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Electrolytic Generation of Nucleophiles. III.[1] Reductive Acetylation of Nitro and Nitroso Compunds

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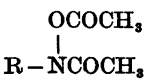
During the current investigations [2] of the reaction between electrophiles and electrolytically generated nucleophiles reductive acetylation of *N*-heterocyclic compounds was found useful.[3] Below is reported the analogous electrolysis of nitro and nitroso compounds in the presence of acetic anhydride to *N*,*O*-diacetyl-*N*-substituted hydroxylamines (I).



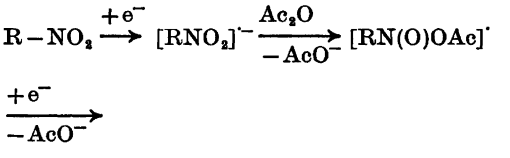
I

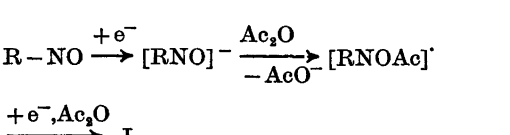
N,*O*-Diacetylhydroxylamines, which are of interest in chemical carcinogenesis,[4,5] mutagenesis,[6] and nucleic acid transformations,[7] have been obtained by acetylation of the corresponding hydroxylamines [8] or monoacetylated derivatives;[9] direct catalytic reduction of nitroarenes in the presence of acetic anhydride to I has only very limited success.[10]

Electrolytic reduction at a suitable potential of nitro or nitroso compounds in an aprotic medium, such as acetonitrile, containing an excess of acetic anhydride gives the desired compounds in one step in fair to good yield (47 – 87 % isolated yield). In Table 1 are given the yields from some electrolytic reductions and some of the properties of the isolated products.

The mechanism of the reaction has not been established; besides the scheme given below, where anion radicals or anions act as nucleophiles towards the electrophile acetic anhydride, there might be the possibility that the anion radicals acts as an electron donor towards acetic anhydride. Acetic anhydride could then cleave into an acetate ion and an acetyl radical, which then could couple with a substrate anion radical. The nucleophilic reaction mechanism is at present thought more likely than the radical coupling, mainly for the following two reasons: (a) *n*-values for the nitro and nitroso compounds are found close to 4 and 2, respectively, which is less likely for a radical process where acetyl radicals may react with other substrates than the nitro anion radicals, and (b) no "catalytic" increase [11] in the polarographic waveheight of *t*-nitrosobutane was obtained in the presence of acetic anhydride.

Nitroso compounds seem to be intermediates during the reductive acetylation of nitro compounds as judged from the fact that a slight blue colour, presumably due to the monomer *t*-nitrosobutane,[12] is observed during the electrolysis of *t*-nitrobutane. The same products have been isolated from the reductive acetylation of either nitro or nitroso compounds, and the following reaction scheme is thus suggested:





The same experimental procedure, which here has been applied to nitro and nitroso compounds and previously to heteroaromatic compounds,[3] has also been applied to the reductive acetyla-

Table 1. Yields and properties of *N,O*-diacetylhydroxylamines from electroreductive acetylations of some nitro and nitroso compounds.

Substrate used	Product I obtained % Yield crude	isolated	Physical properties (isolated sample)	Properties of authentic sample[a] of I
$MeNO_2$	68[b]	54	b.p. 90–100 °C (13 mmHg) n_D^{26} 1.4305	b.p. 87–88 °C (12 mmHg) n_D^{26} 1.4270; Lit.[15]
t-$BuNO_2$	63[b] 59[c]	47	b.p. 90–100 °C (13 mmHg) n_D^{26} 1.4295	b.p. 95–98 °C (18 mmHg) n_D^{26} 1.4320; lit.[16]
t-BuNO	73[b] 75[c]	57[d]	n_D^{26} 1.4320	see above
$PhNO_2$	70[b]	55	m.p. 39–42 °C (43.5–44.5)[e]	lit.[17] m.p. 43 °C
PhNO	83[b]	71	see above	see above
p-$MeC_6H_4NO_2$	–	77	b.p. 118–121 °C (0.5 mmHg)	see Experimental
m-$C_6H_4(NO_2)_2$	88[b]	87	m.p. 113 °C (119 °C)[e]	see Experimental

[a] Unless otherwise indicated, data are for a sample prepared by acetylation of the corresponding hydroxylamine. [b] From NMR analysis. [c] From VPC analysis. [d] By preparative VPC. [e] Analytically pure sample.

tion of anthraquinone, benzoquinone, and 2,3,5,6-tetramethoxybenzoquinone in yields of 70–85 %. The simplicity in controlling the degree of the reduction probably makes the procedure the method of choice where a reductive acylation to a partly reduced substrate is sought.

Experimental. Apparatus. An H-type 3-electrode cell of conventional design[13] has been used in combination with a Juul Electronic 100V/3A or 100V/10A potentiostat. Spectra were recorded on a Varian A60 NMR-spectrometer and a Perkin-Elmer Infracord IR-spectrophotometer. Analytical VPC was performed on a FM810 gas chromatograph and preparative VPC on a Perkin-Elmer F21. Melting and boiling points are uncorrected.

Materials. The nitro and nitroso compounds were either commercially available or prepared according to published procedures.[12,14]

General procedure. Electroreductions were mostly performed at room temperature (water bath surrounding the cell) at a stirred mercury cathode maintained at controlled potential, usually −0.9 to −1.3 V *vs* an Ag/AgI or Ag/Ag *p*-toluenesulfonate reference electrode. The solvent/electrolyte was anhydrous acetonitrile (dried over type A4 molecular sieves) containing 0.8 M sodium perchlorate and 10 % (by volume) of redistilled acetic anhydride throughout the cell. The anode was made of platinum gauze, because a graphite rod rapidly breaks down when used as an anode in aprotic perchlorate medium. The substrate (usually 1–2.3 g) was dissolved in the catholyte (180 ml) and current was passed through at the chosen potential until it ceased, usually after uptake of 5–10 % more than the theoretical consumption. Especially for the aliphatic compounds it was found advantageous to work up immediately and use short electrolysis times to minimize the formation of by-products. During the electrolysis a white precipitate was formed and the catholyte turned more or less yellowish. The precipitate could be filtered off, washed with acetonitrile, and identified as sodium acetate by its IR-spectrum; it was formed in an amount closely corresponding to the amount of electricity consumed.

Typically the resulting catholyte was concentrated *in vacuo*, diluted with methylene chloride or chloroform, filtered to remove the inorganic salts and evaporated *in vacuo*. The residue was analyzed by NMR or VPC (2 m 15 % SE30 on Chromosorb W, isothermal at 50 °C for 5 min, then programmed to 200 °C with 10 °C/min, biphenyl as internal standard). The products were isolated and purified by means of distillation, recrystallization, preparative VPC (2.7 m 15 % SE30, conditions similar to the analytical VPC) or column chromatography (chloroformsilica gel), and identifiel by means of IR (*N*-Ac, 1670–1690; *O*-Ac, 1780–1800 cm^{-1}), NMR and comparison with authentic samples and/or literature data (Table 1).

N,O-Diacetyl-*p*-tolylhydroxylamine, amber

liquid; IR-spectrum (film, cm^{-1}): 1780(s), 1670(s) 1170(br, s), 850(br, m), 820(br, m). NMR-spectrum (CCl_4): δ 1.94 (s, 3 H); δ 2.10 (s, 3 H); δ 2.36 (s, 3 H); δ 7.0 – 7.5 (multiplet, 4 H). The IR- and NMR-spectra correspond to those previously published.[6]

N,N′,O,O′-*Tetraacetyl*-m-*dihydroxylaminobenzene* (IV). *m*-Dinitrobenzene (1.0 g) was reduced at 5 °C in acetonitrile containing $NaClO_4$ in the presence of 10 ml acetic anhydride at -0.2 V *vs* Ag/AgI-electrode, $n = 8$. The solvent was evaporated and the residue extracted with methylene chloride. Evaporation of CH_2Cl_2 left 5.55 g of a residue; from NMR-analysis of the residue a yield of 88 % of tetraacetyl-1,3-dihydroxylaminobenzene was found. The residue was dissolved in 5 ml CH_2Cl_2 and 5 ml ether and then petroleum ether (b.p. < 50 °C) were added to beginning turbidity. A small amount of coloured material was filtered off and the filtrate cooled to -20 °C. The crystals, 1.60 g, m.p. 113 °C was recrystallized from methanol yielding a compound m.p. 119 °C (1 °C/min). NMR δ 2.11 (s, 6 H); δ 2.22 (s, 6 H); δ 7.3 – 7.7 (multiplet, 4 H). (Found: C 54.76; H 5.44; N 9.10. Calc. for $C_{14}H_{16}N_2O_6$: C 54.54; H 5.23; N 9.09).

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