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The Facile Synthesis of Pentane-1, 5-diamines from Glutaraldehyde and Secondary Amines with Tetracarboxylhydridoferrate

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Ethanollic tetracarboxylhydridoferrate solution combined with glutaraldehyde is a very effective reducing agent for the selective transformation of two moles of secondary amines into pentane-1, 5-diamine derivatives. A variety of aliphatic secondary amines react with ferrate-glutaraldehyde at room temperature under carbon monoxide to give the corresponding N-substituted pentane-1, 5-diamines in reasonable yields.

Introduction

Several workers have shown that tetracarboxylhydridoferrate acts as an efficient and highly selective reducing reagent with respect to various functional groups.¹⁻⁶ In the preceding paper, we reported that a large variety of both aliphatic and aromatic amines react with glutaraldehyde in the presence of tetracarboxylhydridoferrate at room temperature under carbon monoxide to give the corresponding N-alkyl- and N-arylpiperidines in good to excellent yields.⁷ Recently, we received a private communication from Laine that catalytic reactions of pyridine with carbon monoxide and water in the presence of $Rh_6(CO)_{16}$ gave dipiperidinopentane-1, 5-diamine and its derivatives.⁸ In this connection, the present study deals with the reaction of secondary amines and the ferrate-glutaraldehyde system under carbon monoxide atmosphere.

Experimental

Potassium tetracarboxylhydridoferrate was prepared according to the method described in previous papers.^{9,10} 11 mmol of the ferrate was used in each run. Pentacarboxyliron, secondary amines, aqueous glutaraldehyde (45 %), and the

other compounds employed were all commercial products, which have been proved to be sufficiently pure by glpc.

A typical reaction procedure is as follows: to the ethanollic tetracarboxylhydridoferrate derived from pentacarboxyliron (11 mmol) and 1M-potassium hydroxide (33 mmol) solution in ethanol, added a secondary amine (22 mmol) using a syringe and then aqueous glutaraldehyde (11 mmol) was added dropwise for 5-10 min. The mixture was stirred vigorously for 24h at room temperature under carbon monoxide. The amount of carbon monoxide absorbed was determined volumetrically. The reaction was readily monitored by glpc analysis of the secondary amine consumed. When most of the secondary amine was consumed, the reaction was stopped and potassium carbonate formed in the reaction was filtered off. The filtrate was concentrated to 3-5 ml on a rotary evaporator and/ or with Kugelrohr apparatus. The products were purified by careful vacuum distillation, and submitted to analysis.


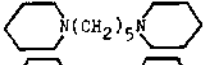

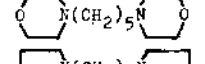

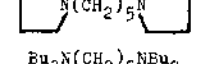
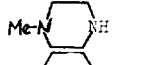
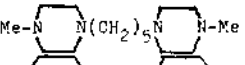

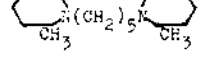


The glpc analysis was made using internal standards; a column (0.3 cm ϕ , 3m) packed with 10 % Versamid on Neopak 60-80 mesh was used. The measurements of the H-NMR and IR spectra were made on a JEOL Model 3H 60-NMR spec-

trometer and a Varian HR 220MHz NMR spectrometer using tetramethylsilane (δ) as an internal standard and CDCl_3 as the solvent unless stated otherwise and on a 215 Hitachi spectrophotometer respectively. Elemental analyses were formed at Microanalytical Center in Kyoto University.

Results and Discussion

A variety of secondary amines except *N*-arylamines reacted with the ferrateglutaraldehyde mixture at room temperature for 24h under an atmosphere of carbon monoxide to give the corresponding *N*-substituted pentane-1, 5-diamine derivatives in reasonable yields. The results obtained are summarized in Table 1 and 2. As shown in Table 1, the yields of pentane-1, 5-diamine derivatives were not obtained more than 45 % in all cases. These moderate yields seem to be partly due to the formation of intractable organic iron com-

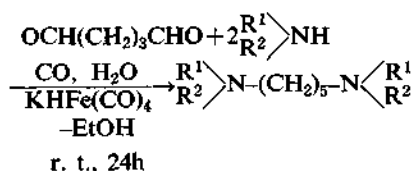
TABLE 1: Preparation of Pentane-1,5-Diamines from Glutaraldehyde Using $\text{KHFe}(\text{CO})_4$ ^a

Exp. No.	Sec-Amine	CO^b Absorbed	Product	Yield(%) ^c
1		1.0		30
2		1.6		40
3		1.1		35
4	Bu_2NH	1.0	$\text{Bu}_2\text{N}(\text{CH}_2)_5\text{NBu}_2$	40
5		1.6		45
6		1.0		25
7		1.8	Tarry material	-
8		1.5	" "	-
9	PhNHCH_3	0.1	No reaction	-
10	Et_2NH	0.0	" "	-

^a Molar ratio; Ferrate/Glutaraldehyde/Sec-Amine 1.0/1.0/2.0, at room temperature under carbon monoxide for 24h. ^bMol/mol-ferrate^c Isolated yield.

plexes¹¹. ¹H-NMR spectra and elemental analyses of these products are shown in Table 2.

The reaction proceeds smoothly with absorption of carbon monoxide and with a color change from pale-yellow to dark-red. Stirring was continued until carbon monoxide absorption ceased. The reaction of glutaraldehyde with aliphatic secondary amines such as piperidine, morpholine, pyrrolidine, and *N*-methylpiperazine in the presence of tetracarbonylhydridoferrate gives easily the corresponding products, *N,N'*-dipiperidino-, *N,N'*-dimorpholino-, *N,N'*-dipyrrolidino-, and *N,N'*-dimethylpiperazinopentane-1, 5-diamines, respectively, but in the cases of *N*-substituted anilines with alkyl and phenyl substituents, no reaction occurred and absorption of carbon monoxide was not observed. These reaction seem to be strongly affected by the basicity of secondary amines.¹² In general, the yields of products were highly promoted with an absorption of carbon monoxide, the absorption, however, was not always proportional to the yields. For example, in the reaction of 1, 2, 3, 6-tetrahydropyridine (Exp. No. 7) with glutaraldehyde an intractable tarry product mixture was obtained. In the case of piperazine (Exp. No. 8) a tarry material was also obtained.



These reactions seem to proceed *via* immonium salts and enamine intermediates and appear to involve reactions of carbon-nitrogen double bonds.¹³ The mechanism of the reaction is not completely known yet at the present time. The results obtained here show that this method can be applied for aliphatic secondary amines but not for aromatic secondary amines under the reaction conditions employed.

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TABLE 2: Analytical Data of Pentane-1, 5-Diamines

Exp. No.	B. P.	E. A.			¹ H-NMR (δ , ppm, CDCl_3)
		H	C	N	
1	65°C/4mmHg	Cald. 12.68	75.57	11.75	1.2-1.8(m, 18H), 2.1-2.6(m, 12H).
		Found. 12.51	75.80	11.59	
2	107/5	10.81	64.43	11.56	1.3-1.8(m, 6H), 2.1-2.7(m, 12H), 3.6-4.0(m, 8H).
		10.60	64.48	11.23	
3	73/10	12.46	74.23	13.32	1.3-2.0(m, 14H), 2.1-2.6(m, 12H).
		12.20	73.81	12.72	
4	63/11	14.20	77.23	8.85	0.6-1.0(t, 12H), 1.0-1.7(m, 22H), 2.1-2.5(m, 12H).
		14.48	77.20	8.30	
5	84/4	12.02	67.11	20.87	1.3-1.7(m, 6H), 2.3-2.4(s, 6H), 2.4-2.5(m, 20H)
		12.02	66.33	20.25	
6	42/5	—	—	—	1.3-1.8(d, 6H), 2.3-2.4(m, 18H), 2.4-2.7(m, 10H)

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