Nitrogen Insertion to Bicyclo[2.2.1]heptanones; the Photo-Beckmann Rearrangement of Oximes of (+)-Fenchone and (+)-Camphor[1,2]

Hiroshi Suginome,* Kenji Furukawa, and Kazuhiko Orito

Organic Synthesis Division, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

The major products of the photolysis of the oximes of two natural bicyclo[2.2.1]heptanones, (+)-fenchone and (+)-camphor, in methanol are nearly equal amounts of two isomeric lactams arising from the photo-Beckmann rearrangement and the corresponding ring-opened amides.

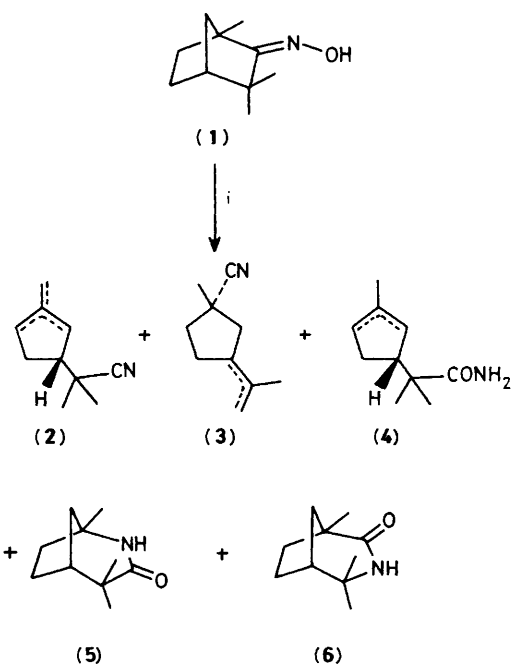
Our studies[3] of the photo-Beckmann rearrangement of several steroidal cyclic ketone oximes have indicated that two structurally isomeric lactams which retain the configuration of the migrating carbon centre are always produced in moderate to good yields in approximately a 1 : 1 ratio. Another feature of the photo-reaction of oximes is their reluctance to give nitriles *via* α-fission; the oximes of cyclic ketones that undergo second-order Beckmann rearrangement on treatment with Lewis acids[4] thus seldom give products resulting from photochemical α-fission,[5] although a highly substituted 6-methyl-2,4,6-tri-t-butylcyclohexadienone oxime has been reported to give, exceptionally, α-fission products as the major products.[6]

The reported result[7] of the photolysis of camphor oxime, however, is a violation of the aforementioned property since a mixture of nitriles resulting from α-fission is claimed to be virtually the exclusive product. Since the major products of the photolysis of the parent norcamphor oxime are reported to be two lactams (28%) accompanied by small amounts of the corresponding ring-opened amides,[8] the formation of the nitriles from camphor oxime cannot be taken as a general property for the photo-reaction of bicyclo[2.2.1]heptanone oximes, but should be considered as anomalous; the observed α-fission, if correct, should be attributed to the effects of the C-1 and C-7 methyl groups. In order to gain more insight into the effects of the methyl group adjacent to the hydroxyimino group in bicyclo[2.2.1]heptanone oxime, we have investigated the photolysis of fenchone oxime (**1**) in which all the carbons adjacent to the hydroxyimino group have methyl substituents.

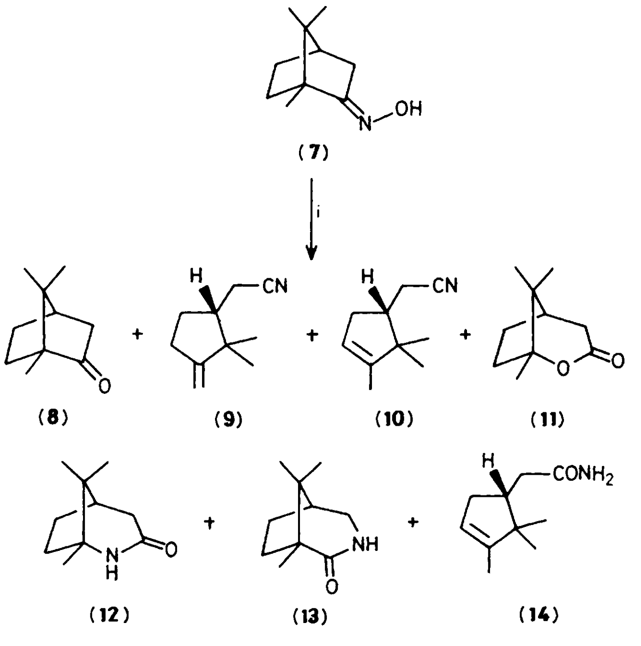
Irradiation of (+)-fenchone oxime (**1**)[9] (400 mg) in methanol (240 ml) using a low pressure Hg arc, in a Rayonet photochemical reactor, for 15 h resulted in a 96% conversion of the oxime and afforded a mixture of products, which on separation by means of preparative t.l.c. and h.p.l.c. gave a mixture of isomeric nitriles (**2**) and (**3**) (11%), a 1 : 1 mixture of crystalline amides (**4**) (10%), 1,4,4-trimethyl-2-azabicyclo-[3.2.1]octan-3-one (**5**)[10] (13%), and a new isomeric lactam, 1,4,4-trimethyl-3-azabicyclo[3.2.1]octan-3-one (**6**),† m.p. 129.5—130 °C (13%).

Thus, the photo-reaction of (**1**) is virtually in line with that of norcamphor oxime. Reinvestigation of the photolysis of camphor oxime then became necessary since this result showed that methyl substitution of all the β-carbons of norcamphor has little effect on the direction of the photo-reaction.

Photolysis of (+)-camphor oxime (**7**) in methanol under the same conditions as oxime (**1**) led to 85% conversion of the oxime and afforded a mixture of products, which on separa-



Scheme 1. *Reagents and conditions:* i, MeOH, *hv*, 15 h.



Scheme 2. *Reagents and conditions:* i, MeOH, *hv*, 15 h.

---

† Details of the isolation and the determination of the structures of all the products in this paper will be described in a forthcoming full paper.

tion by preparative t.l.c. gave (+)-camphor (**8**) (4%), isomeric nitriles (**9**) (4%) and (**10**) (2%), 1,8,8-trimethyl-2-oxabicyclo-[3.2.1]octan-3-one (**11**)[11] (6%), a crystalline 1,8,8-trimethyl-2-azabicyclo[3.2.1]octan-3-one (**12**) (α-camphidone)[12] (12%), an isomeric lactam, 1,8,8-trimethyl-3-azabicyclo-[3.2.1.]octan-2-one (**13**)[13] (12%), and an amide (**14**) (α-campholenic amide)[7,14] (32%).

Thus, in sharp contrast with the results published in the previous report,[7]‡ the major products of the photolysis of camphor oxime are nearly equal amounts of two isomeric lactams arising from the photo-Beckmann rearrangement and ring-opened amides; these results are in line with those for bicyclo[2.2.1]heptanone oxime and fenchone oxime.

Since lactams such as (**6**) and (**12**) are inaccessible by means of the Beckmann rearrangement, the photo-reaction carried out under neutral conditions at room temperature is useful for nitrogen insertion to bicyclo[2.2.1]heptanones.[15]

Financial support from the Ministry of Education of Japan and the Takeda Science Foundation is gratefully acknowledged.

Received, 26th January 1987; Com. 091

---

‡ The previous investigators[7] used a 100 W high pressure Hg arc for the photolysis. It is certain that the difference in the pressure of the lamp does not affect the products and their yields in the photolysis of oximes although the use of a low pressure Hg arc is better since saturated oximes absorb light in the *ca.* 200 nm region.

References

1 Presented at the 26th Symposium on Perfumes, Terpenes and Essential Oils (Yamagata, Japan), 7th October 1977, Abstr., p. 270.

2 Previous paper in this series, H. Suginome, J. B. Wang, and S. Yamada, *Chem. Lett.,* 1987, 783.

3 H. Suginome and F. Yagihashi, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2488, and references cited therein.

4 *E.g.*, J. N. Shah, Y. P. Mehta, and G. M. Shah, *J. Org. Chem.*, 1978, **43**, 2078.

5 H. Suginome and Y. Takahashi, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2920; H. Suginome and Chi-Ming Shea, *ibid.*, 1980, 2268; H. Suginome and Chi-Ming Shea, *Synthesis*, 1980, 229; H. Suginome, N. Maeda, Y. Takahashi, and N. Miyata, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 846.

6 R. Okazaki, M. Watanabe, and N. Inamoto, *Tetrahedron Lett.*, 1977, 4515.

7 T. Satoh and H. Obase, *Tetrahedron Lett.*, 1967, 1633; T. Satoh, T. Inoue, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1176.

8 B. L. Fox and H. M. Rosenberg, *J. Chem. Soc., Chem. Commun.*, 1969, 1115.

9 O. Wallach, *Liebigs Ann. Chem.*, 1890, **263**, 136.

10 R. W. Cottingham, *J. Org. Chem.*, 1960, **25**, 1473.

11 A. Baeyer and V. Villiger, *Chem. Ber.*, 1899, **32**, 3625; H. Suginome and S. Yamada, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3055.

12 G. R. Krow and S. Szczepanski, *Tetrahedron Lett.*, 1980, 4593.

13 M. Nakazaki and K. Naemura, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 532.

14 F. Tiemann, *Chem. Ber.*, 1895, **28**, 2168.

15 For a review on nitrogen insertions of bridged bicyclic ketones, see G. R. Krow, *Tetrahedron*, 1981, **37**, 1283.