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Electroörganic Preparations

XXVI. Polarography and Reduction of some Oxaziridines

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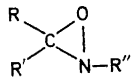
The electrochemical reduction of some oxaziridines has been investigated. The first polarographic wave of oxaziridines starts at all pH at the dissolution wave of mercury and the corresponding reduction is a hydrogenation of the nitrogen-oxygen bond. At low pH is found a second wave which is caused by the reduction of the azomethine compound formed by loss of water from the primarily formed *gem*-aminoalcohol. At higher pH the aminoalcohol loses ammonia and the further wave is due to the reduction of the carbonyl compound.

In connection with the electrolytic reduction of oximes [1–4] and related compounds it was of interest to investigate the polarographic behaviour of oxaziridines. The electrode reactions were investigated by means of controlled potential reduction.

The following compounds were included in the investigation: 2-*tert*-Butyl-3-phenyloxaziridine (I), 2-*tert*-butyl-3-(4′-pyridyl)oxaziridine (II), and 2-benzoyl-3,3-pentamethylene oxaziridine (III).



I	R = H	R′ = C_6H_5	R″ = *t*-C_4H_9
II	R = H	R′ = NC_5H_4	R″ = *t*-C_4H_9
III	R,R′ = $CH_2CH_2CH_2CH_2CH_2$		R″ = C_6H_5CO

Polarographic investigation. The oxaziridines investigated are polarographically reducible and the first wave (Ia, IIa, IIIa) starts at the dissolution wave of mercury at all pH; 2-benzoyl-3,3-pentamethylene oxaziridine gives no further waves.

2-*tert*-Butyl-3-phenyloxaziridine (I) yields three waves (Ia, Ib, and Ic). The first wave (Ia) is found at very positive potentials, the second one (Ib)

at the same potentials as those of *N-tert*-butylbenzaldimine, and the third one (Ic) at those of benzaldehyde.

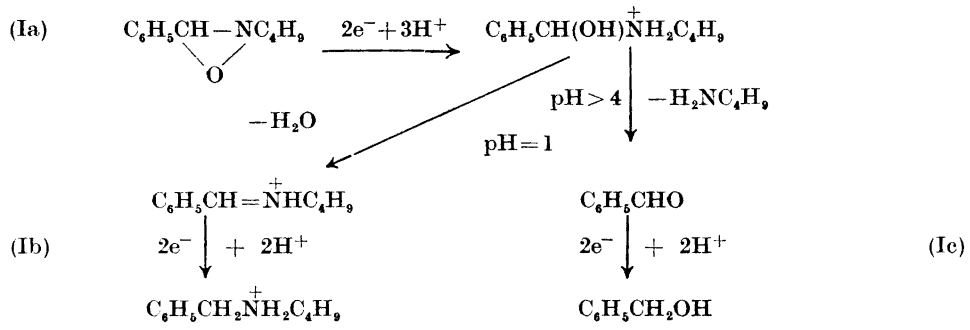
In strongly acid solution I is hydrolysed,[5] but at pH >1 polarograms of I are readily obtained. At 1<pH<4 the three waves Ia, Ib, and Ic are found; Ic is small at low pH but grows at the expense of Ib when pH rises. At pH>4 only the waves Ia and Ic are seen. In Table 1 are given the half-wave potentials of the second wave of I (Ib) at 1<pH<4. *N-tert*-butylbenzaldimine is in this region stable enough for a polarographic investigation.

2-*tert*-Butyl-3-(4'-pyridyl)oxaziridine (II) behaves polarographically in a similar way, but the wave (IIb) of the aldimine is visible only at pH<2. The height of the third wave (IIc) corresponds to a two electron reduction of 4-pyridinecarbaldehyde even at pH 2, and no appreciable hydration of the aldehyde seems to occur. In acidic aqueous solution 4-pyridinecarbaldehyde is normally highly hydrated which influences the polarographic behaviour.[6]

Table 1. Half-wave potentials of the second wave (due to the reduction of N-benzylidene-*tert*-butylamine) of 2-*tert*-butyl-3-phenyloxaziridine at 1 <pH <4. The medium contained 40 % alcohol.

Buffer	pH	$-E_{\frac{1}{2}}$ V
HCl	0.20	0.75_5
HCl	0.80	0.75_5
HCl	1.20	0.77_5
HCl	1.65	0.80
Glycine	2.20	0.82
Citric acid	2.95	0.84
Citric acid	3.50	0.85
Citric acid	4.30	0.87

Preparative reductions. Reduction of I in cold 0.3 N HCl at a potential corresponding to the first wave yielded benzylidene-*tert*-butylamine, which was not isolated but characterised by its polarographic behaviour. Reduction of I at a potential at the plateau of the second wave yielded mainly *N-tert*-butyl benzylamine, together with some benzylalcohol. The reduction may be formulated as:



Discussion. Oxaziridines are easily reduced by chemical reagents; thus iodide [5] and lithium aluminium hydride [5] reduce such compounds to the parent Schiff's base; the latter reagent reduces some oxaziridines to the secondary amine, and such amines are products in catalytic hydrogenation with platinum as catalyst.[7]

The first step in the electrochemical reaction is a hydrogenation of the nitrogen-oxygen bond whereby a *gem*-aminoalcohol is formed; a similar cleavage has been postulated as the first step in the reduction of oximes [1,2] and nitrones,[1,4] but in these cases the product of the first reduction is an azomethine compound which most often is easier reducible than the parent oxime or nitrone and can thus not be isolated from a reduction; in some cases, however, the reduction proceeds in two distinct steps.[2,4]

The *gem*-aminoalcohol is not reducible as such but loses either water or amine depending on pH. The investigations by Cordes and Jencks [8] show that the loss of water would be fastest at low pH and the loss of amine at higher pH, which is in agreement with the results obtained in the polarographic investigation. The optimum conditions for the reduction to the secondary amine is thus a low pH and temperature.

The wave height of wave IIc of 2-*tert*-butyl-3-(4′-pyridyl)oxaziridine, which is due to the reduction of 4-pyridinecarbaldehyde, corresponds to a two-electron reduction at all pH, although an equimolar solution of 4-pyridinecarbaldehyde at, *e.g.*, pH 2 would give only a small wave due to the predominant hydratisation of the protonated compound.[6] This is in accordance with the assumption that a proton is removed from the oxygen atom of the protonated *gem*-aminoalcohol before the amine is expelled leaving the carbonyl group, which then is reduced before it is attacked by water. A somewhat similar situation is found in the reduction of 4-chloroquinazoline [9] where the second wave is due to the reduction of unhydrated quinazoline even under conditions where quinazoline is predominantly hydrated in the nucleus.

The parent Schiff's base of II is in acid solution at a given pH less stable than that of I. This is in accordance with the lower rate of hydrolysis of benzylidene-*tert*-butylamine compared to that of *p*-nitrobenzylidene-*tert*-butylamine at low pH.[8]

EXPERIMENTAL

The power supply for the electrolysis was a transistorised potentiostat (Tage Juhl Electronics, Copenhagen) capable of delivering 25 A at 40 V.

Materials. 2-*tert*-Butyl-3-phenyloxaziridine (I) (NMR spectrum ($CDCl_3$, Ref. TMS): $\delta = 1.05$ (singlet) $\sum H = 9$; $\delta = 4.56$ (singlet), $\sum H = 1$; $\delta = 7.0-7.4$ (multiplet), $\sum H = 5$) was prepared according to Emmons;[5] analogously was prepared 2-*tert*-butyl-3-(4′-pyridyl)oxaziridine (II), m.p. 82–83° (light petrol, b.p. 60–80°). (Found: C 67.81; H 8.09; N 15.68. Calc. for $C_{10}H_{14}N_2O$: C 67.39; H 7.92; N 15.72). NMR spectrum ($CDCl_3$, Ref. TMS): $\delta = 1.18$ (singlet) $\sum H = 9$; $\delta = 4.70$ (singlet) $\sum H = 1$; $\delta = 7.32-7.45$ (multiplet) $\sum H = 2$; $\delta = 8.58-8.71$ (multiplet) $\sum H = 2$. 2-Benzoyl-3,3-pentamethyleneoxaziridine was prepared according to Schmitz and Schramm.[10]

Reduction of 2-tert-butyl-3-phenyloxaziridine (I) (1. wave). I (1 g) was reduced in 0.3 N HCl containing 30 % alcohol at −0.3 V (SCE) at −5 to 0°. The reduction was followed polarographically and the first wave disappeared after the consumption of two electrons per molecule. The second wave corresponding to the reduction of benzylidene-*tert*-butylamine remained and no wave of benzaldehyde was visible immediately after the reduction. The Schiff's base was not isolated.

Reduction of I (2. wave). I (1 g) was reduced as above but the potential was kept at −1.1 V (SCE), $n=3.8$. The reduction completed, part of the solvent was removed *in vacuo* and the aqueous solution extracted with ether. Removal of the ether left 0.2 g benzylalcohol. The aqueous layer was made strongly alkaline and extracted with ether which was dried with potassium carbonate. Addition of dry hydrogen chloride produced a precipitate (450 mg) identified as *tert*-butylbenzylamine hydrochloride from the m.p. 230–232° (228 [11]) and the analysis. (Found: C 66.69; H 9.12; N 7.08. Calc. for $C_{11}H_{18}NCl$: C 66.15; H 9.08; N 7.01). NMR spectrum (CF_3COOH): $\delta=1.62$ (singlet) $\sum H=9$; $\delta=4.10-4.43$ (5 major lines) $\sum H=2$; $\delta=6.5-7.8$ (broad band) $\sum H=2$; $\delta=7.43$ (singlet) $\sum H=5$. The methylene protons and the two protons on nitrogen couple and form an AA'XX'-system.

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