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New Addition Reactions of Cyclic Ethers with Esters and Thioesters Catalyzed by Quaternary Ammonium Salts or Crown Ether Complexes

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A new addition reaction of 3-benzyloxymethyl-3-methyloxetane with S-phenyl thioacetate proceeded to give 3-benzyloxy-2-methyl-2-phenylthiomethylpropyl acetate catalyzed by 18-crown-6 - potassium phenoxide complex. N-(2-Acetoxyethyl)-N-(2-phenoxyethyl)acetamide was also synthesized in high yield by the addition reaction of 5-methyl-4,6-dioxa-1-azabicyclo[3.3.0]octane with phenyl acetate, using tetrabutylammonium salts as catalysts.

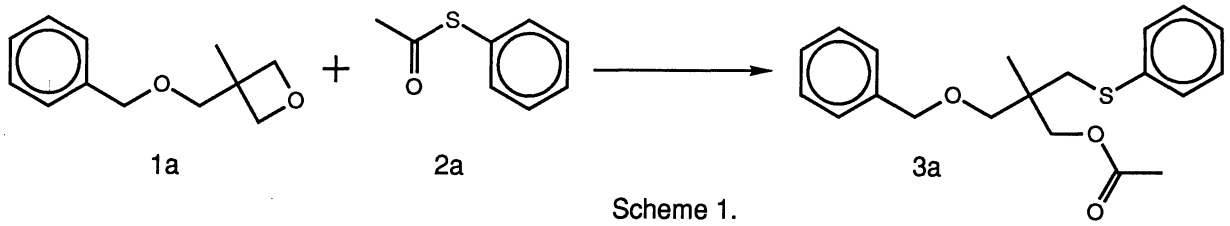
Addition reactions of oxirane with electrophilic reagents such as acyl halide,[1] alkyl halide,[2] carbon dioxide,[3] aldehyde,[4,5] and ketone[5] as well as with nucleophilic reagents such as amine, phenol, and carboxylic acid have been used for synthetic organic chemistry and chemical modification of polymers. Recently, we reported[6,7] regioselective addition reactions of oxiranes with aryl (thio)esters catalyzed by quaternary onium salts, crown ether complexes, or t-amines. However, there has been no study of the addition reactions of other cyclic ethers such as oxetane, oxorane, or bicyclic amide acetal with aryl or alkyl (thio)esters. Furthermore, the successful addition reactions of oxirane with alkyl (thio)esters have not been reported so far, although these reactions are likely to be very important for synthetic organic chemistry and polymer

synthesis.

In this paper, we wish to report new addition reactions of 3-benzyloxymethyl-3-methyloxetane (**1a**) and 5-methyl-4,6-dioxa-1-azabicyclo-[3.3.0]octane (**1c**) with S-phenyl thioacetate (**2a**) and/or phenyl acetate (**2b**) as well as successful addition reactions of 2-phenoxymethyloxirane (**1d**) with S-benzyl thioacetate (**2c**) and S-dodecyl thioacetate (**2d**).

A typical addition reaction was carried out as follows: **1a** [1.92 g (10 mmol)], 1.52 g (10 mmol) of **2a**, and 0.132 g (0.5 mmol) of 18-crown-6 (CR) and 0.066 g (0.5 mmol) of KOPh as catalysts were mixed, and then the mixture was stirred at 110 ^{o}C for 48 h. The crude product thus obtained was purified with a silica gel (Merck Co., Kiesegel 60) column by using dichloromethane as an eluent. The yield of 3-benzyloxy-2-methyl-2-phenylthiomethylpropyl acetate (**3a**) was 2.69 g (78.1%). IR spectrum; 1740 (ν C=O), 1240 (ν C-O-C, ester), and 1100 cm^{-1} (ν C-O-C, ether). ^{1}H-NMR spectrum ($CDCl_3$); δ 1.04 (s, 3H, CH_3), 1.92 (s, 3H, $COCH_3$), 3.05 (s, 2H, SCH_2), 3.32 (s, 2H, OCH_2), 4.02 (s, 2H, $OCOCH_2$), 4.38 (s, 2H, $ArCH_2O$), and 7.0-7.4 ppm (m, 10H, aromatic protons). Found: C, 69.48; H, 6.95%. Calcd for $C_{20}H_{24}O_3S$: C, 69.74; H, 7.02%.

Addition reaction of the oxetane ring of **1a** with **2a** gave the corresponding adduct **3a** by using 5 mol% of CR-KOPh or CR-KSCN complexes as catalysts in 76 and 17% yields at 110 ^{o}C for 48 h, respectively (Scheme 1). However, the reaction did not proceed when tetrabutylammonium chloride (TBAC) was used under the same conditions. This result indicates that crown ether complexes have higher catalytic activity than quaternary onium salt for the addition reaction of the oxetane ring with active ester.



Scheme 1.

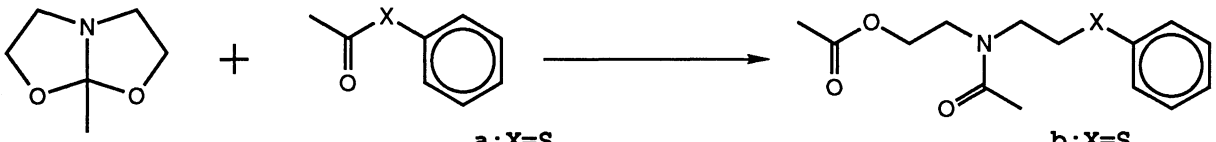
No reaction took place between 2-benzyloxymethyloxolane (**1b**) and **2a**, although it was performed using CR-KOPh as the catalyst under the same con-

ditions. It seems that the reactivity of the oxorane ring toward active ester is much lower than that of the oxetane ring.

Table 1. Reactions of cyclic ethers with (thio)esters

Run No.	Cyclic ether (mmol)	Ester (mmol)	Catalyst (mmol)	Temp °C	Time h	Yield of 3[a] %
1	**1a** (10)	**2a** (10)	CR/KOPh (0.5)	110	48	76.4
2	**1a** (10)	**2a** (10)	CR/KSCN (0.5)	110	48	17.1
3	**1a** (10)	**2a** (10)	TBAC (0.5)	110	48	0
4	**1b** (10)	**2a** (10)	CR/KOPh (0.5)	110	48	0
5	**1c** (4)	**2a** (4)	None	90	5	56.1(47.4)[b]
6	**1c** (4)	**2a** (4)	TBAB (0.2)	90	5	59.3
7	**1c** (4)	**2b** (4)	None	90	5	4.8
8	**1c** (4)	**2b** (4)	TBAC (0.12)	90	5	66.4(53.6)[b]
9	**1c** (4)	**2b** (4)	TBAB (0.12)	100	5	76.7
10	**1d** (10)	**2c** (10)	CR/KOPh (0.5)	90	5	95.0(80.3)[c]
11	**1d** (10)	**2d** (10)	CR/KOPh (0.5)	90	5	93.3(86.6)[d]
12	**1d** (50)	**2e** (50)	CR/KOPh (2.5)	90	5	27.6(4.7)[d]

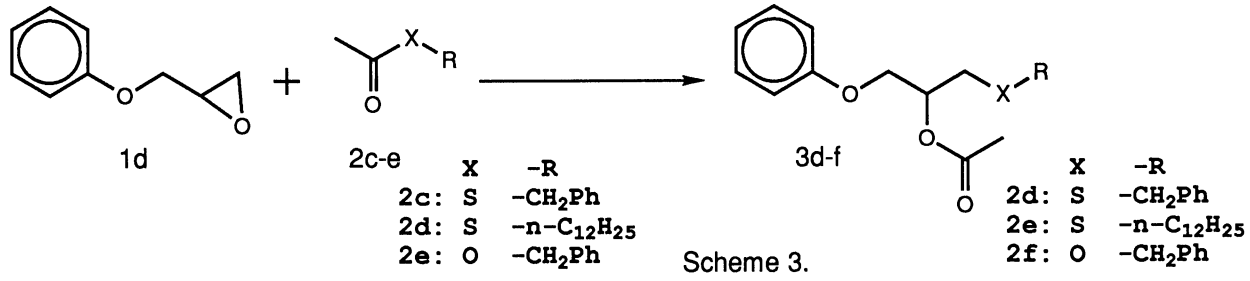
a) Determined by GLC. b) Isolated yield (the reaction was carried out for 24 h). c) Isolated yield (the reaction was carried out at 50 °C for 3 h). d) Isolated yield.



Scheme 2.

When the addition reaction of **1c**, which is a bicyclic amide acetal compound, with **2a** was carried out in the presence or absence of the catalyst, TBAB, at 90 °C for 5 h, N-(2-acetoxyethyl)-N-(2-thiophenoxyethyl)acetamide (**3b**) was obtained in 59 and 56% yields, respectively (Scheme 2). The addition reaction of **1c** with phenyl acetate (**2b**) also proceeded to give N-(2-acetoxyethyl)-N-(2-phenoxyethyl)acetamide (**3c**) in 66-77% yields by using TBAC or tetrabutylammonium bromide (TBAB) as a catalyst at 90-100 °C for 5 h (Scheme 2). When the same reaction, however,

was carried out without any catalyst at 90 °C for 5 h, the yield of **3c** was only 5%. Comparably, the reaction behavior of **1c** with **2b** was markdely different from the reaction of **1c** with **2a**, in which the reaction smoothly proceeded without any catalyst.



Scheme 3.

Addition reactions of oxirane compound **1d** with alkyl (thio)esters were performed catalyzed by 5 mol% of CR-KOPh complex at 90 °C for 5 h (Scheme 3). The reactions with alkyl thioesters **2c** and **2d** gave the corresponding adducts **3d** and **3e** in 95 and 93% yields, respectively. On the other hand, the reaction with alkyl ester **2e** produced adduct **3f** in only 28% yield under the same conditions. These results indicate that the addition reaction of oxirane with alkyl ester and alkyl thioesters proceed satisfactorily by using crown ether complex.

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