New Simple Synthesis of N-Substituted 1,3-Oxazinan-2-ones

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Abstract: An efficient and simple synthesis of N-substituted 1,3-oxazinan-2-ones was developed that involves a three-component, one-pot reaction of readily available tetraethylammonium bicarbonate, 1,3-dibromopropane, and a primary amine in methanol at room temperature. L-Alanine can be used as the amino component to give the chiral product (2*S*)-2-(2-oxo-1,3-oxazinan-3-yl)propanoic acid.

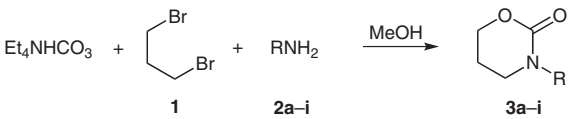
Key words: cyclizations, urethanes, oxazinanones, amines

1,3-Oxazinan-2-ones, which are six-membered cyclic urethanes, are an important class of compounds that can serve as small building blocks for the synthesis of pharmaceutical compounds[1] or 1,3-amino alcohols.[2] Although there are only a few reports in the literature on the synthesis of nonurethane 1,3-oxazinanes,[3] several types of starting substrate have been used in syntheses of 1,3-oxazinan-2-one or its derivatives. All the reactions used in these syntheses can be divided into two groups: intermolecular cyclizations or intramolecular cyclizations.

The starting materials that are used for the first group of reactions are mainly 1,3-bifunctional compounds in which at least one functional group contains an oxygen or nitrogen atom, and in most cases the substrates are compounds containing both oxygen and nitrogen separated by the same distance as that in the target molecule. Thus, 1,3-oxazinan-2-one or its derivatives have been prepared by the reaction of 1,3-amino alcohols with carbonic acid derivatives such as ethylene carbonate,[4] urea,[5] 1,1′-carbonyldiimidazole,[6] or triphosgene.[3b,c] The insertion of a carbonyl group between the oxygen and nitrogen atoms in these substrates to give the required six-membered cyclic urethanes has also been achieved by reaction with carbon monoxide catalyzed by palladium(II) complexes[7] or selenium[8] or with carbon dioxide catalyzed by phosphorus(III) reagents, in carbon tetrachloride or perchloroethane.[9] Trichloroacetates,[10] trifluoroacetamides,[11] or *N*-benzyloxycarbonyl derivatives[12] of 1,3-amino alcohols, as well as their *N*-*tert*-butoxycarbonyl tosylates[13] and *N*-aroyl nitrates,[14] can likewise be converted into 1,3-oxazinan-2-ones. Synthesis of six-membered cyclic urethanes can also be achieved by using 3-chloropropanol as the starting material, via the chloroformyl ester and the carbamate,[15] or by reaction with cyanate ion in anhydrous *N*,*N*-dimethylformamide.[16] 3-Bromopropan-1-amine, on the other hand, can be converted into unsubstituted 1,3-oxazinan-2-one by treatment with tetraethylammonium bicarbonate,[17] or by the electrochemical reduction of oxygen in the presence of the substrate and carbon dioxide.[18]

Six-membered cyclic urethanes and their derivatives can also be prepared by intramolecular cyclization reactions, such as the reaction of 1-chloro-3-isocyanatopropane with bis(tributyltin) oxide,[19] Hofmann rearrangements of 4-hydroxy amides,[20] Curtius rearrangements of 4-hydroxy hydrazides,[21] thermolyses of 4-hydroxy *N*-ammonio amidates[22] or alkyl azidoformates,[23] halocyclizations of allyl,[24] homoallyl,[2,25] or allenyl[26] carbamates, halocyclization of allyl amines in the presence of carbon dioxide,[27] or Sharpless asymmetric dihydroxylation of homoallylic carbamates.[28]

Here we report a new, simple synthesis of N-substituted six-membered cyclic urethanes from 1,3-dibromopropane, tetraethylammonium bicarbonate, and a primary amine. Thus, a methanolic solution of 1,3-dibromopropane (**1**), benzylamine (**2a**, Scheme 1), and commercially available tetraethylammonium bicarbonate was refluxed for one hour to give a mixture from which *N*-benzyl-1,3-oxazinan-2-one (**3a**) was isolated in 15% yield by evaporation of the solvent, dissolution of the residue in 2 M hydrochloric acid, and extraction with diethyl ether.



1 **2a–i** **3a–i**

a R = benzyl
b R = 2-thenyl
c R = 2-phenylethyl
d R = 2-(4-methoxyphenyl)ethyl
e R = phenyl
f R = 4-tolyl
g R = cyclohexyl
h R = octyl
i R = dodecyl
j R = *tert*-butyl

Scheme 1 Synthesis of N-substituted 1,3-oxazinan-2-ones

The composition of the crude reaction mixture was analyzed in detail by gas chromatography–mass spectrometry (GC/MS) and quantified by estimations of the areas under

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the peaks of the total ion chromatograms, which are expressed as the corresponding relative percentage. This analysis showed that the mixture consisted mainly of the unchanged starting reagents (dibromide **1** and primary amine **2a**), together with the oxazinanone **3a** (about 20%). The mixture also contained small amounts of several other components. Although the mass spectral fragmentation patterns in GC/MS analysis are insufficient to give an unambiguous identification of a compound, we believe that among these components were 3-bromopropanol (traces), 3-methoxy-1-bromopropane (traces), 1-benzylazetidine (up to 1.5%), *N*-benzyl-3-bromopropan-1-amine (traces), and 3-bromopropyl benzylcarbamate (up to 1.5%).

Prolonged heating of the mixture resulted in increased amounts of oxazinan-2-one and a compound that we identified as 1-benzylazetidine (up to about 60 and 3.5%, respectively, after refluxing for six hours), whereas the compounds that we tentatively identified as *N*-benzyl-3-bromopropan-1-amine and 3-bromopropyl benzylcarbamate had almost completely disappeared.

The best yield of compound **3a** (60%) was achieved when the mixture was kept at room temperature overnight. 3-Benzyl-1,3-oxazinan-2-one (**3a**) was easily isolated from the acidic mixture and characterized by spectral methods, since the unconsumed 1,3-dibromopropane was removed by evaporation under in a vacuum, and the starting amine **2** was washed out as its water-soluble salt, which was insoluble in ether. The absence of the component that we identified as 1-benzylazetidine in the ethereal extract confirmed its basic character.

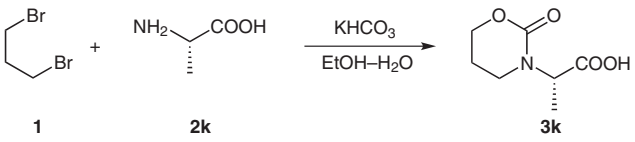
Several primary amines were then submitted to the same reaction conditions. The results for these reactions are listed in Table 1. The benzylic-type amine **2b** and amines **2c** and **2d** behaved similarly to benzylamine, giving the corresponding N-substituted 1,3-oxazinan-2-ones (**3b–d**, respectively) in moderate isolated yields. Two aromatic amines, aniline (**2e**) and *p*-toluidine (**2f**), were found to be unsuitable as substrates for this reaction. Although both of these amines gave the corresponding oxazinanones according to GC/MS analysis, we were able to isolate only the toluidine derivative **3f** in a low yield. A high yield of the cyclic urethane was achieved when cyclohexanamine was used as the substrate, whereas the aliphatic amines **2h** and **2i** gave the corresponding cyclic urethanes in similar yields to amines **2a–d**. Surprisingly, 2-methylpropan-2-amine (**2j**) did not react at all.

We believe that the probable intermediates in this reaction are 3-bromopropyl benzylcarbamate and *N*-benzyl-3-bromopropan-1-amine, because we observed these two components in the reaction mixtures at an early stage, but they disappeared as the reaction progressed.

Because of the possible applications of 1,3-oxazinan-2-ones in asymmetric syntheses, we considered the possibility of using a chiral amino acid as the amine component of our reaction. L-Alanine (**2k**), the most readily available chiral amino acid, was chosen, but it was necessary to adapt our procedure for this substrate. As no suitable solvent is capable of dissolving all three reaction components (L-alanine, 1,3-dibromopropane, and a bicarbonate), we decided to use a combination of two miscible solvents, water and ethanol, because L-alanine is soluble in aqueous potassium bicarbonate solution, whereas 1,3-dibromopropane soluble in ethanol. When a solution of 1,3-dibromopropane in ethanol was added dropwise to a boiling aqueous solution of L-alanine and potassium bicarbonate, the target urethane (*S*)-2-(2-oxo-1,3-oxazinan-3-yl)propanoic acid (**3k**) was obtained in 32% isolated yield (Scheme 2).

Table 1 Synthesis of N-Substituted 1,3-Oxazinan-2-ones **3a–i**

Entry	Amine	Oxazinanone	Yield (%)
1	**2a**	**3a**	60
2	**2b**	**3b**	61
3	**2c**	**3c**	57
4	**2d**	**3d**	54
5	**2e**	**3e**	–
6	**2f**	**3f**	7
7	**2g**	**3g**	80
8	**2h**	**3h**	62
9	**2i**	**3i**	52
10	**2j**	–	–



1 2k 3k

Scheme 2 Synthesis of (2*S*)-2-(2-oxo-1,3-oxazinan-3-yl)propanoic acid (**3k**)

The structure of (2*S*)-2-(2-oxo-1,3-oxazinan-3-yl)propanoic acid (**3k**) was confirmed by X-ray analysis (see Figure 1).[29]

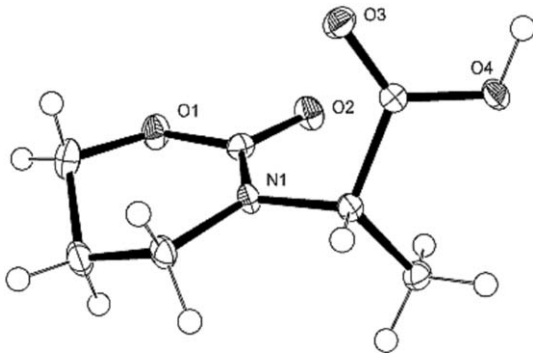


Figure 1 Thermal ellipsoid plot of **3k** showing ellipsoids at the 50% probability level

In summary, we have developed a new method for the synthesis of N-substituted 1,3-oxazinan-2-ones that is simple, can be conducted in any laboratory, and requires only cheap and readily available starting materials. The most important advantage of the method is ease of separation and purification of the oxazinanone products from the reaction mixtures, which require only extraction and evaporation procedures.

All starting materials were obtained from commercial suppliers (Aldrich, Fluka, Merck) and were used without further purification. The solvents were purified by distillation. Melting points (uncorrected) were determined on a Mel-Temp capillary melting points apparatus (Model 1001). The ^{1}H and ^{13}C NMR spectra of samples dissolved in $CDCl_3$ or DMSO-d_6 were recorded on a Varian Gemini (200 MHz) spectrometer. Chemical shifts are expressed in δ (ppm), relative to residual solvent protons as internal standards ($CDCl_3$: δ = 7.26 ppm for ^{1}H; δ = 77 ppm for ^{13}C; DMSO-d_6: δ = 2.50 ppm for ^{1}H, δ = 39.43 ppm for ^{13}C). IR spectra were recorded on a Perkin-Elmer FTIR 31725-X spectrophotometer. Microanalyses of carbon, hydrogen, nitrogen, and sulfur were carried out with a Carlo Erba 1106 microanalyzer; the results agreed well with the calculated values. The GC/MS analyses were carried out by using a Hewlett-Packard 6890N gas chromatograph equipped with a fused silica capillary column HP-5MS [5% phenyl(methyl)siloxane, 30 m × 0.25 mm, film thickness 0.25 μm, Agilent Technologies, USA] coupled to a Hewlett-Packard 5975B mass-selective detector. The injector and interface were operated at 250 °C and 300 °C, respectively. The oven temperature was increased from 70 to 290 °C at 5 °C min^{-1} and then held for 10 min. The carrier gas was He at a flow rate of 1.0 mL min^{-1}. The samples were injected in a pulsed split mode at 1.5 mL min^{-1} for the first 0.5 min and then 1.0 mL min^{-1} throughout the remainder of the analysis at a split ratio of 40:1. MS conditions were as follows: ionization voltage 70 eV, acquisition mass range 35–500, scan time 0.32 s. Optical rotations were measured on a Perkin-Elmer SP Polarimeter.

N-Substituted 1,3-Oxazinan-2-ones 4a–j; General Procedure

Et_4NHCO_3 (3.82 g, 20 mmol), $Br(CH_2)_3Br$ (2.02 g, 10 mmol), and an amine **2a–j** (10 mmol) were dissolved in MeOH (20 mL) and the mixture was stirred overnight at r.t. MeOH and residual $Br(CH_2)_3Br$ (if present) were evaporated in vacuo, and the resulting oily mass was diluted with 1 M H_2SO_4 (20 mL). The mixture was extracted with several 20-mL portions of Et_2O, and the combined organic layers were dried (Na_2SO_4) and concentrated. The resulting oxazinanones were sufficiently pure for spectroscopic analysis. Compounds **3a** and **3f** are known, and their spectral data have been reported elsewhere.[19,30]

3-(2-Thienylmethyl)-1,3-oxazinan-2-one (3b)

Colorless solid; yield: 61%; mp 128–130 °C.

IR (neat): 3054, 2969, 2925, 1681, 1537, 1264, 1131, 691, 630 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.00 (m, 2 H), 3.31 (t, *J* = 6.2 Hz, 2 H), 4.23 (t, *J* = 5.4 Hz, 2 H), 4.68 (s, 2 H), 6.93–7.02 (m, 2 H), 7.23–7.26 (m, 1 H).

^{13}C NMR ($CDCl_3$): δ = 22.1, 44.1, 47.2, 66.4, 125.6, 126.6, 126.8, 138.9, 153.4.

MS (EI, 70 eV): *m/z* (%) = 97 (100), 197 (60) [M]$^+$, 152 (52), 124 (35), 110 (33), 45 (15), 41 (12), 53 (11), 125 (10), 39 (9).

Anal. Calcd for $C_9H_{11}NO_2S$ (197.25): C, 54.80; H, 5.62; N, 7.10; S, 16.26. Found: C, 54.67; H, 5.68; N, 7.01; S, 16.22.

3-(2-Phenylethyl)-1,3-oxazinan-2-one (3c)

Colorless solid; yield: 57%; mp 65–67 °C.

IR (neat): 3024, 2930, 1669, 1519, 1447, 1280, 1115, 1011, 755, 725, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.90 (m, 2 H), 2.94 (t, *J* = 6.2 Hz, 2 H), 3.07 (t, *J* = 7.2 Hz, 2 H), 3.51 (t, *J* = 7.2 Hz, 2 H), 4.14 (t, *J* = 5.3 Hz, 2 H), 7.19–7.33 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 21.7, 33.1, 45.6, 50.9, 66.0, 126.0, 128.1, 128.4, 138.4, 153.0.

MS (EI, 70 eV): *m/z* (%) = 114 (100), 104 (66), 205 (62) [M]$^+$, 42 (61), 91 (42), 70 (32), 41 (26), 65 (14), 77 (13), 105 (13).

Anal. Calcd for $C_{12}H_{15}NO_2$ (205.25): C, 70.22; H, 7.37; N, 6.82. Found: C, 70.16; H, 7.44; N, 6.81.

3-[2-(4-Methoxyphenyl)ethyl]-1,3-oxazinan-2-one (3d)

Colorless solid; yield: 54%; mp 87–88 °C.

IR (neat): 3032, 2925, 1685, 1672, 1612, 1441, 1237, 1116, 1032, 756 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.83 (m, 2 H), 2.78 (t, *J* = 7.3 Hz, 2 H), 3.01 (t, *J* = 6.2 Hz, 2 H), 3.41 (t, *J* = 7.3 Hz, 2 H), 3.71 (s, 3 H), 4.10 (t, *J* = 7.3 Hz, 2 H), 6.74–6.78 (m, 2 H), 7.05–7.10 (m, 2 H).

^{13}C NMR ($CDCl_3$): δ = 22.1, 32.6, 46.0, 51.5, 55.1, 66.2, 113.8, 129.7, 130.8, 153.3, 158.1.

MS (EI, 70 eV): *m/z* (%) = 134 (100), 121 (24), 42 (12), 135 (11), 91 (6), 41 (6), 119 (6), 77 (6), 78 (6), 235 (4) [M]$^+$.

Anal. Calcd for $C_{13}H_{17}NO_3$ (235.28): C, 66.36; H, 7.28; N, 5.95. Found: C, 66.21; H, 7.22; N, 5.95.

3-Phenyl-1,3-oxazinan-2-one (3e)

Not isolated.

MS (EI, 70 eV): *m/z* (%) = 104 (100), 77 (82), 177 (74) [M]$^+$, 105 (43), 91 (38), 132 (33), 51 (20), 119 (11), 78 (8), 178 (8).

3-Cyclohexyl-1,3-oxazinan-2-one (3g)

Colorless solid; yield: 80%; mp 60–61 °C.

IR (neat): 2927, 2852, 1666, 1484, 1432, 1286, 1108, 756 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.03–1.17 (m, 1 H), 1.34–1.48 (m, 4 H), 1.72–1.82 (m, 5 H), 2.0 (m, 2 H), 3.23 (t, *J* = 6.1 Hz, 2 H), 4.07–4.17 (m, 1 H), 4.21 (t, *J* = 5.3 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 22.2, 25.4, 25.5, 29.4, 39.3, 55.5, 65.8, 153.2.

MS (EI, 70 eV): *m/z* (%) = 102 (100), 140 (68), 56 (43), 41 (37), 183 (34) [M]$^+$, 55 (31), 74 (24), 54 (22), 68 (16), 39 (13).

Anal. Calcd for $C_{10}H_{17}NO_2$ (183.25): C, 65.54; H, 9.35; N, 7.64. Found: C, 65.63; H, 9.40; N, 7.69.

3-Octyl-1,3-oxazinan-2-one (3h)

Colorless semi-solid; yield: 62%.

IR (neat): 2922, 2854, 1652, 1534, 1466, 1215, 1025, 724, 576 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3 H), 1.27 (m, 12 H), 1.40–1.66 (m, 2 H), 2.04 (m, 2 H), 3.31 (t, *J* = 6.4 Hz, 2 H), 4.25 (t, *J* = 5.4 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 14.0, 22.2, 22.5, 26.6, 27.0, 29.1, 29.2, 31.7, 45.0, 49.6, 66.5, 153.9.

MS (EI, 70 eV): *m/z* (%) = 114 (100), 42 (47), 115 (45), 70 (37), 41 (34), 142 (22), 184 (18), 156 (14), 43 (13), 213 (13) [M]$^+$.

Anal. Calcd for $C_{12}H_{23}NO_2$ (213.32): C, 67.57; H, 10.87; N, 6.57. Found: C, 67.50; H, 10.84; N, 6.69.

3-Dodecyl-1,3-oxazinan-2-one (3i)

Colorless semi-solid; yield: 52%.

IR (neat): 2919, 2851, 1681, 1533, 1497, 1247, 1220, 1146, 1039, 871, 721, 574 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3 H), 1.26 (m, 20 H), 1.40–1.68 (m, 2 H), 2.03 (m, 2 H), 3.31 (t, *J* = 6.3 Hz, 2 H), 4.24 (t, *J* = 5.04 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 14.0, 22.3, 22.6, 26.7, 27.0, 29.2, 29.3, 29.3, 29.5, 29.6, 29.6, 31.8, 45.1, 49.6, 66.4, 153.7.

MS (EI, 70 eV): *m/z* (%) = 114 (100), 115 (51), 70 (31), 42 (30), 41 (25), 142 (24), 240 (19), 156 (19), 269 (15) $[M]^+$, 43 (15).

Anal. Calcd for $C_{16}H_{31}NO_2$ (269.42): C, 71.33; H, 11.60; N, 5.20. Found: C, 71.35; H, 11.52; N, 5.11.

(2*S*)-2-(2-Oxo-1,3-oxazinan-3-yl)propanoic Acid (3k)

L-Alanine (8.9 g, 0.1 mol) was added to a soln of $KHCO_3$ (30 g, 0.3 mol) in H_2O (60 mL), and the mixture was heated to reflux. A soln of $Br(CH_2)_3Br$ (2.02 g, 10 mmol) in EtOH (20 mL) was slowly added dropwise to the clear boiling mixture over 1 h. The mixture was refluxed for a further 5 h, then concentrated to 60 mL by evaporation in vacuo, acidified to pH 3.5, and kept at r.t. overnight. The precipitate was filtered off, washed with EtOH and Et_2O, and dried ($CaCl_2$) to give **3k**; yield: 5.6 g (32 mmol; 32%); mp 210 °C (H_2O); $[\alpha]_D^{20}$ –4.40 (*c* 0.5%, H_2O). For X-ray crystal structure analysis, the product was recrystallized (H_2O).

IR (KBr): 3431, 3266, 2911, 2582, 1728, 1654, 1639, 1502, 1305, 1248, 1086, 960, 767 cm^{-1}.

^1H NMR (DMSO-d_6): 1.32 (d, *J* = 7.4 Hz, 3 H), 1.86–1.99 (m, 2 H), 3.13–3.40 (m, 2 H) 4. 16 (t, *J* = 5.5 Hz, 2 H), 4.51 (q, *J* = 7.4 Hz, 1 H).

^{13}C NMR (DMSO-d_6): 14.2, 22.0, 42.3, 54.8, 66.5, 153.2, 173.3.

MS (EI, 70 eV): *m/z* (%) = 128 (100), 84 (73), 56 (70), 41 (65), 42 (36), 114 (27), 70 (22), 44 (20), 129 (16), 45 (15), 173 (12) $[M]^+$.

Anal. Calcd for $C_7H_{11}NO_4$ (173.17): C, 48.55; H, 6.40; N, 8.09; Found: C, 47.98; H, 6.40; N, 8.13.

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