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THE ANODIC TETRAMERIZATION OF THE N-BENZYLAZIRIDINE : A CHAIN PROCESS

by

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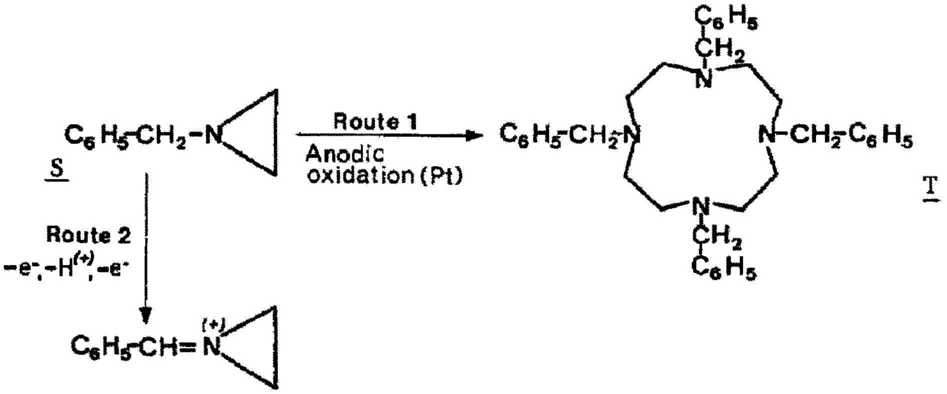
Summary - *Benzylaziridine is oxidized anodically in organic solvents. The tetramer (tetra-az lododecane) is obtained in good yield and the electrical consumption is very low. Authors pr pose a chain process mechanism in comparison with the chemical method.*

The synthesis of 1, 4, 7, 10 tetra-aza-cyclododecane T has been reported several ye ago by HANSEN and BURG[1]. The tetramerization of the N-benzylaziridine S was performed in the presence of p-toluenesulfonic acid (PTSA) in catalytic amount by reflux during several hours alcohol.

Attempts to perform the tetramerization by anodic means (route 1) was successful (t 1 experiments n° 1-4 by potentiostatic methods) ant this result appears to be unique since th oxidation of tertiary amines leads very generally to iminium salts (route 2[2,3]) .



On the other hand, the low electricity consumption (especially exp. n° 2, 4, 7) does confirm an oligomerization is occuring and suggests also a chain process. It is probably worth comparing here the chemical and the electrochemical method. This comparison brings us to sugge that the action of H^+ (used as catalyst in the chemical tetramerization) may be an oxidizing reagent : the chemical tetramerization in the absence of light occurs in much lower yields (fo example, the experiment (10) shows a dramatic decay of the efficiency of the reaction).

TABLE 1 : ANODIC TETRAMERIZATION OF THE N-BENZYLAZIRIDINE*

Experiments N°	Mass of N-benzylaziridine submitted to tetramerization (g)	Solvent (with nBu_4N^+, ClO_4^-, 0.1 M)	Condition of the electrolysis	Fixed applied potential or applied current	Amount of electricity[a] ($F.mol^{-1}$)	Yield in tetramer (%)
1	1	MeOH	direct	+ 1.20 V	0.37	(60)
2[k]	1.5	MeOH	direct	+ 1.20 V	0.15	(57)
3	1.5	CH_2Cl_2	direct	+ 1.3 V	0.25	(66)
4[k]	2	CH_2Cl_2	direct	+ 1.1 V	0.20	(67)
5	0.5	CH_2Cl_2	direct	10 mA	0.05	(7)
6	0.6	CH_2Cl_2	direct	3 mA	0.05	(19)
7	0.4	CH_2Cl_2	direct	2 mA	0.05	(43)
8[d]	0.5	CH_2Cl_2	electrolysis conditions	no current	-	(0)
9[e]	0.5	CH_2Cl_2	electrolysis conditions +PTSA		-	(0)
10[f]	0.75	MeOH	-	-	-	(20)
11[g]	0.6	CH_3CN	indirect	+ 0.75 V	0.04	(6)
12[h]	1	CH_3CN	indirect	+ 0.75 V	0.95	(66)
13[i]	0.5	CH_3CN	indirect	+ 0.80 V	0.14	(70)
14[j]	0.87	CH_3CN	indirect	+ 0.85 V	0.54	(80)

* Electrochemical tetramerization at an anode of polished platinum (area : 7 cm^2). Volume of the anolyte : 70 ml. A H cell is used : volume of the catholyte 30 ml. Cathode : rod of graphite ; anolyte and catholyte are separated by means of a glass frit. [a] Vs aqueous saturated calomel electrode, [b] Vs Ag/Ag^+ 0.1 M system, [c] calculated on the basis of the starting material.

[d, e, f] Effect of the absence of light (in the presence of p. toluenesulfonic acid (PTSA)):the mixture was stirred during 6 hours in the absence [d] or in the presence (61 mg), of PTSA [e] - [f] The mixture reproduces the experimental conditions of reference (1) but in the darkness (10 mg of PTSA in 30 ml of MeOH).

[g, h, i, j] Indirect oxiding reagents : [g] N-benzylaziridine was added after a partial oxidation of the tetramer (50 mg) and stirred during 6 hours without current in the darkness - [h, i, j]: mixed electrolysis in the presence of tetramer (150 mg) tris-p-bromophenylamine (100 mg) and thiantren (300 mg) respectively.

By means of electrochemistry, a certain number of additional experiments were performed. The results are briefly summarized below :

(a) The formation of the tetramer is shown to be not catalyzed by the more or les partial appearance of electrogenerated acids(which might be produced according to the route The mixing of PTSA (amount calculated on the basis of the reaction N°2 occuring at 50 %) wit aziridine in the cell and the electrolytes chosen in table 1 does not lead to the formation of tetramere in the absence of light, even after 6 hours of stirring (experiments 8, 9).

(b) The tetramerization is also possible by means of an electrogenerated oxidizing reagent (experiments : 12, 13 and 14). The anodic oxidation then occurs at less positive potentials (gain in potential of the order of 0.4V with the mentionned electron carriers in table 1). Electrochemically, it may be shown that the radical cation of the mediator transfe fast the electron to the arizidine (increase of the peak current of mediator in the presence of $C_6H_5CH_2N\triangleleft$). This exchange thermodynamically unfavourable is then made possible when a fa chemical reaction follows up the SET. This is just the foundation of the redox catalysis already developped [4, 5].

DISCUSSION :

This work demonstrates that the electrochemical tetramerization of the benzylaziridine proceeds via the radical cation formed either by direct or indirect electron transfer. On the other hand, the formation of this transient may be possible in the presence of a chemical oxidant (e.g. H^+ or some metallic cations [7]) and accelerated by photoirradiation. The experimental results reported in this note exclude the prevalence of the deprotonation process of the radical cation and are obviously in favor of a fast opening process of the three-membered ring. Accordingly, the polymerization mechanism could be summarized as follows

Initiation :

$S \xrightarrow[\text{slow}]{-e^-} S^{\cdot+}$ (at the anodic interface) (1)

$S^{\cdot+} \xrightarrow[\text{fast}]{\text{opening}} (S')^{\cdot+}$ (2)

$(S')^{\cdot+} \xrightarrow{S} \xrightarrow{S} \xrightarrow{S} (S'S_3)^{\cdot+}$ (3)

$(S'S_3)^{\cdot+} \xrightarrow[\text{of the ring}]{\text{closing}} T^{\cdot+}$ (4)
tetramer
radical cation

Propagation :
(in solution)

$T^{\cdot+} + S \rightleftharpoons T + S^{\cdot+}$ (5)

Termination :

$S^{\cdot+}$ or $T^{\cdot+}$ → two faraday "normal" anodic oxidation leading to the iminium salt. (6)

The reaction 2 must be fast : it is the driving force of the homogeneous electron exchange in the presence of mediator radical cation. The occurence of the propagation reaction 5 is totally in agreement with the experimental data since $T^{\cdot +}$ is an oxidant of the N-benzylaziridine. The mechanism is consequently of the type $\overrightarrow{E}\ C\ \overleftarrow{E}$: the electricity consumption is very low and its increase appears to be only due to the termination steps (reaction 6) such as iminium salts formation from the substrate or from the tetramer .

The described reaction shown to be induced by monoelectronic transfer similar to other $\overrightarrow{E}\ C\ \overleftarrow{E}$ processes induced by a reduction SET (see for example, reference (6) on electrochemically induced aromatic nucleophilic substitution and references on the work of BUNNETT cited therein).

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