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단 신

삼플루오르화붕소에 의한 산화스티렌의 자리옮김

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The Boron Trifluoride Etherate Catalyzed Rearrangement of Styrene Oxide to Phenylacetaldehyde

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There have been several reported studies of the rearrangement of substituted oxirane to a carbonyl compound in the presence of Lewis acids[1,4] (magnesium bromide, boron trifluoride, or aluminum chloride), lithium salt[2,4] or Grignard reagent[3,4]. However, no systematic investigation on the rearrangement of styrene oxide in the presence of boron trifluoride etherate has been reported. We therefore undertook a systematic study of this rearrangement in diethyl ether solution. The systems were examined under the various reaction temperature (25°C, 0°C, and −18°C) and in the various mole ratio of boron trifluoride to styrene oxide (100 mole %, 50 mole %, 25 mole %, and 10 mole %), to understand the influence of reaction temperature and the proportion of Lewis acid on the formation of the rearranged product, phenylacetaldehyde. The results of this investigation are reported in the present paper.

The reactions were carried out at a constant concentration of 0.25 *M* in styrene oxide in diethyl ether. After appropriate reaction intervals, 16 m*l* of the solution (4 mmol of compound) was removed and treated immediately with sufficient amount of 2,4-dinitrophenylhydrazine solution. In every experiment, the reactions of the short time intervals (1 min. and 3 min.) were carried out in separate flasks, containing 4 mmol of styrene oxide in 16 m*l* of diethyl ether solution in each flask. The crystallized hydrazone was weighed and the results are summarized in *Table* 1. Styrene oxide itself also underwent rearrangement under the strong acidic condition on the way of formation of hydrazone to give 4-5% of the hydrazone. However, since the amount of unrearranged styrene oxide after reaction intervals should be very small, the influence might be neglected.

As shown in *Table* 1, in the case of mole ratio of 1:1 at 25°C, the amount of hydrazone decreased as the reaction progressed, showing 65.2% in 1 min, 62.1% in 3 min, 57.4% in 15 min, and only 8.8% in 1 h, respectively. These results might be attributed to the formation of polymer, possibly formed from the self-polymerization of aldehyde in the presence of boron trifluoride. However, as the proportion of boron trifluoride in the reaction mixture was decreased, although the rates of rearrangement were to be slower, the maximum yields of the hydrazone increased. Thus, the maximum yields were 72.4% at 5 min in the mole ratio of 1:0.5, 77.0% at 0.5 hr in 1:0.25, and 70.1% at 1 h

Table 1. Rearrangement of styrene oxide with boron trifluoride etherate in diethyl ether.

Temp, °C	Compd: BF_3	yield of Phenylacetaldehyde 2,4-dinitrophenylhydrazone, %[a]										
		1min[b]	3min[b]	5min	10min	15min	0.5hr	1.0hr	3.0hr	6.0hr	9.0hr	24hr
25	1:1	65.2	62.0	61.5	61.3	57.4[d]	35.9	8.8				
25	1:1[c]	69.0	65.2	63.5								
25	1:0.5	61.6	65.5	72.4	69.8	66.6[d]	64.9	57.6	31.9			
25	1:0.5[c]			71.6	70.3	65.0[d]						
25	1:0.25	67.6	72.8	73.4	73.8	74.3	77.0	75.7	69.7			
25	1:0.25[c]	71.2	72.2		74.4		76.0	73.4				
25	1:0.1	51.6	55.8	61.1	65.7	68.2	69.2	70.1	68.8	68.0	66.9	
0	1:1	71.3	72.0	80.0	73.2	72.4	64.5	61.0	27.6[d]			
0	1:1[c]	69.9	71.7	78.7	69.5	68.5	66.4	61.3				
0	1:0.5	70.8	74.4	74.7	74.0	73.5	73.2	72.6	72.4	70.6	66.1	
0	1:0.25	72.1	73.2	75.5	74.4	72.3	71.8	71.6	70.1	68.6	68.4	
0	1:0.1	48.4	52.8	55.2	58.2	61.3	63.4	66.7	67.0	68.9	68.8	66.6
−18[e]	1:1	67.7	68.1	69.3	68.2	67.7	66.3	65.0	62.6	trace		
−18[e]	1:0.5	62.5	64.4	65.7	66.4	67.2	67.3	66.8	66.5	66.2	65.4	

a. In every case where only one product was obtained, the melting point of the product was within the range 180–181 °C. *b.* Batch experiment. *c.* 2nd run for each of sets of proportion. *d.* It began form polymer, and the products were recrystallized with 95% ethanol. *e.* Immersed in ice-NaCl bath.

in 1:0.1, respectively. Therefore, the case of 25 mole % of boron trifluoride to styrene oxide appeared as the most optimum condition at 25°C.

The influence of reaction temperature, when lowered to 0°C, appeared only in the case of 1:1, showing the remarkable increase of maximum yield (80%) in 5 min. However, when treated with the lower proportion of boron trifluoride at the same temperature, the maximum yields were invariable, compared to the reaction at 25°C. Moreover, when the reaction temperature was lowered to -18°C, since the rates of formation of the rearranged product was slowed down, the yields were somewhat reduced.

EXPERIMENTAL

The following procedure for the reaction in the case of 1:0.25 at 25°C is representative[5]. A carefully dried 200 m*l* reaction flask with a septum inlet is assembled with a reflux condenser connected to a mercury bubbler. In this flask is placed 0.84 m*l* of boron trifluoride etherate(6.5 mmol) and 90.2 m*l* of anhydrous diethyl ether with hypodermic syringe. The flask was immersed in a water bath at 25°C. Then 13.0 m*l* of 2.00 *M* diethyl ether solution of styrene oxide was added rapidly with syringe through the septum cap to the well stirred boron trifluoride solution. At the appropriate time of intervals, 16m*l* of solution (4 mmol) was removed and poured into the pre-prepared 2,4-dinitrophenylhydrazine solution. The crystallized hydrazone was separated and weighed as in the usual manner[6]. Test experiments were carried out by using authentic phenylacetaldehyde. In these yields of 98–99% of the pure derivatives were realized.

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