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The Catalytic Hydrogenolysis of Alkyl-substituted Aziridines

Yoshihiro SUGI,* Mitsuru NAGATA, and Sekio MITSUI
Department of Applied Science, Faculty of Engineering, Tohoku University, Aramaki aza Aoba, Sendai 980

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Synopsis. Alkyl-substituted aziridines were hydrogenolysed, mainly at the less-substituted C–N bonds over Raney Ni, to yield β-amines. This hydrogenolysis occurred with the retention of the configuration. The differences in behavior between aziridines and oxiranes may be ascribed to the difference in polarisation between C–N and C–O bonds in the transition state of the hydrogenolysis.

Previous publications from our laboratory[1,2] have shown that 2-phenylaziridines undergo selective hydrogenolyses at the benzylic C–N bonds. However, there has no systematic work on the hydrogenolysis of 2-alkylaziridines. This paper will present our results for the hydrogenolysis of some 2-alkyl and 2-benzylaziridines over Raney Ni. One aspect of this investigation has been an examination of the differences in effect between alkyl and phenyl groups and in behavior between aziridine and oxirane.

Results

The results of the hydrogenolysis of 2-alkyl and 2-benzylaziridines are listed in Table 1. 2-Methyl (I), 2-ethyl (II), and 2,2-dimethyl (III) aziridines underwent rapid hydrogenolyses to yield β-amines**: *iso*-propyl, *sec*-butyl, and *t*-butylamines respectively. Karabinos and Seigen,[3] and Campbell, Sommers, and Campbell[4] have also reported the selective formation of *t*-butylamine in the hydrogenolysis of III over Raney Ni. I and II yielded small amounts of α-amines: *n*-propyl and *n*-butylamines respectively, in addition to β-amines. 1-Methyl-7-azabicyclo[4.1.0]heptane (IV) was also hydrogenolysed to a mixture of 1- and *trans*-2-methylcyclohexylamines in a ratio of 4: 1, and scarcely any *cis*-2-methylcyclohexylamine was obtained. The hydrogenolysis of 2-benzylaziridine (V) gave 1-methyl-2-phenylethylamine (82%) and 3-phenylpropylamine (18%).

Discussion

Aziridines undergo facile hydrogenolyses even under mild conditions because of their strains. 2-Alkyl and 2-benzylaziridines (1—V) were mainly hydrogenolysed at the less-substituted C–N bonds to yield β-amines. This is quite different from the hydrogenolysis of 2-phenylaziridines.[1,2] This difference may be ascribed to the fact that the latter can form π-benzyl complexes by the C–N bond fission, while the former can not.

The hydrogenolysis of IV gave *trans*-2-methylcyclohexylamine (20%) in addition to 1-methylcyclohexylamine. This suggests that the aziridine, which has no phenyl group adjacent to the ring, will be hydrogenolysed with the configurational retention over Raney Ni.

Because of the tetrahedral character of the nitrogen, the aziridine **1** will be adsorbed inclined cornerwise on the catalyst, and the nucleophilic attack to the carbon atom from the catalyst will occur to form two α,γ-diadsorbed species, **2** and **3**.[1,2] The Cα-atom*** has a

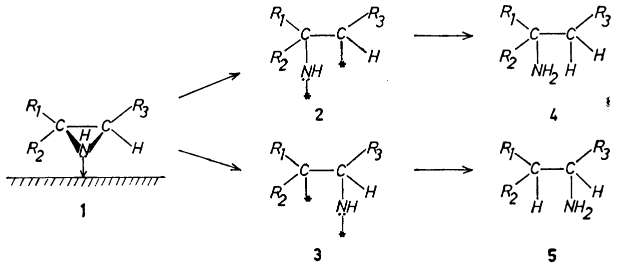
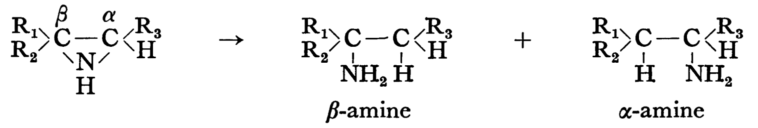


TABLE 1. CATALYTIC HYDROGENOLYSIS OF 2-SUBSTITUTED AZIRIDINES OVER RANEY Ni



$$\underset{\text{H}}{\overset{\beta\quad\alpha}{R_1R_2C\text{—}CR_3H}}\ (\text{N bridge}) \rightarrow \underset{\beta\text{-amine}}{\underset{NH_2\ H}{R_1R_2C\text{—}CR_3H}} + \underset{\alpha\text{-amine}}{\underset{H\ NH_2}{R_1R_2C\text{—}CR_3H}}$$

Compd (mol)	R_1	R_2	R_3	Time (hr)	Solvent (ml)	Conv (%)	Products β-amine (%)	Products α-amine (%)
I 1/200	Me	H	H	1	*n*-BuOH 10	98	87	13
II 1/200	Et	H	H	1	*n*-BuOH 10	98	87	13
III 1/200	Me	Me	H	1/2	*n*-BuOH 10	67	100	trace
IV 1/800	Me	$(CH_2)_4$		1/4	EtOH 5	80	80	20[a]
V 1/400	$PhCH_2$	H	H	1/4	EtOH 5	90	82	18

Catalyst: 500 mg (wet weight with EtOH). At 25 °C and 1 atm of H_2. a) *trans*-2-methylcyclohexylamine

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* Present address: National Chemical Laboratory for Industry, 2-19-19, Mita, Meguro-ku, Tokyo 153. Any correspondence should be addressed to him.

** β-Amine is the more substituted one; the alternative is α-amine.

*** The C_α-atom is the less-substituted one; the alternative is the C_β-atom.

larger positive charge than the Cβ-atom, and it is also less hindered than the Cβ-atom because of the steric hindrance of the alkyl group. Moreover, the α,γ-diadsorbed species **2** may be more stable than the alternative **3**, because the stability of the carbon–metal bond is usually in this order: primary>secondary>tertiary.[5]† The result of these effects is that the Cα–N bond fission predominates over the C_β–N bond fission.

2-Methyl-1,2-epoxyoctane (VI) was hydrogenolysed at the Cβ–O bond to yield an almost equimolar mixture of α-alcohol†† and 2-methyloctane, while the isomeric β-alcohol was obtained in a trace.[6] The hydrogenolysis of 1,2-epoxyoctane (VII) led to the formation of α- and β-alcohols in a ratio of 3: 2.[6] These results are in contrast with those of the aziridines (I—III). These differences we may ascribe to the difference in electronegativity between the nitrogen and oxygen atoms. The hydrogenolysis of the oxiranes VI and VII will proceed *via* carbonium ions, and the direction of the C–O bond fission will be governed by the relative stabilities of the carbonium ions: tertiary≫secondary>primary.[6] Howevev, it is unreasonably that the hydrogenolysis of the aziridines (I—V) occurs *via* the carbonium ions because more than 80% of the β-amines were obtained, in contrast with the oxiranes VI and VII. The polarisation of the C–N bond in the transition state of the hydrogenolysis may be lower than that of the C–O bond, because the nitrogen atom has a lower electronegativity than the oxygen atom. The direction of the C–N bond fission will be governed by such factors as the positive charge on the carbon, the steric hindrance of the alkyl group, and the stability of the α,γ-diadsorbed species, as has been discussed above.

Experimental

Materials. The 2-methyl (I), 2-ethyl (II), and 2,2-dimethyl (III) aziridines were prepared by the procedure of Campbell *et al.*[4] The 2-benzylaziridine (V) was obtained by the Brois method[7] from 3-phenyl-1-aminopropanol-2.

1-Methyl-7-azabicyclo[*4.1.0*]*heptane (IV).* Methyl *N*-(1-methyl-*trans*-2-iodocyclohexane)carbamate was obtained by the procedure of Hassner *et al.*[8] The carbamate, without isolation, was treated with a NaOH solution in water. The usual work-up gave IV; bp 58—64 °C/25 mmHg.

Hydrogenolysis. The hydrogenolyses of I, II, and III were conducted over W-4 Raney Ni at 25 °C and 1 atm of hydrogen, using *n*-BuOH as a solvent. IV and V were hydrogenolysed in EtOH under similar conditions. The reaction mixtures were analysed by gas chromatography (liquid phase: Carbowax 4000 dispersed on firebrick†††).

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† When R_1 is phenyl, **3** will be more stable than **2**, as has previously been discussed.[1,2]

†† α-Alcohol is the less-substituted one.

††† The firebrick was treated with KOH.