Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2017, **27**, 160–162
Mendeleev Communications

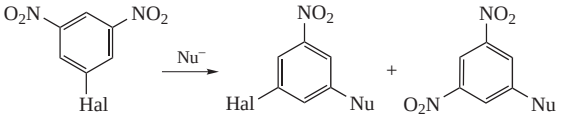
Dual reactivity of 1-chloro- and 1-bromo-3,5-dinitrobenzenes in aromatic nucleophilic substitution

Mikhail D. Dutov,*[a] Svyatoslav A. Shevelev,[a] Vladimir N. Koshelev,[b] David R. Aleksanyan,[b] Olga V. Serushkina,[a] Olga D. Neverova,[a] Evgeniya V. Kolvina[b] and Egor S. Bobrov[c]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: dutov@ioc.ac.ru*
[b] *I. M. Gubkin Russian State University of Oil and Gas, 119991 Moscow, Russian Federation. Fax: +7 499 507 8877*
[c] *D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation. Fax: +7 499 978 8657*

DOI: 10.1016/j.mencom.2017.03.018

Aromatic nucleophilic substitution reactions in 1-halo-3,5-dinitrobenzenes (where the halogen is bromine or chlorine) can occur with replacement of either a nitro group or a halogen atom, depending on the nature of anionic nucleophile Nu^- as a Lewis base (hard, soft or intermediate), as well as on the polarity of the dipolar aprotic solvent.



Hal = Br, Cl
NuH = 1,2,4-triazole, ArSH, PhOH, CF_3CH_2OH, PhC(Me)=NOH

This paper reports a part of our studies on aromatic nucleophilic substitution (S_NAr) in the series of 1-X-3,5-dinitrobenzenes (X = NO_2, SO_2R, *N*-azolyl),[1–6] in which activation of substitution is determined only by the inductive effect (*–I*) of substituents. Herein, specific features of 1-chloro- and 1-bromo-3,5-dinitrobenzenes in the S_NAr reaction are studied. It is known that the substitution rate and the pathway in the S_NAr reaction are generally determined by the first stage, *i.e.*, reversible formation of anionic *ipso*-σ-complexes, which is usually determined by the enthalpy factor.[7,8]

Only the halogen atom (F, Cl, Br, I) is replaced in 1-halo-2,4-dinitrobenzenes, irrespective of the reaction conditions and the character of the nucleophile nature, which is associated with the high thermodynamic stability of the corresponding *ipso*-σ-complex that is caused by considerable delocalization of the negative charge due to *–M* and *–I* effects of the *o*/*p*-nitro groups. In the case of 1-halo-3,5-dinitrobenzenes, activation of substitution decreases abruptly due to the absence of conjugation. In 1-fluoro-3,5-dinitrobenzene, the fluorine atom is replaced on treatment with alkoxides,[9] however, the rate of replacement on treatment with the MeO^-/MeOH system is ~5 orders smaller than that of 1-fluoro-2,4-dinitrobenzene under the same conditions.[8(a)] At the same time, unlike in 1-fluoro-3,5-dinitrobenzene, only a nitro group is replaced in 1-chloro- and 1-bromo-3,5-dinitrobenzenes treated with sodium methoxide in MeOH[10–13] or $PhCH_2OH$ + KOH in tetramethylurea.[14] The only example of nucleophilic substitution of a chlorine atom in 1-chloro-3,5-dinitrobenzene on treatment with morpholine in DMSO at 100 °C, which gives a mixture of a chlorine atom replacement (35%) and a nitro group replacement (14%) products, is reported.[15]

We assumed that, due to the weakening of activation of the halogen atoms in 1-bromo-3,5-dinitrobenzene **1a** and in 1-chloro-3,5-dinitrobenzene **1b** under the effect of *meta* nitro groups (only the *–I* effect), the reaction pathway may be affected by external factors, *i.e.*, the nature of the nucleophile and the nature of the solvent. In this work, the direction of nucleophilic substitution in **1a**,**b** is considered in terms of hard and soft Lewis acids and bases.[16]

As noted above, reactions of **1a** and **1b** with alkoxides, which are hard Lewis bases, with replacement of a nitro group are reported in literature. It may be assumed that carbon atoms bound to chlorine or bromine atoms are softer Lewis acids than a carbon atom bound to a nitro group, since the C–Hal moiety (Hal = Cl, Br) is more polarizable (the *+M* effect of a halogen) and is bound to a less electronegative atom than in the $C–NO_2$ moiety. Therefore, hard Lewis bases would more easily form an *ipso*-σ-complex with the carbon atom in a $C–NO_2$ moiety. It may be expected that softer Lewis acids would be capable of forming an *ipso*-σ-complex with a C–Hal moiety.

As concerns the effect of solvents, their ability to solvate an *ipso*-σ-complex would favour the thermodynamic stability of these complexes and thus affect the course of the reaction. In accordance with the hard and soft acids and bases principle,[16] dipolar aprotic solvents (DAS) are more capable of solvating easily polarizable (soft) large anions. In this study we used the following DAS listed in ascending order by polarity and basicity: MeCN, *N*-methylpyrrolidone (NMP) and hexamethylphosphortriamide (HMPA).

The following nucleophiles (Nu^-) with various properties were used as Lewis bases: (1) 1,2,4-triazolate anion, a hard Lewis base due to its high basicity, difficult oxidation and low polarizability of the nucleophilic center (which is within the aromatic system); (2) phenoxide, a softer Lewis base as compared to aliphatic alkoxides (lower basicity, easier oxidation and higher polarizability of the nucleophilic center); (3) arenethiolates, soft Lewis bases (easy oxidation, low basicity and high polarizability of the nucleophilic center); (4) acetophenone oximate $Ph(Me)C=NO^-$, a Lewis base with intermediate properties since its basicity is close to that of phenoxide (pK_a 11 for acetophenone oxime[17(a)] and pK_a 10 for phenol[18]), at the same time oximates possess higher nucleophilicity;[17(b)–(d)] (5) 2,2,2-trifluoroethoxide $CF_3CH_2O^-$, a softer anion than the non-fluorinated analogue as it has a much smaller basicity.

We used the NuH + K_2CO_3 system, molar ratio **1a** (**1b**) : NuH : K_2CO_3 of 1 : 1 : 2, in order to generate Nu^- from NuH. The reac-

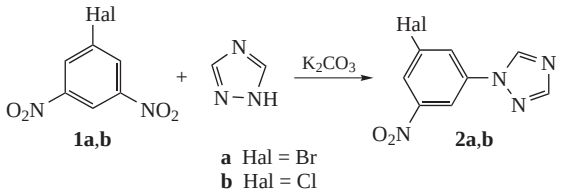
Table 1 Reactions of 1-halo-3,5-dinitrobenzenes with nucleophiles.

Entry	Starting compounds		Products, HPLC ratios and isolated yields (%)		
	1-halo-3,5-dinitro-benzene	NuH	MeCN	NMP	HMPA
1	**1a**	1,2,4-triazole	**2a** (20)	Resin	Resin
2	**1b**	1,2,4-triazole	**2b** (18)	Resin	Resin
3	**1a**	PhSH	Resin	**3** (43)	**3** (44)
4	**1b**	PhSH	Resin	**3** (45)	**3** (41)
5	**1a**	4-ClC_6H_4SH	Resin	**4** (40)	**4** (38)
6	**1b**	4-ClC_6H_4SH	Resin	**4** (35)	**4** (42)
7	**1a**	PhOH	**5a** (60)	**5a** + **7**, ~6:1	**5a** + **7**, ~1:1 (12, 19)
8	**1b**	PhOH	**5b** (66)	**5b** + **7**, ~6:1	**5b** + **7**, ~1:1 (15, 11)
9	**1a**	CF_3CH_2OH	**6a** (75)	**6a** + **8**, ~6:1	**6a** + **8**, ~1:1
10	**1b**	CF_3CH_2OH	**6b** (80)	**6b** + **8**, ~6:1	**6b** + **8**, ~1:1
11	**1a**	PhC(Me)=NOH	**9a** (60)	**9a** (66)	**9a** + **10**, ~1:1 (30, 41)
12	**1b**	PhC(Me)=NOH	**9b** (65)	**9b** (61)	**9b** + **10**, ~1:1 (29, 39)

tions were carried out at 80 °C or, in the case of highly nucleophilic ones, at 20 and 80 °C (Table 1).†

In our experiments the nucleophilic substitution could proceed in a more complex manner than in 1,3,5-trinitrobenzene itself and always occurred incompletely. No principal differences between the bromo and chloro derivatives were found (except for the diversity of admixtures). The choice of the solvents followed from previous experience.[19]

The reaction of **1a**,**b** with 1,2,4-triazole in both NMP and HMPA gave only resinous products. On using MeCN, the main products **2a**,**b** of the nitro group replacement were isolated (Scheme 1).



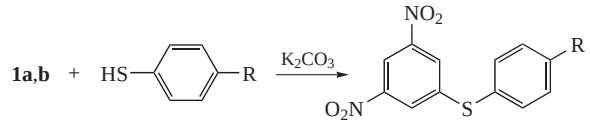
1a,**b** **2a**,**b**

a Hal = Br
b Hal = Cl

Scheme 1

Reactions of **1a**,**b** with arenethiols (Scheme 2) in NMP or HMPA resulted only in halogen substitution products to give known[4,20] 1-arylsulfanyl-3,5-dinitrobenzenes **3**, **4** in 35–45% yields.

The reaction of **1a**,**b** with phenol in NMP led to both **5a**,**b** and **7**[1] in an approximate ratio of 6:1, *i.e.*, the product of the



3 R = H
4 R = Cl

Scheme 2

† ^{1}H NMR spectra were recorded on a Bruker AMX-300 instrument. Chemical shifts in DMSO-d_6 are reported relative to TMS. Mass spectra (EI, 70 eV) were obtained on a Finnigan MAT INCOS 50 spectrometer with a direct inlet system. The melting points were determined on a Boetius hot stage using Koffler's technique (the heating rate was 4 K min^{-1}). The course of the reactions and the purity of the compounds were monitored by HPLC (MeCN–H_2O, 3:2; reversed phase C18), Waters 1525 pump with Waters 2996 photodiode detector. Column chromatography was carried out using 0.035–0.070 mm silica gel. All chemicals used in this study were commercially available.

Method A. Reactions in MeCN. A mixture of a nucleophile (0.001 mol), K_2CO_3 (0.002 mol), MeCN (5 ml) and 1-halo-3,5-dinitrobenzene **1a**,**b** (0.001 mol) was refluxed with stirring for 20–40 h until the consumption of the starting compounds stopped (the reactions of all the nucleophiles did not go to completion, and we judged that the reactions ceased when the HPLC chromatogram did not change anymore). The reaction mixture was cooled to room temperature and filtered. The solvent was evaporated *in vacuo*. The residue was dissolved in dichloromethane (30–50 ml) and filtered through a thin layer of silica gel. The filtrate was partially concentrated *in vacuo* to a volume of 5–10 ml. After cooling, the solid was filtered off.

Method B. Reactions in N-*methylpyrrolidone*. A mixture containing 1-halo-3,5-dinitrobenzene **1a**,**b** (0.001 mol), a nucleophile (0.001 mol), K_2CO_3 (0.002 mol) and NMP (5 ml) was stirred for 18–19 h at room temperature (or heated to 80 °C and kept for 11–12 h) until the reaction stopped (HPLC). The reaction mixture was poured into ice water with vigorous stirring, kept for 10–15 min, and filtered *in vacuo*. The product was dried, dissolved in chloroform, and filtered through a short pad of silica gel, then recrystallized from ethanol.

Method C. Reactions in HMPA. A mixture containing 1-halo-3,5-dinitrobenzene **1a**,**b** (0.001 mol), a nucleophile (0.001 mol), K_2CO_3 (0.002 mol) and HMPA (5 ml) was stirred for 16–17 h at room temperature (or heated to 80 °C and kept for 10–11 h) until the reaction stopped (HPLC). The reaction mixture was poured into ice water with vigorous stirring, kept for 10–15 min, and filtered *in vacuo*. The residue was separated by column chromatography.

1-(3-Bromo-5-nitrophenyl)-1,2,4-triazole **2a**. Yield 20% (method A, MeCN, 38 h), mp 107–109 °C. ^{1}H NMR, δ: 8.35 (s, 1H), 8.41 (s, 1H), 8.62 (s, 1H), 8.69 (s, 1H), 9.60 (s, 1H). MS, *m*/*z*: 270/268 $[M]^+$. Found (%): C, 35.62; H, 1.99; N, 20.93. Calc. for $C_8H_5BrN_4O_2$ (%): C, 35.81; H, 1.87; N, 20.67.

1-(5-Chloro-3-nitrophenyl)-1,2,4-triazole **2b**. Yield 18% (method A, MeCN, 40 h), mp 101–103 °C. ^{1}H NMR, δ: 8.23 (s, 1H), 8.35 (s, 1H), 8.65 (s, 1H), 8.71 (s, 1H), 9.65 (s, 1H). MS, *m*/*z*: 226/224 $[M]^+$. Found (%): C, 42.88; H, 2.46; N, 24.83. Calc. for $C_8H_5ClN_4O_2$ (%): C, 42.58; H, 2.24; N, 24.99.

1-Bromo-3-nitro-5-phenoxybenzene **5a**. Yield 60% (method A, MeCN, 20 h), yellow oil. ^{1}H NMR, δ: 7.19 (d, 2H, ^2J 7.9 Hz), 7.29 (t, 1H, ^2J 7.3 Hz), 7.51 (t, 2H, ^2J 7.7 Hz), 7.62 (s, 1H), 7.71 (s, 1H), 8.12 (s, 1H). MS, *m*/*z*: 295/293 $[M]^+$. Found (%): C, 49.31; H, 2.52; N, 4.93. Calc. for $C_{12}H_8BrNO_3$ (%): C, 49.01; H, 2.74; N, 4.76.

1-Chloro-3-nitro-5-phenoxybenzene **5b**. Yield 66% (method A, MeCN, 22 h), yellow oil. ^{1}H NMR, δ: 7.15 (d, 2H, ^2J 8 Hz), 7.29 (t, 1H, ^2J 7.3 Hz), 7.41 (t, 2H, ^2J 7.7 Hz), 7.51 (s, 1H), 7.68 (s, 1H), 8.02 (s, 1H). MS, *m*/*z*: 251/249 $[M]^+$. Found (%): C, 57.61; H, 3.00; N, 5.47. Calc. for $C_{12}H_8ClNO_3$ (%): C, 57.73; H, 3.23; N, 5.71.

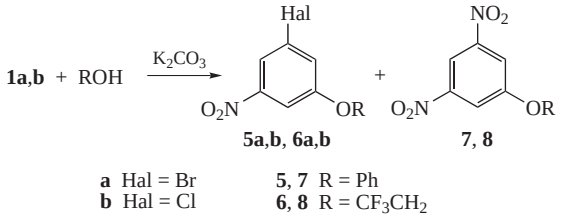
1-Bromo-3-nitro-5-(2,2,2-trifluoroethoxy)benzene **6a**. Yield 75% (method A, MeCN, 23 h), mp 55–57 °C. ^{1}H NMR, δ: 5.10 (q, 2H, ^2J 8 Hz), 7.65 (s, 1H), 7.84 (s, 1H), 7.95 (s, 1H). MS, *m*/*z*: 301/299 $[M]^+$. Found (%): C, 32.25; H, 1.91; N, 4.77. Calc. for $C_8H_5BrF_3NO_3$ (%): C, 32.03; H, 1.68; N, 4.58.

1-Chloro-3-nitro-5-(2,2,2-trifluoroethoxy)benzene **6b**. Yield 80% (method A, MeCN, 24 h), mp 61–63 °C. ^{1}H NMR, δ: 5.00 (q, 2H, ^2J 8 Hz), 7.54 (s, 1H), 7.73 (s, 1H), 7.89 (s, 1H). MS, *m*/*z*: 257/255 $[M]^+$. Found (%): C, 37.48; H, 1.69; N, 5.63. Calc. for $C_8H_5ClF_3NO_3$ (%): C, 37.60; H, 1.97; N, 5.48.

O-*(3-Bromo-5-nitrophenyl) acetophenone oxime* **9a**. Yield 60% (method A, MeCN, 16 h), 78% (method B, NMP, 20 °C, 18 h), 66% (method B, NMP, 80 °C, 11 h), 35% (method C, HMPA, 20 °C, 17 h), 30% (method C, HMPA, 80 °C, 10 h), mp 79–81 °C. ^{1}H NMR, δ: 2.46 (s, 3H), 7.51–7.53 (m, 3H), 7.84–7.86 (m, 2H), 7.95 (s, 1H), 8.05 (s, 2H). MS, *m*/*z*: 336/334 $[M]^+$. Found (%): C, 49.89; H, 3.08; N, 8.54. Calc. for $C_{14}H_{11}BrN_2O_3$ (%): C, 50.17; H, 3.31; N, 8.36.

O-*(5-Chloro-3-nitrophenyl) acetophenone oxime* **9b**. Yield 65% (method A, MeCN, 18 h), 72% (method B, NMP, 20 °C, 19 h), 61% (method B, NMP, 80 °C, 12 h), 38% (method C, HMPA, 20 °C, 16 h), 29% (method C, HMPA, 80 °C, 11 h), mp 72–74 °C. ^{1}H NMR, δ: 2.47 (s, 3H), 7.52–7.55 (m, 3H), 7.83–7.89 (m, 2H), 7.95 (s, 1H), 8.05 (s, 2H). MS, *m*/*z*: 292/290 $[M]^+$. Found (%): C, 57.99; H, 4.03; N, 9.38. Calc. for $C_{14}H_{11}ClN_2O_3$ (%): C, 57.84; H, 3.81; N, 9.64.

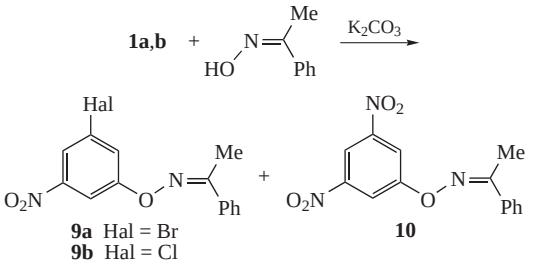
nitro group replacement predominated. In HMPA, such a ratio becomes ~1:1, *i.e.* the rate of halogen substitution becomes higher. In MeCN, only the nitro group is replaced to give products **5a** (60%) and **5b** (66%) (Scheme 3).



Scheme 3

The substitution with trifluoroethanol in HMPA afforded a mixture of 1-halo-3-nitro-5-(2,2,2-trifluoroethoxy)benzene **6a** or **6b** and 1,3-dinitro-5-(2,2,2-trifluoroethoxy)benzene **8**[2] in ~1:1 ratio. In MeCN, only products of the nitro group replacement **6a** (75%) and **6b** (80%) were obtained (see Scheme 3).

The reactions of **1a**,**b** with acetophenone oxime in NMP (Scheme 4) occurred with replacement of the nitro group to give *O*-(3-halo-5-nitrophenyl) derivatives **9a**,**b**. No halogen replacement product **10**[21] was detected. The reactions proceeded with complete conversion of the starting compounds **1**, both at 80 °C and at 20 °C. In HMPA, both types of products **9** and **10** were obtained in ~1:1 ratio. In MeCN, only products of the nitro group substitution, **9a** (76%) or **9b** (80%), were formed.



Scheme 4

The results obtained demonstrate that the nucleophilic substitution pathway depends on the nucleophile and the solvent nature. They can be rationalized in view of the Lewis Hard and Soft Acids and Bases (HSAB) principle: the softer base the anionic nucleophile (Nu^-) is, the higher the degree of halogen replacement, since a carbon atom bound to a halogen is a softer Lewis acid than a carbon atom bound to a nitro group. The reaction pathway depends considerably on the properties of dipolar aprotic solvents: other conditions being equal, an increase in the solvent polarity (in the series MeCN < NMP < HMPA) favours the replacement of a halogen atom.

It is noteworthy in the data obtained (see Table 1) that only the halogen atom is replaced in the case of the softest Lewis bases, *i.e.*, arenethiolate anions (in NMP and HMPA). On the other hand, in the case of 1,2,4-triazolate anion, which is the hardest Lewis base of the nucleophiles studied, only products of the nitro group replacement were detected. In all the other cases, the nucleophiles are Lewis bases with intermediate hardness (softness) and undergo both possible processes, the ratio of the latter depending on the nucleophile and solvent properties. The phenoxide anion is a characteristic example: nitro group replacement products were obtained in high yields in MeCN; in NMP, along with nitro group replacement products, halogen replacement products are also formed (the product ratio is ~6:1 with predominance of the nitro group replacement product), whereas in HMPA both possible products are also formed, but in 1:1 ratio. Similar results were obtained in the case of trifluoroethoxide anion: in HMPA, both possible substitution processes are observed in ~1:1 ratio.

In conclusion, dual reactivity of 1-bromo and 1-chloro-3,5-dinitrobenzenes in aromatic nucleophilic substitution has been identified. Regioselectivity (only one reaction pathway) is observed either in the case of nucleophiles that are hard Lewis bases (1,2,4-triazolate anion, non-substituted alkoxides) – only a nitro group is replaced, or soft Lewis bases (arenethiolates) – only a halogen atom is replaced. In the case of intermediate Lewis bases, both pathways occur in NMP and HMPA, whereas in MeCN, only a nitro group is replaced.

This work was supported by the Russian Foundation for Basic Research (grant no. 13-03-01276).

References

1 S. A. Shevelev, M. D. Dutov, I. A. Vatsadze, O. V. Serushkina, A. L. Rusanov and A. M. Andrievskii, *Mendeleev Commun*., 1995, 157.
2 S. A. Shevelev, M. D. Dutov, M. A. Korolev, O. Yu. Sapozhnikov and A. L. Rusanov, *Mendeleev Commun*., 1998, 69.
3 G. V. Kokurkina, M. D. Dutov, S. A. Shevelev, S. V. Popkov, A. V. Zakharov and V. V. Poroikov, *Eur. J. Med. Chem.*, 2011, **46**, 4374.
4 O. V. Serushkina, M. D. Dutov, O. Yu. Sapozhnikov, B. I. Ugrak and S. A. Shevelev, *Russ. J. Org. Chem.*, 2002, **38**, 1758 (*Zh. Org. Khim.*, 2002, **38**, 1819).
5 O. Yu. Sapozhnikov, M. D. Dutov, M. A. Korolev, V. V. Kachala and S. A. Shevelev, *Mendeleev Commun*., 2001, 232.
6 M. D. Dutov and O. V. Serushkina, *Mendeleev Commun*., 2013, **23**, 174.
7 J. Miller, *Nucleophilic Aromatic Substitution*, Elsevier, Amsterdam, 1968.
8 (*a*) F. Terrier, *Nucleophilic Aromatic Displacement. The Influence of the Nitro Group*, VCH, New York, 1991; (*b*) F. Terrier, *Modern Nucleophilic Aromatic Substitution*, Wiley-VCH, Weinheim, 2013; (*c*) V. M. Vlasov, *Russ. Chem. Rev.*, 2003, **72**, 681 (*Usp. Khim.*, 2003, **72**, 764).
9 C. W. L. Bevan, A. J. Foley, J. Hirst and W. O. Uwamu, *J. Chem. Soc. B*, 1970, 794.
10 V. N. Knyazev, V. N. Drozd and A. A. Klimov, *Russ. J. Org. Chem.*, 1976, **12**, 2319 (*Zh. Org. Khim.*, 1976, **12**, 2387).
11 P. Martin, *Helv. Chim. Acta*, 1988, **71**, 344.
12 P. S. Hameed, V. Patil, S. Solapure, U. Sharma, P. Madhavapeddi, A. Raichurkar, M. Chinnapattu, P. Manjrekar, G. Shanbhag, J. Puttur, V. Shinde, S. Menasinakai, S. Rudrapatana, V. Achar, D. Awasthy, R. Nandishaiah, V. Humnabadkar, A. Ghosh, C. Narayan, V. K. Ramya, P. Kaur, S. Sharma, J. Werngren, S. Hoffner, V. Panduga, C. N. Naveen Kumar, J. Reddy, K. N. Mahesh Kumar, S. Ganguly, S. Bharath, U. Bheemarao, K. Mukherjee, U. Arora, S. Gaonkar, M. Coulson, D. Waterson, V. K. Sambandamurthy and S. de Sousa, *J. Med. Chem.*, 2014, **57**, 4889.
13 O. V. Miroshnikova, T. H. Hudson, L. Gerena, D. E. Kyle and A. J. Lin, *J. Med. Chem.*, 2007, **50**, 889.
14 F. Effenberger, M. Koch and W. Streicher, *Chem. Ber.*, 1991, **124**, 163.
15 A. J. Belfield, G. R. Brown, A. J. Foubister and P. D. Ratcliffe, *Tetrahedron*, 1999, **55**, 13285.
16 R. G. Pearson, *Hard and Soft Acids and Bases*, Dowden, Hutchinson and Ross, Stroudsburg, PA, 1973.
17 (*a*) G. Guillot-Edelheit, M. Laloi-Diard and O. Eisenstein, *Tetrahedron*, 1978, **34**, 523; (*b*) E. Buncel, C. Cannes, A.-P. Chatrousse and F. Terrier, *J. Am. Chem. Soc.*, 2002, **124**, 8766; (*c*) M. Laloi-Diard, J. Verchere, P. Cosselin and F. Terrier, *Tetrahedron Lett.*, 1984, **25**, 1267; (*d*) F. Terrier, P. Rodriguez-Dafonte, E. Le Guével and G. Moutiers, *Org. Biomol. Chem.*, 2006, **4**, 4352.
18 D. A. Pratt, R. P. Pesavento and W. A. van der Donk, *Org. Lett.*, 2005, **7**, 2735.
19 O. V. Serushkina, M. D. Dutov, V. N. Solkan and S. A. Shevelev, *Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2406 (*Izv. Akad. Nauk, Ser. Khim.*, 2001, 2297).
20 S. A. Shevelev, M. D. Dutov and O. V. Serushkina, *Russ. Chem. Bull.*, 1995, **44**, 2424 (*Izv. Akad. Nauk, Ser. Khim.*, 1995, 2528).
21 S. A. Shevelev, I. A. Vatsadze and M. D. Dutov, *Mendeleev Commun.*, 2002, **12**, 196.

Received: 12th July 2016; Com. 16/4993