Tetrahedron Letters,Vol.30,No.38,pp 5119-5120,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

FORMATION OF NITRONES FROM TERTIARY NITROALKANES

Walter Huggenberg and Manfred Hesse*
Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

Summary: In the presence of KOtBu/THF the nitroesters **5** - **8** cyclize to the nitrones **9** - **12**.

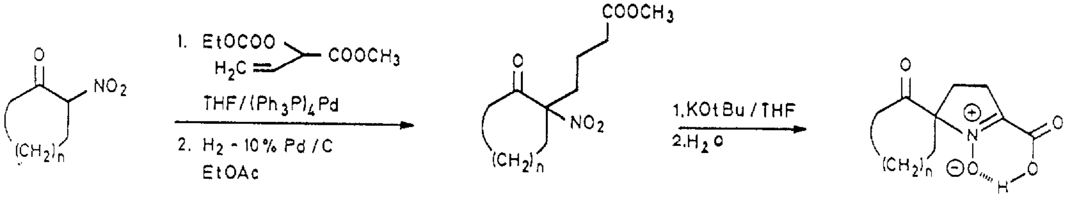
The aim of this investigation was to prepare ring enlarged carbocyclic compounds. Starting with the nitroesters **5** - **8** it was expected[1] to get expansions by three carbon atoms. The nitroesters **5** - **8** were formed by alkylation of the 2-nitrocycloalkanones[2] **1** - **4** with ethyl (1-methoxycarbonylprop-2-enyl)carbonate[3] in the presence of $(Ph_3P)_4Pd$ in THF[5] followed by the hydrogenation (H_2/10% Pd-C) with yields: **5** (76%), **6** (89%), **7** (88%), **8** (98%)[6]. Main experiments were done with the twelve-membered ring compound **8**. Without success was its treatment with Bu_4NF and with lithium 2,2,6,6-tetramethylpiperidineamide, both in THF (main component: **8**). The treatment of **8** with KOtBu in THF gave the nitrone **12**, (67%). The structure elucidation was done by X-ray analysis[7]. The analogues **9**, **10**[7], and **11** were prepared too, (see Table).

By crystallization of the chromatographical pure products partly decomposition occurred, which lead to significant lower yields of the pure products given in the Table. The eight-membered **11** could not be isolated in pure form, it was registered in an unseparated mixture with other products. - The lower homologues of **5** - **8** with a C_3-side chain do not form nitrones.

The nitrone formation is explained by a nucleophilic attack of the carbanion in α-position to the ester group at the nitrogen atom [8], followed by loss of water. It is not clear whether the ester hydrolysis happened during the ring closure or by the work up.

The formation of nitrones from tertiary nitroalkanes seems to be a hitherto unknown process[9].

Acknowledgement. The support of this work by the Schweizerischer Nationalfonds is gratefully acknowledged.



1	n = 4	**5**	**9**
2	n = 5	**6**	**10**
3	n = 6	**7**	**11**
4	n = 10	**8**	**12**

	Yield [%]		m.p.	IR ($CHCl_3$) [cm^{-1}]		^{13}C-NMR[c] ($CDCl_3$)		CIMS[d] m/z (rel.%)		e)
				C=O	C=N	C=O COOH	C=N C-N	$[M+1]^+$	$[M-CO_2+1]^+$	
9	(48)[a] 28	$C_{10}H_{13}NO_4$	140.9–141.6°[b]	1740 1728	1558	201.5 159.4	140.2 88.0	212 (5)	168 (27)	355 (100)
10	(38)[a] 20	$C_{11}H_{15}NO_4$	95.5–97.0°[b]	1743 1722	1555	204.5 159.4	139.9 88.8	226 (27)	182 (100)	363 (52)
12	(93)[a] 67	$C_{16}H_{25}NO_4$	141.0–141.6°	1745 1720	1547	202.3 159.4	139.3 90.4	296 (3)	252 (100)	503 (49)

[a] in (): yield of the crude product, t.l.c. pure.
[b] m.p. under decomposition.
[c] chemical shifts in $CDCl_3$
[d] Varian MAT 112S, isopropane.
[e] $[2(M-CO_2)+1]^+$

References and Notes

Part of the PhD Thesis of W.H., University of Zürich.

1 Y. Nakashita, M. Hesse, *Helv. Chim. Acta* **1983**, *66*, 845; H. Stach, M. Hesse, *Tetrahedron* **1988**, *44* 1573.

2 R. Fischer, H. Weitz, *Synthesis* **1980**, 261.

3 Ethyl (1-methoxycarbonylprop-2-enyl)carbonate from methyl 2-hydroxy-3-butenoate with ethyl carbonochloridate[4,5].

4 R. Palm, H. Ohse, H. Cherdron, *Angew. Chem.* **1966**, *78*, 1093, Int.Ed. Engl.**1966**, 5, 994; A.R. Katritzky, J.M. Lagowski, *The Chemistry of the Heterocyclic N-Oxides*, in A.T. Blomquist, *Organic Chemistry, A Series of Monographs*, Academic Press, London, **1971**, 120.

5 V.I. Ognyanov, M. Hesse, *Synthesis* **1985**, 645.

6 The compounds **1** - **8** were completely characterized by IR, ^{1}H- and ^{13}C-NMR, CIMS, and combustion analysis.

7 We are indepted to Dr. R. Prewo for X-ray analysis.

8 Reactions of this type are known by attack of carbanions to nitrate and nitrite ester: H. Feuer, P.M. Pivawer, *J.Org.Chem.* **1966**, *31*, 3152; H.O. House, *Modern Synthetic Reactions*, 2nd Ed.,Benjamin, Menlo Park CA, 1972, p. 754, and the Kröhnke reaction in which aromatic nitroso and active methylene compounds react with each other[9].

9 K.B.G. Torssell, *Nitrile Oxides, Nitrones, and Nitronates in Organic Syntheses. Novel Strategies in Synthesis*. VCH Verlagsgesellschaft, Weinheim 1988.

(Received in Germany 29 June 1989)