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STEREOSELECTIVE SYNTHESIS OF CIS-2,3-DIPHENYL-2-CYANOOXIRANE BY REACTION OF 2-BROMODEOXYBENZOIN WITH CYANIDE ION ON SOLID ADSORBENTS

Kazumasa Takahashi*, Toshio Nishizuka and Hirotada Iida
Department of Synthetic Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba 260 Japan

Summary: Treatment of 2-bromodeoxybenzoin with cyanide ion in the presence of solid adsorbent (silica gel or alumina) stereoselectively gives cis-2,3-diphenyl-2-cyanooxirane in a good yield. The mechanism is discussed.

Usual synthetic methods of 2,3-diphenyloxiranes are Darzens condensation[1] and oxidation of stilbenes.[2] There is, however, no report for stereoselective synthesis of oxiranes by reaction of 2-halodeoxybenzoin with cyanide ion. We now wish to report that the reaction, when conducted in the presence of solid adsorbent (silica gel or alumina), stereoselectively gives cis-2,3-diphenyl-2-cyanooxirane (2).

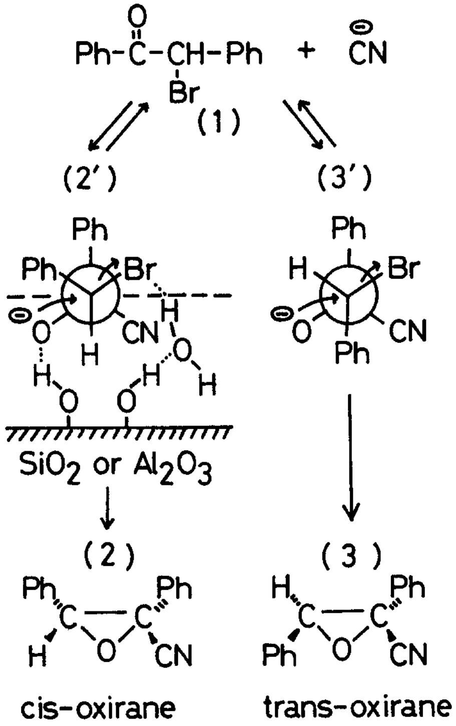
The reaction of 2-bromodeoxybenzoin (1) dissolved in dichloromethane with 40% aqueous KCN solution adsorbed on silica gel at 20 ℃ for 4 hr gave cis-oxirane (2) in 88% yield and trans-oxirane (3) in 7% yield (total yield, 95%). The products were identified by direct comparison with the authentic samples.[3] The ratio of cis- to trans-isomer was determined from the integral ratio of cis- and trans-methyne protons (cis: 4.73 ppm, trans: 4.16 ppm) in the NMR

Table 1[a]

Adsorbent (10g)	Solvent (20ml)	Total yield, (%) (2) + (3)	Composition, (%) (2) : (3)
None	DMF	61	48 : 52
Silica gel[b]	CH_2Cl_2	95	93 : 7
None	CH_2Cl_2	0	-
Silica gel[b]	Benzene	82	96 : 4
None	Benzene	0	-
Alumina[b]	CH_2Cl_2	91	97 : 3
Zeolite (13Y)[c]	CH_2Cl_2	38	100 : 0
Zeolite (4A)[c]	CH_2Cl_2	10	100 : 0
Celite[c]	CH_2Cl_2	0	-
Active carbon	CH_2Cl_2	0	-

a: 1g (3.6 mmol) of (1) and 14.4 mmol of KCN were used. b: Commercial silica gel (70-230 mesh) and alumina (ca. 300 mesh) were used. c: Two types of synthetic zeolites and diatom earth, which are commercially named as molecular sieves (13Y and 4A) and Celite 545, respectively, were used.

Scheme 1



spectrum. The reaction was also examined using other adsorbents and solvents as shown in Table 1. Only cis-oxirane was obtained, though in lower yields, in the case of molecular sieves. In contrast, when celite or active carbon was used, no reaction occurred. In the absence of adsorbent, no reaction took place except in dimethyl formamide (DMF) in which both KCN and (1) are soluble.

In the present reaction, silica gel or alumina presumably acts as an adsorbent[4] both for (1) and for cyanide ion. Unlike celite[5] and active carbon[6], silica gel, alumina and molecular sieves have numerous hydroxy groups, i.e., HO-Si or HO-Al.[4] Hydrogen bonding formed between these hydroxy groups and the polar groups of (1) seems to play an important role in determining the stereochemistry of the product. In DMF, products (2) and (3) are formed via anti-elimination from the corresponding bromohydrin anions (2') and (3'). When adsorbed on the adsorbent surface, intermediate (3') appears not able to undergo anti-elimination efficiently since the conformation required for anti-elimination involves unfavorable phenyl-surface interaction as depicted in Scheme 1. Intermediate (2') is free from such an interaction and appears to undergo anti-elimination efficiently, surmounting the sterically unfavorable phenyl-phenyl interaction. Intermediate (3') seems to be converted to (2') in the course of reaction. Control experiment indicates that epimerization of (2) does not occur under the experimental conditions and suggests that the formation of (3) (6-7% yield) is due to partial desorption of (3') from the adsorbent.

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