), 2.83 (s, 3 H), 2.80 (t, J = 3, 2 H), 2.66 (t, J = 3, 2 H), 2.54–2.25 (m, 1 H), 1.52–1.27 (m, 4 H), 1.00 (d, J = 7, 6 H), 0.83 (t, J = 6, 3 H)	**11A**: 158.9, 85.7, 53.3, 44.0, 42.8, 40.1, 32.5, 32.3, 19.8, 18.7, 13.6 **12A**: 171.1, 157.0, 59.2, 50.1, 40.2, 34.6, 33.7, 32.2, 19.9, 18.0, 13.6
11B + 12B	C, 67.90 H, 8.55 N, 16.98	67.86 8.46 17.00	**11B**: 7.47–6.85 (m, 5 H), 6.55 (br s, 1 H), 4.27 (d, J = 6, 1 H),[c] 3.74–3.49 (m, 1 H), 3.39–3.03 (m, 3 H), 2.38 (s, 3 H), 2.07–1.60 (m, 1 H), 0.97 (d, J = 7, 2 H), 0.94 (d, J = 7, 2 H) **12B**: 8.15 (br s, 1 H), 7.52 (d, J = 4, 1 H),[c] 7.47–6.85 (m, 5 H), 2.94 (s, 3 H), 2.89–2.65 (m, 4 H), 2.54–2.25 (m, 1 H), 1.06 (d, J = 7, 6 H)	**11B**: 154.4, 139.0, 128.2, 122.3, 119.8, 85.6, 53.3, 43.9, 43.1, 32.3, 18.7, 18.0 **12B**: 172.3, 156.8, 139.5, 128.3, 121.8, 119.1, 58.6, 50.3, 34.4, 33.9, 18.9
11C + 12C	C, 58.81 H, 7.24 N, 18.29	58.84 7.19 18.23	**11C**: 8.19 (d, J = 9, 2 H), 7.61 (d, J = 9, 2 H),[c] 4.86 (s, 1 H), 4.33 (br t, 1 H), 3.78–3.61 (m, 3 H), 3.40–3.18 (m, 1 H), 3.30–3.15 (m, 2 H), 2.30 (s, 3 H), 1.5–1.15 (m, 4 H), 0.82 (t, J = 6, 3 H) **12C**: 8.36 (s, 1 H), 8.27 (d, J = 9, 2 H), 7.88 (d, J = 9, 2 H),[c] 4.92 (br t, 1 H), 3.25–3.11 (m, 2 H), 2.93 (s, 3 H), 2.82 (t, J = 8, 2 H), 2.73 (t, J = 8, 2 H), 1.53–1.21 (m, 4 H), 0.86 (t, J = 6, 3 H)	**11C**: 156.2, 149.2, 148.5, 128.8, 123.6, 81.4, 53.8, 45.1, 40.3, 39.1, 32.3, 20.0, 13.7 **12C**: 160.4, 158.8, 147.9, 141.3, 128.8, 123.9, 60.5, 50.2, 40.6, 35.2, 32.6, 20.1, 13.8
11D + 12D	C, 62.57 H, 5.56 N, 17.17	62.61 5.60 17.14	**11D**: 8.20 (d, J = 8, 2 H), 7.63 (d, J = 8, 2 H),[c] 7.40–6.90 (m, 5 H), 6.25 (br s, 1 H), 4.94 (s, 1 H), 3.98–3.82 (m, 3 H), 3.40–3.18 (m, 1 H), 2.31 (s, 3 H) **12D**: 8.42 (s, 1 H), 8.26 (d, J = 8, 2 H), 7.92 (d, J = 8, 2 H),[c] 7.40–6.90 (m, 5 H), 7.20 (br s, 1 H), 3.03 (s, 3 H), 2.98 (t, J = 8, 2 H), 2.79 (t, J = 8, 2 H)	**11D**: 153.5, 149.3, 148.0, 138.4, 128.8, 123.6, 123.3, 119.8, 81.4, 53.8, 45.5, 39.0 **12D**: 161.4, 156.4, 147.9, 140.8, 139.5, 128.8, 123.9, 122.7, 119.5, 60.0, 50.6, 35.1
11E + 12E	C, 64.69 H, 11.28 N, 17.41	64.71 11.28 17.49	**11E**: 4.56 (br t, 1 H), 4.26 (s, 1 H),[c] 3.81–3.60 (m, 2 H), 3.33–3.06 (m, 2 H), 2.85–2.60 (m, 2 H), 2.43 (s, 3 H), 1.53–1.22 (m, 4 H), 0.97–0.84 (m, 3 H), 0.92 (s, 9 H) **12E**: 7.51 (s, 1 H),[c] 5.37 (br t, 1 H), 3.48–3.42 (m, 4 H), 3.33–3.06 (m, 2 H), 2.88 (s, 3 H), 1.53–1.22 (m, 4 H), 1.04 (s, 9 H), 0.97–0.84 (m, 3 H)	**11E**: 158.0, 87.9, 54.8, 46.0, 45.0, 40.1, 35.7, 32.1, 26.2, 19.7, 13.4 **12E**: 173.6, 159.0, 59.1, 50.1, 40.1, 35.7, 34.5, 32.2, 26.3, 19.7, 13.4
11F + 12F	C, 68.93 H, 8.87 N, 16.08	68.88 8.89 16.17	**11F**: 7.46–6.91 (m, 5 H), 6.66 (br s, 1 H), 4.40 (s, 1 H), 3.88–3.70 (m, 2 H), 2.85–2.60 (m, 2 H), 2.45 (s, 3 H), 0.95 (s, 9 H)[c] **12F**: 7.74 (br s, 1 H), 7.56 (s, 1 H), 7.46–6.91 (m, 5 H), 3.44–3.19 (m, 4 H), 2.93 (s, 3 H), 1.05 (s, 9 H)[c]	**11F**: 155.8, 139.2, 128.5, 122.5, 119.7, 88.1, 55.0, 46.2, 45.5, 38.3, 26.4 **12F**: 175.1, 156.8, 139.6, 128.5, 122.0, 119.2, 58.8, 50.4, 36.2, 34.3, 26.6

Table VI (Continued)

product	elem. anal. calcd	elem. anal. found	^{1}H NMR (δ, 100 MHz)[g]	^{13}C NMR (δ)
11G[a]	C, 70.55	70.58	7.31–7.15 (m, 2 H), 6.80–6.59 (m, 3 H), 5.45 (d, J = 3, 1 H), 4.52 (br t, 1 H), 3.96–3.12	156.9, 146.3, 129.1, 117.1,
	H, 9.40	9.42	(m, 6 H), 2.39–2.12 (m, 1 H), 1.63–1.25 (m, 4 H), 1.03 (d, J = 7, 3 H), 0.92	112.9, 76.3, 47.2, 44.4, 40.5,
	N, 14.52	14.60	(t, J = 6, 3 H), 0.87 (t, J = 7, 3 H)	33.4, 32.5, 19.9, 19.0, 17.2, 13.6
11H[f]	C, 73.76	73.69	7.42–7.04 (m, 7 H), 6.85–6.64 (m, 3 H), 6.26 (br s, 1 H), 5.62 (d, J = 3, 1 H), 4.08–3.90	154.2, 146.2, 138.6, 128.9,
	H, 7.49	7.52	(m, 1 H), 3.70–3.54 (m, 3 H), 2.46–2.09 (m, 1 H), 1.06 (d, J = 7, 3 H),	128.7, 123.2, 120.1, 117.4,
	N, 13.58	13.52	0.91 (d, J = 7, 3 H)	113.0, 76.3, 47.3, 44.7, 33.4, 19.0, 17.2

[a] Product was a viscous liquid. [b] Recrystallized from toluene/hexane: mp 105–106 °C. [c] Integration of these two peaks was used to calculate the product composition (see Tables I, II, and IV). [d] Recrystallized from toluene: mp 130 °C. [e] Recrystallized from ethanol: mp 189–190 °C. [f] Recrystallized from ethanol: mp 135–136 °C. [g] J values are in hertz.

The product composition of the reaction of aminal **9b** with butyl isocyanate was found to be influenced by the polarity of the solvent and the use of catalysts (Table IV). The formation of the urea aminal **11C** was favored by nonpolar solvents and by the presence of a catalyst. No solvent or catalyst effect was observed on the reaction of aminal **9a**.

Mechanism. On the basis of the results discussed above, it is proposed that the reaction of cyclic aminals with isocyanates proceeds via two different mechanisms A and B depending on the substituents and the ring size of the heterocycle (Scheme V). Mechanism A involves the attack of the lone pair of the tertiary amino group on the isocyanate and may proceed either in a concerted or in a stepwise fashion. This mechanism is favored by electron-donating substituents in the 2-position of the aminal that increase the nucleophilicity of the tertiary nitrogen. Electron-withdrawing substituents in the 2- or in the N-position decrease the nucleophilicity of the tertiary amino group and hence inhibit mechanism A. In such cases, the reaction with isocyanates involves the nucleophilic attack of the less hindered secondary amino group to provide the corresponding urea aminal either via a concerted or a stepwise mechanism (mechanism B). The reaction of imidazolidines with isocyanates is also influenced by kinetic effects. The reactive phenyl isocyanate reacts with the less hindered secondary nitrogen of the imidazolidine preferentially (mechanism B). With the less reactive butyl isocyanate, the reaction involving the attack of the most nucleophilic nitrogen becomes more competitive (mechanism A).

Conclusion. The investigation described above provided a method to control the course of the reaction of isocyanates with cyclic aminals based on the substituents and the ring size of the heterocycle and on the reactivity of the isocyanate. The significance of this reaction is that it is possible to functionalize isocyanates through urea linkages and introduce at the same time either an imine functionality or a heterocycle. This process, which can provide products of well-defined structure in quantitative yield and high purity from readily available materials, is a convenient tool for polymer modification and a variety of other applications.

Experimental Section

Infrared spectra were recorded on a Nicolet 20 2X FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker WP-100-SY (100 MHz) or a Bruker WM-250 (250 MHz) or a Varian XL-300 (300 MHz) or a Bruker AM-360 (360 MHz) spectrometer with tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded on a Varian XL-300 (75 MHz) or a Bruker AM-360 (90 MHz) spectrometer with tetramethylsilane (δ 0.0) or chloroform (δ 77.0) as the internal standard. Unless otherwise stated, the spectra were obtained in deuteriochloroform.

Melting points are uncorrected. Gas chromatographic analyses were carried out on a Perkin-Elmer Model 8300 using a CPMS/1701 fused-silica capillary column (25 m length × 0.32 mm i.d., 0.25 mm film thickness) with a flame ionization detector and helium as the carrier gas. All starting materials were purchased from Fluka.

General Procedure for the Preparation of Cyclic Aminals.[7a,9] A solution of 1 mol of aldehyde (or ketone) in 100 mL of toluene was added dropwise to 1 mol of the appropriate diamine. The reaction was generally exothermic and the rate of addition was adjusted in order to maintain the temperature below 30 °C. At the end of the addition, the mixture was heated at reflux under an inert atmosphere of nitrogen until the calculated amount of water was collected in a Dean–Stark trap. The solvent was evaporated and the product was purified by distillation or recrystallization. The physical characteristics of the products are listed in Table V.

General Procedure for the Reaction of Cyclic Aminals with Isocyanates.[7a,8] A solution of 0.1 mol of butyl isocyanate (or phenyl isocyanate) in 30 mL of dry toluene was added dropwise to a solution of 0.1 mol of cyclic aminal in 20 mL of dry toluene. The reaction was exothermic and the rate of addition was adjusted in order to maintain the temperature below 30 °C. At the end of the addition the solution was stirred at room temperature until no more isocyanate was detected by IR spectroscopy (1–2 h). The solvent was removed on a rotary evaporator. In the case of reactions that provided a mixture of urea aminal and urea imine, every attempt to separate the components by conventional techniques (distillation, recrystallization, solvent extraction, and chromatography) was unsuccessful. The yields are reported in Tables I and III. The physical characteristics of the products are listed in Table VI.

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Registry No. **1a**, 31952-00-8; **1b**, 70231-94-6; **1c**, 124821-12-1; **1d**, 124821-13-2; **1e**, 124821-14-3; **1f**, 51461-66-6; **1g**, 61327-69-3; **3**, 124821-48-3; **4**, 70233-87-3; **7A**, 124821-15-4; **7B**, 124821-16-5; **7E**, 124821-19-8; **7F**, 124821-21-2; **7G**, 124821-23-4; **7H**, 124821-25-6; **7K**, 124821-29-0; **7L**, 124821-30-3; **7M**, 124821-31-4; **7N**, 124821-32-5; **8C**, 124821-17-6; **8D**, 124821-18-7; **8E**, 124821-20-1; **8F**, 124821-22-3; **8G**, 124821-24-5; **8H**, 124821-26-7; **8I**, 124821-27-8; **8J**, 124821-28-9; **9a**, 124821-33-6; **9b**, 75817-16-2; **9c**, 124821-34-7; **9d**, 42163-87-1; **10c**, 124821-35-8; **10d**, 42163-96-2; **11A**, 124821-36-9; **11B**, 124821-38-1; **11C**, 124821-40-5; **11D**, 75817-27-5; **11E**, 124821-42-7; **11F**, 124821-44-9; **11G**, 124821-46-1; **11H**, 124821-47-2; **12A**, 124821-37-0; **12B**, 124821-39-2; **12C**, 124821-41-6; **12D**, 75817-28-6; **12E**, 124821-43-8; **12F**, 124821-45-0; $MeNH(CH_2)_3NH_2$, 6291-84-5; $HOCH_2CH_2NH(CH_2)_3NH_2$, 4461-39-6; $NH_2(CH_2)_3NH_2$, 109-76-2; HCHO, 50-00-0; *i*-PrCHO, 78-84-2; PhCHO, 100-52-7; *p*-$NO_2C_6H_4CHO$, 555-16-8; $Me(CH_2)_3NCO$, 111-36-4; PhNCO, 103-71-9; $HCOC(CH_3)_3$, 630-19-3; $MeNHCH_2CH_2NH_2$, 109-81-9; $PhNHCH_2CH_2NH_2$, 5700-56-1; $OCN(CH_2)_6NCO$, 822-06-0; cyclohexanone, 108-94-1.

Supplementary Material Available: IR spectral data of aminals and of the reaction products of aminals with isocyanates (2 pages). Ordering information is given on any current masthead page.

Amine-Induced Reactions of Diacyl Peroxides

Shamala Srinivas and K. Grant Taylor*

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

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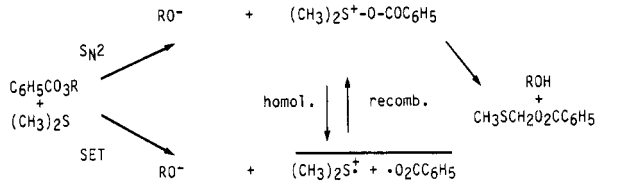
The decompositions of 3-chlorobenzoyl cyclobutylformyl peroxide (**3a**), and 3-chlorobenzoyl cyclopropylacetyl peroxide (**3b**) induced by 1-azabicyclo[2.2.2]octane (Q), N^1,N^1,N^4,N^4-tetramethyl-1,4-benzenediamine (W), 1,4-diazabicyclo[2.2.2]octane (DABCO), and *N,N*-dimethylaniline (DMA) were investigated. Peroxides **3** were selected for study because distinctive product patterns were expected from decompositions induced by the alternative S_N2 and SET pathways. Q and W were selected as amines likely to react by the S_N2 and SET pathways, respectively. Q reacted with **3** to give products characteristic of the intermediacy of an ion pair (general structure: $R_3NOCOC_4H_7^+ArCO_2^-$) formed by the S_N2 pathway, while W reacted with **3** to give rapid formation of the $C_4H_7CO_2$ radical, indicative of an SET pathway. Based on the results with Q and W, we interpret the results with DABCO and DMA to indicate that both induce the decomposition of **3** by the S_N2 pathway. Thus, peroxides **3** have been shown to be structurally sensitive to the modes of their induced decomposition, and are, potentially, mechanistic probes for ascertaining the mechanism of induced peroxide decomposition by closed-shell molecules.

Background and Introduction

Organic peroxides have varied applications ranging from the initiation of industrially useful free-radical polymerizations to their use in hair dye and acne medication formulations. Studies have shown that peroxides are carcinogenic and mutagenic.[1] For example, peroxide **3a** has been found to be marginally mutagenic in the *Salmonella* LT-2 and *B. subtilis* FB-13 tester strains.[1c] Little is known, however, about their mechanism of action. Pryor has pointed out that peroxides in vivo likely undergo bimolecularly assisted rupture of the O–O bond to initiate their decomposition.[2] Such induced decomposition of peroxides by odd-electron as well as closed-shell molecules is well known in peroxide chemistry. The mechanism by which closed-shell electron donors cause O–O bond rupture has received intensive study.[3-5] These reactions occur by

Scheme I



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