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The base-induced cascade rearrangement of 4-acetylamino-3-arylazo-1,2,5-oxadiazole 2-oxides (furoxans) into 4-acetylamino-2-aryl-5-nitro-2*H*-1,2,3-triazoles

Ekaterina L. Baryshnikova, Alexander S. Kulikov*, Igor V. Ovchinnikov, Vladimir V. Solomentsev and Nina N. Makhova

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5328; e-mail: mnn@ioc.ac.ru

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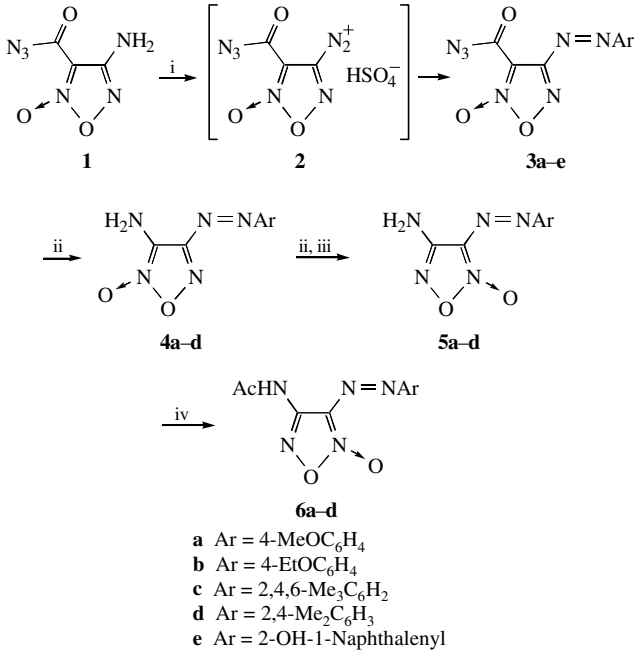
4-Acetylamino-3-arylazo-1,2,5-oxadiazole 2-oxides (furoxans) undergo two successive (cascade) mononuclear heterocyclic rearrangements in an aqueous basic medium with the formation of 4-acetylamino-2-aryl-5-nitro-2*H*-1,2,3-triazoles.

Mononuclear heterocyclic rearrangements of uncondensed furoxan derivatives (as distinct from benzofuroxans[1]) are not clearly understood.[2,3] Several examples of the mononuclear heterocyclic rearrangements of the oximes of carbonyl derivatives of furoxans to form α-nitroalkylfurazans were described.[4–6] The mononuclear heterocyclic rearrangements of furoxans can be useful for the synthesis of other heterocyclic systems. Thus, recently we found the thermal recyclisation of 4-acetyl(benzoyl)-3-methylfuroxan phenylhydrazones into 5-acetyl-4-methyl(phenyl)-2-phenyl-2*H*-1,2,3-triazole 1-oxide oximes and the base-induced mononuclear heterocyclic rearrangement of the above phenylhydrazones into 4-methyl(phenyl)-5-(1-nitroethyl)-2-phenyl-2*H*-1,2,3-triazoles.[7] Moreover, the thermal recyclisation of a diazenofuroxanyl unit into 4-nitro-2*H*-1,2,3-triazole was discovered.[8] It was suggested[8] that this reaction includes two successive (cascade) rearrangements: a 1,2,4-oxadiazole ring is formed at the first step; next, this ring is transformed into a 1,2,3-triazole ring with the participation of an azo group. In this work, we examined an analogous rearrangement of 4-acetylamino-3-arylazofuroxans **6**.

4-Amino-3-azidocarbonylfuroxan **1**[9] served as a common parent compound for azofuroxans **6**. On this basis, diazonium salt **2** was prepared by the well-known procedure,[10] and this salt was entered into azo coupling reactions with corresponding aromatic compounds. The diazotization of aminofuroxan **1**, which is a weakly basic amine (like other aminofuroxans[11]), was performed in a mixture of concentrated sulfuric and phosphoric acids. Of aromatic compounds, we studied anisole (its azo coupling reaction was described previously[10]), phenetole, 2-hydroxynaphthalene, mesitylene, *m*-xylene, toluene and *tert*-butylbenzene. We failed to enter only the two last-named compounds into the azo coupling reaction with diazonium salt **2** with the formation of 4-arylazo-3-azidocarbonylfuroxans **3**. This result additionally points to the fact that a furoxan ring is a strong electron acceptor:[12] diazonium salt **2** entered azo coupling reactions even with passive substrates such as mesitylene and *m*-xylene.



a Ar = 4-$MeOC_6H_4$
b Ar = 4-$EtOC_6H_4$
c Ar = 2,4,6-$Me_3C_6H_2$
d Ar = 2,4-$Me_2C_6H_3$
e Ar = 2-OH-1-Naphthalenyl

Scheme 1 *Reagents and conditions*: i, $NaNO_2$, conc. H_2SO_4 and H_3PO_4, 1 h, 0–2 °C, then ArH in Py, 0–2 °C → 20 °C; ii, dioxane–water, 80 °C, 15 min; iii, (only for **3a**,**c**) toluene, reflux, 2 h; iv, Ac_2O, H_2SO_4 (2 drops), 30 min.

Next, an azidocarbonyl group in azo compounds **3** was transformed into an amino group using the Curtius rearrangement in accordance with a previously developed procedure.[9] It would be expected that 3-amino derivatives are formed as a result of this reaction. However, in the case of compounds **3b**,**d**, 4-amino isomers **5b**,**d** were immediately formed because it is well known that 3-aminofuroxans are prone to thermal isomerisation into 4-aminofuroxans.[13] In the case of compounds **3a**,**c**, a mixture of 3- and 4-aminofuroxans **4a**,**c** and **5a**,**c** was formed, which was completely isomerised without separation into 4-aminofuroxans **5a**,**c** by refluxing in toluene according to a published procedure.[13] 3-Amino and 4-amino groups in furoxans can be easily identified by ^{1}H NMR spectroscopy: a 3-amino group exhibits an upfield signal with respect to that of a 4-amino group.[13]

We failed to rearrange an azidocarbonyl group in 2-hydroxy-1-naphthyl derivative **3e** into a corresponding amine. Under reaction conditions, the rate of rearrangement of azidocarbonyl group in this compound was insignificant, and the azo compound underwent almost complete degradation on standing without the formation of an amino derivative. Amino groups in amino derivatives **5a–d** were acylated with acetic anhydride in the presence of a catalytic amount of sulfuric acid with the formation of desired 4-acetylamino-3-arylazofuroxans **6** (Scheme 1).[†,‡,§] All of the compounds were obtained in high yields (80–85 or ~100%). The peculiarity of some compounds **6** is doubled signals of MeCO and NH groups in their ^{1}H NMR spectra due to the hindered rotation of acetylamino fragments.

† *4-Amino-3-arylazofuroxans* **5b**,**d** (general procedure). A solution of 10 mmol of **4b**,**d** in 10 ml of dioxane and 0.3 ml of water was stirred at 80 °C during 15 min. The reaction mixture was cooled to room temperature and 40 ml water was slowly added with stirring. The precipitate of **5b**,**d** was filtered, washed with a 20% dioxane–water mixture (2×5 ml) and dried in air.

4-Amino-3-arylazofuroxans **5a**,**c** (general procedure). The precipitate obtained as described above (10 mmol) was refluxed with toluene (35 ml) for 2 h. Then, the reaction mixture was cooled, 70 ml of hexane was added, the precipitate was filtered off, washed with hexane (5 ml) and dried in air.

4-Acetylamino-3-arylazofuroxans **6a–d** (general procedure). A suspension of 2 mmol of **5a–d** in 1.5 ml (10 mmol) of Ac_2O was stirred for 30 min, 2 drops of conc. H_2SO_4 was added and stirring was continued during 30 min. The reaction mixture became homogeneous and then a precipitate of **6a–d** was formed. It was filtered off, washed with water (3×5 ml) and dried in air.

*4-Acetylamino-2-aryl-5-nitro-2*H*-1,2,3-triazoles* **9a–d** (general procedure). A solution of 1 mmol of acetylamino derivative **6a–d** in 10 ml of 15% NaOH was stirred for 20 min at room temperature, then the reaction mixture was acidified with 15% HCl. The precipitate was filtered off, washed with cold water (2×20 ml), dried in air and dissolved in a mixture of EtOAc and $CHCl_3$ (1:1). The solution was filtered through SiO_2 and the solvent was evaporated at a reduced pressure.

The rearrangement of prepared compounds **6** into 4-acetylamino-2-aryl-5-nitro-2*H*-1,2,3-triazoles **9** was initially examined by the example of 4-acetylamino-3-(4-methoxyphenylazo)furoxan **6a**. Attempts to perform its thermal rearrangement (boiling in ethyl acetate, dioxane or toluene) by analogy with that described in ref. 9 were unsuccessful. In all cases, thermal degradation with the liberation of initial compound **6a** was observed. The rearrangement was successfully performed only under conditions of basic catalysis in water at room temperature for 20 min. The reaction conditions were found suitable for the rearrangement of other prepared acetylamino derivatives **6**. Target nitrotriasoles **9** were precipitated after neutralising the reaction mixture with hydrochloric acid, and the precipitates were filtered off.†,¶ In all cases, the yields of nitrotriasoles were higher than 50% (54–62%).

By analogy with ref. 8, we may believe that compounds **9** are formed *via* two successive (cascade) rearrangements. As a result of the first rearrangement *via* intermediate **7**, 1,2,4-oxadiazole derivatives **8** are formed, which are rearranged into final 4-acetylamino-2-aryl-5-nitro-2*H*-1,2,3-triazoles **9** under reaction conditions in accordance with Scheme 2.

The formation of nitrotriazoles **9** was supported by the appearance of a signal due to the nitro group in the ^{14}N NMR spectra and a peak due to the molecular ion in the mass spectra (note that the fragment ions [M$^+$ – NO] and [M$^+$ – 2NO], which are typical of furoxans, are absent). Moreover, upfield signals (110–130 ppm), which correspond to the C-3 atom of a furoxan ring, are absent from the ^{13}C NMR spectrum. To provide an

‡ All new compounds exhibited satisfactory elemental analyses, and their structures were confirmed by IR and NMR spectroscopy and mass spectrometry. Spectroscopic data: ^{1}H NMR (250, 300 MHz), ^{13}C NMR (75.47 MHz) standard TMS; ^{14}N NMR (21.6 MHz), internal standard $MeNO_2$ (Bruker WM-250 and Bruker AM-300 spectrometers). Compounds **3** were characterised by only spectral methods owing to their capacity to explode. Mass spectra were measured on a Finnigan MAT INCOS-50 spectrometer. IR spectra were recorded on a UR-20 spectrometer.

3-Azidocarbonyl-4-(4-methoxyphenylazo)furoxan **3a**: 86% yield, mp 85–87 °C (lit.,[10] 85–87 °C).

3-Azidocarbonyl-4-(4-ethoxyphenylazo)furoxan **3b**: yield 100%, mp 71–73 °C, R_f 0.35 (eluent: $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 1.50 (t, 3H, Me), 4.20 (q, 2H, CH_2), 7.03, 8.05 (4H, AA′BB′, ^3J 7.2 Hz). IR (ν/cm^{-1}): 2176 (N_3), 2144 (N_3), 1688 (CO), 1616, 1600 (fur. ring), 1488 (N=N), 1388, 1268, 1196, 1040, 868, 800.

3-Azidocarbonyl-4-(2,4,6-trimethylphenylazo)furoxan **3c**: 100% yield, mp 82–84 °C, R_f 0.65 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.40 (s, 3H, 4-Me), 2.55 (s, 6H, 2,6-Me), 7.10 (s, 2H, CH). IR (ν/cm^{-1}): 2928 (CH), 2184 (N_3), 2136 (N_3), 1700 (CO), 1608 (fur. ring), 1488 (N=N), 1432, 1392, 1332, 1304, 1288, 1200, 1120, 1080, 984, 864, 808, 752, 720, 704.

3-Azidocarbonyl-4-(2,4-dimethylphenylazo)furoxan **3d**: 82% yield, mp 94–95 °C, R_f 0.18 (eluent: $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 2.45 (s, 3H, 4-Me), 2.67 (s, 3H, 2-Me), 7.15, 7.75 (2H, ^3J 7.4 Hz), 7.25 (s, 1H, CH). IR (ν/cm^{-1}): 2184 (N_3), 2136 (N_3), 1692 (CO), 1608 (fur. ring), 1484 (N=N), 1392, 1328, 1180, 808, 712.

3-Azidocarbonyl-4-(2-hydroxy-1-naphthylazo)furoxan **3e**: 100% yield, mp 100–101 °C, R_f 0.30 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 5.0 (br. s, 1H, OH), 7.10–7.80 (m, 6H, naphth.). IR (ν/cm^{-1}): 3072 (OH), 2168 (N_3), 1712, 1672 (CO), 1616, 1592 (fur. ring), 1584, 1576, 1560, 1536, 1508, 1464 (N=N), 1456, 1400, 1312, 1256, 1192, 1136, 1096, 984, 968, 848, 776, 736. MS, *m*/*z*: 325 (M$^+$), 255 (M$^+$ – N_3CO), 224 (M$^+$ – N_3CO – NO – 1), 194 (M$^+$ – N_3CO – 2NO – 1), 171 (M$^+$ – N_3CO – – fur), 143 (M$^+$ – N_3CO – fur – N=N).

4-Amino-3-(4-methoxyphenylazo)furoxan **5a**: 65% yield, mp 161–163 °C, R_f 0.18 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 3.90 (s, 3H, MeO), 6.75 (br. s, 2H, NH_2), 7.15, 8.10 (4H, AA′BB′, ^3J 7.2 Hz). IR (ν/cm^{-1}): 3431, 3322 (NH), 1632, 1625 (NH), 1588, 1194.

4-Amino-3-(4-ethoxyphenylazo)furoxan **5b**: 78% yield, mp 160–162 °C, R_f 0.11 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.42 (t, 3H, Me), 4.19 (q, 2H, CH_2), 6.75 (br. s, 2H, NH_2), 7.10, 8.00 (4H, AA′BB′, ^3J 7.4 Hz). ^{13}C NMR ([$^2H_6$]DMSO) δ: 15.90 (Me), 64.10 (CH_2), 114.4 (*m*-Ar), 121.58 (C-3 fur. ring), 125.55 (*o*-Ar), 125.70 (*ipso*-Ar), 151.30 (C-4 fur. ring), 160.60 (*p*-Ar). IR (ν/cm^{-1}): 3424 (NH_2), 3304 (NH_2), 3008, 1604, 1592, 1556, 1524, 1480, 1432, 1392, 1360, 1336, 1316, 1304, 1248, 1204, 1192, 1164, 1148, 1128, 1112, 1068, 1024, 1016, 920, 872, 840. MS, *m*/*z*: 249 (M$^+$), 233(M$^+$ – O), 219 (M$^+$ – NO), 189 (M$^+$ – 2NO), 149 (M$^+$ – fur – NH_2 – 1), 121 (M$^+$ – N=N – fur – NH_2 – 1).

4-Amino-3-(2,4,6-trimethylphenylazo)furoxan **5c**: 56% yield, mp 119–120 °C, R_f 0.70 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.35 (s, 3H, Me), 2.55 (s, 6H, 2Me), 6.85 (br. s, 2H, NH_2), 7.10 (s, 2H, CH). IR (ν/cm^{-1}): 3425 (NH_2), 3316 (NH_2), 1655, 1600, 1542, 1524, 1494, 1395, 1385, 1324, 1282, 1210, 1196, 999, 872, 868, 706.

4-Amino-3-(2,4-dimethylphenylazo)furoxan **5d**: 77% yield, mp 151–153 °C, R_f 0.21 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.35 (s, 3H, 4-Me), 2.60 (s, 3H, 2-Me), 6.70 (br. s, 2H, NH_2), 7.15, 7.55 (2H, ^3J 7.4 Hz), 7.25 (s, 1H, CH). IR (ν/cm^{-1}): 3464 (NH_2), 3336 (NH_2), 2960, 1592, 1192, 1008, 864, 824, 712.

§ *4-Acetylamino-3-(4-methoxyphenylazo)furoxan* **6a**: 82% yield, mp 130–132 °C, R_f 0.25 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.20 (s, 3H, MeCO), 3.95 (s, 3H, MeO), 7.10, 7.90 (4H, AA′BB′, ^3J 7.3 Hz), 10.50 (br. s, 1H, NH). IR (ν/cm^{-1}): 3304 (NH), 1728 (CO), 1616, 1584, 1576, 1568, 1544, 1504, 1496, 1464, 1416, 1368, 1312, 1264, 1240, 1220, 1148, 1016, 1000, 848.

4-Acetylamino-3-(4-ethoxyphenylazo)furoxan **6b**: 80% yield, mp 137–139 °C, R_f 0.20 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.45 (t, 3H, Me), 2.13, 2.21 (2s, 3H, MeCO), 4.19 (q, 2H, CH_2), 7.10, 7.90 (4H, AA′BB′, ^3J 7.4 Hz), 10.50, 10.85 (2br. s, 1H, NH). IR (ν/cm^{-1}): 3288 (NH), 2984, 1704 (CO), 1616, 1584, 1568, 1532, 1480, 1472, 1460, 1448, 1432, 1424, 1372, 1328, 1304, 1288, 1256, 1192, 1144, 1128, 1040, 1000, 952, 840.

4-Acetylamino-3-(2,4,6-trimethylphenylazo)furoxan **6c**: 80% yield, mp 119–120 °C, R_f 0.52 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.00 (s, 3H, MeCO), 2.10 (s, 3H, 4-Me), 2.35 (s, 6H, 2-Me), 7.10 (s, 2H, CH), 10.50, 10.85 (2br. s, 1H, NH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 16.41 (MeCO), 20.45 (4-Me), 22.55 (2,6-Me), 129.09 (C-3 fur. ring), 128.92, 134.45, 135.51, 140.47 (Ar), 147.90 (C-4 fur. ring), 168.33 (CO). IR (ν/cm^{-1}): 3320 (NH), 1728 (CO), 1604, 1568, 1528, 1456, 1440, 1372, 1304, 1296, 1288, 1280, 1272, 1208, 1152, 992.

4-Acetylamino-3-(2,4-dimethylphenylazo)furoxan **6d**: 85% yield, mp 145–147 °C, R_f 0.12 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.08, 2.15 (2s, 3H, MeCO), 2.35 (s, 3H, 4-Me), 2.60 (s, 3H, 2-Me), 7.20, 7.60 (2H, ^3J 7.2 Hz), 7.30 (s, 1H, CH), 10.70, 11.05 (2br. s, 1H, NH). IR (ν/cm^{-1}): 3280 (NH), 2928, 1700 (CO), 1616, 1592, 1372, 1308, 1232, 1176, 1000, 832.

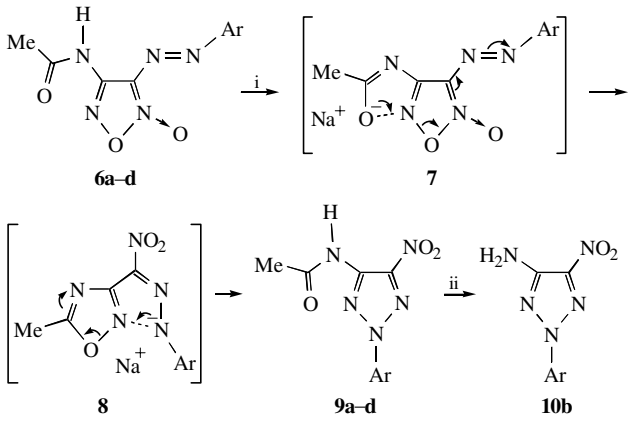
¶ *4-Acetylamino-2-(4-methoxyphenyl)-5-nitro-2H-1,2,3-triazole* **9a**: 54% yield, mp 143–145 °C, R_f 0.22 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.15 (s, 3H, MeCO), 3.85 (s, 3H, MeO), 7.15, 7.95 (4H, AA′BB′, ^3J 7.2 Hz), 10.95 (s, 1H, NH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 22.63 (MeCO), 55.47 (MeO), 114.82 (*m*-Ar), 120.53 (*o*-Ar), 131.32 (*ipso*-Ar), 138.27 (C–NH), 144.80 (C–NO_2), 159.88 (*p*-Ar), 168.38 (CO). ^{14}N NMR ($CDCl_3$) δ: –26.83 (NO_2). IR (ν/cm^{-1}): 3240 (NH), 3212 (NH), 3202(NH), 2978, 1690 (CO), 1554, 1514, 1442, 1178, 1124, 1088, 920, 670. MS, *m*/*z*: 278 (M$^+$ + 1), 277 (M$^+$), 247 (M$^+$ – NO), 236, 235 (M$^+$ – CH_2CO), 205 (M$^+$ – NO_2 – CN), 190, 189, 135 ($MeOPhN_2$), 107 (MeOPh).

4-Acetylamino-2-(4-ethoxyphenyl)-5-nitro-2H-1,2,3-triazole **9b**: 60% yield, mp 189–191 °C, R_f 0.25 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.35 (t, 3H, Me), 2.15 (s, 3H, MeCO), 4.15 (q, 2H, CH_2), 7.15, 7.95 (4H, AA′BB′, ^3J 7.2 Hz), 11.05 (br. s, 1H, NH). ^{14}N NMR ([$^2H_6$]acetone) δ: –25.82 (NO_2). IR (ν/cm^{-1}): 3248 (NH), 3208 (NH), 3204 (NH), 3064, 2976, 1692 (CO), 1544, 1512, 1448, 1252, 1176, 1120, 1084, 920, 672.

4-Acetylamino-5-nitro-2-(2,4,6-trimethylphenyl)-2H-1,2,3-triazole **9c**: 57% yield, mp 145–147 °C, R_f 0.22 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.15 (s, 3H, MeCO), 2.35 (s, 3H, 4-Me), 2.63 (s, 6H, 2,6-Me), 7.10 (s, 2H, CH), 10.80 (br. s, 1H, NH). ^{14}N NMR ([$^2H_6$]acetone) δ: –25.69 (NO_2). IR (ν/cm^{-1}): 3184 (NH), 2976, 1680 (CO), 1576, 1540, 1524, 1404, 1376, 1368, 1360, 1340, 1320, 1304, 1288, 1272, 1200, 1176, 1036, 1016, 976, 856, 804, 736. MS, *m*/*z*: 289(M$^+$), 272 (M$^+$ – OH), 247 (M$^+$ – CH_2CO), 230 (M$^+$ – NO_2COMe), 147 (Me_3PhN_2), 119 (Me_3Ph).

4-Acetylamino-2-(2,4-dimethylphenyl)-5-nitro-2H-1,2,3-triazole **9d**: 62% yield, mp 139–141 °C, R_f 0.19 (eluent: $CHCl_3$–isooctane 1:1). ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.15 (s, 3H, MeCO), 2.30 (s, 3H, 4-Me), 2.38 (s, 3H, 2-Me), 7.25, 7.55 (2H, ^3J 7.6 Hz), 7.31 (s, 1H, CH), 10.90 (br. s, 1H, NH). ^{14}N NMR ($CDCl_3$) δ: –27.26 (NO_2). IR (ν/cm^{-1}): 3360 (NH), 3200 (NH), 3080, 3056, 1692 (CO), 1568, 1496, 1324, 1240, 1176, 968, 832, 804.

4-Amino-2-(4-ethoxyphenyl)-5-nitro-2H-1,2,3-triazole **10b**: 68% yield, mp 133–135 °C, R_f 0.17 (eluent: $CHCl_3$). ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.47 (t, 3H, Me), 4.13 (q, 2H, CH_2), 6.74 (br. s, 2H, NH_2), 7.05, 7.90 (4H, AA′BB′, ^3J 7.4 Hz). ^{13}C NMR ([$^2H_6$]acetone) δ: 15.16 (Me), 64.90 (OCH_2), 116.16 (*m*-Ar), 121.50 (*o*-Ar), 133.15 (*ipso*-Ar), 140.55 (C–NO_2), 150.30 (C–NH_2), 160.70 (*p*-Ar). ^{14}N NMR ([$^2H_6$]acetone) δ: –23.18 (NO_2), –139.34 (N-2 tr. ring), –342.60 (NH_2). IR (ν/cm^{-1}): 3480 (NH), 3368 (NH), 2992 (CH), 2944 (CH), 1640, 1600, 1568, 1512, 1476, 1396, 1324, 1248, 920, 832. MS, *m*/*z*: 249 (M$^+$), 221 (M$^+$ – C_2H_4), 203 (M$^+$ – NO_2), 121 (M$^+$ – NH_2 – tr-NO_2 – 1), 93 (PhO).



Scheme 2 *Reagents and conditions*: i, 15% NaOH, 20 min, 20 °C, then HCl; ii, H_2SO_4 (2 drops), MeOH, 40 °C, 4 h.

additional support for the structure of **9**, using compound **9b** (Ar = 4-$EtOC_6H_4$) as an example, we hydrolysed the acetyl group and examined resulting amino derivative **10b** by NMR spectroscopy. The ^{14}N NMR spectrum was found to be most informative. It exhibited signals due to the nitro group (–23.20 ppm), the amino group (–342.60 ppm) and the N-2 atom of a triazole ring (–139.34 ppm), which are consistent with published data on the ^{14}N NMR spectra of 2-substituted 1,2,3-triazoles.[14]

Thus, we found the base-induced cascade mononuclear heterocyclic rearrangement of 4-acetylamino-3-arylazofuroxans into 4-acetylamino-2-aryl-5-nitro-2*H*-1,2,3-triazoles, and this rearrangement can be convenient for the synthesis of these structures.

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