ACTA CHEMICA SCANDINAVICA 27 (1973) 271–275

Seven-membered Heterocyclic Rings

III. Thermolysis and Hydrolysis of 2,4,5,7-Tetraphenyl-1,3-oxazepine. Pyrrole Formation[1]

CHRISTIAN L. PEDERSEN and OLE BUCHARDT

Chemical Laboratory II, University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

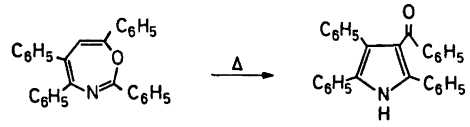
The thermolysis of 2,4,5,7-tetraphenyl-1,3-oxazepine (I) results in an almost quantitative rearrangement to 2,4,5-triphenyl-3-benzoylpyrrole (II), whereas acid hydrolysis leads to II, *N*-benzoyl-2,3,5-triphenylpyrrole (III), 2,3,5-triphenylpyrrole (IV), and 1,2,4-triphenyl-1,4-butanedione (V). Hydrolysis under basic conditions gives compounds II and V.

The chemistry of seven-membered rings has been the subject of an increasing number of investigations,[2] and this has led to the observation of many novel and interesting reactions.

We therefore found it of interest to examine some of the chemistry of the new heterocyclic system 1,3-oxazepine. Compounds containing this system can be obtained in high chemical yield ($\sim 70-90$ %) as well as high quantum yield ($\sim 10-20$ %) from pyridine *N*-oxides upon irradiation,[3,4] but appear only to be stable when they are highly substituted with phenyl [3,4] or cyano [5] groups. Thus we decided to concentrate our studies on 2,4,5,7-tetraphenyl-1,3-oxazepine (I).

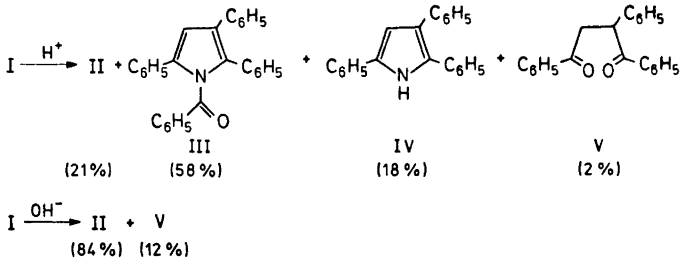
RESULTS

2,4,5,7-Tetraphenyl-1,3-oxazepine upon heating to 240°C in the pure state rearranged in almost quantitative yield to give an isomeric product which was identified as 2,4,5-triphenyl-3-benzoylpyrrole (II).



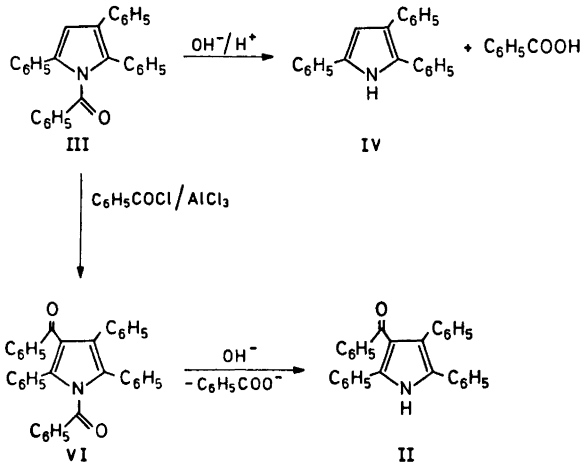
I II

Acid hydrolysis of I in aqueous ethanol gave a mixture of four compounds, which were identified as 2,4,5-triphenyl-3-benzoylpyrrole (II), *N*-benzoyl-2, 3,5-triphenylpyrrole (III), 2,3,5-triphenylpyrrole (IV), and 1,2,4-triphenyl-1, 4-butanedione (V), whereas basic hydrolysis in aqueous ethanol gave a mixture of II and V.



IDENTIFICATION OF PRODUCTS

Compounds II – V all showed the expected spectral characteristics (Table 1), but the spectra do not permit their identification. However, compound IV and V were shown to be identical (IR, mixed m.p.) with authentic samples.[6,7] The remaining compounds were identified by the following chemical reactions.



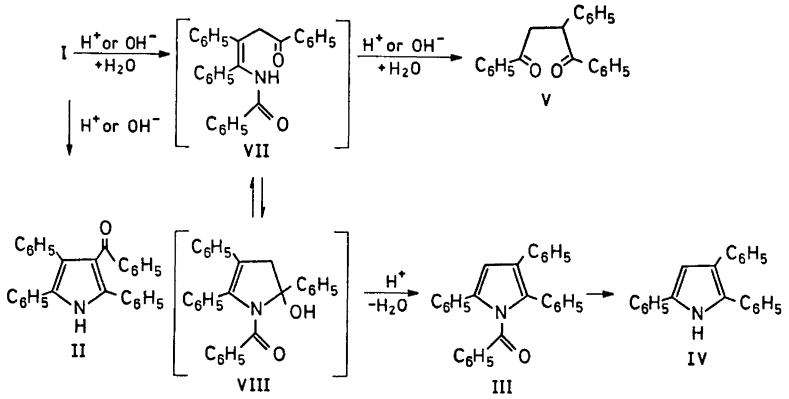
Mild basic hydrolysis of compound III gives in almost quantitative yield 2,3,5-triphenylpyrrole (IV) and benzoic acid. The *N*-benzoyltriphenylpyrrole (III) could be converted to 2,4,5-triphenyl-3-benzoylpyrrole (II) by treatment with benzoyl chloride and aluminium chloride followed by hydrolysis of the product (VI).*

*In view of the mild conditions under which these reactions were performed, it seems unlikely that any rearrangements could occur. The chemistry combined with the spectroscopy is regarded as ample evidence for the structural identifications.

A kinetic study of the rearrangement of I to II in nitrobenzene-d_5, using NMR spectroscopy, showed that the reaction was first order with a rate constant of 4.6×10^{-4} sec^{-1} at 204°C.

DISCUSSION

By analogy with what was proposed for the related reaction of benz[d] [1,3]-oxazepines [8] we suggest that the thermal rearrangement of compound I may be concerted. The formation of compound II in the hydrolytic experiments was shown to be acid or base catalyzed and not due to the thermal rearrangement. The reaction under acid conditions to give compounds III, IV, and V is believed to be due to hydrolysis of the oxazepine (I). The latter can be formulated as an imidoester of an enol which is expected to hydrolyze to give compound VII, which can react as shown in the scheme below. Again these reactions are analogous to what has been found for benz[d] [1,3]oxazepines;[9-11] however, for the latter compounds intermediates analogous to VII and VIII could be isolated and characterized.



The difference in product distribution in the experiments under acid and basic conditions is presumably due to acid catalysis of the dehydration of VIII.

EXPERIMENTAL

Microanalysis were performed in the microanalysis department of this laboratory.

Melting points (uncorr.) were determined on a Reichert melting point microscope.

Infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Ultraviolet spectra were recorded on a Unicam SP 1800 Ultraviolet spectrophotometer.

Nuclear magnetic resonance spectra were recorded on a Varian A60A spectrometer.

Preparative layer chromatography (PLC) was performed using 20×100 cm plates with a 2.5 mm thick layer of silica gel (Merck $PF_{254+366}$). The plates were developed 2 – 3 times. The fractions were isolated by continuous extraction with chloroform in a Soxhlet apparatus.

Thermolysis of 2,4,5,7-tetraphenyl-1,3-oxazepine (I). Compound I (1.00 g) was thermolyzed without solvent at 240°C for 12 min. After cooling the melt was dissolved in benzene,

Table 1. Characteristic IR and UV absorptions, and NMR spectra of compounds II, III, and VI.

	UV						IR (in KBr)	NMR[a] (in $CDCl_3$)	
	λ_{max} nm	log ε	λ_{max} nm	log ε	λ_{max} nm	log ε	cm^{-1}	aromatic τ	other τ
II[b]	207	4.57	243	4.35	283	4.32	3270 (N−H), 1625 (C=O)	2.23−3.15 (20 H)	1.42 (1 H) broad[d]
III[b]	206	4.55	257	4.41	273sh	4.36	1710 (C=O)	2.42−3.03 (20 H)	3.38 (1 H)
VI[c]	210	4.73	259	4.63	280	4.46	1705, 1656 (C=O)	2.23−3.20	

[a] Spectra recorded at 60 MHz with tetramethylsilane as interna l reference. Relative intensities are given in parantheses. [b] Absolute ethanol. [c] 96 % ethanol. [d] Singlet disappeared by shaking with D_2O.

and petroleum ether was added until crystallization began. After cooling the crystals were isolated by filtration (0.96 g, ~96 %). (Found: C 87.50; H 5.67; N 2.90. Calc. for $C_{29}H_{21}NO$: C 87.19; H 5.30; N 3.51.) M.p. 200–201° from benzene/petroleum ether.

Acid catalyzed hydrolysis of I. Compound I (1.003 g) was dissolved in ethanol (100 ml, 96 %) and hydrochloric acid (10 ml, 2 N) was added. The mixture was refluxed for 75 min. After cooling *N*-benzoyl-2,3,5-triphenylpyrrole (III) crystallized out. After filtration of the crystals (551 mg), the mother liquor was separated by PLC (developant, benzene/petroleum ether 1:1) into 2,3,5-triphenylpyrrole (IV) (131 mg, ~18 %), *N*-benzoyl-2,3,5-triphenylpyrrole (III) (28 mg, total yield 58 %). (Found: C 87.30; H 5.30; N 3.29. Calc. for $C_{29}H_{21}NO$: C 87.19, H 5.30; N 3.51.) M.p. 154–155° from hexane), 1,2,4-triphenyl-1,4-butanedione (V) (19 mg ~2 %), and 3-benzoyl-2,4,5-triphenylpyrrole (II) (212 mg, ~21 %).

Base catalyzed hydrolysis of I. Compound I (501 mg) was dissolved in ethanol (50 ml, 96 %) and sodium hydroxide (5 ml, 2 N) was added. The mixture was refluxed for 42 h. After evaporation the residue was separated by PLC (developant, toluene/petroleum ether/acetone 7:7:1) into 1,2,4-triphenyl-1,4-butanedione (V) (46 mg, ~12 %) and 3-benzoyl-2,4,5-triphenylpyrrole (II) (422 mg, ~84 %).

Basic hydrolysis of III. Compound III (132 mg) was dissolved in ethanol (25 ml, 96 %) and sodium hydroxide (2 ml, 2 N) was added. The mixture was refluxed for 25 h and evaporated to dryness. Extraction with chloroform followed by evaporation gave 2,3,5-triphenylpyrrole (IV) (97 mg, ~99 %). The residue was acidified with dilute hydrochloric acid and extracted with chloroform. The extract after evaporation yielded benzoic acid.

Benzoylation of III. Compound III (1.00 g) was dissolved in carbon disulfide (20 ml). Benzoyl chloride (0.37 g) and aluminium chloride (1.00 g) were added. The mixture was stirred at room temperature for 14 h and refluxed on a steam bath for 3 h. The reaction mixture was poured on ice and hydrochloric acid, and extracted twice with chloroform. The extract was separated by PLC (developant, toluene/petroleum ether/acetone 7:7:1) into starting material (458 mg) and 1,3-dibenzoyl-2,4,5-triphenylpyrrole (VI) (586 mg, ~86 %, calculated from reacted starting material). (Found: C 85.86; H 5.31; N 2.59. Calc. for $C_{36}H_{25}NO_2$: C 85.86; H 5.00; N 2.78.) M.p. 177–178° from benzene/petroleum ether.

Basic hydrolysis of VI. Compound VI (100 mg) was dissolved in ethanol (10 ml, 96 %) and sodium hydroxide (1 ml, 2 N) was added. The mixture was refluxed for 40 min and evaporated to dryness. Extraction with chloroform gave 3-benzoyl-2,4,5-triphenylpyrrole (III) (78 mg, ~99 %).

REFERENCES

1. For the previous paper in this series, see Svanholm, U. *Acta Chem. Scand.* **25** (1971) 640.
2. *Ann. Repts. on Progr. Chem. (Chem. Soc. London)* **66** (1969) 460; **67** (1970) 460; Spence, G. G., Taylor, E. C. and Buchardt, O. *Chem. Rev.* **70** (1970) 231.
3. Kumler, P. L. and Buchardt, O. *Chem. Commun.* **1968** 1321.
4. Buchardt, O., Pedersen, C. L. and Harrit, N. *J. Org. Chem.* **37** (1972) 3592.
5. Ishikawa, M., Kaneko, C., Yokoe, I. and Yamada, S. *Tetrahedron* **25** (1969) 295.
6. Angelico, F. and Calvello, E. *Gazz. Chim. Ital.* **31** (1901) 4.
7. Smith, A. *J. Chem. Soc.* **57** (1890) 643.
8. Buchardt, O., Kumler, P. L. and Lohse, C. *Acta Chem. Scand.* **23** (1969) 2149.
9. Buchardt, O., Kumler, P. L. and Lohse, C. *Acta Chem. Scand.* **23** (1969) 159.
10. Buchardt, O., Becker, J., Lohse, C. and Møller, J. *Acta Chem. Scand.* **20** (1966) 262.
11. Buchardt, O., Becker, J. and Lohse, C. *Acta Chem. Scand.* **20** (1966) 2467.

Received July 4, 1972.