Studies on the Chemistry of Lichens, XV

New Synthetic Nitrogen-Derivatives of Pulvinic Acid

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Lichen, Pulvinic Acid Lactams

Pulvinic acid lactams have been synthesized by reaction of the lichen compound vulpinic acid and 2-hydroxyethoxy-acetamide. The structure were established by consideration of infrared, mass and nuclear magnetic resonance spectra.

The lichen compound pulvinic acid and its derivatives have been described in a series of communications [1–8]. Karrer *et al.* [1] synthesized *p*-dimethyl pulvinic acid amide (yellow crystals) by the reaction of di(*p*-tolyl)-ketipinic acid dilactone with ammonia in a bomb tube.

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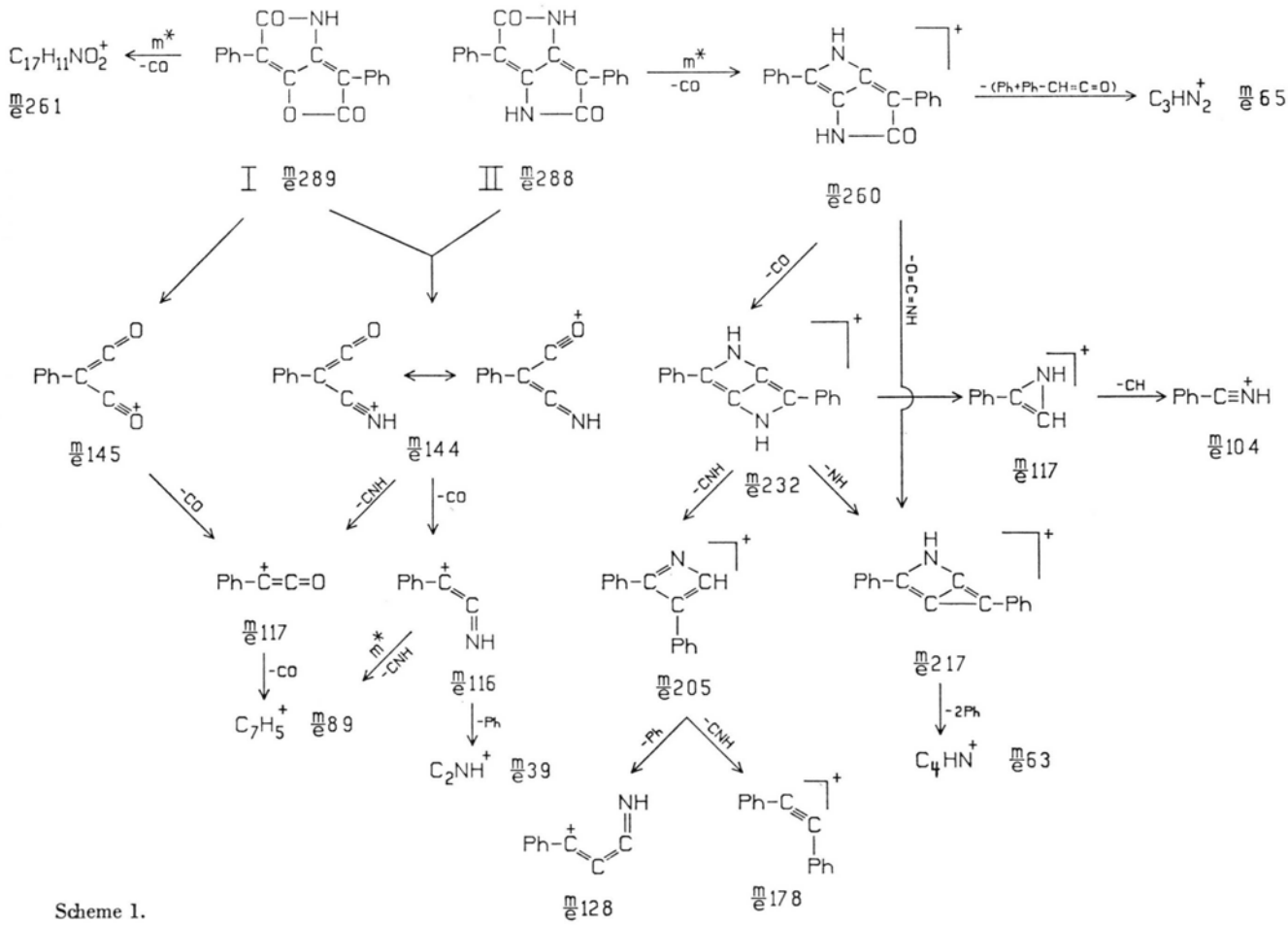
During our work concerning chemical studies on Norwegian lichen species, we succeeded in preparing two new nitrogen-derivatives of the lichen compound vulpinic acid. The reaction of vulpinic acid with an excess of 2-hydroxyethoxy-acetamide produced a splended mass of red-orange crystals. The recrystallized reaction product decomposed above 300 °C and was almost insoluble in the usual organic solvents except dimethyl sulfoxide. By elementary analyses, IR, NMR and mass spectrometry the product obtained was shown to be a mixture of pulvinic acid monolactam (**I**) and pulvinic acid dilactam (**II**), Scheme 1. Attempts to separate the components did not succeed, but it was found expedient to carry out the investigations on the lactam mixture.

Mass spectra of some pulvinic acid derivatives have already been reported [9, 10]. The compound **I** and **II** in this communication showed characteristic



Scheme 1.

fragmentation patterns for this type of compounds. The molecular ion of **II** is the base peak in the spectrum and the fragmentation may be rationalised as outlined in Scheme 1. Loss of CO from the molecular ions **I** and **II** produced the fragments *m/e* 261 and 260 respectively. Metastable peaks were observed in the LrMS establishing this elimination. Cleavage of the parent ions gave the resonance stabilized ions *m/e* 145 and 144, which subsequently lost molecules of CO and CNH respectively to produce the ion *m/e* 117 (C_8H_5O). The elimination of CO from the ion *m/e* 144 afforded the characteristic fragment *m/e* 116.

The fragment *m/e* 217 appeared to be formed from the ion *m/e* 260 by loss of the molecule HN=C=O. The formation of the ion *m/e* 65 (C_3HN_2) could be rationalised from the ion *m/e* 260 by elimination of a phenyl rest and the molecule Ph−CH=C=O. A hydrogen atom rearrangement must be assumed. It was considered that the peak at *m/e* 117 (C_8H_7N) arose by cleavage of the molecule *m/e* 232 by the transfer of hydrogen to the cleaved amide ion. In the lower part of the mass spectrum a strong peak was seen at *m/e* 89. This ion is postulated to have the benzcyclopropenyl or the dehydrotropylium structure [11].

Experimental

Material and methods. Elemental analyses were performed by Mikroanalytisches Laboratorium, Elbach-BRD. The melting point is not corrected. Chemical shifts in NMR spectra were recorded in δ values (ppm downfield from internal standard tetramethylsilane).

Low and high resolution mass spectra recorded in this communication were obtained by direct insertion technique and carried out by Shrader Analytical, Detroit-USA. In some cases, the charge is not localized on a particular group in the ions drawn in Scheme 1.

The reagent O-(2-hydroxyethyl)-glycolamide (2-hydroxyethoxyacetamide) was delivered from Aldrich Chemical Co., Milwaukee-USA. Vulpinic acid was an extract from the lichen species *Letharia vulpina*.

Synthesis of pulvinic acid lactams. Vulpinic acid (5 mM) was added to 2-hydroxyethoxy-acetamide ($HO-CH_2CH_2-O-CH_2CONH_2$) (10 mM) and heated in a closed teflon vessel for 6 h at 155–160 °C. During that time the mixture turned deep red-orange in colour and solidified to a crystalline mass. After cooling the product was extracted with $CHCl_3$, EtOH and Et_2O and the insoluble part recrystallized from boiling acetic acid. A mixture of pulvinic acid monolactam (**I**) and pulvinic acid dilactam (**II**) was obtained as red-orange needles, yield 4%, m.p. above 300 °C(d). The compounds gave no colour reaction with $FeCl_3$ in ethanol. With conc. sulfuric acid they produced a very strong red colour. IR(KBr): 3170 [(s), NH stretch. vibr.], 1775 (m) and 1710 (s) [C=O stretch.], 1635 cm^{-1} [(s), sec. amide band]. UV (ethanol): 360, 238 nm. ^1H NMR (60 MHz, DMSO-d_6, 38 °C): δ 7.25–8.0 (aromatic protons, 10 H), 10.91 (nitrogen proton, 1 H). Found: C 74.84, H 4.26, N 7.73, O 13.14. A mixture of $\frac{2}{5}$ $C_{18}H_{11}NO_3$ (**I**) and $\frac{3}{5}$ $C_{18}H_{12}N_2O_2$ (**II**) requires: C 74.89, H 4.05, N 7.76, O 13.29.

Accurate mass determinations were carried out on the following fragment ions:

Ion *m/e*	R.I.	Formula of ion	Found accurate mass	Calculated accurate mass
289	5	$C_{18}H_{11}NO_3$	289.0739	289.0739
288	100	$C_{18}H_{12}N_2O_2$	288.0907	288.0898
260	4	$C_{17}H_{12}N_2O$	260.0924	260.0949
259	2.2	$C_{17}H_{11}N_2O$	259.0891	259.0870
217	2.9	$C_{16}H_{11}N$	217.0876	217.0891
205	1.0	$C_{15}H_{11}N$	205.0901	205.0890
145	1.5	$C_9H_5O_2$	145.0310	145.0342
144	6.0	C_9H_6NO	144.0462	144.0449
117	30.2	C_8H_7N	117.0569	117.0578
116	13.5	C_8H_6N	116.0493	116.0500
115	4.4	C_8H_5N	115.0408	115.0421
104	0.8	C_7H_6N	104.0509	104.0499
103	0.8	C_7H_5N	103.0413	103.0421
89	34.1	C_7H_5	89.0393	89.0391
65	3.2	C_3HN_2	65.0135	65.0139
63	4.8	C_4HN	63.0119	63.0108

R.I. = Relative intensity.
The peak at *m/e* 117 is a double-ion, C_8H_7N and C_8H_5O.

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