to Westman and Nordmark [3]) or both cannot be decided at the present stage.

Samples quenched from temperatures 800°C–400°C in the composition range $x = 0.90$ to 1.05 show strong diffuse scattering; two types of pattern have been noted.

The authors are indebted to Dr. P. Kofstad and his colleagues at the Central Institute of Industrial Research for use of their equipment and for advice in preparing the samples. Financial support from the *Royal Norwegian Council for Scientific and Industrial Research* is gratefully acknowledged.

1. Schönberg, N. *Acta Chem. Scand.* **8** (1954) 221.
2. Andersson, G. *Acta Chem. Scand.* **8** (1954) 1599.
3. Westman, S. and Nordmark, C. *Acta Chem. Scand.* **14** (1960) 465.
4. Stenström, G. and Westman, S. *Acta Chem. Scand.* **22** (1968) 1712.
5. Koch, F. and Cohen, J. B. *Acta Cryst.* **B 25** (1969) 275.

Received June 5, 1970.

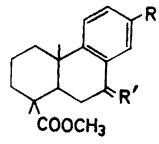
The Beckmann Rearrangement of the Oxime of 7-Ketodehydroabietate. A Side Reaction

HOLGER ERDTMAN and LENNART MALMBORG

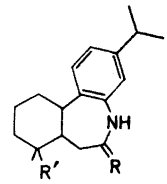
Division of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

Dedicated to Professor K. Mothes on his 70th birthday

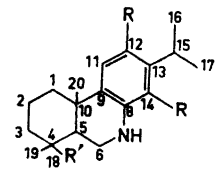
Controlled oxidation of methyl dehydroabietate with chromic acid [1] gave methyl 7-ketodehydroabietate (*1*, R=ipr, R′=O) in about 75 % yield. Prolonged oxidation yielded increasing amounts of the diketone *1* (R=$COCH_3$, R′=O). When subjected to Beckmann rearrangement (polyphosphoric acid) the oxime of ketone *1* (R=ipr, R′=O) furnished the expected lactam (*2*, R=O, R′=$COOCH_3$), $C_{21}H_{29}NO_3$. In addition, a weak base, $C_{20}H_{29}NO_2$, was formed, the spectral data of which indicated structure *3* (R=H, R′=$COOCH_3$). This base exhibited a characteristic colour reaction with $SbCl_5$.



1



2



3

The unexpected formation of this base indicates that, in studies of Beckmann rearrangement, it may sometimes be worth-while looking not only for the normal amides but also for basic reaction products.

Experimental. Methyl dehydroabietate (10 g) in acetic acid (5.5 g) was added dropwise at 50° with stirring to chromic acid (5 g) in 75 % acetic acid (15 g). After 10 h at 20° an equal amount of chromic acid solution was added and the mixture heated to 90–100°. At intervals samples were examined by gas chromatography. The heating was continued until almost all the methyl dehydroabietate had disappeared (about 3 h). The reaction products were isolated and separated on silica gel. Light petroleum:benzene (4:1) eluted the unchanged starting material and the methyl 7-ketodehydroabietate was obtained from the benzene:ether (9:1) fraction as an oil which slowly crystallized. Recrystallization from light petroleum gave crystals melting at 66–67.5° (Lit.[1] m.p. 67–68°), yield 75 %. Pure ether eluted the diketone *1* (R=$COCH_3$, R′=O), m.p. 145–145.5°, $[\alpha]_D$ 29.3° ($CHCl_3$, $c=1.6$). Lit.[1] m.p. 144–145°, $[\alpha]_D$ 30.8° ($CHCl_3$).

The oxime of methyl 7-ketodehydroabietate was prepared in the usual way and purified by chromatography on silica (benzene:ether, 9:1). From isooctane crystals were obtained, melting at 127.5–129°, $[\alpha]_D$ −49.3° ($CHCl_3$, $c=0.9$).

The oxime (6.5 g) and polyphosphoric acid (150 g) were heated to 130° for 10 min with stirring. After cooling the reaction mixture was diluted and subsequently extracted several times with ether. (Ether solution=A). Reesterification of the partially hydrolyzed reaction product was effected with diazomethane. Examination by TLC now indicated the presence of two main constituents. The reaction product was submitted to column chromatography on silica gel. The crude base *3* (R=H, R′=$COOCH_3$) (about 1 g) was eluted with light petroleum:ether (9:1). It was recrystallized twice from dilute methanol and sublimed at 95° under reduced pressure. Yield 0.5 g. M.p. 108−109°, $[\alpha]_D$ 3.3° ($CHCl_3$, c=1.3). (Found: C 76.2; H 9.2; N 4.4; m.w. 315, determined by MS. Calc. for $C_{20}H_{29}NO_2$: C 76.15; H 9.3; N 4.4; m.w. 315). IR 3390 cm^{-1} (NH) and 1720 cm^{-1}. No peak at about 1700 cm^{-1}. λ_{max}(EtOH) 253, 305 nm (ε 12 600, 3900). NMR: signals at (δ ppm from internal standard TMS in $CDCl_3$) δ 1.18 (6 H, doublet, J 7 cps), C(16) H_3 and C(17) H_3; δ 1.11 and 1.32 (singlets, each 3 H), C(20) H_3 and C(19) H_3; complex unresolved multiplet centered at δ 1.52 (7 H), C(1) H_2, C(2) H_2, C(3) H_2 and C(5) H; δ 2.18 (2 H, multiplet), C(6) H_2; δ 2.75 (1 H, septet, J 7 cps), C(15) H; δ 3.60 (3 H, singlet), C(18) $COOCH_3$; δ 6.24 (1 H, doublet, J 2 cps), C(14) H; δ 6.43 (1 H, quartet, J 8 and 2 cps), C(12) H; δ 6.92 (1 H, doublet, J 8 cps), C(11) H. On TLC plates sprayed with $SbCl_5$ in $CHCl_3$ this base gave a characteristic, initially weak reddish violet spot which gradually became intense.

For complete extraction of the base from ether solutions strong acids were required (20 % H_2SO_4 or HCl) and for complete *N*-acetylation heating with acetic anhydride and pyridine for *ca.* 10 h at 100° was needed. The *acetyl derivative* melted at 112−113.5°. $[\alpha]_D$ 154° ($CHCl_3$, c=1.0). λ_{max}(EtOH) 258 nm (ε 11 400). (Found: C 74.2; H 8.8; N 3.8. Calc. for $C_{22}H_{31}NO_3$: C 73.9; H 8.7; N 3.9).

At room temperature the base readily gave a *dinitro derivative*, formulated as *3* (R=NO_2, R′=$COOCH_3$) with nitric acid in acetic acid. Crystals, m.p. 100−101.5°, $[\alpha]_D$ −53.9° ($CHCl_3$, c=0.7). λ_{max}(EtOH) 243, 375 nm (ε 8800, 8300). (Found: C 59.0; H 6.7; N 10.1. Calc. for $C_{20}H_{27}N_3O_6$: C 59.2; H 6.7; N 10.4).

A second fraction was eluted with ether to give lactam *2* (R=O, R′=$COOCH_3$), which crystallized on trituration with light petroleum. Recrystallization from isooctane and sublimation under reduced pressure gave pure lactam, melting at 150−151°, $[\alpha]_D$ −191° ($CHCl_3$, c=0.8). λ_{max}(EtOH) 245 nm (ε 12 200). (Compare acetanilide: 240 and benzamide: 285 nm). (Found: C 73.5; H 8.5; N 3.9; m.w. 343 [MS]. Calc. for $C_{21}H_{29}NO_3$: C 73.4; H 8.5; N 4.1; m.w. 343).

When the lactam *2* (R=O, R′=$COOCH_3$) was treated in the same way as the oxime of methyl 7-ketodehydroabietate with polyphosphoric acid or, less advantageously, with conc. sulphuric acid, the presence of base *3* (R=H, R′=$COOCH_3$) in the reaction mixture could be demonstrated by spraying the TLC plates with $SbCl_5$.

The lactam *2* (R=O, R′=$COOCH_3$) was reduced with $LiAlH_4$ in the usual way to the aminoalcohol *2* (R=H_2, R′=CH_2OH). This compound was chromatographed on silica gel and recrystallized from light petroleum. M.p. 104−109°. $[\alpha]_D$ −30° ($CHCl_3$, c=0.8). λ_{max} (EtOH) 245, 287 nm (ε 7100, 2200). (Found: C 79.8; H 10.6; N 4.3. Calc. for $C_{20}H_{31}NO$: C 79.7; H 10.4; N 4.65).

From the above ether fraction A, alkali removed the amino acid *3* (R=H, R′=COOH). It was sublimed under reduced pressure at 150° to give crystals, melting at 194−195°. (Found: C 75.7; H 9.0. Calc. for $C_{19}H_{27}NO_2$: C 75.7; H 9.0).

Acknowledgements. We thank Svenska Malros AB, Borås, for financial support and Dr. D. Donnelly, Dublin, for improving the English of our manuscript.

1. Ritchie, P. F., Sanderson, T. F. and McBurney, L. F. *J. Am. Chem. Soc.* **76** (1954) 723.

Received July 6, 1970.

Spin Trapping of the Radicals Formed by γ-Irradiation of Sodium Phosphite in the Solid State

GÖRAN ADEVIK and CARL LAGERCRANTZ

Department of Medical Physics, University of Göteborg, S-400 33 Göteborg 33, Sweden

The nitroxide method for trapping short-lived free radicals has now been applied to a large number of reactions.[1-11] The es-