NEW RING OPENING REACTIONS OF THREE MEMBERED HETEROCYCLES, OXIRANES, AZIRIDINES, AND THIIRANES, WITH PHENYL ACETATE

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The reactions of oxirane, aziridine or thiirane with phenyl acetate in the presence of bases such as pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and tributylamine afford 2-phenoxyethyl acetate, N-(2-phenoxyethyl)acetamide or S-(2-phenoxyethyl) thioacetate, respectively.

Ring-opening addition reactions of three-membered heterocycles such as oxiranes, aziridines and thiiranes with a variety of reagents via heterocyclic cleavage of a C-Z bond (Z; O, NH and S) are well known, O0 but the addition reactions with esters were not known.

We have now found that these heterocycles react with phenyl acetate in the presence of a base to give the ring-opening addition products as shown in the following scheme.

R; H, 
$$CH_3$$
 a;  $Z=O$ , b;  $Z=NH$ , c;  $Z=S$ 

For example, a mixture of phenyl acetate (2.72 g, 20 mmol), methyloxirane (1.28 g, 22 mmol), and tributylamine (0.11 g, 0.6 mmol) in THF (15 ml) was placed in an autoclave and stirred at 170°C for 3 h. The reaction mixture was subjected to distillation under reduced presure, giving 3.26 g (84%) of pure 2-acetoxy-1-phenoxypropane (2a, R=CH<sub>3</sub>): bp 141°C/23 Torr; IR (neat) 1740 cm<sup>-1</sup> (alkyl ester C=0); MS (70 ev): m/e (rel intensity) 194 (2), 134 (2), 101 (46), 77 (13), and 43 (100); NMR (CDCl<sub>3</sub>):  $\delta$  (ppm from TMS) 1.32 (3H, d, j=7.1 Hz, C-CH<sub>3</sub>), 2.01 (3H, s, OCOCH<sub>3</sub>), 3.95 (2H, d, j=5.2 Hz, CH<sub>2</sub>-OPh), and 5.22 (1H, m, CH<sub>3</sub>CO<sub>2</sub>-CH). The product was identified as 2a by comparing with an authentic sample that was prepared by acetylation of 1-phenoxy-2-propanol. 2)

In a similar procedure, the reaction of aziridine (1.03 g, 24 mmol) with phenyl acetate (2.72 g, 20 mmol) in the presence of pyridine (0.05 g, 0.6 mmol) was carried out at  $90^{\circ}\text{C}$  for 2 h. The reaction mixture was dissolved in ether (30 ml), washed with 5% aqueous boric acid (25 ml), and distilled under reduced pressure.

Substrate	Temp.	Bp (°C/Torr)	°co (cm <sup>-1</sup> )	Product <sup>4)</sup> (isomer distribution)	Yield <sup>b)</sup> (%)
Oxirane	140	131/20	1745	<u>2</u> a (R=H) <sup>5</sup> )	77
Methylaziridine	100	159-169/2 <sup>c)</sup>	1630	$\underline{2}b$ (R=CH <sub>3</sub> ), $\underline{3}b$ (R=CH <sub>3</sub> )	6) 24
Thiirane	160	99/2	1690	(68) (32) $\underline{2}c (R=H)$ 7)	2

Table 1. The reaction of three-membered heterocycles with phenyl acetate in the presence of  $\mathrm{DBU}^{a}$ )

- a) The molar ratio of substrates. phenyl acetate / heterocycles / DBU = 1 / 1.2 / 0.03. Reaction time; 4 h.
- b) Total isolated yield based on phenyl acetate used.
- c) Mixture of  $\underline{2}b$  (R=CH<sub>3</sub>) and  $\underline{3}b$  (R=CH<sub>3</sub>).

The distillate was recrystallizad from cyclohexane to give N-(2-phenoxyethyl)acetamide (2b, R=H), (0.72 g, 20%): mp 88-89°C; IR (KBr) 1645 and 1540 (amide C=O) and 1250 cm<sup>-1</sup> (phenyl ether Ph-O); NMR (CDCl $_3$ ):  $\delta$  1.98 (3H, s, CH $_3$ ), 3.62 (2H, m, NHCH $_2$ ), 4.01 (2H, t, j=4.8 Hz, PhOCH $_2$ ), and 5.98 (1H, br, s, CH $_3$ CONH). The product was identified by comparing with an authentic sample that was prepared by acetylation of 2-phenoxyethylamine. In this reaction, the polymerization of aziridine also took place and reduced the yield of the product.

The results of the other reactions are summarized in Table 1. The reactions can be useful for synthetic purposes and the further investigation is in progress.

## References and notes

- 1) a) A. Rosowsky, P. E. Fanta, D. D. Reynolds, and D. L. Fields, "Heterocyclic compounds with three- and four-membered rings," ed by A. Weissberger, Wiley-Interscience, London (1964).
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- 2) A. R. Sexton and E. C. Britton, J. Am. Chem. Soc., 70, 3606 (1948).
- 3) A. Uffer and E. Schlittler, Helv. Chim. Acta., 31, 1397 (1948).
- 4) All products gave satisfactory elemental analyses.
- 5) The product was identified by comparing with an authentic sample. W. J. Svirbely, W. M. Eareckson III, K. Matsuda, H. B. Pickard, I. S. Solet, and W. B. Tuemmler, J. Am. Chem. Soc., 71, 508 (1949).
- 6) The product isomer distibution of these compounds was determined by gas chromatography using a 2 m column of Apiezon grease L on Celite.
- 7) NMR (CDC1<sub>3</sub>) :  $\delta$  2.23 (3H, s), 3.17 (2H, t, j=4.8 Hz) and 3.97 (2H, t, j=4.8 Hz).

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