Tetrahedron Letters,Vol.30,No.27,pp 3577-3578,1989 0040-4039/89 \$3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

SYNTHESIS OF 2,8-DIDEHYDRO-9-NORADAMANTANONE

Marija Šindler-Kulyk[‡], Zdenko Majerski[†],
Dražen Pavlović and Kata Mlinarić-Majerski*

Ruder Bošković Institute, 41000 Zagreb, Croatia, Yugoslavia
[‡]Organic Chemistry Department, Faculty of Technology, Zagreb

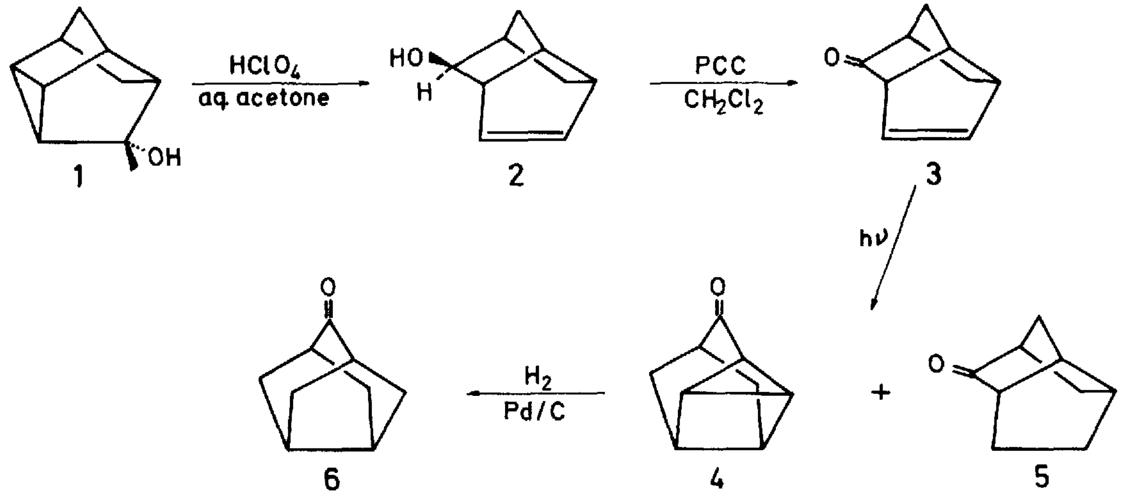
Summary: Hitherto unknown 2,8-didehydro-9-noradamantanone (**4**) has been synthesized involving oxa-di-π-methane photorearrangement of 4-brenden-2-one (**3**) as a key step.

In the course of our studies in the chemistry and properties of the noradamantane system[1,2] we were prompted to prepare the so far unknown, novel 2,8-didehydronoradamantane skeleton. Previous attempts at the preparation of this strained cage systems were all unsuccessful. Pyrolysis of the sodium salt of the p-toluensulfonylhydrazone of 2-noradamantanone[3], 2-noradamantyl mesylates[4] as well as dehydrochlorination of noradamantyl chloride derivative[5] gave the least strained hydrocarbons, triaxanes. No formation of 2,8-didehydronoradamantane was observed. Moreover, our attempts to get the olefin-cycloaddition product by 2,8-ring closure in the noradamantane derivative resulted instead in γ-CH bond insertion giving the 2,4-didehydronoradamantane derivative[2].

Therefore, we focused our efforts on photochemical transformation[6] of cyclic unsaturated β,γ-ketones, which might result in the formation of cyclopropyl ketone structures[7], and choose 4-brenden-2-one (**3**) as a starting material. 4-Brenden-2-one (**3**)[8] was readily prepared from 2,4-didehydro-5-endo-hydroxybrendane (**1**). Treatment of **1**, obtained by $LiAlH_4$ reduction of tetracyclo$[4.3.0.0^{2,9}.0^{4,8}]$nonan-3-one[9], with a catalytic amount of perchloric acid in 80% aqueous acetone[10] at 40°C for 40 h gave 4-brenden-2-ol (**2**) in 80% yield [νO-H 3420, ν=C-H 3050 cm^{-1}; δ($CDCl_3$) 5.95 (br,s, 2H olefinic), 3,4 (s, 1H)]. Oxidation of tricyclic alcohol **2** with PCC in dichloromethane provided ketone **3** in 40% yield [ν=C-H 3050, νC=O 1740 cm^{-1}; δ($CDCl_3$) 6.2 (m, 1H olefinic), 5,8 (m, 1H olefinic), 3.4 (m, 1H), 2.6-2.8 (m, 3H), 1.5-2.1 (m, 4H)]. Irradiation of an acetone solution (0.03 M) of **3** through a Pyrex filter with a high pressure mercury lamp (400 W) affords **4** and **5** in a 4:1 ratio along with some unidentified high molecular weight material. The products were isolated in 25% (**4**) and 7% (**5**) yield, respectively, by column chromatography on silica gel using 0→10% ether-pentane as eluent and identified by spectroscopic means. The spectral data of the minor product (**5**) were in full agreement with the known 2-brendanone[9]. The major photoproduct was identified as the desired 2,8-didehydro-9-noradamantanone (**4**)[11]. Moreover, the structure of **4** was confirmed

---

[†] Prof. Dr. Z. Majerski deceased August 28, 1988.



by hydrogenolysis to ketone **6**, which was found to be identical with an authentic sample of 9-noradamantanone (**6**)[12].

We are continuing to explore the chemistry of 2,8-didehydro-9-noradamantanone (**4**).

Acknowledgment: This research was supported by a Grant from the Research Council of the Republic of Croatia and by the U.S.-Yugoslav Joint Fund for Scientific and Technological Cooperation with the NSF under Grant JF-832.

References and Notes

1. Majerski, Z.; Hameršak, Z. J. Org. Chem. **1984**, 49, 1182, and the references cited therein.
2. Majerski, Z.; Hameršak, Z.; Mlinarić-Majerski, K. J. Chem. Soc., Chem. Commun. **1985**, 1830; Majerski, Z.; Hameršak, Z.; Šarac-Arneri, R. J. Org. Chem. **1988**, 53, 5053.
3. Nickon, A.; Pandit, G.D. Tetrahedron Lett. **1968**, 3663.
4. Farcasiu, D.; Slutsky, J.; Schleyer, P.v.R.; Overton, K.H.; Luk, K.; Stothers, J.B. Tetrahedron **1977**, 33, 3269.
5. Nickon, A.; Simons, J.R.; Ho, B. J. Org. Chem. **1977**, 42, 800.
6. For reviews on these photorearrangements see: Hixon, S.S.; Mariano, P.S.; Zimmerman, H.E. Chem. Rev. **1973**, 73, 531; Houk, K.N. ibid. **1976**, 76, 1; Schuster, D.I. in "Rearrangements in ground and excited states", P. de Mayo, Ed., Academic Press, New York, **1980**, p. 167.
7. Similar oxa-di-π-methane rearrangement was observed in 2-protoadamantenone (Ref. 10).
8. Satisfactory elemental analyses and mass spectra have been obtained for all new compounds (2, 3, and 4).
9. Nickon, A.; Kwasnik, H.R.; Mathew, C.T.; Swartz, T.D.; Williams, R.O.; DiGiorgio, J.B. J. Org. Chem. **1978**, 43, 3904.
10. According to: Murray, Jr. R.K.; Babiak, K.A. Tetrahedron Lett., **1974**, 319; Murray, Jr. R.K.; Morgan, T.K.; Babiak, K.A. J. Org. Chem. **1975**, 40, 1079.
11. Spectral data of **4**: IR (film): ν3035, 2950, 2920, 2850, 1695 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS): δ3.0 (br.s, 2H), 2.6-2.8 (m, 1H), 2.4-2.6 (m, 2H), 1.4-2.2 (m, 5H); ^{13}C NMR (CDCl$_3$, TMS): δ 211.3 (s), 51.8 (d), 38.2 (t, 2C), 34.1 (d, 2C, J=148 Hz), 31.6 (d, 2C, J=184 Hz), 26.4 (d, J=167 Hz).
12. For the synthesis of 9-noradamantanone see: Vegar, M.R.; Wells, R.J. Tetrahedron Lett. **1969**, 2565.; Gravel, D.; Rahal, S. Can. J. Chem. **1975**, 53, 2671.

(Received in UK 25 May 1989)