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Proton NMR Spectrum of *N*-Phenethyl-*o*-anisidine[1]

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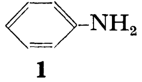
It was reported that anionic telomerizations where anisidines and phenetidines were allowed to react as a telogen with styrene as a taxogen in the presence of alkali metals gave phenethylamines.[1] Each of the telomers showed two methylene triplets in the NMR spectrum, the assignment of which was not elucidated.

This paper reports on the preparation of mixed telomers composed of *N*-phenethyl-*o*-anisidine and *N*-phenethyl-*β*-*d*-*o*-anisidine and the assignment of NMR spectrum of *N*-phenethyl-*o*-anisidine done by analyzing the NMR spectra of the mixed telomers.

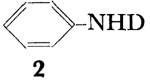
Results and Discussion

Exchange Reaction between O-*Anisidine and Deuterium Oxide*

The exchange reaction between *o*-anisidine and deuterium oxide in the presence of a small amount of potassium deuteroxide gave mixed amines, *i.e. o*-anisidine **1**, *o*-anisidine-*N*-*d* **2**, and *o*-anisidine-*N*-d_2 **3**.



1



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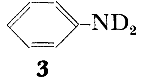

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Since the above is an equilibrium reaction, the partly deuterated *o*-anisidine may be composed of **1**, **2**, and **3**. The extent of deuteration of the amino group calculated from the integral curve of NMR spectrum was 55%. On treating *o*-anisidine with deuterium oxide, the intensity of –NH– stretching vibration of the amine at 3350—3450 cm^{-1} decreased and –ND– stretching vibration appeared at 2400—2600 cm^{-1}. This is consistent with the fact that the amino group of *o*-anisidine was partly deuterated.

Anionic Telomerization of Mixed o-*Anisidine with Styrene.*

In the first place the mixed *o*-anisidine was allowed to react with an alloy of sodium and potassium to form organometallic compounds **5** and **6**, which acted as an initiator (I). In the next place telomerization was carried out by dropping styrene into the amine-alloy system (II,III). Finally, the reaction product was washed with water and dried, and thereafter purified by vacuum distillation (IV) : bp 156°C/2mmHg, n_D^{25} 1.5747, mol wt by VPO 229. Found: C, 79.02 ; H, 7.73; N, 6.40 %. Calcd for $[C_{15}H_{16}NO]_{0.48}[C_{15}H_{15}DNO]_{0.52}$: C, 79.08; H and D, 7.79; N, 6.15 %.

These reactions are summarized as follows.

Thus, a mixture of *N*-phenethyl-*o*-anisidine **13** and *N*-phenethyl-*β*-*d*-*o*-anisidine **14** was prepared by the telomerization of styrene with the mixed amines.

Proton NMR Spectrum of Mixed Telomers **13** *and* **14**.

Figures 1 and 2 show the proton NMR spectrum of *N*-phenethyl-*o*-anisidine and that of the mixed telomers derived from the partly deuterated *o*-anisidine, respectively. In Fig. 1 two triplets with equal intensities appear at 2.79 ppm and 3.27 ppm, while in Fig. 2 the area of the triplet at 2.79 ppm decreases and the shape of the signal at 3.27 ppm is modified.

It may be derived from the reaction scheme and the consideration on the spectra that a triplet signal at 2.79 ppm should originate from the methylene group neighboring to the phenyl group and the other triplet at 3.27 ppm should be assigned to the methylene group attached to the nitrogen atom. The extent of deuteration of the obtained telomers, calculated from the integral curve in Fig. 2, reached 52 % of the mixed telomers.

The proton NMR spectra of *N*-phenethyl-*m*-anisidine, *N*-phenethyl-*p*-anisidine, *N*-phenethyl-*o*-phenetidine, *N*-phenethyl-*m*-phenetidine, and *N*-phenethyl-*p*-phenetidine previously reported[1] can be interpreted in the same manner.

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[1] Anionic Telomerizaions. VI. Part V of this series: T. Asahara, M. Senō, S. Tanaka, and M. Akiyama, *Bull. Jap. Petrol. Inst.*, to be published.

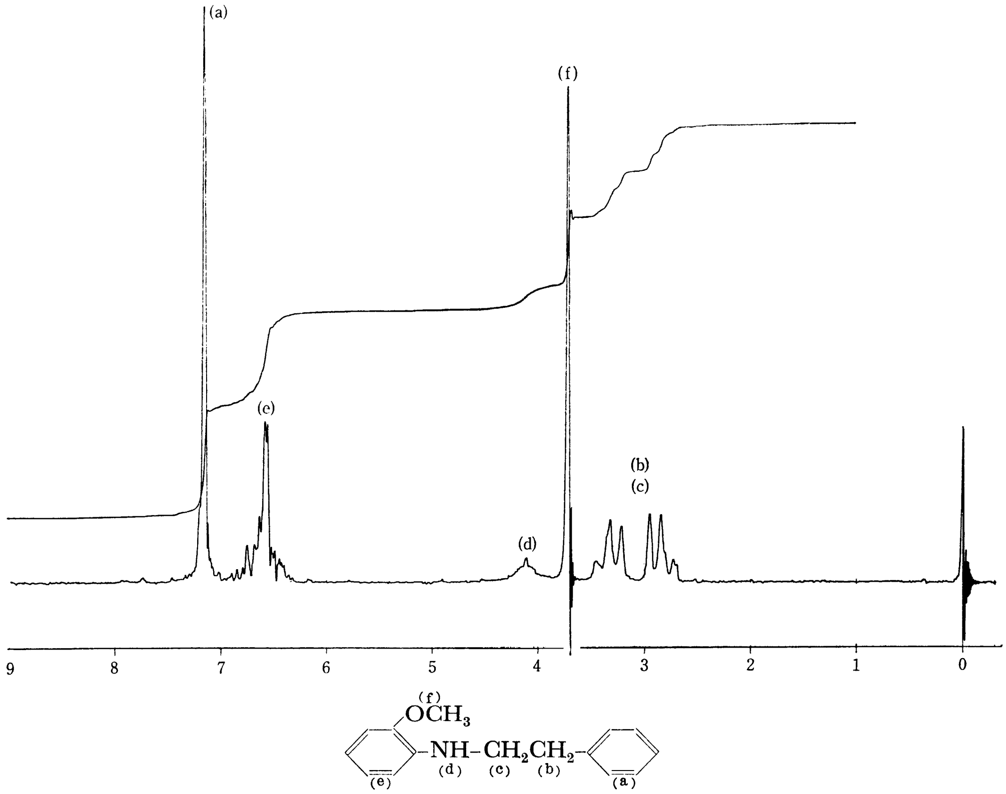


Fig. 1. Proton NMR spectrum of *N*-phenethyl-*o*-anisidine.

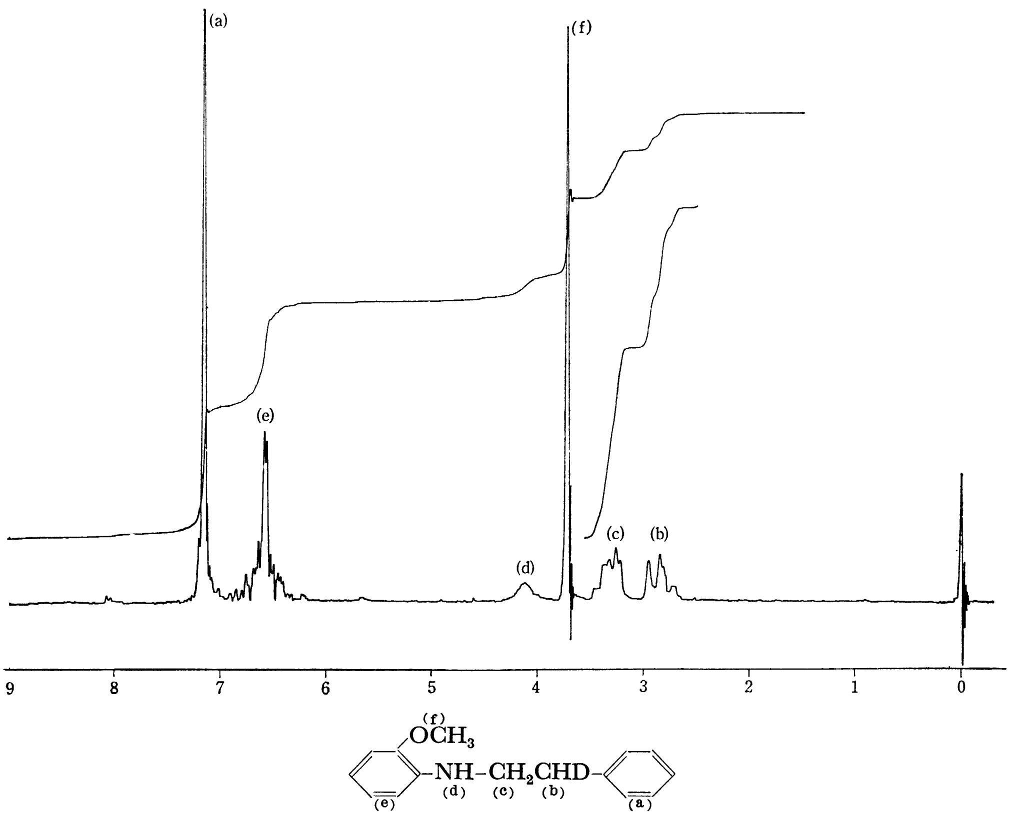
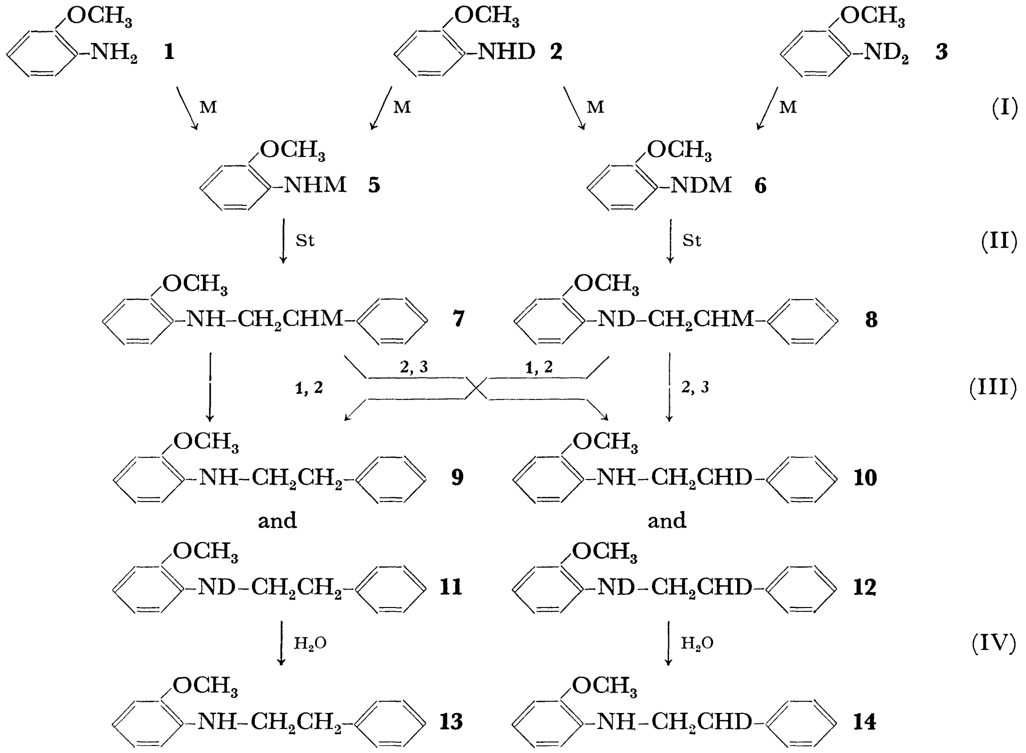


Fig. 2. Proton NMR spectrum of the mixed telomers composed of *N*-phenethyl-*o*-anisidine and *N*-phenethyl-*β*-*d*-*o*-anisidine.


OCH3
-NH2 1
-NHD 2
-ND2 3
M
(I)
-NHM 5
-NDM 6
St
(II)
-NH-CH2CHM- 7
-ND-CH2CHM- 8
1, 2
2, 3
(III)
-NH-CH2CH2- 9
-NH-CH2CHD- 10
and
-ND-CH2CH2- 11
-ND-CH2CHD- 12
H2O
(IV)
-NH-CH2CH2- 13
-NH-CH2CHD- 14

M: Na or K