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ISOMERIZATION OF 1,6- OXIDO[10]ANNULENE TO 1-NAPHTHOL BY POTASSIUM AMIDE

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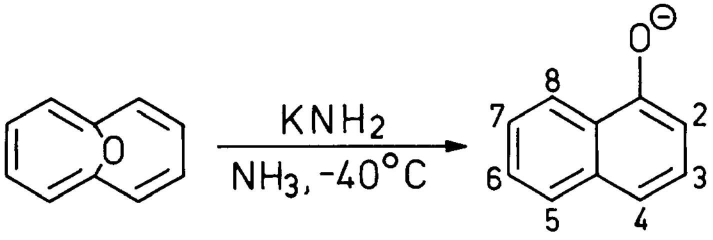
Abstract *1,6-Oxido(10)annulene (1) forms -according to nmr- quantitatively the 1-naphtholate anion (3) upon reaction with potassium amide in liquid ammonia at low temperature*

Since the first synthesis of 1,6-oxido[10]annulene (1) in 1964 1)2) the chemistry of this interesting compound has been investigated by several groups 3).
Under acidic conditions 1 is reported to rearrange, forming 1-benzoxepin, 1-naphthol and/or 2-naphthol 4). The compound seems to be fairly stable both thermally and under basic conditions It is even possible to prepare 2,5,7,10-tetradeutero-oxido[10]annulene (2) from 1 in DMSO-d_6, using a catalytic amount of potassium t-butoxide 5).
As far as we are aware, no other reactions of 1 under basic conditions are known.

We now report the behaviour of 1 in liquid ammonia containing one equivalent of potassium amide When 1 4) and one equivalent of KNH_2 are mixed in liquid ammonia at low temperature (-40°C) a reaction takes place instantaneously The ^{1}H-nmr spectrum, recorded immediately at -45°C shows a multiplet ([3H]), centered at 7 2 ppm besides two low-field doublets (at 8 28 and 7 53 ppm respectively) and two high-field doublets (6 51 ppm, 6.21 ppm), all doublets have the same coupling constant of about 7 5 hz and the same intensity ([1H])
The ^{1}H-nmr spectrum, which is shown in the figure, is identical with that of a solution of the 1-naphtholate anion (3), prepared similarly as described above from 1-naphthol The same applies to the (proton decoupled) ^{13}C-nmr spectra. When treated with one equivalent of potassium amide, 1 and 1-naphthol give rise to the same spectrum in liquid ammonia at -40°C, showing signals at 106 4, 109.2, 120 6, 124 7, 125.3, 127 2, 129 4, 131 4, 137 0 and

169.6 ppm (values underlined correspond to signals that are singlets in an off-resonance proton decoupled ^{13}C-nmr spectrum).
Indeed, quenching of both solutions with ammonium chloride yields, after standard work-up, 1-naphthol as the sole product (according to m.p., IR, MS, ^{1}H- and ^{13}C-nmr).



1 3

The ^{1}H-nmr spectrum of 1-naphthol in CCl_4 has been analysed completely [6]. The chemical shifts of 1-naphthol in liquid ammonia at low temperature differ only slightly from the values in CCl_4 at room temperature. It is possible to bring those signals into a one-to-one correspondence with the ^{1}H-nmr signals of 3 in NH_3 by studying samples in which the 1-naphthol is only partly ionized (i.e. samples, differing in the 3 : 1-naphthol ratio), using less than one equivalent of base. This is due to the fact that the anion 3 and 1-naphthol, when both present in liquid ammonia, are in rapid equilibrium (on the nmr time scale) under the conditions used. This leads to the assignments shown in the figure. Plotting the position of the ^{1}H-nmr signals in the 1-naphthol/1-naphtholate(3) system as a function of the degree of ionization shows that the slopes of the resulting straight lines are not equal. Their relative magnitudes (H-2 > H-4 > H-5,H-8) are as intuitively would be expected and thus confirm the assignments.

When the reaction between 1 and KNH_2 is performed in liquid ND_3, the ^{1}H-nmr spectrum of the formed 1-naphtholate anion shows specific deuterium incorporation; in the ^{1}H-nmr spectrum the multiplet at 7.2 ppm is decreased in intensity ([2H] instead of [3H]) and the doublet at 7.53 ppm ([1H]) is now a (broad) singlet ([0.4H]) as shown in the figure.
The observed incorporation of deuterium (100 % deuteration at position 6 and 60 % at position 5) is in agreement with MS data of the 1-naphthol that is formed upon quenching.
(A solution of 3 -prepared from 1-naphthol- in ND_3 showed no detectable exchange upon several days of standing at -15°C).

When 2 5) is added to a KNH_2/NH_3 suspension, a ^{1}H-nmr spectrum is obtained in which the high-field doublet at 6.2 ppm is completely missing (see figure)

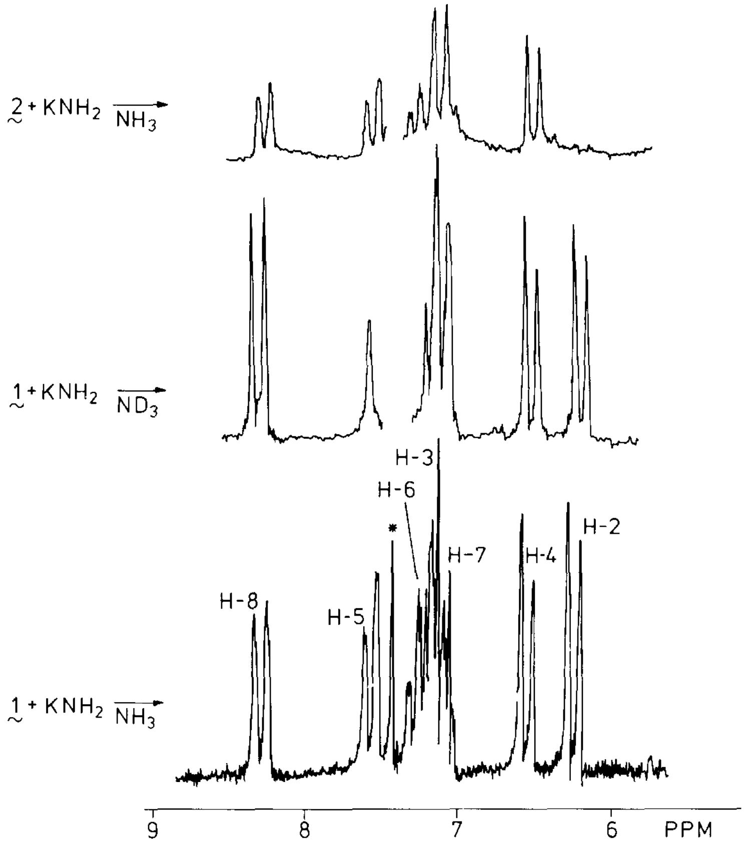
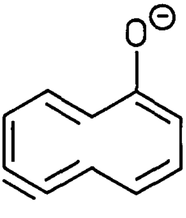


Figure Resulting ^{1}H-nmr spectra when 1 is treated with potassium amide in liquid NH_3 (bottom) or in liquid ND_3 (middle) and when 2 is treated with KNH_2 in liquid NH_3 (top) Benzene (marked signal) was used as an internal reference

It is possible that a benzyne-like intermediate (e g 4) plays an important role in the rearrangement of 1 to 3. This might be formed from 1 by (alpha-) proton abstraction followed or accompanied by a ring opening Via ring-closure and a hydrogen migration 3 can than be formed. It is however possible that other mechanistic pathways are involved. At this stage a clear distinction between them cannot be made.

From the second labeling experiment described it is evident however that the oxygen atom is bound to the same carbon atom in 1 and in 3

A similar reaction is not observed for the corresponding 1,6-methano[10]annulene. Reaction of this substance with KNH_2 under similar conditions as described above followed by quenching with ammonium chloride gave 1,6-methano[10]annulene as the only observable product.



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