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2-아미노와 2-니트로-3, 4-디히드로-5, 6-디메톡시-1(2H) 나프탈레논으로부터 5, 6-디메톡시-1, 2, 3, 4-테트라히드로 -2(1H)나프탈레논 생성물의 메카니즘과정. 정정

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(1679. 7. 3 접수)

Mechanistic Pathways in the Transformation Product of 5, 6-Dimethoxy-1, 2, 3, 4-tetrahydro-2(1H) naphthalenone from the Respective 2-amino and, 2-Nitro-3, 4-dihydro -5, 6-dimethoxy-1(2H) naphthalenone. A Correction

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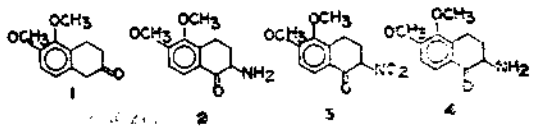
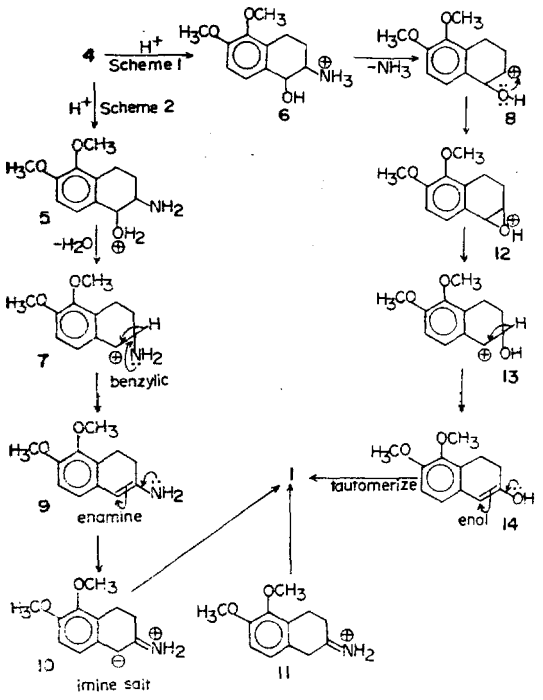
In a previous publication "Isolation and Characterization of 5, 6-dimethoxy-1, 2, 3, 4-tetrahydro-2(1H)naphthalenone from the catalytic reductions of the catalytic reductions of the respective 2-amino, and 2-nitro-3, 4-dihydro-5, 6-dimethoxy-1(2H)naphthalenone" (*J. Kor. Chem. Soc.*, **23**, 94 (1979), from this laboratory[1] we isolated an unusual rearranged product of 5, 6-dimethoxy-2(1H)naphthalenone **1** from the respective 2-amino, **2**, and 2-nitro-3, 4-dihydro -5, 6-dimethoxy-1(2H)naphthalenoe **3**. In these synthetic routes, the intermediate, 2-amino-5, 6-dimethoxy-1, 2, 3, 4-tetrahydro-naph-thalen-1 -ol, **4** was isolated before the perchloric acid treatment in the catalytic hydrogenation operations (See Experimental Sectiou of the *J. Kor. Chem. Soc.*, **23**, 94 (1979), and treated the **4** with a few drops of conc. HCl(or $HClO_4$). At this condition, the structure of a unknown crystalline was proved to be the **1** on the basis of the spectroscopic data and the result of the elemental analysis. And also we proposed a plausible mechanism (*Scheme* 1) for the rearranged product **1** formation from the intermediate **4**.

Regrettably, we report the previously published plausible mechanism of the *Scheme* **1** in error in the following reasons: A central



1 2 3 4

Scheme 1.



Scheme 2.

problem in the fundamental understanding of a plausibl emechanism of the *Scheme* 1 at the amino-alcohol intermediate **4** stage, is the question of whether the intermediate amino-alcohol **4** appears to involve[2] either kinetically controlled protonation at the hydroxyl oxygen to form oxonium ion **5** (*Scheme* 2), or thermodynamically controlled protonation at the basic nitrogen atom to from ammonium salt **6** (*Scheme* 1) in the acidic medium condition of the catalytic hydrogenation step.

Both of the protonated species, **5** and **6** will give rise to the respective carbonium ions, **7** and **8**, after the leaving groups, OH_2 and NH_3 come off as a free entity. However, best leaving groups will be those that can best stabilize an extra pair of electrons, that is a weak Lewis base[3]; the strong base, NH_3 is so hard to leave as a leaving group[4] as in **6**→**8** step, and weaker base, OH_2 is a better leving group.

Secondly, the structural features of the generated carbonium ions **7** and **8** have relatively good deal of influences on the proposed mechanism; the speed of this ionization partly depends upon the stability of the carbonium ions formed. The much more stable longlived benzylic carbonium ion **7** will predominantly favor the mechanistic in **5**→**7**, rather than in **6**→**8**.

With these two controlling factors in mind, the stable benzylic carbonium ion **7** will drive to form the enamine **9** initially,[5] Analogous to the keto-enol system, the enamine **9** rapidly tautomerizes into the imion form **10**. The generated ambident character of the **10** may be protonated acidic medium used) to form more stable iminium sait **11**.[6] Then the equilibrium favors the formation of **9**→**10**→**11** and the relatively stable iminium salt **11** will be attacked by the nucleophilic H_2O (obtained from the steps **5**~**7**, or from the medium used) to give the rearranged product **1**.

On the basis of the presently available data, the enamine-followed mechanistic *Scheme* **2** is more compatible, and it is reasonable to discard the epoxide-followed *Scheme* **1**.

REFERENCES

1. (a) J. C. Kim, S. K. Han, S. K. Choi. *J. Kor. Chem. Soc.*, **20**, 91 (1976). (b) J. C. Kim, *J. Kor. Chem. Soc.*, **21**, 187 (1977); (c) J. G. Cannon and J. C. Kim, *J. Med. Chem.*, **15**, 348 (1972). (d) J. G. Cannon, J. C. Kim, ASPET MEETING, East Lansing, Mich., 1973, Abstract 129; (e) J. P. Long, S. Heinz, J. G. Gannon and J. C. Kim, *J. Pharmacol. Exp. ther.*, **192**, 336 (1975); (f) J. G. Cannon and J. C. Kim, *U. S. Patent*, **374,170** (June 27, 1974). (g) J. G. Cannon and J. C. Kim, *J. Heterocycl. Chem.*, **9**, 731 (1972); (h) J.C. Kim, *J. Kor. Chem. Soc.*, **23**, 94 (1979).
2. H. O. House, "Modern Synthetic Reactions", P. 504, 573~75, 2nd Ed., W. A. Benjamin, Inc., 1972.

3. J. March, "Advanced Organic Chemistry, Reaoticn Mechanism and Structure, P. 296~94, "McGraw-Hill Book Co., NewYork, 1968.
4. The strong base such as a NH_3 as al eaving group is seldom seen, except in the treatment of amino function with HNO_2.
5. T. H. Lowry and K. H. Richardson "Mechanism and Theory in Organic Chemistry", P. 192~94, 223~26, Harper and Row Publishing, 1976.
6. P. Y. Sollenberger and R. B. Martin, *J. Amer. Chem. Soc.*, **92**. 4261 (1970); J. Eicini and A. Krief, *Tetrahedron Letters*, **17**, 1397 (1970).