Novel, Efficient and Regiospecific Alkylation/Arylation/Heteroarylation of Unsymmetrical Azo Compounds

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Received 6 September 2005

Abstract: Excellent regioselectivity is observed in the addition of diverse organometallic nucleophiles to unsymmetrical azo compounds. Primary/secondary/tertiary alkyl, aryl and heteroaryl substituents were introduced this way in high yields.

Key words: azo compounds, hydrazines, regioselectivity, neighboring group effects, protecting groups

Many hydrazines with general formula $R^1R^2NNR^3R^4$ (R^1–R^4 = alkyl, acyl or aryl substituent) exhibit incredible biological activity and are used in the treatment of various diseases. A few vivid examples can refer to tuberculosis, Parkinson disorder and hypertension. Chemical structure of atazanavir, which represent an example of extremely useful peptidomimetics, also includes genuine hydrazine skeleton.[1]

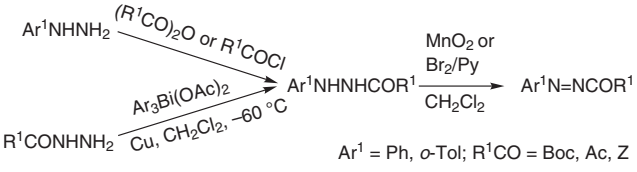
As a consequence, a remarkable number of strategies have been developed in order to systematize the synthesis of multi-substituted hydrazines, making it robust and suitable for industry.[2] Basic approach employs a set of relevant protecting groups and stepwise introduction of substituents. Each step is in fact an NH substitution reaction: alkylation, acylation or arylation. Alkylation is normally performed under phase-transfer catalysis or Mitsunobu conditions; both alkylation and acylation depend strongly on the pKa of the substrate.[3] The introduction of aryl substituent is more complicated, requiring organobismuth reagents or palladium catalysis.[4]

Contrary to NH substitution as a way to derivatize a hydrazine precursor, another approach would use direct addition reaction to the N=N bond. Actually, azo compounds with two alkoxycarbonyl groups are known as versatile electrophiles (DEAD, DBAD). The corresponding electrophilic aminations are widely used in the preparation of hydrazines, which in turn are employed as the source of derivatized amines and amino acids via the cleavage of N–N bond.[5]

Surprisingly, there are only two reports regarding nucleophilic addition to unsymmetrically substituted azo compounds. Evans used chiral Cu complexes in enantioselective amination of enol silanes with unsymmetrical azoimides.[6] Knochel generated diarylamines by amination of substituted aryl azo tosylates with arylmagnesium, followed by subsequent one-pot allylation, reduction and hydrolysis.[7] Regioselectivity of such addition is presumably thermodynamically controlled by the difference in the electronegativities of the both nitrogen-attached functional groups.

However, due to the reasons mentioned above, our main interest is to preserve hydrazine skeleton intact. It is well known that alkyl azo compounds are labile and tend to regroup to corresponding hydrazones, thus making no use for practical synthesis. Unlike them, azo compounds containing aryl and acyl/alkoxycarbonyl groups are sufficiently stable and readily available.[4d]

1-Alkoxycarbonyl-2-arylhydrazines were synthesized by two methods: highly selective catalytic arylation of alkoxycarbonylhydrazines with triarylbismuth diacetates[4d] or acylation of monoarylhydrazines (yields 80–90%). Further oxidation in very mild conditions furnishes azo compounds in high yields (90–100%) as it is demonstrated in Scheme 1.[8] However, only Troc and PhCO groups could be introduced into $DNPNHNH_2$ (DNP = 2,4-dinitrophenyl) by direct acylation (yields: 43 and 84%, respectively). Attempts to use Ac, Boc or Cbz were unsuccessful due to side reactions. Also, it was not possible to oxidize either TrocNHNHDNP or PhCONHNHDNP, despite the plenty of reagents we have tested [MnO_2, Br_2/Py, $NaBO_3$, PyN-oxide, MCPBA, CF_3CO_3H, $H_2O_2{\cdot}(NH_2)_2CO$].

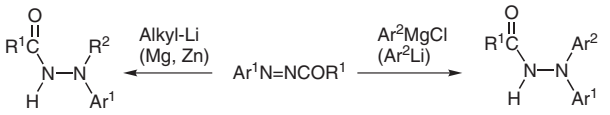


Scheme 1 Synthesis of unsymmetrical aryl azo compounds

The reaction, as outlined in Scheme 2, was never reported before. The process can be easily monitored by TLC. Regardless of the fact that the reaction closely resembles titration (extremely fast, ca. 15–20 min at –80 °C), the addition is still regiospecific, as it was confirmed by the ^1H NMR analysis of the crude mixtures. Namely, R^1CONH proton is clearly distinguishable from ArNH, which should appear if the addition happens to be nonselective. Also, the reaction of BuLi with BocN=NPh yield-

SYNTHESIS 2006, No. 5, pp 0843–0846
Advanced online publication: 07.02.2006
DOI: 10.1055/s-2006-926331; Art ID: Z16605SS

ed BocNHNPh(Bu), a compound which was described previously.[4d] ^{1}H, ^{13}C NMR data and HRMS spectra were identical in both cases (see experimental).



Scheme 2 Regioselective alkylation/arylation

The results of the derivatization are shown in Table 1. Organolithium and organomagnesium compounds gave extremely fast alkylation. The yield and the purity increase with lowering of the temperature. However, according to NMR studies, the formation of side products is not due to the nonselectivity of addition. The only case where we have observed nonspecific addition, was actually the reaction between *i*-PrMgCl and BocN=NPh, probably due to the extreme reactivity of such organomagnesium reagents (PhNH proton was clearly visible in the ^{1}H NMR of the product). Organozinc compounds, which are easily prepared from organolithiums just before use, were found to be versatile alkylating reagents. The reaction time is still the same 15 minutes, but side products are not detected.

Metal–halogen exchange reactions were used to generate heteroarylmagnesium derivatives in situ.[9] For arylation, organomagnesium reagents seem to be most convenient.

Table 1 Addition of Nucleophiles to $Ar^1N=NCOR^1$

Substrate	Nucleophile	Product	Yield (%)
BocN=NPh	3-PyMgCl	**1a**	81
BocN=NPh	*i*-PrZnCl	**1b**	92
BocN=NPh	3-ThienylMgCl	**1c**	91
BocN=NPh	BuLi	**1d**	82[a]
BocN=NPh	BuZnCl	**1d**	ca. 100
BocN=NPh	*p*-TolMgBr	**1e**	81
BocN=NPh	*p*-TolMgBr	**1e**	ca. 100[a]
BocN=NPh	*t*-BuZnCl	**1f**	97
ZN=NPh	BuLi	**2a**	70
ZN=NPh	BuZnCl	**2a**	85
ZN=NPh	*i*-PrMgCl	**2b**	77
AcN=NPh	BuZnCl	**3a**	96
AcN=NPh	*i*-PrMgCl	**3b**	88
AcN=NPh	*t*-BuZnCl	**3c**	54
BocN=N(*o*-Tol)	BuZnCl	**4a**	91
BocN=N(*o*-Tol)	*p*-TolMgCl	**4b**	93

[a] Reaction was conducted at –100 °C.

Arylzinc was too slow to react and aryllithium might sometime pose a problem, e.g. as in the case of the formation of 2-thienyllithium, where BuLi attacked 50% of aromatic H instead of performing the halogen–metal exchange. A solution of citric acid in THF was found to be the best option to quench the reaction at low temperatures.

The reasonable explanation of the unusual selectivity of the addition is still not known. At the first sight, it seems that the reaction is ruled mostly by the difference in electronegativities of R^1CONH and NHAr, but it is difficult to imagine that the process is thermodynamically controlled and there is a fast equilibrium between two possible anions $RCON^-$–NRAr and $RCONHN^-$–Ar at –80 °C. Therefore, a possibility of kinetic control via steric hindrance was checked using AcN=NPh as starting material. Despite low steric hindrance on AcNH in comparison to bulky BocNH, the latter compound still gave very selective addition of alkylzinc compounds. Finally, steric hindrance on aryl substituent was increased using *ortho*-tolyl substituent [see examples with BocN=N(*o*-Tol)] where no difference from BocN=NPh was detected.

BuLi and ArMgHal were added directly to azo compounds, since the reverse version – addition of azo compounds to BuLi resulted in the incomplete reaction and formation of side products. However, in the case of organozinc reagents the reverse addition sequence is more convenient from the practical point of view and was accomplished with no problems.

In conclusion, the described procedure is an efficient way to introduce alkyl or aryl substituents into protected azo compound. The reaction has a number of substantial advantages: high yields and high selectivity, the introduction of secondary and tertiary alkyl substituent is not far different from primary. The addition is fast and sensitivity to steric hindrance is diminished. Organozinc reagents seem to be more suitable for alkylation in comparison to organolithium, while organomagnesium is the reagent of choice for arylation.

NMR spectroscopy was performed on a Bruker AC 200P spectrometer, operating at 200 MHz (^{1}H NMR) and 50 MHz (^{13}C NMR). TMS was used as internal standard. Melting points were determined on a Gallenkamp melting point apparatus. High-resolution mass spectrometry was carried out on a Ettan ESI-ToF electrospray time-of-flight instrument.

Oxidation of Hydrazines with MnO_2; (1-*tert*-Butoxycarbonyl)phenyldiazene; Typical Procedure

BocNHNHPh (1.52 g, 7.5 mmol) was dissolved in CH_2Cl_2 (10 mL). Activated MnO_2 (3.26 g, 5 equiv) was added and the reaction was monitored by TLC (1:4 EtOAc–hexane). After the starting material had been consumed (15–20 min), the suspension was filtered and the filtrate evaporated, furnishing 1.35 g of BocN=NPh as dark orange oil (90%).

^{1}H NMR ($CDCl_3$): δ = 1.67 [s, 9 H, $C(CH_3)_3$], 7.5–7.6 (m, 3 H, C_6H_5), 7.8–7.9 (m, 2 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 28.0 ([$C(CH_3)_3$], 123.5, 129.2, 133.3, 151.8 (C_6H_5), 161.3 (C=O).

Addition of Nucleophiles to Azo Compounds; *tert*-Butyl 1-Isopropyl-2-phenylhydrazine-1-carboxylate (1b); Typical Procedure

An oven-dried flask was charged with a melt of $ZnCl_2$ (100 mg, 0.74 mmol, 1.3 equiv) under argon, then evacuated and backfilled with argon. At 0 °C, THF (2 mL) was added to dissolve the solid, followed by a 1.6 M solution of *i*-PrMgCl in THF (0.46 mL, 0.74 mmol). The reaction mixture was stirred for 0.5 h and then cooled down to –80 °C. A solution of BocN=NPh (117 mg, 0.567 mmol) in THF (2 mL) was added dropwise and the obtained mixture stirred for 20 min. TLC (1:4 EtOAc–hexane) confirmed that the starting material had been consumed. The reaction was quenched by adding a solution of citric acid (240 mg, 2 equiv) in THF (3 mL). The mixture was stirred, then partitioned between H_2O (5 mL) and CH_2Cl_2 (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic phases were dried ($MgSO_4$) and evaporated, to give the crude product as a white solid. Purification by chromatography (1:4 EtOAc–hexane) furnished 136 mg (92%) of **1b** pure by TLC; white crystals (hexane–$CHCl_3$); mp 97–99 °C.

In general the chemical shifts of conformers in the ^{1}H NMR spectra are given in decreasing order of intensity and separated by slashes.

^{1}H NMR ($CDCl_3$): δ = 1.14 [d, *J* = 3.8 Hz, 6 H, $(CH_3)_2CH$], 1.50/1.39 [s, 9 H, $C(CH_3)_3$], 4.15 [m, 1 H, $(CH_3)_2CH$], 6.13 (s, 1 H, NH), 6.75–6.85 (m, 3 H, C_6H_5), 7.15–7.3 (m, 2 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 18.2 [$(CH_3)_2CH$], 28.3 [$C(CH_3)_3$], 50.6 [$(CH_3)_2CH$], 80.4 [$C(CH_3)_3$], 113.5, 119.2, 129.2, 148.7 (C_6H_5), 155.9 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{23}N_2O_2$ $[MH]^+$: 251.1760; found: 251.1791.

Structures of all compounds prepared (Table 1) were confirmed with the help of spectral and analytical data. Analytical samples were obtained by crystallization from hexane–$CHCl_3$.

1a

Yellow oil.

^{1}H NMR ($CDCl_3$): δ = 1.41/1.31 [s, 9 H, $C(CH_3)_3$], 7.05–7.45 (m, 7 H, NH + C_6H_5 + $H_{pyridyl}$), 7.71, 8.18, 8.42 (br s, 3 $H_{pyridyl}$).

^{13}C NMR ($CDCl_3$): δ = 28.2 [$C(CH_3)_3$], 81.6 [$C(CH_3)_3$], 120.4, 123.4, 124.0, 124.9, 129.4, 140.2, 142.7, 143.0, 145.3 (C_6H_5 + pyridyl CH, C), 155.3 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{20}N_3O_2$ $[MH]^+$: 286.1556; found: 286.1601.

1c

Grey crystals; mp 69–71 °C.

^{1}H NMR ($CDCl_3$): δ = 1.44 [s, 9 H, $C(CH_3)_3$], 6.8–7.2 (m, 9 H, NH + C_6H_5 + 3 $H_{thienyl}$).

^{13}C NMR ($CDCl_3$): δ = 28.2 [$C(CH_3)_3$], 81.5 [$C(CH_3)_3$], 114.4, 120.8, 121.9, 122.1, 125.4, 128.8, 147.9, 149.2 (C_6H_5 + thienyl CH, C), 154.8 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{19}N_2O_2S$ $[MH]^+$: 291.1167; found: 291.1154.

1e

White crystals; mp 110–112 °C.

^{1}H NMR ($CDCl_3$): δ = 1.47/1.32 [s, 9 H, $C(CH_3)_3$], 2.31 (s, 3 H, $ArCH_3$), 6.85 (br s, 1 H, NH), 6.8–7.4 (m, 9 H, C_6H_5 + H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 20.8 ($ArCH_3$), 28.3 [$C(CH_3)_3$], 81.2 [$C(CH_3)_3$], 117.7, 121.0, 121.7, 129.0, 129.7, 133.2, 143.7, 146.9 (C_6H_5 + aryl CH, C), 155.7 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{23}N_2O_2$ $[MH]^+$: 299.1760; found: 299.1727.

1f

White crystals; mp 123–124 °C.

^{1}H NMR ($CDCl_3$): δ = 1.17 [s, 9 H, $(CH_3)_3CN$], 1.42 [s, 9 H, $C(CH_3)_3$], 6.42 (br s, 1 H, NH), 7.1–7.3 (m, 5 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 26.8 [$(CH_3)_3CN$], 28.4 [$C(CH_3)_3$], 58.9 [$(CH_3)_3CN$], 79.8 [$C(CH_3)_3$], 124.9, 125.9, 128.2, 148.1 (C_6H_5), 155.7 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{25}N_2O_2$ $[MH]^+$: 265.1916; found: 265.1956.

2a

White crystals; mp 67–69 °C.

^{1}H NMR ($CDCl_3$): δ = 0.91 (t, *J* = 7.2 Hz, 3 H, $CH_3CH_2CH_2CH_2$), 1.31 (m, 2 H, $CH_3CH_2CH_2CH_2$), 1.56 (m, 2 H, $CH_3CH_2CH_2CH_2$), 3.41 (m, 2 H, $CH_3CH_2CH_2CH_2$), 5.13/5.11 (s, 2 H, CH_2OCO), 6.6–6.9 (m, 3 H, NH + C_6H_5), 7.1–7.4 (m, 8 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 13.9 ($CH_3CH_2CH_2CH_2$), 20.2 ($CH_3CH_2CH_2CH_2$), 28.4 ($CH_3CH_2CH_2CH_2$), 52.5 ($CH_3CH_2CH_2CH_2$), 67.3 (CH_2OCO), 113.1, 119.4, 128.2, 128.5, 129.1, 136.2, 149.2 (C_6H_5), 155.8 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{22}ClN_2O_2$ $[MCl]^-$: 33.1370; found: 333.1410.

2b

Yellow oil.

^{1}H NMR ($CDCl_3$): δ = 1.13 [t, *J* = 5.4 Hz, 6 H, $(CH_3)_2CH$], 4.13 [m, 1 H, $(CH_3)_2CH$], 5.16/5.10 (m, 2 H, CH_2OCO), 6.47/6.53 (s, 1 H, NH), 6.7–6.9 (m, 3 H, C_6H_5), 7.1–7.4 (m, 7 H, C_6H_5).

^{13}C NMR ($CDCl_3$): δ = 18.1 [$(CH_3)_2CH$], 50.9 [$(CH_3)_2CH$], 67.3 (CH_2OCO), 113.8, 119.7, 128.2, 128.5, 130.0, 136.2, 148.4 (C_6H_5), 156.8 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{20}ClN_2O_2$ $[MCl]^-$: 319.1213; found: 319.1233.

3a

Yellowish crystals; mp 93.5–95 °C.

^{1}H NMR ($CDCl_3$): δ = 0.95 (t, *J* = 9.6 Hz, 3 H, $CH_3CH_2CH_2CH_2$), 1.34 (m, 2 H, $CH_3CH_2CH_2CH_2$), 1.96 (m, 2 H, $CH_3CH_2CH_2CH_2$), 1.97/1.91 (s, 3 H, CH_3CO), 3.35 (t, *J* = 7.6 Hz, 2 H, $CH_3CH_2CH_2CH_2$), 6.7–6.9 (m, 3 H, C_6H_5), 7.1–7.3 (m, 2 H, C_6H_5), 7.73/8.54 (s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 13.87/13.92 ($CH_3CH_2CH_2CH_2$), 19.2/20/8 (CH_3CO) 20.23/20.21 ($CH_3CH_2CH_2CH_2$), 28.0/28.8 ($CH_3CH_2CH_2CH_2$), 54.8/52.1 ($CH_3CH_2CH_2CH_2$), 114.0/113.0, 120.6/119/1, 129.4/129.0, 149.2/148.8 (C_6H_5), 169.6/176.5 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{12}H_{18}ClN_2O$ $[MCl]^-$: 241.1108; found: 241.1156.

3b

Yellow crystals; mp 100–102 °C.

^{1}H NMR ($CDCl_3$): δ = 1.02/1.29/1.17 [d, *J* = 6.4 Hz, 6 H, $(CH_3)_2CH$], 2.01/2.11 (s, 3 H, CH_3CO), 4.17 [m 1 H, $(CH_3)_2CH$], 6.8–7.0 (m, 3 H, C_6H_5), 7.2–7.35 (m, 2 H, C_6H_5), 7.43 (br s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 19.1/15.6/18.3 [$(CH_3)_2CH$], 20.2/20.8 (CH_3CO), 52.9/50.6 [$(CH_3)_2CH$], 115.3/114.0, 121.1/119.7, 129.5/129.3, 149.1/147.9 (C_6H_5), 177.1/170.1 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}ClN_2O$ $[MCl]^-$: 227.0951; found: 227.1029.

3c
Yellow crystals; mp 111–113 °C.

^{1}H NMR ($CDCl_3$): δ = 1.15 [s, 9 H, $C(CH_3)_3$], 2.14 (s, 3 H, CH_3CO), 7.1–7.3 (m, 5 H, C_6H_5), 9.22 (s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 20.1 (CH_3CO), 26.8 [$C(CH_3)_3$], 59.2 [$C(CH_3)_3$], 125.7, 126.7, 128.4, 147.4 (C_6H_5), 176.6/179.4 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{25}N_2O_2$ $[MH]^+$: 265.1916; found: 265.1956.

4a
Yellowish crystals; mp 73.5–74.5 °C.

^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 3 H, $CH_3CH_2CH_2CH_2$), 1.3–1.7 [overlapped signals, 13 H, $C(CH_3)_3$ + $CH_3CH_2CH_2CH_2$), 2.34 ($ArCH_3$), 3.14 (m, 2 H, $CH_3CH_2CH_2CH_2$), 6.24 (s, 1 H, NH), 6.9–7.1 (m, 4 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 14.0 ($CH_3CH_2CH_2CH_2$), 18.5 ($CH_3CH_2CH_2CH_2$), 20.3 (CH_3CO), 28.4 [$C(CH_3)_3$], 29.6 ($CH_3CH_2CH_2CH_2$), 55.8 ($CH_3CH_2CH_2CH_2$), 80.1 [$C(CH_3)_3$], 119.8, 124.2, 126.0, 131.1, 132.8, 149.3 (C_6H_5), 155.2 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{26}N_2NaO_2$ $[MNa]^+$: 301.1892; found: 301.1876.

4b
White crystals; mp 115–116 °C.

^{1}H NMR ($CDCl_3$): δ = 1.44 [s, 9 H, $C(CH_3)_3$], 2.22/2.19 (s, 6 H, 2 × $ArCH_3$), 2.34 ($ArCH_3$), 6.56 (d, 2 H_{arom}), 6.9–7.4 (m, 7 H, NH + H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 18.2, 20.3 ($ArCH_3$), 28.3 [$C(CH_3)_3$], 80.7 [$C(CH_3)_3$], 114.1, 126.4, 127.0, 129.0, 129.5, 131.1, 135.4, 144.2, 145.7 (arom CH, C), 155.0 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{24}ClN_2O_2$ $[MH]^+$: 347.1549; found: 347.1526.

Acknowledgment

This work was financially supported by the Estonian Science Foundation (No. 5255).

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