

selective *N*-protonation and a too slow selective rearrangement to the alternative *C*-protonated ammonium salt. At 0 °C and even at room temperature the reaction is selective and gives an isomer ratio in solution *2a:1a* = 95:5 (<sup>1</sup>H NMR), with yields 90–95 % (internal standard, <sup>1</sup>H NMR) after 30 min. No change was found by increasing this time to 2 h. A preparative scale experiment (40 mmol) gave 86 % as isolated yield with the isomer ratio *2a:1a* = 92:8. Evaporation of the solvent inevitably gave some isomerisation since <sup>1</sup>H NMR analysis prior to removal of solvent showed 95 % *2a*. Selectivity was also found in benzene solution; after 30 min at room temperature an isomer distribution *2a:1a* = 92:8 was obtained. In chloroform no selectivity was found.

Unfortunately, the scope of the method is limited since no selectivity in protonation by ion exchange resin was observed to occur with the enamines obtained from cyclopentyl methyl and cyclohexyl methyl ketone. However, using trifluoroacetic acid as described in Ref. 1, *2b* was obtained in 98 % isolated yield with a purity better than 99 %, and *2c* was obtained in quantitative yield with a purity of 96 %.

Attempts at liberating the enamine from the resin bound ammonium salt by treatment with base have not been successful. The ammonium salt seems to be rather inert and tightly bound to the resin, such that not even a concentrated solution of amine base at reflux temperature was effective in liberating the enamine.

**Experimental.** The enamines were prepared by the titanium tetrachloride method.<sup>2</sup> Ion exchange resin Amberlyst 15 was purchased from FLUKA and washed with diethyl ether, finally with pentane boiling from a piece of sodium in a Soxhlet apparatus and dried *in vacuo* over solid paraffin. The capacity was determined to 4.5 mmol H<sup>+</sup>/g of resin.

**Selective protonation of 1a using Amberlyst 15.** To 6.21 g of a mixture of *1a:2a* = 30:70 (40 mmol) in 40 ml of pentane was added 3.00 g of Amberlyst 15. After stirring at room temperature for 30 min the resin was removed by filtration and washed three times with 5 ml of pentane. A few crystals of 1,8-bis(dimethylamino)naphthalene were added to the filtrate to suppress acid catalyzed isomerisation and the solvent was removed by evaporation under reduced pressure giving 3.72 g of enamine *2a:1a* 92:8, (86 % calculated from the amount of *2a* present in the starting material). When this isomeric mixture was dissolved in 25 ml of pentane and treated with 0.60 g of Amberlyst 15 the amount of *1a* dropped to less than 5 % within 30 min.

**Acknowledgements.** A grant from CNRS (France) to R.C. and financial support from the Swedish Natural Science Research Council are gratefully acknowledged.

Acta Chem. Scand. B 31 (1977) No. 8

1. Nilsson, L., Carlson, R. and Rappe, C. *Acta Chem. Scand. B* 30 (1976) 271.
2. White, W. A. and Weingarten, H. *J. Org. Chem.* 32 (1967) 213.

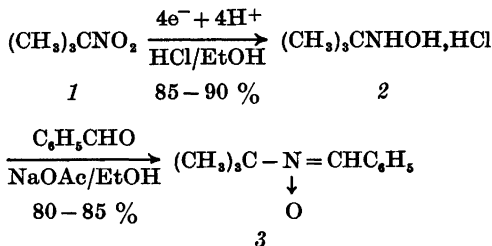
Received July 14, 1977.

## Organic Electrosyntheses. X.<sup>1</sup> Preparation of *N*-Benzylidene-*tert*-butylamine-*N*-oxide

PALLE E. IVERSEN and  
TORBEN B. CHRISTENSEN

Department of Organic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

The title compound **3** has been used as a radical scavenger<sup>2</sup> and is normally obtained by isomerization of the corresponding oxaziridine<sup>3</sup> or by direct condensation of the components.<sup>4</sup> We here describe a simple procedure for its preparation using as a key step the cathodic reduction of 2-methyl-2-nitropropane **1**:



The electrochemical reduction of *tert*-nitroalkanes to the corresponding *N*-alkylhydroxylamines is a general reaction proceeding with high yields<sup>5</sup> and in the present case has the advantage that the crude, wet **2** from the permanganate oxidation of *tert*-butylamine<sup>2</sup> can be used directly in the electrolytic step.<sup>6</sup> Furthermore, the product *N*-*tert*-butylhydroxylamine **2** from simple evaporation of the catholyte (giving the hydrochloride) is also used without purification for the condensation with benzaldehyde in the presence of sodium acetate to form the desired nitrene **3** in about 50 % overall yield from *tert*-butylamine on a 0.5 mol scale. Thus the handling of the free base of **2** (which is easily oxidized)<sup>2</sup> is avoided and manual work kept at a minimum by using essentially the same approach as for 2-methyl-2-nitropropane.<sup>6</sup> Also unsophisticated electrolytic

equipment can be applied. Only a divided cell is indispensable; the electrolysis can be run in unattended constant current mode with a simple rectifier, as there is no risk of over-reduction in strongly acidic medium (hydrogen evolution).

*Experimental.* N-tert-Butylhydroxylamine hydrochloride, 2. Crude 1<sup>2</sup> (0.6–0.7 mol) was reduced at a mercury cathode in 1:1 conc. hydrochloric acid/ethanol at 30–40°C in a conventional H-type cell<sup>4</sup> of about 400 ml catholyte volume surrounded by a water bath. A current of 2–3 A from an ordinary selenium rectifier (some voltage ripple is easily tolerated) was found satisfactory (very little hydrogen evolution from the cathode) for about 90% of the reaction. Towards the end the current was reduced stepwise to minimize hydrogen evolution. Alternatively potentiostatic control at –0.9 V vs. Ag | AgCl | 4 NHCl has been used.<sup>6</sup> Work-up by simple evaporation of the catholyte gave the crude hydrochloride of 2.<sup>6</sup> To obtain a dry product the solid residue was evaporated once more with 75–100 ml of absolute ethanol.

The procedure has been tested on a larger scale (up to 2.5 mol) in a similar cell of 1000 ml capacity with automatic temperature control by means of a contact thermometer in the cathode compartment regulating a magnetic valve and a heat exchanger. The yield of recrystallized 2 hydrochloride (1:5 absolute ethanol/ether) was usually 75–85%, m.p. 182–183°C (uncorr.). The cathodic reduction of pure 1 to 2 has been found to give 90% yield (or more) by anodic polarography.<sup>5</sup>

N-Benzylidene-tert-butylamine-N-oxide, 3. Crude, dry 2 hydrochloride (0.5–0.6 mol) was refluxed for 45–48 h with the equivalent amount of anhydrous sodium acetate in absolute ethanol (150–200 ml) and 5% less of benzaldehyde (the amount based on a 90% conversion in the cathodic reduction step). After cooling to room temperature dichloromethane (200 ml) and water (200–300 ml) was added, and after separation the aqueous phase was extracted further with 2 × 25 ml of dichloromethane. The combined organic extracts were washed with aqueous sodium bicarbonate and water, dried over anhydrous magnesium sulfate, and the solvent evaporated to give about 85% of crude 3, m.p. 65–71°C, with a slight smell of benzaldehyde. Recrystallization from 1:3 dichloromethane/light petroleum gave 70–75% of pure 3 (white needles), m.p. 73–74°C (uncorr., lit<sup>4</sup> 75–76°C) with a further small crop of 5–6%, m.p. 69–71°C by working up the mother liquor.

This step, tested with pure 2 hydrochloride, gave a total yield of 84–85% of recrystallized 3. The use of an equivalent amount of benzaldehyde gave greater losses, as several recrystallizations were necessary to remove traces of unreacted benzaldehyde. It was found advantageous to use an equimolar amount of sodium acetate for neutralization, as 25% less or excess

both resulted in a 10–15% lower yield of the pure nitron. The procedure has not been tested with other carbonyl compounds, but ought to be generally applicable.

1. Falsig, M. and Iversen, P. E. *Acta Chem. Scand. B* 31 (1977) 15. Part IX.
2. Calder, A., Forrester, A. R. and Hepburn, S. P. *Org. Synth.* 52 (1972) 77.
3. Emmons, W. D. *J. Am. Chem. Soc.* 78 (1956) 6208.
4. Emmons, W. D. *J. Am. Chem. Soc.* 79 (1957) 5739.
5. Iversen, P. E. and Duggirala, G. K. *Acta Chem. Scand. To be published.*
6. Iversen, P. E. *J. Chem. Educ.* 51 (1974) 489.

Received July 18, 1977.