TRAPPING MECHANISM OF ETHANAL WITH DEODORANT SODIUM p-AMINOBENZOATE IN AMBIENT AIR: QUINOLINE RING FORMATION TO PREVENT ITS RELEASE

Masahiro Sugiura, *¹ Kazuhiro Fukumoto¹ and Masatomi Ohno² ¹ Toyota Central R&D Labs. Inc., Nagakute, Aichi 480-1192, Japan ² Toyota Technological Institute, Hisakata, Tempaku, Nagoya, 468-8511, Japan

Abstract: The trapping experiment of vapor ethanal (1) with solid sodium *p*-aminobenzoate (2-Na) to prove the effectiveness as a deodorant prompted us to examine their aqueous reaction. After GLC monitoring to show the prerequisite formation of 2-butenal (3), the final product was elucidated as sodium 4-hydroxy-2-methyl-1,2,3,4- tetrahydro-quinoline-6-carboxylate (4-Na), indicating that trapping of 1 with 2-Na proceeded *via* not simple condensation to a Shiff base but heterocyclization to the quinoline ring, which is a reasonable intermediate in the Döbner-Miller reaction, and irreversible formation of this ring reflects on high deodorant activity of 2-Na.

Cigarette smoke, exhaust gas from heat engine, and odor of rotten vegetables contain more or less aldehydic compounds. In particular, ethanal (1) is prescribed as one of the offensive odorants by the Offensive Odor Control Law of the Environment Agency of Japan.¹ Therefore, it is a crucial problem in daily life to remove contaminating 1 from ambient air.

In the previous paper,^{2a} we have shown that such aldehydes could be trapped efficiently with various amino acids and their sodium salts and hydrochlorides, and those of *p*-aminobenzoic acid (2-Na, 2-HCl) were shown to be one of the best trapper or deodorant among them especially for 1. The aldehyde is well known to react with a primary amine to form an aldimine.³ Then, the trapping of 1 with 2 might be straightforwardly explained by the condensation reaction as shown below. However, reversibility of this type of reaction allows the formed imine to undergo hydrolysis and release 1 under a humid atmosphere. This is incompatible with the observed efficiency. Thus, it is significant to have an insight into the mechanism of reaction of 1 with 2 and discern whether the product is nonvolatile and hence odorless.



In the present study, we revealed that the reaction of **1** with **2-Na** could afford a cyclized product, sodium 4-hydroxy-2-methyl-1,2,3,4-tetrahydro-quinoline-6-carboxylate (4), which was in fact nonvolatile and less likely to return to **1** and **2-Na**.

The trapping experiment in ambient air (30% relative humidity) was conducted in a 5 dm³-bag including gaseous 1 (0.300 g, 6.81 mmol) and powdered 2-Na (0.100 g, 0.628 mmol) at 25°C, while the consumption of 1 was monitored with the apparatus as described in the previous papers.^{2b-d} After 24 h, brownish solid was formed as a product. This was first inspected with IR spectrum, which indicated strong and broad absorptions at 3400 and 1540 cm⁻¹ due to hydroxyl and carboxylate groups, respectively.^{2a} In order to follow up the chemical behavior of 1 and suffice a quantity of the product for other analyses, we decided to undertake the more convenient reaction in an aqueous solution.

This was carried out in deionized water with nearly the same ratio of 1/2-Na and much higher concentration (ca. 300 fold), while a small amount of the mixture was sampled out and analyzed directly by gas chromatography. As a result, intermediate 2-butenal (3) was recognized to appear after a few

minutes. Therefore, the relative amounts of the starting and dimeric aldehydes 1 and 3 were both monitored occasionally. Fig.1 shows the relative ratio of consumed 1 to used 2-Na (mol/mol) to be approximately constant (~ 2) after even shorter and long period, demonstrating smooth dimerization to occur⁴ (*vide supra*). Fig. 2 shows the concentration of 1 and 3 as a function of time, demonstrating that 3 increased initially, reached maximum after about 1 min, and then decreased gradually, while 1 decreased throughout the course. These observations are indicative of the chemical behavior of 1 toward 2-Na; self aldol-condensation of 1 is preceding possibly with catalytic action of 2-Na, and the resulting enal 3 may be converted to the final 2:1 adduct of 1 and 2-Na, which, in fact, could be furnished by the direct reaction of 3 with 2 under the same conditions. Notably, this adduct obtained from the solution reaction resembled that formed by the gaseous reaction (*vide infra*). With these results in hand, we next turned to isolation and characterization of the product from the former reaction.

The preparative experiment was carried out similarly at 25 °C for 1 day with stirring. After removal of the insoluble by-products by filtration, the filtrate was evaporated in vacuo and dried with heating (80 °C) to give the brown solid (~95% yield based on 2-Na). The product was subjected as prepared to spectral (IR, NMR, FAB-MS) and elemental analyses, and identified as sodium 4-hydroxy-2methyl-1.2.3.4-tetrahydro-quinoline-6-carboxylate (4-Na), which fulfills the desire of "trapping aldehvde". The structure was determined as follows. Firstly, the elemental and FAB-MS analyses showed the molecular formula to be best fitting with $C_{11}H_{12}NO_3Na$ as a 2:1 monodehydrated adduct of 1 and 2-Na.⁵ The 1R spectrum indicated the presence of functional groups due to characteristic absorptions at 3400 cm⁻¹ (OH), 1605 cm⁻¹ (benzene ring), and 1540/1390 cm⁻¹ (COO⁻) together with no aldehydic absorption. It is essential that the IR spectrum of the product obtained above resembled that of the product formed by the gaseous reaction. Finally, the full assignments for the ¹H and ¹³C NMR spectra (in D₂O, 400 MHz and 100 MHz, respectively) allowed us to deduce the 2,4,6-trisubstituted 1,2,3,4tetrahydro-quinoline ring system as 4-Na. The requisite coupling patterns for the benzene ring and the fused -HN-CH(CH₃)-CH₂-CH(OH)- unit were compatible with ¹H-NMR signals at δ 7.78 (d), 7.69 (dd), and 6.67 (d) (C₅-H, C₇-H, and C₈-H, respectively, J_{57} =2.2 Hz, J_{78} =8.5 Hz), and at δ 4.76 (dd, C₄-H), 3.45 (ddq, C₂-H), 1.99 (dt, C₃-H), 1.48 (ddd, C₃-H), and 1.21 (d, CH₃) with coupling constants J_{2Me}=6.4 Hz, $J_{23}=12.2$ and 2.6 Hz, $J_{33}=14.2$ Hz, and $J_{34}=3.4$ and 2.6 Hz).^{6a} This ring structure was also interpreted in the ¹³C NMR spectra using DEPT: 23.1 (CH₃), 39.5 (C₃), 43.9 (C₂), 67.4 (C₄), 116.9 (C₈), 123.6 (C_{4a}), 127.2 (C₆), 132.9 (C₇), 134.5 (C₅), 150.1 (C_{8a}), 177.8 (COO), and C-H COSY was well correlated as assigned above. It is noted here that these signals were accompanied in most cases by resembling ones at their neighborhood. This pattern is suggestive of the product to be mixed with stereoisomers, trans and cis.^{6b} As a matter of fact, in the reported quinoline synthesis using *p*-methyl and *p*-chloroanilines with 3, such stereoisomerism was observed for the intermediate compounds.

The present reaction is categorized as Skraup reaction or related Döbner-Miller reaction (reaction of aniline derivatives with α,β -unsaturated aldehydes and ketones).⁸ The employed amino acid 2 (entitled as vitamin B_x) is known as a bioactive compound. In the old patent, this type of reaction using 2 with 3 was recorded to give 2-methylquinoline-6-carboxylic acid.⁹ Alternatively, the catalyzed gas phase reaction was documented for the case of aniline with 3;¹⁰ although the same gaseous conditions was employed as in our work, much higher reaction temperature might fall into a different mechanism giving 4-methylquinoline as a result of consecutive condensation, electrocyclization, dehydrogenation reactions. The reaction aptitude of 2-Na with 3 at ambient temperature, of course, follows the normal 1,4-addition/Friedel-Crafts cyclization mechanism ($3 \rightarrow 4'$ -Na $\rightarrow 4$ -Na) as shown above. Thus, it is apparent that the trapping efficiency of 2 is ascribable to the efficient conversion of 1 with 2-Na into a quinoline ring. Usually, acids are utilized as a catalyst in Skraup/Döbner-Miller reaction, but these tend to resinify the products.¹¹ This is also the case for the reaction of 2 with 1 in the presence of HCl, where polymeric products were formed mainly, and such a result may explain the high deodorant activity for 2-HCl.^{2a} While usefulness of 2 as an acetaldehyde scavenger against air pollution has often been claimed by us¹²

and others¹³, mechanistic considerations in this work are informative of a deodorizing role of **2**. Indeed, **2** and **2-Na** have put into practical use globally as a deodorant to remove ethanal in ambient air.



Fig. 1 The molar ratio of the consumed ethanal (1) to the used sodium p-aminobenzoate (2-Na) in aqueous solution (25°C).



Fig. 2 The molar concentration of ethanal $(1: \bigcirc)$ and 2-butenal $(3: \bigoplus)$ as a function of time for the reaction of 1 with sodium *p*-aminobenzoate (2-Na) in aqueous solution (25°C).



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- 6. a) These coupling constants supported the trans-relationship between C_2 and C_3 -H. b) From relative intensity of ¹H-NMR signals due to CH₃ groups, the trans/cis ratio was estimated to be 85/15.
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#Present Address of the corresponding author (M. Sugiura) : Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan.

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