ELECTRODE TRANSFORMATIONS OF CARBANIONS AND HETEROANIONS.

1. ELECTROLYTIC SYNTHESIS OF 1-PHENYL-3-NITRO-1,2,4-TRIAZOLE AND ITS ^{1}H, ^{13}C, AND ^{15}N NMR SPECTRA

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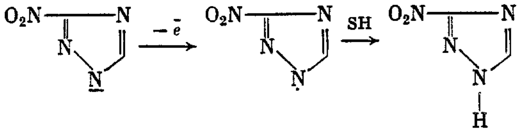
The radical intermediates generated by the electrolytic oxidation (EO) of the anions of CH acids react with benzene and its derivatives to give the corresponding alkylarenes [1]. In principle, similar transformations under EO conditions are also possible for the anions of NH acids. This was experimentally verified in the present research in the case of the 3-nitro-1,2,4-triazole (NT) anion as the model.

The NT anion in absolute MeCN with 0.1 N $LiClO_4$ as the inert electrolyte on a Pt disk electrode has one oxidation wave with $E_{1/2}$ = 1.85 V. The dependences of the heights of the limiting current on the depolarizer concentration and the square root of the number of revolutions of the electrode have linear character and pass through the origin. This constitutes evidence for the diffusion nature of the wave of the EO of the NT anion. Coulometric determination of the number of electrons at potential E = 2.0 V gives an n value close to one. Analysis of the solution after electrolysis at a controllable potential showed that the principal product is nonionized NT, the yield of which with respect to the substance is 90%.

It might be assumed that the radical generated on transfer of one electron detaches an H atom from a solvent molecule (see [2]) to give NT:



Dimeric products were not detected in the products of electrolysis of the NT anion; this is probably due to the electrophilic properties of the NT radical (see [1, 2]).

In analogy with the data in [1], we attempted to subject the NT radical to homolytic substitution. We found that the potentiostatic electrolysis (E = 1.8 V) of the tetramethylammonium salt of NT in a diaphragm cell in a 0.2 N solution of $LiClO_4$ in MeCN in the presence of 10% by volume benzene leads, in addition to the formation of nonionized NT (60% yield with respect to the substance, 63% yield with respect to the current), to N-phenyl-NT (18% yield with respect to the substance, 20% yield with respect to the current) (PNT). The structure of PNT was confirmed by the results of elementary analysis and data from the IR, NMR, and mass spectra (see the experimental section).

The PMR spectrum [δ, ppm: 7.47-7.64 m ($H^{3'}$, $H^{4'}$), 7.89 m ($H^{2'}$), 9.56 s (H^5)] confirms the presence in the molecule of a Ph group and an H atom of the triazole ring. In addition to signals of a Ph group, the ^{13}C NMR spectrum (Table 1) contains two doublets at 144.5 (C^5, $^1J_{C^5-H^5}$ = 222.0 Hz) and 162.6 ppm (C^3, $^3J_{C^3-H^5}$ = 14.0 Hz). Similar chemical shifts are known for the C^5 atom of 1-methyl-1,2,4-triazole (144.7 ppm) [3] and the C^3 atom of 1-phenyl-3-amino-5-methylthio-1,2,4-triazole (165 ppm) [4]; this confirms the structure of PNT as 1-phenyl-3-nitro-1,2,4-triazole.

The ^{15}N NMR spectrum gives unambiguous structural information (Table 2). On the basis of the data in [5], the signals at −151.6, −92.5, and −133.9 ppm were assigned to the N^1, N^2, and N^4 atoms of the 1,2,4-triazole ring, in which the substituent is attached to the N^1 or N^2 atom but not to the N^4 atom. It is known [5, 6] that the effect of replacement of the Me group by a Ph group in 1-methylpyrazole is −18.7 ppm. In fact, the difference in the

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TABLE 1. ^{13}C NMR Chemical Shifts (δ, ppm) and $^{13}C-^{1}H$ Spin–Spin Coupling Constants (SSCC) (Hz) of 1-Phenyl-3-nitro-1,2,4-triazole

C^3	C^5	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$
162,6 ($^2J_{C^3-H^5}$= =14,0 d	144,5 (222,0 d)	135,6 (9,0 t, 2,7 t)	120,0 (166,0 d, 8,9 d 4,3 d)	129,8 (162,0 d 8,1 d)	129,3 (163,5 d 7,4 t)

TABLE 2. ^{15}N NMR Chemical Shifts (δ, ppm) and $^{15}N-^{1}H$ SSCC (Hz) of 1-Phenyl-3-nitro-1,2,4-triazole

N^1	N^2	N^4	3-NO_2 *
−151,6 ($^2J_{N^1-H^5}$=10,6 d) ($J_{N^1-H^2}$=1,8 t)	−92,5 –	−133,9 ($^2J_{N^4-H^5}$=12.0 d)	−26,7 –

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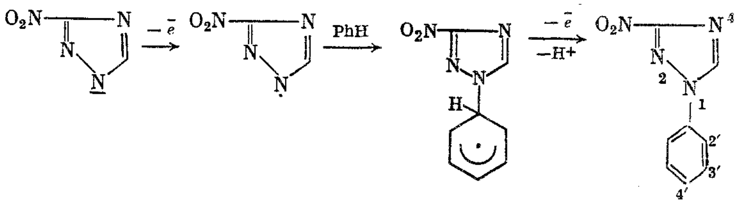
*A signal of the 3-nitro group also shows up in the ^{14}N NMR spectrum: −26.7 ppm ($\nu_{1/2}$ = 180 Hz).

chemical shifts of the N^1 atoms in 1-methyl-1,2,4-triazole [5] and in 1-phenyl-3-nitro-1,2,4-triazole is close, viz., −19.7 ppm. In addition, the location of the Ph group at N^1 is confirmed by the existence of a vicinal SSCC $^3J_{^{15}N-H}$ = 1.8 Hz for coupling of the N^1 atom with the ortho protons. The absence of a substituent in the 5 position of the 1,2,4-triazole ring is confirmed by the SSCC for coupling of the H^5 atom with the N^1 ($^2J_{^{15}N^1-H^5}$ = 10.6 Hz) and N^4 ($^2J_{^{15}N^4-H^5}$ = 12.0 Hz) atoms, as well as by the absence of an SSCC for coupling of the H^5 atom with the N^2 atoms [7]. In the absence of a substituent in the 3 position one should observe SSCC for coupling of the H^3 atom not only with the N^1 and N^4 atoms but also with the N^2 atom [7].

The signal at −26.7 ppm was assigned to the N atom of the NO_2 group in the 3 position, which also shows up in the ^{14}N NMR spectrum at −26.7 ppm ($\nu_{1/2}$ = 180 Hz).

In addition, a product, which is evidently a mixture of two other PNT isomers (2% yield with respect to the substance), was isolated from the reaction mixture in small amounts. According to the results of elementary analysis and the IR spectral data, it virtually does not differ from 1-PNT. However, in addition to signals of a Ph group, the PMR spectra contain singlets at 8.9 and 8.4 ppm, which apparently correspond to the protons of a 1,2,4-triazole ring substituted in the 4 and 2 positions. Judging from the integral intensities, the ratio of 4-PNT and 2-PNT in the mixture is 4:1. Thus, 1-, 2-, and 4-PNT in a ratio of 10:1: 0.25 are formed in 20% yield in the electrolysis of the NT anion in the presence of benzene.



The yield of PNT increases somewhat (28% yield with respect to the substance, 30% yield with respect to the current) in a diaphragmless electrolyzer. The nonionized NT that is formed during the process probably undergoes partial reduction on the cathode to the anion (compare with [8]), which is again oxidized on the electrode to the NT radical. In this connection it should be noted that the yield of PNT increases if, in addition to the NT salt, nonionized NT is added to the electrolyte. Electrolysis under these conditions leads to the formation of PNT in 67% yield with respect to the substance and 75% yield with respect to the current.

EXPERIMENTAL

The methods used to make the volt–ampere measurements and carry out the electrolysis, as well as the purification of the solvents, were described in [1, 2]. The reference electrode in all of the experiments was an Ag/0.1 N Ag^+ electrode in MeCN. The diaphragmless electrolysis was carried out in a thermostatted cell (20°C) equipped with Pt electrodes in the form of plates with $S = 6\ cm^2$. Stirring was accomplished with a magnetic stirrer. All of the experiments were carried out in absolute MeCN with 0.1-0.2 N $LiClO_4$ as the inert electrolyte. The 3-nitro-1,2,4-triazole (NT) was synthesized by the method in [9].

The ^{13}C, ^{14}N, and ^{15}N NMR spectra of solutions of the compounds in DMSO-d_6 were recorded with a Bruker AM-300 spectrometer with tetramethylsilane (TMS) as the internal standard; the ^{14}N and ^{15}N NMR spectra were also recorded with respect to $Me^{15}NO_2$ as the external standard (the high-field shifts were negative).

Tetramethylammonium Salt of NT. An equimolar amount of Me_4NOH (4.8 g in 10 ml of EtOH) was added with stirring to a solution of 6 g of NT in 20 ml of EtOH, after which the solvent was removed by vacuum distillation, and the residue was crystallized from CCl_4–MeCN (5:1) to give 5 g (51%) of the salt with mp 136-137°C. Found, %: C 38.5; H 7.60; N 37.43. $C_6H_{13}N_5O_2$. Calculated, %: C 38.3; H 7.45; N 37.23.

Electrolysis of the Tetramethylammonium Salt of NT. A solution of 0.2 g of the salt in 20 ml of 0.2 N $LiClO_4$ in MeCN was placed in the anode space of the electrolyzer, 15 ml of the inert electrolyte solution was poured into the cathode compartment, and electrolysis was carried out at E = 2.0 V until the NT anion was completely consumed. After electrolysis, the anolyte was evaporated in vacuo. Preparative TLC of the residue on Silufol UV-254 plates [benzene–ether (2:3)] gave 0.11 g of nonionized NT (90% yield with respect to the substance, 95% yield with respect to the current). Monitoring of the change in the anion concentration during the electrolysis was accomplished by spectrophotometry and from the limiting current for the oxidation of the NT anion. The NT was identical to a genuine sample according to the results of TLC and the UV and IR spectra.

Electrolysis of the Tetramethylammonium Salt of NT in the Presence of Benzene. A solution of 0.5 g of the NT salt in 20 ml of the inert electrolyte containing 10% by volume benzene was placed in the anode compartment of the electrolyzer, and electrolysis was carried out at E = 1.8 V until the NT anion was completely consumed. After electrolysis, the anolyte was evaporated in vacuo. Preparative TLC of the residue gave 90 mg (18% yield with respect to the substance, 20% yield with respect to the current) of 1-PNT, 10 mg (2% yield with respect to the substance, 2.2% yield with respect to the current) of a mixture of 2- and 4-PNT, and 180 mg (60% yield with respect to the substance, 65% yield with respect to the current) of NT. The 1-PNT had mp 130-132°C. Mass spectrum, m/z: 190 M^+. IR spectrum (ν, cm^{-1}, KBr): 760 s, 840 s, 985 m, 1095 m, 1230 w, 1250 w, 1310 s (NO_2), 1370 w, 1410 w, 1430 m, 1470 w, 1510 m, 1570 s (NO_2), 1600 w, 1680 vw, 3160 w (aromatic CH). Found, %: C 51.20; H 3.17; N 29.24. $C_8H_6N_4O_2$. Calculated, %: C 50.52; H 3.16; N 29.47. The IR spectrum of the mixture of 2- and 4-PNT was identical to the spectrum of 1-PNT. Mass spectrum, m/z: 190 M^+. Found, %: C 49.9; H 3.17; N 29.51.

Diaphragmless Electrolysis of the Tetramethylammonium Salt of NT in the Presence of Benzene. A) The electrolyzer was charged with 20 ml of MeCN, 2 ml of benzene, and 0.6 g of the NT salt, and electrolysis was carried out at a constant current of 0.25 A with stirring until 1.8 F/mole of electricity had been passed. After electrolysis, the solvent was removed by distillation, and the residue was subjected to column chromatography [neutral Al_2O_3, benzene–ether (2:3)] to give 150 mg (25% yield with respect to the substance, 27% yield with respect to the current) of 1-PNT and 16 mg (3% yield with respect to the substance, 3% yield with respect to the current) of a mixture of 2- and 4-PNT.

B) A 0.8-g sample of the NT salt, 0.5 g of NT, 20 ml of MeCN, and 2 ml of benzene were placed in the electrolyzer, and electrolysis was carried out as in experiment A. After removal of the solvent by distillation, column chromatography of the residue gave 470 mg (58% yield with respect to the substance, 65% yield with respect to the current) of 1-PNT and 70 mg (9% yield with respect to the substance, 10% yield with respect to the current) of a mixture of 2- and 4-PNT.

CONCLUSIONS

The electrolytic oxidation of the 3-nitro-1,2,4-triazole anion is realized through an intermediate radical, which splits out an H atom on reaction with the medium and reacts with benzene to give N-substituted phenyl-3-nitro-1,2,4-triazoles.

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C-ALKYLATION OF INDOLES WITH IMINES AND HEXAFLUOROACETONE AZINE

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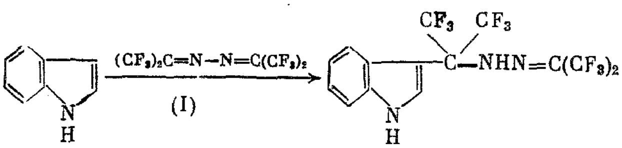
Uncatalyzed C^3 alkylation of indole with imine, fluorobenzoyl-, benzenesulfonyl-, and trifluoroacetylimines of hexafluoroacetone have been described earlier [1]. In this paper the results of further study of similar reactions are presented.

C^3 alkylation of indole under mild conditions can be carried out with weak electrophiles such as hexafluoroacetone azine (I). Reaction of (I) with indole in abs. $CHCl_3$ at 20°C over a prolonged time (3 months) leads to 3-[2,5-di(trifluoromethyl)-3,4-diaza-3H-perfluorohex-4-en-2-yl]indole (II) in 91% yield. Compound (II) does not react with indole even in refluxing CCl_4.



(II)

Conditions for C alkylation with acylimines of hexafluroacetone are determined apparently by the electrophilic properties of the C=N bond and do not depend substantially on steric effects of the substituents at the N atom. For example, the perfluorovaleroylimine of hexafluoroacetone (IIIa) reacts with indole under conditions analogous to those described for the trifluoroacetylimine of hexafluoroacetone (IIIb) [1]. Mixing the reagents in abs. $CHCl_3$ at −50°C causes spontaneous warming of the reaction mixture to 20°C and leads nearly quantitatively (Table 1) to 3-(α-perfluorovaleroylamidohexafluoroisopropyl)indole (IVa) (see scheme top of following page). The substituent in position 2 of the indole ring has relatively little influence on the reaction conditions. Compound (IIIb) under these conditions reacts with 2-methyl- and 2-phenylindoles to form the corresponding derivatives (Vb) and (VIb).

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