Reaction of Silylimines with Ester Enolates. Synthesis of *N*-Unsubstituted Azetidinones Starting from Nitriles

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The reduction of aromatic, vinylic, and aliphatic nitriles with several 'metal–aluminium hydrides' produces an addition product which is readily converted to a β-lactam derivative by treatment with Me_3SiCl followed by the addition of lithium ester enolates. The factors influencing the course of the cycloaddition-type reaction are discussed. A relatively simple synthetic procedure for the preparation of *N*-unsubstituted azetidin-2-ones in satisfactory yields is reported.

N-Unsubstituted azetidin-2-ones are key intermediates in the synthesis of β-lactam antibiotics such as the carbapenems, penems, and the monobactams.[1,2] Routes to such potentially valuable compounds have hitherto involved either the assembly of an *N*-functionalized β-lactam followed by liberation or degradation of a naturally occurring bicyclic β-lactam.[1]

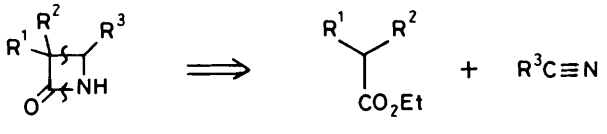
Recently *N*-trimethylsilylimines[3] have been shown, when treated with ester enolates, to be versatile starting materials for the preparation of *N*-unsubstituted β-lactams, in good yields.[4]

Nevertheless, this approach is subject to the ready availability of the corresponding aldehydes, since the starting silylimines are prepared from the reaction of aldehydes with lithium bis(trimethylsilyl)amide.[4a]

In connection with our studies[4c] on the synthesis of the azetidin-2-one ring, as a part of a general program dealing with the synthesis of non-classical β-lactam antibiotics, we became interested in studying the chemistry of metallo imines with particular regard to their applicability as electrophilic partners of ester enolates in the synthesis of the β-lactam ring.

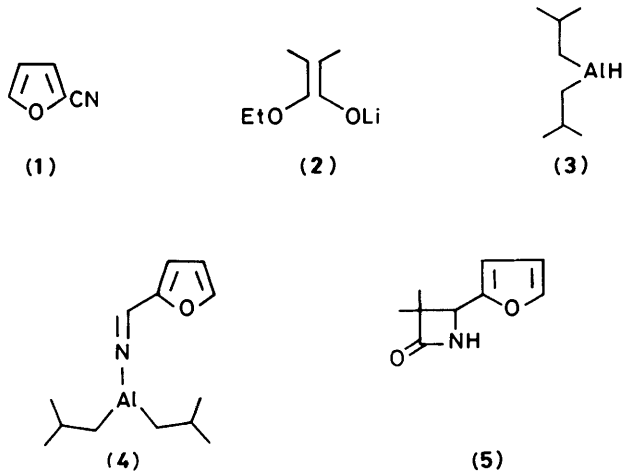
Among the metallo imines known in the literature,[5] those arising from the reduction of nitriles with a range of aluminium hydrides seemed to us very interesting because of their accessibility. It is known, in fact, that *N*-aluminium imines, particularly dialkylaluminium-alkylidene or -arylideneimines are intermediates[6] in the production of aldehydes by reduction of nitriles with dialkylaluminium hydrides such as di-isobutylaluminium hydride (DIBAH).

In a recent letter[7] we briefly described a novel synthesis of *N*-unsubstituted azetidinones starting from nitriles. This novel reaction takes place by the reduction of a nitrile by lithium triethoxyaluminium hydride (LTAH)[8] and the reaction of the adduct thus obtained with chlorotrimethylsilane, followed by the addition of a lithium ester enolate to give the cyclic compound in good yield.



In this paper we report the results of a detailed study on the reaction of aluminium imines and ester enolates for the preparation of the β-lactam ring. A range of nitriles and aluminium hydrides of widely varying structural types have been employed in the production of the starting aluminium imines.

In a preliminary study 2-furonitrile (**1**), selected as representative nitrile, was treated with several aluminium hydrides under different conditions. The complexes, thus generated, were then



(**1**) (**2**) (**3**) (**4**) (**5**)

treated *in situ* with 2 equivalents * of the lithium enolate of ethyl isobutyrate (**2**), obtained by metallation of the ester with lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) at −78 °C.

Alternatively, to the aluminium adduct was added trimethylsilyl chloride at 0 °C and the reaction mixture allowed to react for 3 h, whereupon the ester enolate (2 equiv.) was added at −78 °C.

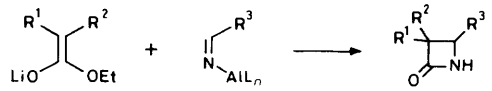
Results and Discussion

The first aluminium hydride we considered was the commercially available di-isobutylaluminium hydride (DIBAH) (**3**). Treatment of a solution of 2-furonitrile (**1**) in toluene with DIBAH (**3**) at −78 °C, produced a colourless solution of the aluminium imine (**4**). When kept in the absence of moisture and oxygen, (**4**) was indefinitely stable. Typical infrared spectra (in $CHCl_3$) show the absence of the C≡N group and absorption assigned to C=N–Al(Bu^i)$_2$ stretching near to 1 635 cm^{-1}. The aluminium imine structure of (**4**) was confirmed by the ^1H n.m.r. spectrum obtained in $CDCl_3$ solution, which shows the presence of a vinylic proton at 8.6 p.p.m.

Reaction of this aluminium imine (**4**) in toluene with the lithium enolate of the ethyl isobutyrate (**2**) in THF at −78 °C gave a complex mixture of products. Careful chromatography

* As reported in the previous paper,[7] although the stoicheiometry of the reaction requires equimolar amounts of the aluminium complex and ester enolate the use of a 2:1 ratio of enolate anion and metal complex appears to improve the yields.

Table 1. Preparation of *N*-unsubstituted azetidinones (**5**)—(**17**)



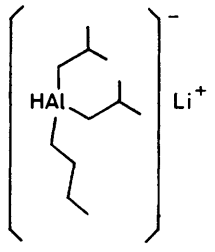
Entry	R^1	R^2	R^3	Method	(Product) Yield (%)	*cis*:*trans* ratio
1	Me	Me	2-Furyl	A	(**5**) 4	
2	Me	Me	2-Furyl	B	(**5**) 6	
3	Me	Me	2-Furyl	C	(**5**) 60	
4	Me	Me	2-Furyl	D	(**5**) 45	
5	Me	Me	2-Furyl	E	(**5**) 60	
6	H	Et	2-Furyl	C	(**9**) 40	80:20[a]
7	H	Et	2-Furyl	D	(**9**) 50	75:25[a]
8	H	Et	2-Furyl	E	(**9**) 56	70:30[a]
9	H	$Me_2SiCH_2CH_2Si(Me_2)N$	2-Furyl	C	(**10**) 38[c]	95:5[a]
10	H	$Me_2SiCH_2CH_2Si(Me_2)N$	2-Furyl	D	(**10**) 40[c]	95:5[a]
11	H	$Me_2SiCH_2CH_2Si(Me_2)N$	2-Furyl	E	(**10**) 43	95:5[a]
12	H	Et	Pr	C	(**11**) 0	
13	H	Et	Pr	D	(**11**) 0	
14	H	Et	Pr	E	(**11**) 40	75:25[a]
15	H	Et	C_6H_5OMe-*p*	D	(**12**) 68	89:11[a]
16	Me	Me	CH≡CHPh	A	(**13**) 21[b]	
17	Me	Me	2-Thienyl	D	(**14**) 45	
18	H	Et	2-Thienyl	D	(**15**) 50	75:25[a]
19	H	$Me_2SiCH_2CH_2Si(Me_2)N$	2-Thienyl	D	(**16**) 35[d]	90:10[a]
20	H	Isopropenyl	2-Furyl	D	(**17**) 30[e]	10:90[a]

[a] Analysed as *cis*/*trans* mixture. The *cis*:*trans* ratio was determined by ^1H n.m.r. spectroscopy by integration of characteristic protons. [b] Overnight at room temperature and then 1 h at reflux. [c] Isolated as 3,4-*cis*-3-(benzoyloxycarbonyl)amino-4-(2-furyl)azetidin-2-one. [d] Isolated as 3,4-*cis*-3-(benzoyloxycarbonyl)amino-4-(2-thienyl)azetidin-2-one. [e] Isolated as 3,4-*trans*-3-propen-1-en-2-yl-4-(2-furyl)azetidin-2-one.

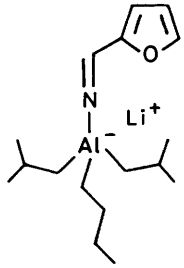
of this mixture produced the expected azetidin-2-one (**5**) (4%) (Method A, see Table 1).

The low yield is probably due to the competitive nucleophilic attack of the ester enolate at the aluminium atom of the metallo imine. However, the use of an excess of ester enolate in addition to Me_3SiCl, as previously reported,[7] did not increase the yield (Method B).

In an attempt to improve the azetidinone yields we used, as the reducing agent, the ate complex (**6**), generated *in situ* from DIBAH and butyl-lithium.[9] Reaction of the hydride (**6**) with furonitrile at 0 °C in toluene furnished, after hydrolysis of the reaction product, furfural in 70% yield.*



(**6**)



(**6a**)

However, the reaction of the aluminium adduct (**6a**) with 2 equiv. of the enolate of the ethyl isobutyrate ester, as described above, gave only traces of the expected azetidin-2-one (**5**). More drastic conditions (high temperature, prolonged reaction time), resulted in increased yields of side products.

* 2-Furonitrile appears to be more reactive towards this reagent than other nitriles *cf.* ref. 9.

Since the imino aluminates showed poor reactivity towards the ester enolates, we tried to convert these intermediates into the corresponding silylimines by trans-metallation with Me_3SiCl as it is known that silylimines are appropriately reactive towards ester enolates to give the azetidin-2-one ring.[4]

For this purpose, the imino aluminate (**6a**) was treated at 0 °C with 2 equiv. of Me_3SiCl and the homogeneous solution was stirred at 0 °C for 3 h. To the resulting reaction mixture, the lithium enolate (2 equiv.) of ethyl isobutyrate, prepared as described above, was added at −78 °C *via* syringe. The reaction was then allowed to reach room temperature over a period of 8 h. After decomposition of the reaction mixture with ammonium chloride, chromatography of the crude material yielded the azetidinone (**5**) in 60%. (Method C, see Table 1). Employing this general technique the range of the β-lactams shown in Table 1 was obtained.

Although rewarding, the procedure described was limited by the restricted number of nitriles which could be reduced by the ate complex (**6**).[9,*]

We felt that the alkali metal alkoxy aluminium reagents, which are known to be good reducing agents of the nitrile function to give the corresponding aldehyde, should be more useful and show greater reactivity because the oxygen-atoms, linked directly to the aluminium, should increase the ionic character of the aluminium–nitrogen bond, thus allowing easier transmetallation with Me_3SiCl.

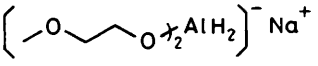
As reagents of this class we chose the lithium triethoxy-aluminium hydride (LTAH) (**7**), easily obtainable from lithium aluminium hydride and ethyl acetate, according to Brown's procedure,[8] and the commercially available sodium bis(2-methoxyethoxy)aluminium hydride 'Red-Al' (**8**).[10]

A preliminary communication on the use of LTAH has been reported,[7] (Method E, Table 1) however, as for regards 'Red-Al', treatment of the imino aluminates, obtained by the reduction of

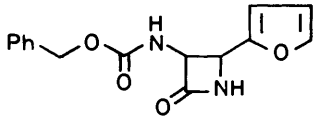
Table 2. Analytical data for the azetidinones (5)—(17)

Compound (Formula)	$\nu_{max.}$(cm^{-1})	Found (%) (Required) C	H	N	M.p. (°C)	*m/z*	δ_H(90 MHz; $CDCl_3$; Me_4Si)
(5) ($C_9H_{11}NO_2$)	3 410, 1 765	65.33 (65.44)	6.7 (6.7)	8.47 (8.48)	99—101	165	0.85 (3 H, s), 1.4 (3 H, s), 4.45 (1 H, s), 6.35 (2 H, m), 6.5 (1 H, br s), and 7.4 (1 H, m)
cis-(9) ($C_9H_{11}NO_2$)	3 400, 1 750	65.35 (65.44)	6.71 (6.71)	8.49 (8.48)		165	0.80 (3 H, t), 1.1—1.9 (2 H, m), 3.35 (1 H, q, *J* 6 Hz), 4.8 (1 H, d, *J* 6 Hz), 6.4 (2 H, m), 6.8 (1 H, br s, NH), and 7.4 (1 H, m)
trans-(9)	3 400, 1 750						1.05 (3 H, t), 1.4—2.1 (2 H, m), 3.35 (1 H, t, *J* 3 Hz), 4.4 (1 H, d, *J* 3 Hz), 6.4 (3 H, m), and 7.4 (1 H, m)
cis-(10) ($C_{15}H_{14}N_2O_4$)	3 315, 3 200, 1 790, 1 730	63.03 (62.93)	4.92 (4.93)	9.77 (9.79)	136—138	286	4.9 (1 H, d, *J* 6 Hz), 5.05 (2 H, s), 5.4 (2 H, m), 6.35 (3 H, m), and 7.4 (6 H, m)
cis-(11) ($C_8H_{15}NO$)	3 400, 1 750	67.93 (68.04)	10.7 (10.75)	9.94 (9.92)		141	1.05 (6 H, m), 1.25—1.85 (6 H, m), 3.1 (1 H, m, 3-H), 3.7 (1 H, m, 4-H), and 6.9 (1 H, br s, NH)
trans-(11)	3 400, 1 750						1.05 (6 H, m), 1.3—1.9 (6 H, m), 2.8 (1 H, m, 3-H), 3.7 (1 H, m, 4-H), and 6.9 (1 H, br s, NH)
cis-(12) ($C_{12}H_{15}NO_2$)	3 395, 1 745	70.09 (70.22)	7.35 (7.37)	6.83 (6.82)	113—115	205	0.75 (3 H, t), 0.9—1.6 (2 H, m), 3.3 (1 H, q, *J* 6 Hz), 3.8 (3 H, s), 4.8 (1 H, d, *J* 6 Hz), and 6.8—7.4 (5 H, m)
trans-(12)	3 395, 1 745						1.05 (3 H, t), 1.7 (2 H, m), 2.85 (1 H, t, *J* 3 Hz), 3.8 (3 H, s), 4.3 (1 H, d, *J* 3 Hz), and 6.8—7.4 (5 H, m)
(13) ($C_{13}H_{15}NO$)	3 405, 1 760	77.7 (77.58)	7.5 (7.51)	6.90 (6.95)		201	1.1 (3 H, s), 1.3 (3 H, s), 3.95 (1 H, d, *J* 6 Hz), 6.20 (1 H, dd, *J* 6 and 16 Hz), 6.65 (1 H, d, *J* 16 Hz), 6.70 (1 H, br s, NH), and 7.3 (5 H)
(14) ($C_9H_{11}NOS$)	3 475, 1 750	59.58 (59.64)	6.1 (6.12)	7.73 (7.74)	113—115	181	0.85 (3 H, s), 1.35 (3 H, s), 4.65 (1 H, s), 6.95 (2 H, m), and 7.3 (2 H, m)
cis-(15) ($C_9H_{11}NOS$)	3 400, 1 750	59.58 (59.64)	6.13 (6.12)	7.74 (7.73)		181	0.85 (3 H, t), 1.1—1.8 (2 H, m), 3.35 (1 H, m), 5.1 (1 H, d, *J* 6 Hz), 6.5 (1 H, br s, NH), 7 (2 H, m), and 7.2 (1 H, m)
trans-(15)	3 400, 1 750						1.1 (3 H, t), 1.80 (2 H, m), 3.2 (1 H, t, *J* 3 Hz), 4.65 (1 H, d, *J* 3 Hz), 7.07 (3 H, m), and 7.25 (1 H, m)
cis-(16) ($C_{15}H_{14}N_2O_3S$)	3 410, 1 790, 1 730	59.5 (59.59)	4.6 (4.67)	9.25 (9.27)		302	4.60 (1 H, d, *J* 7 Hz), 5.15 (2 H, s), 5.9 (2 H, m), 6.7 (1 H, br s), and 6.9—7.5 (8 H, m)
trans-(17) ($C_{10}H_{11}NO_2$)	3 250, 1 760	67.89 (67.78)	6.27 (6.26)	7.92 (7.9)		177	1.7 (3 H, s), 3.8 (1 H, d, *J* 3 Hz), 4.4 (1 H, d, *J* 3 Hz), 4.95 (2 H, m), 6.35 (2 H, m), 7.0 (1 H, br s, NH), and 7.4 (1 H, m)

$LiHAl(OEt)_3$ (7)



(8)



(10)

a number of nitriles with this reagent, followed by the sequential addition of Me_3SiCl (2 equiv., 0 °C 3 h) and ester enolates (2 equiv., −78 °C, overnight), afforded the expected azetidinones in yields ranging from 40—70% (Method D, Table 1).

Analysis of the data summarized in Table 1 (Method C, D, and E; entries 3—14), shows, in accordance with the aims outlined above, that these reagents are more reactive than the ate complex (6). Moreover, while (6) is inert towards aliphatic nitriles,[9] LTAH, in contrast, is able to form alkyl imino aluminates which, through transmetallation with Me_3SiCl and reaction with ester enolates, are converted to the corresponding azetidinone derivatives, thus allowing the first synthesis of β-lactams starting from enolizable imines.

Concerning the stereochemistry of the cycloaddition, a certain *cis*-stereoselectivity, in the formation of the azetidinones has been, in most cases, observed.

The procedure we have reported opens new routes to the synthesis of the azetidinone ring starting from nitriles and ester enolates. Nevertheless, the possibility of using other metallo imines in this reaction needs further investigation. These studies are being actively carried out in our laboratory.

Experimental

General.—All melting points are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 710 B spectrophotometer. ^1H N.m.r. spectra were recorded for samples in $CDCl_3$ on a Varian EM 390 instrument. Chemical shifts are expressed as δ values in p.p.m. from internal standard $SiMe_4$. T.l.c. was performed on silica gel sheets (DC-Plasticfolien Kieselgel 60 F_{254}, Merck) and medium pressure chromatography was performed on a Chromatospac Prep. 10 (Jobin–Yvon instrument) using silica gel (H 60 Merck).

Materials.—Commercially available starting materials were used without prior purification, unless otherwise stated. THF was obtained anhydrous and oxygen free by distillation over sodium diphenylketyl under argon. Toluene was distilled over sodium under argon. Di-isopropylamine and hexamethyldisilazane were refluxed over molecular sieves (type 4 A, Fluka) and distilled at atmospheric pressure. 'Red-Al' was purchased from Aldrich as 3.5M-solution in toluene.

Analytical data for the azetidinones (5)—(17) are given in Table 2.

Preparation of the β-Lactam (5) *starting from the Nitrile* (1) *and the Lithium Enolate of Ethyl Isobutyrate* (2).—*Method A.*

Reduction of nitrile by DIBAH. Neat Bu'$_2$AlH (0.89 ml, 5 mmol) was added to a stirred solution of the nitrile (0.44 ml, 5 mmol) in toluene (10 ml) at −78 °C. The solution was maintained at −78 °C for 1 h. A THF solution (20 ml) of ester enolate (10 mmol) (prepared from ethyl isobutyrate (1.34 ml, 10 mmol) and lithium di-isopropylamide (LDA) [4.2 ml, 10 mmol; prepared from butyl-lithium (2.4M in hexane) and di-isopropylamine (1.4 ml, 10 mmol)] was added at the same temperature. This solution was maintained at −78 °C for 1 h, allowed to warm to room temperature, and stirred overnight. The resulting mixture was cooled to 0 °C, decomposed with saturated aqueous NH_4Cl, extracted with ethyl acetate and dried (Na_2SO_4). After the solvent had been removed under reduced pressure, flash chromatography [cyclohexane–ethyl acetate (6:4)] of the residue yielded azetidinone (**5**) (4%).

Method B. To the homogeneous solution obtained from reduction of the nitrile with DIBAH (see above), was added Me_3SiCl (1.25 ml, 10 mmol), the reaction mixture stirred at 0 °C for 3 h, and the ester enolate added at −78 °C. The mixture was allowed to reach room temperature and stirred overnight whereupon it was decomposed as in Method A, flash chromatography of the residue yielded the azetidinone (**5**) (6%).

Method C. Reduction of the nitrile by the ate complex (**6**). A solution of DIBAH (0.89 ml, 5 mmol) in toluene (20 ml) was stirred under argon with ice-cooling. Buthyl-lithium (2.4M-solution in hexane, 2.08 ml) was slowly added to the flask with stirring, and the resulting solution was stirred for an additional 30 min. To this solution was added dropwise furonitrile (0.44 ml, 5 mmol), dissolved in toluene (5 ml) and the resulting solution was stirred until g.c. analysis showed complete reduction of the nitrile. Trimethylsilyl chloride (1.25 ml, 10 mmol) was then added at the same temperature and the resulting reaction mixture was stirred for 3 h. A solution of the lithium enolate of ethyl isobutyrate [10 mmol; prepared from lithium di-isopropylamide (10 mmol) and ethyl isobutyrate (10 mmol) at −78 °C in THF (20 ml)] was added at −78 °C. The reaction mixture was allowed to reach room temperature and stirred overnight. The flask was immersed in an ice bath, neutralized with 0.25M-H_2SO_4 and extracted with ethyl acetate. The combined organic layers were washed with water and saturated NaCl solution, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. Flash chromatography [ethyl acetate-cyclohexane (1:1)] of the residue yielded the azetidinone (**5**) (60%).

Method D. Reduction of the nitrile by 'Red-Al' (**8**). To a solution of 'Red-Al' (3.5M in toluene; 1.43 ml, 5 mmol), furonitrile (0.44 ml, 5 mmol) in THF (15 ml) was added at 0 °C with stirring in an argon atmosphere. When g.c. analysis showed complete disappearance of the nitrile, Me_3SiCl (0.625 ml, 5 mmol) was added, followed by the addition, at −78 °C, of the ester enolate (10 mmol) of ethyl isobutyrate, prepared as above described. The reaction mixture was allowed to reach room temperature and stirred overnight. The reaction was hydrolysed with H_2SO_4 (0.25M; 20 ml) and worked up in the usual way. The combined organic layers were washed with saturated aqueous NaCl and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue chromatographed to give the β-lactam (**5**) (45%).

Method E. Reduction of nitrile by LTAH (**7**). A solution of $LiAlH_4$ in ether (1M; 11 ml) was stirred under argon. To this was added freshly distilled anhydrous ethyl acetate (1.61 ml, 16.5 mmol) in ether (10 ml). After 15 min, the resulting solution was treated with 2-furonitrile (0.88 ml, 10 mmol) in ether (10 ml). The reaction mixture was stirred for 1 h at 0 °C. At this point chlorotrimethylsilane (1.25 ml, 10 mmol) was added and the mixture was allowed to warm to room temperature. After 2 h, the lithium enolate of ethyl isobutyrate (10 mmol), obtained following standard procedure (see above), was added at −78 °C and the reaction mixture was stirred overnight while the temperature was allowed to reach room temperature. The reaction was quenched at 0 °C with solid NH_4Cl and water was rapidly extracted with ethyl acetate. After the solvent had been removed from the dried ($MgSO_4$) extract, chromatography of the residue yielded the target compound in 60% yield.

Preparation of 3,4-cis-3-*Benzyloxycarbonylamino*-4-(2-*furyl*)-*azetidin*-2-*one* (**10**).—*Method D.* Red-Al (3.5M-solution in toluene; 2.85 ml, 10 mmol) was treated with freshly distilled THF (30 ml) and 2-furonitrile (0.88 ml, 10 mmol) in THF (10 ml) under argon. The reaction mixture was stirred for 2 h at 0 °C. At this point chlorotrimethylsilane (1.25 ml, 10 mmol) was added and the mixture was allowed to warm to room temperature. After a further 2 h the lithium enolate of ethyl *N*,*N*-(1,1,4,4-tetramethyl-1,4-disilatetramethylene)glycinate (STABASE),[11] (20 mmol in THF obtained following standard procedure from STABASE and LDA[12]), was added at −78 °C and the reaction mixture was stirred overnight during which time the temperature was allowed to reach room temperature. The reaction mixture was cooled to 0 °C and NaF[13] (12.85 g) was added. The resulting mixture was stirred vigorously for 0.5 h whereupon water (8 ml) was added. This mixture was stirred for 45 min at 0 °C and 1 h at room temperature. The precipitate was removed by filtration, the concentrated filtrate was diluted with acetone (30 ml), and a solution of $NaHCO_3$ (30 mmol) in water (20 ml) was added. The mixture was cooled to 0 °C and benzylchloroformate (3.40 g, 20 mmol) in acetone (10 ml) was added dropwise. The solution was stirred for 2 h at 0 °C, the solvent was removed under reduced pressure, and the residue was taken up with ethyl acetate (20 ml) and extracted. The organic layers were washed sequentially with saturated aqueous $NaHCO_3$, water, and brine and then dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue chromatographed [cyclohexane–ethyl acetate (6:4)] to give (**10**) (40%).

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