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New Concept in Synthesis of Fused Six-Membered Nitrogen Heterocycles. Silane-Mediated Direct Condensation of Nitroarenes with Allylic Carbanions.

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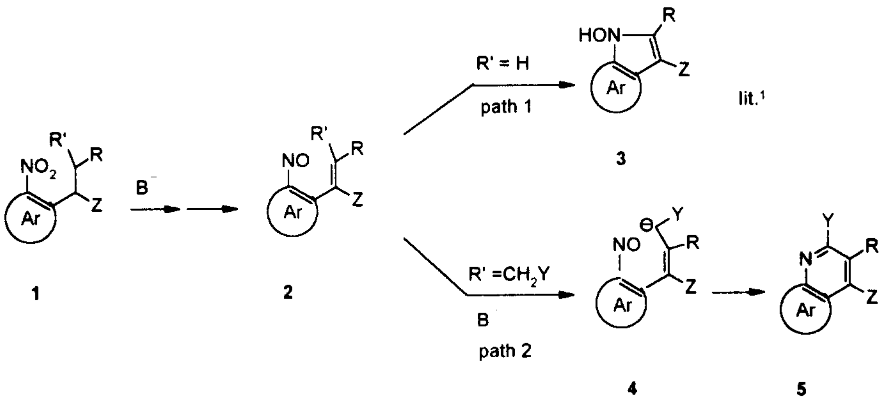
Abstract: Six-membered nitrogen containing ring was constructed *via* double condensation of allylic CH-acids with nitoarenes. The reactions proceed with high regioselectivity. Mechanism of the transformation was discussed. © 1997 Elsevier Science Ltd.

Recently we have shown that some α,β-functionalized *ortho*-nitroarylethanes **1** can be transformed into 1-hydroxyindoles **3** under basic conditions most probably *via* deprotonation at the benzylic position, followed by transformation of the anion to unstable 1-nitroso-2-ethene derivative **2** and subsequent intramolecular

Scheme 1



conversion **4** to **5** :

a.: Ar =benzene, Z=CN, R=Y=CO_2Me; K_2CO_3/ Bu_4NBr cat./ MeCN/ 7 days; 76%

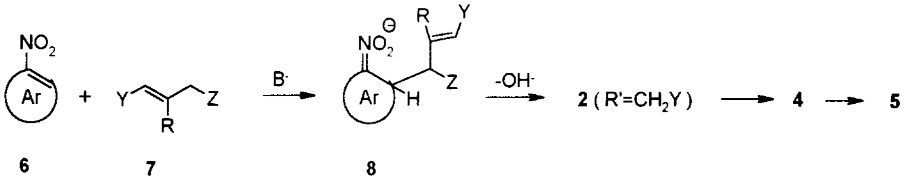
b.: Ar =naphthalene, Z=SO_2Ph, R=H, Y=Ph, DBU/ MeCN/ 30 days, 15%

electrocyclization to form five-membered ring (Scheme 1, path 1).[1]

Another way of the nitroso group trap may be realized *via* its intramolecular condensation with the carbanion center in allylic position (if present), leading to six-membered ring (Scheme 1, path 2). Only two examples of the latter reaction were observed.[2]

Since it is well known that the nitroso compounds can also be formed from σ^H adducts of various anions to nitroarenes with loss of the hydroxide anion[3] (some parallels between σ^H adducts and *ortho*-nitrobenzylic anions have been recently disscussed[1]) one can expect formation of **4** and subsequently **5** when the allylic system is introduced directly to the nitroarene as a fragment of the carbanion moiety (Scheme 2).

Scheme 2

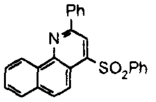
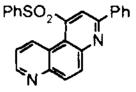
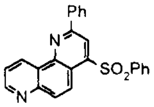
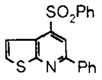
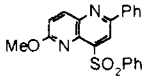
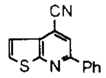
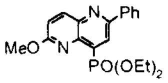


Nevertheless, when the equimolar DMF solution of 1-nitronaphthalene (**6**, Ar=naphthalene) and cinnamyl phenyl sulfone (**7**, Y=Ph, R=H, Z=SO_2Ph) was stirred in the presence of 5 eq. of DBU at RT only substrates were observed even after 48h. However, after addition of 5 eq. of Me_3SiCl, 2-phenyl-4-phenylsulfonylbenzo[*h*]quinoline **5a** was formed in 44% yield during 24h. Some other active nitroarenes react similarly[4] (Table 1).

The reaction conditions were not optimized. The best results were obtained with cinnamyl phenyl sulfones as the allylic component although some other cinnamyl derivatives enter also this reaction. Among the other additives examined in the model reaction (1-nitronaphthalene, cinnamyl phenyl sulfone, 5 eq.of DBU, 2.5 eq. of additive, MeCN, RT, 4 days) LiCl and $MgCl_2$ turned out to be effective giving **5a** in 28 and 70% yield respectively, $TiCl_4$ led to only traces of product and $BF_3 \cdot Et_2O$ as well as $ZnCl_2$ induced no reaction. The role of the additive is unclear so far. It is known that silylation as well as complexation with lithium or magnesium cations stabilize σ^H adducts to nitroarenes.[5,6] They are also known to facilitate nitroso- compound formation from σ^H adducts.[7] Their influence on the last step of the reaction namely the intramolecular condensation of carbanion **4** is also possible.

Since the carbanion derived from 7 is ambident it can add to the nitroarene **6** in two possible manners (Y and Z may be interchanged). Actually the same compound **5a** was obtained both from **4b** (Scheme 1) as well as from **6** (Ar= naphthalene) and 7 (Y=Ph, R=H, Z=SO_2Ph). It means that the new σ bond formation engages the carbon atom with higher electron density, namely α to SO_2Ph group.

Table 1.

6	7, Y=Ph, R=H Z	5		cond.[a]	Yield(%)[b]
1-nitronaphthalene	$PhSO_2$		b	A	44
				B	69 (93)[c]
6-nitroquinoline	$PhSO_2$		c	A	43 (61)[d]
5-nitroquinoline	$PhSO_2$		d	B	87
2-nitrothiophene	$PhSO_2$		e	B	37 (68)[d]
2-methoxy-5-nitropyridine	$PhSO_2$		f	B	50 (62)[c]
2-nitrothiophene	CN		g	C	13
2-methoxy-5-nitropyridine	$PO(OMe)_2$		h	B	20 (40)[c,d]

a) **A**: Me_3SiCl (5eq.), DBU (5eq.), DMF, RT, 1-2 days; **B**: t-$BuSiMe_2Cl$ (2.5eq.), DBU (5eq.), MeCN, RT, 1day; **C**: t-$BuSiMe_2Cl$ (2.5eq), Et_3N (5eq.), MeCN, 5 days.; b) isolated *via* column chromatography.; c) based on converted nitroarene.; d) based on converted allylic compound.

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2. NMR (200 MHz, DMSO-d_6): **5a**: 3.98 (3H, s), 4.01 (3H, s), 8.53 (1H, dd, J = 9.0,2.3 Hz), 8.24 (1H, dd, J

=2.3,0.6 Hz), 8.37 (1H, dd, J = 9.0,0.6 Hz); **5b**: 7.60-7.75 (6H, m), 7.79-7.90 (2H, m), 8.03-8.09 (1H, d, J =9.2 Hz), 8.18-8.25 (2H, m), 8.46 (1H, d, J = 9.2 Hz), 8.48-8.52 (2H, m), 8.88 (1H, s), 9.34-9.42 (1H, m).

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4. NMR (200 MHz, DMSO-d_6) data: **5c**: 7.55-7.83 (7H, m), 7.98-8.05 (2H, m), 8.15-8.21 (2H, m), 8.27 (1H, d, J = 9.2 Hz), 8.35 (1H, d, J = 9.2 Hz), 8.41 (1H, s), 8.99 (1H, dd, J = 4.3,1.5 Hz), 9.71 (1H, ddd, J = 8.7,1.5,0.7 Hz); **5d**: 7.60-7.75 (6H, m), 7.85 (1H, dd, J = 8.4,4.4 Hz), 8.17 (1H, d, J = 9.5 Hz), 8.19-8.26 (2H, m), 8.48-8.55 (2H, m), 8.74 (1H, d, J = 9.5 Hz), 8.92 (1H, s), 9.12 (1H, dd, J = 4.4,1.7 Hz), 9.67 (1H, ddd, J = 8.4,1.7,0.8 Hz); **5e** :7.53-7.79 (6H, m), 7.87 (1H, d, J = 6.1 Hz), 8.19-8.27 (5H, m), 8.53 (1H, s); **5f** : 3.89 (3H, s), 7.33 (1H, d, J = 9.2 Hz), 7.56-7.74 (6H, m), 8.11-8.19 (2H, m), 8.24-8.33 (2H, m), 8.41 (1H, d, J = 9.2 Hz), 8.87 (1H, s); **5g**: 7.51-7.60 (3H, m), 7.61 (1H, d, J = 6.1 Hz), 8.15 (1H, d, J = 6.1 Hz), 6.24-6.30 (2H, m), 8.44 (1H, s); **5h** :3.83 (6H, d, J = 11.0 Hz), 3.95 (3H, s), 7.42 (1H, d, J = 9.1 Hz), 7.51-7.62 (3H, m), 7.91-7.98 (2H, m), 8.05 (1H, d, J = 5.5 Hz), 8.46 (1H, d, J = 9.1 Hz).
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