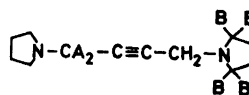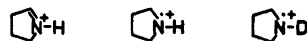# Mass Spectrometry of Acetylenic Amines. II. A Long-range Hydrogen Transfer in the Fragmentation of Some 1,4-Di(*t*-amino)-2-butynes*

CONNY BOGENTOFT and BO KARLÉN
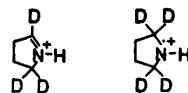
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W̶e have reported a long-range hydrogen transfer in the acetylenic diamine 1,4-diamino-2-butyne (I), in which the amine nitrogen serves as acceptor of the migrating hydrogen.[1] Such hydrogen transfers involving larger rings have been found to occur in the fragmentation of esters and hydroxy derivatives of α-substituted tetrahydrofurans[2] and in several long-chain hydroxyalkyl esters.[3] In I, the acetylenic bond in the propargylic position to the nitrogen favours N−C fission with formation of fragments derived from the pyrrolidine rings. Observed peak shifts in the tetradeutero analogue II of I suggests that the transferred hydrogen originates from the other pyrrolidine ring.[1] This paper presents additional evidence in favour of the proposed site-specific transfer.

In the spectrum of I, the ions *m/e* 70 (a) and *m/e* 71 (b) are the most abundant, *m/e* 71 being the base peak. The observed shifts for these ions to *m/e* 73 (d) and *m/e* 75 (e) in the spectrum of II led us to postulate the structures below for the fragments responsible for these peaks. The formation of *m/e* 73 and *m/e* 75 must involve a primary process, and takes place through an N−C fission in the acetylenic chain of the molecular ion with simultaneous transfer of a hydrogen. The formation of *m/e* 72 (c) in II suggests that the transferred hydrogen at least partly originates from the α-position of the other pyrrolidine ring.[1]

To exclude the possibility of hydrogens from the acetylenic chain being involved in this step, we have examined compound III on electron impact. No shifts of the involved peaks (*m/e* 70, 71) occur, a fact which can only be accounted for by assuming that the transferred hydrogen in the proposed rearrangement originates from the other ring.

* Part I in this series, see Ref. 1.

I: A=H; B=H; II: A=H; B=D; III: A=D; B=H

a, m/e 70   b, m/e 71   c, m/e 72

d, m/e 73   e, m/e 75

Further evidence for the hypothesis that *m/e* 71 is formed by a rearrangement reaction is obtained by comparison of the relative abundance of *m/e* 70 and *m/e* 71, derived from I, at various ionization energies. The ratios between *m/e* 71 and *m/e* 70 at 70, 18, and 15 eV were 1.2, 2.4, and 7.4, respectively. The increasing abundance of *m/e* 71 compared to *m/e* 70 with decreasing energy indicates[4] that *m/e* 71 is formed through a rearrangement.
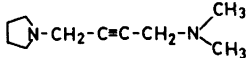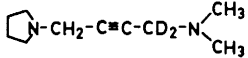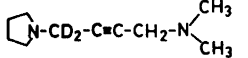
The mechanism for the studied reaction is depicted in Scheme 1 and implies a site-specific hydrogen transfer *via* an 8-membered transition state with loss of a neutral species, which tentatively could be represented as f. The apparent stability of this fragment may be a driving force for this reaction.
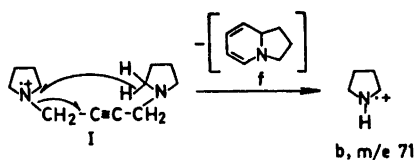
Scheme I

In the fragmentation of compound IV, a dimethylamino analogue of I, prominent ions due to cleavage of the N−C bonds in the acetylenic chain are found at *m/e* 70, 71, 44, and 45 (Table 1). A hydrogen is

Table 1. Relative abundance of mass spectral peaks of compounds IV, V, and VI at 70 eV.

Compound	Fragment structure m/e			
	$\begin{array}{c}CH_2\\ \\ CH_3\end{array}\!\!>\!\!\overset{+}{N}\!-\!H$	$\begin{array}{c}CH_3\\ \\ CH_3\end{array}\!\!>\!\!\overset{+}{N}\!-\!H$	$\overset{+}{N}\!-\!H$ (ring)	$\overset{+}{N}\!-\!H$ (ring)
	44	45	70	71
N-CH₂-C≡C-CH₂-N(CH₃)₂ **IV**	24	40	55	43
N-CH₂-C≡C-CD₂-N(CH₃)₂ **V**	22	79	63	69
N-CD₂-C≡C-CH₂-N(CH₃)₂ **VI**	40	70	40	90

transferred to both of the dimethylamino and pyrrolidine groups.

In the spectra of compounds V and VI, specifically labelled in the acetylenic chain, no peaks occurred at m/e 46 (corresponding to $(CH_3)_2ND^+\cdot$) or at m/e 72 (corresponding to N-deuterated species c), showing that the hydrogens in these positions are not participating in the rearrangement process (Table 1). Evidently, the transferred hydrogen originates either from the pyrrolidine ring (m/e 45) or from the dimethylamino group (m/e 71). No differences in the donating capacities of the two groups are observed. Thus, the discussed hydrogen transfer seems to be of general importance in this series of compounds.

Experimental. Mass spectra were obtained with an LKB 9000 mass spectrometer using a direct probe heated to a suitable temperature. The ionizing energy was maintained at 70 eV except when otherwise stated, the accelerating energy at 3500 V and the temperature of the ion source was kept at 270°C. The infrared spectra of the deutero compounds displayed a $C-D$ band at 2220 cm⁻¹ (Perkin-Elmer 237, KBr). Melting points are uncorrected and were determined with calibrated Anschütz thermometers.

1,4-Dipyrrolidino-2-butyne (I) was prepared as described previously.[1]

1,4-Dipyrrolidino-2-(1,1-d₂-butyne) *(III)* was prepared as described for 1-(2,2,5,5-d_4-pyrrolidino)-4-pyrrolidino-2-butyne (II)[1] except that formaldehyde-d_2, (30 % in D₂O) was used instead of paraformaldehyde. Dihydrochloride: yield 34 %, m.p. 218−220°C (lit.[5] 222°C) (from ethanol-ether).

1-Dimethylamino-4-pyrrolidino-2-butyne (IV was synthesized as described for III from N-propargylpyrrolidine (4.0 g, 37 mmol), dimethylamine (2.7 g, 60 mmol), paraformaldehyde (1.32 g, 44 mmol), acetic acid (4.8 g, 80 mmol) and catalytic amounts of cuprous chloride in dioxane (15 ml). Dihydrochloride: yield 5.5 g (62 %), m.p. 213−214°C (from ethanol-ether). (Found: C 50.0; H 8.66; N 11.7. Calc. for $C_{10}H_{22}Cl_2N_2$: C 50.2; H 8.43; N 11.7).

1-Dimethylamino-4-pyrrolidino-2-(1,1-d₂-butyne) *(V)* and *1-dimethylamino-4-pyrrolidino-2-(4,4-d₂-butyne)* *(VI)* were prepared as described for IV using N-propargylpyrrolidine (333 mg, 3 mmol) and N-propargyl-N,N-dimethylamine (250 mg, 3 mmol), respectively, as starting materials. *V*: dihydrochloride, yield 550 mg (76 %), m.p. 213−214°C. *VI*: dihydrochloride, yield 500 mg (69 %), m.p. 212−214°C.

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Acid Degradation of Lignin

VI.* Formation of Methanol**

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In a previous paper [1] the possibility was considered that cyclohexadienone structures of type I, produced *via* an oxidative phenol coupling, occurred in lignin. Structures II – V constitute some other types of dienone units which conceivably also could arise during the oxidative coupling of phenols involved in the biosynthesis of lignin.[2,3] From the suggested structural elements of the quinone ketal type (IV and V) quinone units may be formed. Thus, hydrolysis of *o*-quinone ketals (IV) with formation of *o*-quinone units of type VII may occur in the plant. Analogously, *p*-quinone units of type VI may arise by hydrolysis of *p*-quinone ketals (V) (see Ref. 4). Alternatively, *p*-quinone units could be thought to be formed in connection with an oxidative elimination of a propyl side chain (Ref. 5, *cf.* also Ref. 6).

In preliminary experiments it was found that methanol was liberated when lignin samples, as well as model compounds for structures II – VII, were subjected to

* Part V, *Acta Chem. Scand. In press.*
** The major part of this work was presented at "Det 13. Nordiske Kemikermøde", Copenhagen, 19—23 August 1968.
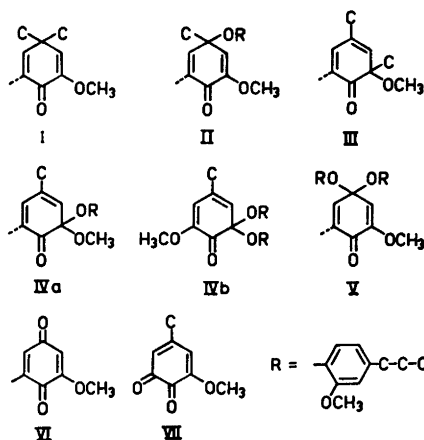
acidolysis by heating with 0.2 M hydrogen chloride in dioxane-water (9:1) at reflux temperature * (concerning the formation of methanol from compounds related to structures III and V on acidic treatment, see Refs. 7, 2, and 4). Evidently the methanol originated from methoxyl groups. In the present work, formation of methanol from lignin and lignin model compounds on acidolysis was studied in order to clarify whether quinonoid and quinone units of types II – VII may occur in lignin. The methanol was determined by gas chromatography.

The amounts of methanol obtained on acidolysis of spruce lignin (Björkman lignin from *Picea abies*) were relatively small; on prolonged treatment the yield was about 0.02 mol/OCH$_3$ (Table 1). Similar results were obtained with a lignin sample which, to avoid contact with acid, had been purified according to a procedure which differed somewhat from that used by Björkman [8] (the precipitation from 90 % acetic acid into water was replaced by precipitation into 1 % aqueous sodium sulphate solution from a dioxane-water (19:1) solution), but an observed difference was that traces of methanol (≈ 0.001 mol/OCH$_3$) were liberated even at room temperature on brief treatment (0.25 h) with the acidolysis reagent. A hardwood lignin (Björkman lignin from *Betula verrucosa*) gave a somewhat higher yield of methanol than spruce lignin on 4 h acidolysis (Table 1).

* Throughout this paper the term "acidolysis" is used specifically for this treatment.