Tetrahedron Letters No.40, pp. 3517-3520, 1969. Pergamon Press. Printed in Great Britain.

THE BECKMANN REARRANGEMENT OF ADAMANTANONE OXIME

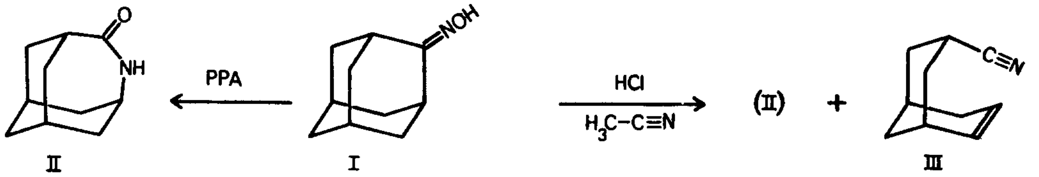
J.G.Korsloot[x] and V.G.Keizer

N.V.Philips-Duphar Research Laboratories, Weesp, The Netherlands

(Received in UK 23 July 1969; accepted for publication 4 August 1969)

Recently Sasaki et al.[1] described the reaction of adamantanone with sodium azide in methanesulphonic acid. Instead of the expected 4-azatricyclo-$[4.3.1.1^{3,8}]$undecan-5-one, these authors obtained as the main product 4-methylsulphonyloxyadamantan-2-one, attributed to a direct substitution of the adamantanone. These results now prompt us to report our findings on the Beckmann rearrangement[2,3] of adamantanone oxime (I) under various conditions. Treatment of (I) with polyphosphoric acid (PPA) yielded 4-azatricyclo-$[4.3.1.1^{3,8}]$undecan-5-one (II) in 57%, as was shown recently[4]. When the rearrangement was carried out with HCl in $CH_3C{\equiv}N$[5], a 40% yield of (II) was obtained. In addition a second product, mp. 176.5 - 181.5°C (dec.) was isolated, characterized as bicyclo [3.3.1]non-6-ene-3-carbonitrile (III)[6] (yield 35%). This nitrile is not obtained after the reaction of (I) with PPA. These reactions are shown in Scheme I.

Scheme I

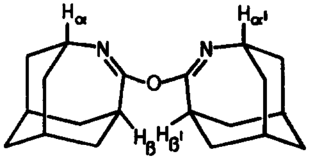


The structure of (III) was assigned on the basis of its spectral properties[7]. (IR: 2230 (C≡N) and 3020 (=C-H) cm^{-1}; NMR ($CDCl_3$): δ 6.20 - 5.74 (m, 2H, HC=CH), 2.96 (tt, J=5.8 Hz, 2.5 Hz, 1H, HC-C≡N) and δ 2.66 - 1.40 (m, 10H, rest of the bicyclononene protons)). The formation of (III) must be due to "Beckmann fission"[3,8] of adamantanone oxime.

---

[x] Abstracted in part from the forthcoming thesis of J.G.Korsloot, University of Groningen, 1969.

The influence of the catalyst employed may be further illustrated by the reaction of (I) with PCl_5 in ether or with p-toluenesulphonyl chloride in DMF. Unexpectedly, PCl_5, prone to give Beckmann fission[2,3], gave the best yield of (II) (82%). Treatment of (I) with p-toluenesulphonyl chloride in DMF[9] afforded the dimer (IV), mp. 180-185°C (dec.), in 80% yield. The structure of (IV) was based on the analytical and spectral data.

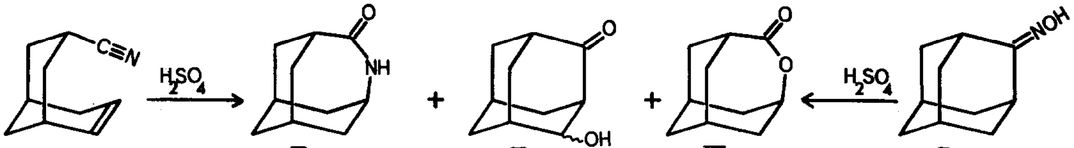


IV

(IR: 1670 and 1630 (C=N) and 1196 (C-O-C) cm^{-1}; NMR ($CDCl_3$): δ 3.30 (m, 2H, $H_\alpha + H_{\alpha'}$), 2.66 (m, 2H, $H_\beta + H_{\beta'}$) and δ 2.20 - 1.70 (m, 24H, rest of the tricycloundecyl protons); mass of the molecular ion: found 312.220; calc. for $C_{20}H_{28}N_2O$ 312.220).

To increase the yield of (II) from the reaction with HCl in $CH_3C{\equiv}N$, we tried a Ritter reaction[10] with (III). However, after a reaction in 96% H_2SO_4 (30 min. at 20°C), only a minor quantity of (II) (1-2%) was detected by GLC. The main product (yield 77%) was shown to be 4-hydroxyadamantan-2-one (V)[11,12] (obtained after acid hydrolysis of its sulphuric acid ester). This hydroxyadamantanone is a useful starting material for the synthesis of 2,4-disubstituted adamantanes[13]. In addition the lactone (VI)[12] was formed (yield 5.4%). This reaction is shown in Scheme II.

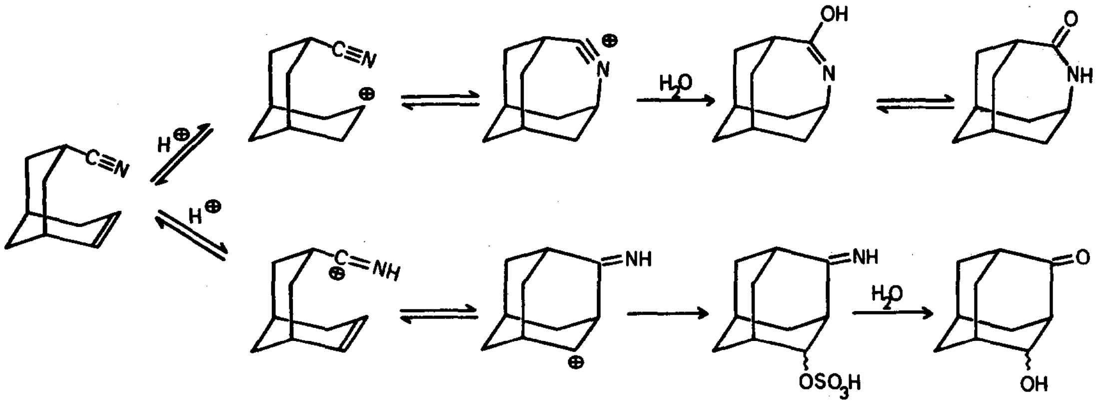
Scheme II



III II V VI I

A reasonable explanation for the formation of (II) and (V) is given in Scheme III. A similar fragmentation and recombination to an iminocarbonium ion in the Beckmann rearrangement has been reported by Hill et al.[8]. The formation of lactones from unsaturated nitriles in 96% H_2SO_4 has been described by Fox and Reboulet[14].

Scheme III



These results urged us to use H_2SO_4 in the Beckmann rearrangement of (I). A treatment with 96% H_2SO_4 (4 hrs. at 20°C) gave the same products as a treatment of (III) with this reagent, with only changed proportions of the quantities of the products isolated (Scheme II). The composition of the isolated mixture was (II) 32%, (V) 56% and (VI) $<1\%$. These results can be explained by a fragmentation reaction of the oxime to the unsaturated nitrile (III), followed by an in situ recombination as shown in Scheme II. This fragmentation reaction competes with a normal Beckmann rearrangement to the lactam (II). A comparison of the yields of the lactam from the nitrile and from the oxime in 96% H_2SO_4 shows that in the last reaction most of the lactam must be formed via a normal Beckmann rearrangement.

Additional evidence for the proposed mechanism of the formation of a 2,4-disubstituted adamantane from adamantanone oxime is provided by a reaction in 30% H_2SO_4 (30 min. at 110°C). The supposed intermediate, the nitrile (III), was shown to be present in considerable amount among the isolated reaction products.

In our opinion the same explanation as given for our findings holds for the results obtained by Sasaki et al., viz. formation of a nitrilium ion[15], followed by fragmentation and recombination, yielding an iminocarbonium ion which reacts to form a methanesulphonic acid ester. This, also, readily explains the need to use sodium azide, the exclusive attack at the 4-position, and the failure with adamantane in the reaction described by Sasaki, facts that can not satisfactorily be explained by a direct substitution mechanism.

Acknowledgement.

We gratefully acknowledge the co-operation of Mr. W.J.Th.Brugman, Mr. F.W. van Deursen, Dr. P.K.Korver and co-workers of the analytical department.

References.

1. T.Sasaki, S.Eguchi and T.Toru, J.Am.Chem.Soc., 91, 3390 (1969).
2. cf. L.G.Donaruma and W.Z.Heldt, Org.Reactions, 11, 1 (1960).
3. cf. P.A.S.Smith, "Molecular Rearrangements", Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, 1963, p.483.
4. J.G.Korsloot, V.G.Keizer and J.L.M.A.Schlatmann, Rec.Trav.Chim., 88, 447 (1969).
5. Stamicarbon, Dutch Pat.Appl. 64.12746.
6. All compounds had satisfactory elemental analyses and mass spectra consistent with the structures assigned to them.
7. NMR spectra were recorded on a Varian HA 100 spectrometer. Chemical shifts are expressed in ppm. TMS was used as an internal standard. IR spectra were measured in KBr on a Perkin Elmer Model 337.
8. R.K.Hill, R.T.Conley and O.T.Chortyk, J.Am.Chem.Soc., 87, 5646 (1965).
9. F.Kohen, Chem. & Ind., 1378 (1966).
10. J.J.Ritter and P.P.Minieri, J.Am.Chem.Soc., 70, 4045 (1948).
11. A mixture of both possible isomers was obtained.
12. The spectral data of this compound were identical with those reported: A.C.Udding, Thesis University of Groningen, The Netherlands, 1968.
13. N.V.Philips Gloeilampenfabrieken, Dutch Pat. Appl. 69.04911.
14. B.L.Fox and J.E.Reboulet, J.Org.Chem., 33, 3639 (1968).
15. The Schmidt reaction is supposed to proceed via the same intermediate as the Beckmann rearrangement[3,16].
16. cf. J.Hine, "Physical Organic Chemistry", McGraw-Hill Book Company, Inc., New York, 1956, p.319.