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Late-stage *N*-functionalization of diazo NH-heterocycles: the Mitsunobu reaction *vs.* alkylation with alkyl halides

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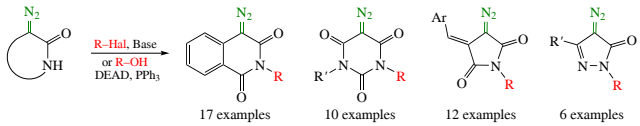
Selective *N*-alkylation of various diazo NH-heterocycles with preserving the diazo function was performed either by classical alkylation with alkyl halides or by the Mitsunobu reaction with alcohols. The substrate variety involved diazo-substituted homophthalimide, arylidenesuccinimides, (thio)-barbituric acids, and pyrazolones. This is the first time the Mitsunobu reaction has been applied for the functionalization of diazo carbonyl compounds.



Convergent approach to libraries of N-heterocyclic diazo reagents

Keywords: diazo carbonyl compounds, *N*-alkylation, Mitsunobu reaction, alkyl halides, NH-heterocycles.

Diazo carbonyl compounds are highly useful reagents in modern organic chemistry. Their diverse reactivity mainly as carbene precursors is widely explored for the construction of complex molecules and biologically relevant frameworks[1] in a concise and efficient manner with high stereochemical control. Generally, the diazo function is introduced into the molecule immediately prior to its replacement. However, the synthesis of certain *N*-alkyl substituted heterocyclic imide and amide frameworks containing active methylene group required for the Regitz diazo transfer reaction is challenging. Exemplarily, the direct alkylation of 2-oxoindoles or homophthalimides with alkyl halides leads to a mixture of mono- and bis-C-alkyl compounds[2–10] rather than to *N*-alkylated products. Another advantage of the approach of introducing a substituent into the prepared diazo heterocyclic reagent is its convergent nature, which allows easy variation of the moiety to be attached in the final step of the synthesis.

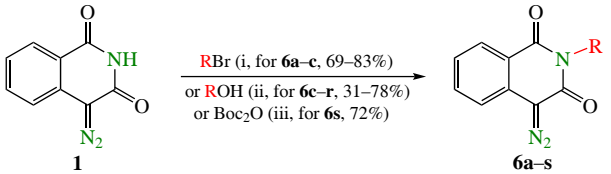
To date several examples of cyclic amide group modification in the preformed diazo scaffolds with alkyl halides[11–17] or acid halides[18–23] prior to metal catalyzed decomposition of the diazo group were described in the literature. The scope was limited by simple alkyl halides. Meanwhile, *N*-alkylation reactions represent a versatile tool for rapid diversification of the molecules, introduction of reactive functionalities into the structure and are actively used in medicinal chemistry and in the synthesis of pharmaceutical compounds.

Most common alkylating agents are undoubtedly alkyl halides; however, their use is limited due to concurrent elimination or overalkylation processes. Besides, some halogen derivatives are hardly accessible, many of them are hazardous. In this respect alcohols are more available, easier to store and to handle and often cheaper as compared to alkyl halides. From industrial prospects alcohols are often preferred alkylating agents.[24] The Mitsunobu reaction finds widespread use in medicinal chemistry and in total synthesis and can be good alternative to alkylation with alkyl halides. To date there is no mention in the literature of the use of the Mitsunobu alkylation for the synthesis of diazo heterocycle derivatives.

Following our continuing interest in the chemistry of diazo heterocycles coupled with its medicinal chemistry applications, we focused on exploration of diverse alkylating agents for *N*-alkylation of selected diazo heterocyclic compounds. Such functionalization will allow one to obtain cyclic diazo scaffolds bearing certain set of substituents which can subsequently be used to generate libraries of compounds for biological studies.

As part of our ongoing studies, we needed a series of *N*-substituted diazo imides as synthetic intermediates. For these purposes, some important from medicinal chemistry view scaffolds **1**–**5** depicted as starting reactants in Schemes 1–5 were selected. Compounds **1**–**5** were synthesized by direct diazo transfer on NH-heterocyclic precursors using 'SAFE' protocol[25] (for **1**, **3**–**5**) or *via* standard procedure (for **2**) (see Online Supplementary Materials).

We began our investigation with the model reaction of diazo homophthalimide **1** with methyl bromoacetate in the presence of



1 **6a–s**

a R = CH_2CO_2Me **g** R = $CH(Me)CO_2Et$ **n** R = $(CH_2)_2NHBoc$
b R = $CH_2CO_2Bu^t$ **h** R = tetrahydrofurfuryl **o** R = $(CH_2)_2N(Bn)Boc$
c R = Bn **i** R = $(CH_2)_2OMe$ **p** R = $(CH_2)_3C(O)Me$
d R = piperonyl **j** R = $(CH_2)_2Cl$ **q** R = $CH_2C{\equiv}CH$
e R = β-picolyl **k** R = $(CH_2)_2Br$ **r** R = $CH_2CH{=}CHPh$
f R = CH_2CO_2Et **l** R = *N*-methylpiperidin-4-yl **s** R = Boc
m R = *N*-Boc-piperidin-4-yl

Scheme 1 *Reagents and optimized conditions*: i, K_2CO_3, DMF, 80 °C, 3–4 h; ii, PPh_3, DEAD, THF, 0–20 °C, ~18 h; iii, DMAP (cat.), MeCN, 20 °C.

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Table 1 Optimization for alkylation of diazo homophthalimide **1** with $BrCH_2CO_2Me$.[a]

Entry	Solvent	Base	*T*/°C	*t*/h	Yield[b] (%)
1	DMF	Cs_2CO_3	65	20	65
2	DMF	K_2CO_3	65	20	69
3	DMF	DBU	80	3	tar formation
4	DMF	DMAP	80	3	NR[c]
5	**DMF**	**K_2CO_3**	**80**	**3.5**	**83**
6	DMF	Bu^tOK	80	3	tar formation
7	1,4-Dioxane	20% aq. KOH	20	20	NR
8	1,4-Dioxane	Bu^tOK	80	20	10
9	1,4-Dioxane	K_2CO_3	80	20	18
10	1,4-Dioxane	NaH	80	20	28
11	Toluene	NaH	65	20	25
12	MeCN	Et_3N	80	72	NR
13	MeCN	DBU	80	72	NR

[a] Reagents: **1** (0.27 mmol), $BrCH_2CO_2Me$ (0.30 mmol), base (0.33 mmol), solvent (1.5 ml). [b] Isolated yields. [c] NR stands for no reaction.

base thus affording product **6a** (see Scheme 1, Table 1). It should be noted that the synthesis of **6a** using other protocols is laborious, whereas direct alkylation of the homophthalimide without diazo function results in *C*-alkylation products. Considering that diazo homophthalimide **1** possesses very low solubility in common organic solvents under standard conditions, we first examined DMF as a solvent under mild heating.

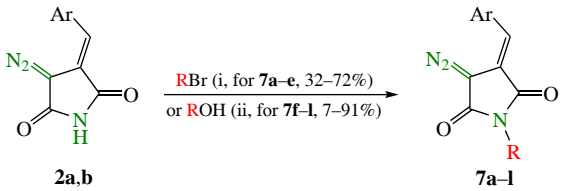
As can be seen from Table 1, cesium and potassium carbonates demonstrated better results (entries 1, 2). Organic bases were found to be not suitable (entries 3, 4, 12, 13). Raising the temperature from 65 to 80 °C significantly improved the yield (*cf.* entries 2 and 5). We also examined 1,4-dioxane with different bases. Unfortunately, the reaction did not proceed with aqueous potassium hydroxide even at elevated temperature. Heating with K_2CO_3 at 80 °C in dioxane resulted in dramatic drop of the yield (entry 9) compared to DMF. The use of stronger bases such as Bu^tOK or NaH did not improve the reaction outcome (entries 8 and 10). Prolonged heating of **1** in acetonitrile resulted in no target product formation, starting diazo compound remained unchanged. This can be explained by low solubility of starting diazo homophthalimide **1** in aforementioned solvents even at heating. Thus, for further studies K_2CO_3, DMF and heating at 80 °C were chosen.

With the optimal conditions in hand, we explored the reaction with other alkyl halides. The reaction worked well with *tert*-butyl bromoacetate and benzyl bromide furnishing the corresponding *N*-alkylated diazo derivatives **6b**,**c** in 79% and 69% yields (see Scheme 1). Alkyl chlorides were not suitable for alkylation of compound **1**, the reaction gave complex mixtures with chloroacetonitrile, 2-chloroethanol, 2-chloro-*N*,*N*-diethylacetamide, and ethyl chloroacetate. Moreover, we were not able to obtain the desired products with several bromides, *viz.* (bromomethyl)cyclobutane, 2-(bromomethyl)isoindoline-1,3-dione, 2-bromo-1,1-diethoxyethane. Thus, *N*-alkylation of diazo homophthalimide **1** can be carried out using a rather limited range of very active bromides.

We next focused on *N*-alkylation of diazo arylidenesuccinimides **2a**,**b** (see Scheme 2). The alkylation with alkyl bromides proceeded smoothly under milder conditions and was completed in 2 h giving substituted diazo compounds **7a–e** in moderate to good yields. In contrast to the homophthalimide analogue, compounds **2** showed higher reactivity, yielding alkylated derivatives with less reactive bromides such as (bromomethyl)cyclobutane or 1,5-dibromopentane (products **7c**,**d**) albeit in decreased yields. Activated secondary alkyl bromides can be also involved into reaction, although it gave a low yield (compound **7b**). The low yield of diazo imide **7d** can be attributed to the formation of unidentified by-products. When chloroacetonitrile was attempted as the alkylating agent, decomposition of the reaction mixture was observed.

Non-symmetrically substituted barbituric acid fragment is present in some biologically active compounds.[26,27] Besides, previously we showed that monosubstituted diazo barbituric acid did not undergo metal-catalyzed decomposition with the formation of oxazole in acetonitrile.[28] Therefore, methods for the preparation of diversely substituted (including mono-*N*-protected) diazo barbituric acids are in demand. Barbituric acid **3a**,**b** readily reacted with alkyl bromides giving the corresponding derivatives in moderate to high yields (see Scheme 3). In contrast to aforementioned diazo imides, compound **3a** smoothly reacted with chloroacetonitrile to afford product **8c** in 84% yield.

Thiobarbituric acid **4** has two reaction centers which can undergo alkylation. In fact, heating diazo compound **4** with alkyl bromides in DMF at 80 °C for 2 h resulted in the formation of *S*-alkylated derivatives only (see Scheme 4). The obtained sulfides **9a**,**b** are representatives of diazo pyrimidines hitherto

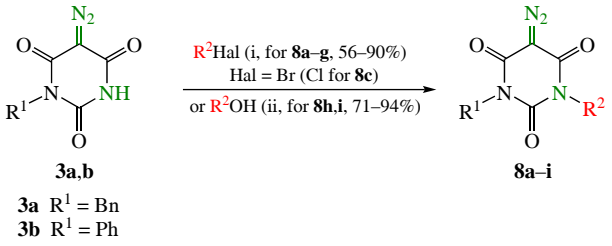


2a,**b** **7a–l**

2a Ar = Ph
2b Ar = 4-MeOC(O)C_6H_4

7a R = CH_2CO_2Me, Ar = Ph
7b R = CH(Me)CO_2Et, Ar = 4-MeOC(O)C_6H_4
7c R = CH_2Bu^c, Ar = Ph
7d R = $(CH_2)_5Br$, Ar = Ph
7e R = Bn, Ar = 4-MeOC(O)C_6H_4
7f R = $(CH_2)_2N$(Bn)Boc, Ar = Ph
7g R = $(CH_2)_2NHBoc$, Ar = Ph
7h R = menthyl, Ar = Ph
7i R = $(CH_2)_2NHBoc$, Ar = 4-MeOC(O)C_6H_4
7j R = cholesteryl, Ar = Ph
7k R = adamantan-1-yl, Ar = Ph
7l R = adamantan-1-ylmethyl, Ar = Ph

Scheme 2 *Reagents and conditions*: i, K_2CO_3, DMF, 50 °C, 2 h; ii, PPh_3, DEAD, THF, 0–20 °C, ~18 h.

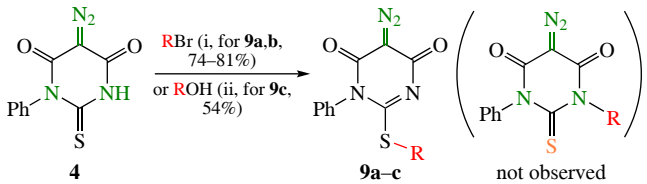


3a,**b** **8a–i**

3a R^1 = Bn
3b R^1 = Ph

8a R^1 = Bn, R^2 = $CH_2CO_2Bu^t$
8b R^1 = Bn, R^2 = 2-$NCC_6H_3CH_2$
8c R^1 = Bn, R^2 = CH_2CN
8d R^1 = Bn, R^2 = CH_2Bu^c
8e R^1 = Bn, R^2 = CH_2CO_2Me
8f R^1 = Ph, R^2 = $CH_2CO_2Bu^t$
8g R^1 = Ph, R^2 = Bn
8h R^1 = Bn, R^2 = $(CH_2)_2NHBoc$
8i R^1 = Bn, R^2 = piperonyl

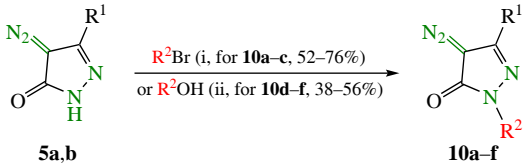
Scheme 3 *Reagents and conditions*: i, K_2CO_3, DMF, 80 °C, 2 h; ii, PPh_3, DEAD, THF, 0–20 °C, ~18 h.



4 **9a–c** not observed

a R = $CH_2CO_2Bu^t$
b R = Bn
c R = piperonyl

Scheme 4 *Reagents and conditions*: i, K_2CO_3, DMF, 80 °C, 2 h; ii, PPh_3, DEAD, THF, 0–20 °C, ~18 h.



5a,**b**

a $R^1 = CO_2Et$
b $R^1 = 4\text{-}MeOC_6H_4$

10a–f

a $R^1 = CO_2Et$, $R^2 = 4\text{-}FC_6H_4CH_2$
b $R^1 = CO_2Et$, $R^2 = CH_2CO_2Bu^t$
c $R^1 = 4\text{-}MeOC_6H_4$, $R^2 = 3\text{-}FC_6H_4CH_2$
d $R^1 = CO_2Et$, R^2 = piperonyl
e $R^1 = 4\text{-}MeOC_6H_4$, $R^2 = (CH_2)_2NHBoc$
f $R^1 = 4\text{-}MeOC_6H_4$, R^2 = menthyl

Scheme 5 *Reagents and conditions*: i, K_2CO_3, DMF, 80 °C, 2 h; ii, PPh_3, DTBAD, THF, 0–20 °C.

not described in the literature. Their chemical behavior and possible application in synthesis remain to be investigated.

The reactivity of diazo pyrazolones **5a**,**b** in *N*-alkylation reaction with activated alkyl halides was found to be dependent on the 3-positioned substituent (see Scheme 5). The electron-withdrawing ester group provoked higher reactivity and the reaction was finished in 1 h in DMF at 80 °C in the presence of potassium carbonate as a base to give products **10a**,**b**. When 4-methoxyphenyl-substituted diazo pyrazolone **5b** was used instead, the reaction was completed in 6 h and gave a lower yield. The higher temperature did not improve the yield of **10c**, but rather caused degradation.

Since the alkylation of selected diazo heterocycles with alkyl halides was limited mostly by the use of alkyl bromides and turned out to be dependent on both the halide reactivity and the electronic nature of substituents in the diazo molecule, we next focused on the use of alcohols as alkylating agents for the functionalization of diazo NH-heterocycles. We assumed the Mitsunobu reaction would serve well for this purpose. To test the feasibility of *N*-alkylation of diazo imides with alcohols in terms of the Mitsunobu reaction we reproduced the synthesis of derivative **6c** using benzyl alcohol (see Scheme 1). To our delight, the reaction proceeded smoothly at room temperature yielding the target *N*-benzyl diazo homophthalimide **6c** in comparable yield (64% *vs.* 69%). The low solubility of the starting compound was not an obstacle in this case, the diazo imide **1** fully dissolved during the course of the reaction.

In order to evaluate the scope and limitations of the method, we synthesized a series of *N*-alkyl diazo homophthalimides **6c**–**r** (see Scheme 1). In contrast to alkyl bromides, primary and secondary alcohols proved to be the alkylating agents of choice for diazo homophthalimide **1** yielding wide scope of diversely functionalized diazo derivatives. The order of the reagent loading had no effect on the reaction outcome. Intriguingly, ethyl 2-hydroxyacetate was less effective as compared to methyl 2-bromoacetate, giving compound **6a** in 20% yield (83% for bromoacetate).

Diazo arylidenesuccinimides **2a**,**b** likewise smoothly underwent alkylation with alcohols (see Scheme 2). It was found that the order of the reagent adding played a crucial role in this case. When triphenylphosphine was pre-stirred with DEAD before diazo NH-heterocycle and alcohol adding (reverse order), the yields were twice higher compared to addition of DEAD to a pre-stirred mixture of PPh_3, diazo imide, and alcohol (direct order). A possible reason for this may be the side phosphazene formation during the reaction of the diazo group with triphenylphosphine. Taking into account that the Mitsunobu alkylation proceeds *via* the S_N2 mechanism with the formation of carbon–heteroatom bond with a stereoselective outcome, we performed a reaction of **2a** with menthol and cholesterol. In both cases, the inversion of stereocenter configuration was observed (products **7h**, **7j**). When diazo substrate **2a** was involved into the reaction with adamantan-1-ol, the target product **7k** was obtained only in 7% yield.

Diazo barbituric acid **3a** was readily alkylated with alcohols to give compounds **8h**,**i** in high yields (see Scheme 3). The reagent loading order had almost no impact on the reaction outcome. In contrast to the *N*-alkylation of 5,5-dimethylthiobarbituric acid derivative previously described,[29] the Mitsunobu reaction of diazo thiobarbituric acid **4** proceeded exclusively as *S*-alkylation yielding only the product **9c** (see Scheme 4).

Alkylation of diazo pyrazolones **5a**,**b** with alcohols was slightly less effective than that with alkyl bromides, resulting in moderate yields of the corresponding products **10d**,**e** (see Scheme 5). At the same time, the use of the Mitsunobu reaction allowed the introduction of a sterically demanding *sec*-alkyl substituent into the diazo heterocycle **10f**. Diethyl azodicarboxylate was replaced by di-*tert*-butyl azodicarboxylate (DTBAD) since the formed in the course of the reaction diethyl hydrazine-1,2-dicarboxylate had chromatographic mobility close to that of the target compounds and could not be separated from them. The reverse order of reagents adding was required.

It is of note that despite the known ability of diazocarbonyl compounds to react with triphenylphosphine to form phosphazenes,[30,31] the alkylation of diazo heterocycles under the Mitsunobu reaction conditions can be carried out with high chemoselectivity, avoiding this side reaction (also by using the reverse order of mixing reagents).

The structure of products **6q**, **7g** and **9b** was unambiguously confirmed by the X-ray analysis data (Figure 1).†

In order to improve the solubility profile and to introduce a substituent that can be easily removed afterwards, we performed a reaction of diazo homophthalimide **1** with Boc_2O (see Scheme 1). The *N*-Boc-protected derivative **6s** was isolated in high yield.

In conclusion, we expanded the scope of alkyl halides which can be employed for the alkylation of diazo NH-heterocycles and demonstrated the utility of the Mitsunobu reaction in the synthesis of *N*-funcionalized diazo derivatives with maintaining the diazo function. The efficiency of both *N*-alkylation methods

† *Crystal data for* **6q**. $C_{16}H_{9.33}N_4O_{2.67}$, $M = 300.27$, monoclinic, space group $P2_1/c$, $a = 8.9562(2)$, $b = 14.1531(3)$ and $c = 7.9069(2)$ Å, $\beta = 91.615(2)°$, $V = 1001.86(4)$ Å^3, $Z = 3$. At 100.00(15) K: $\mu = 0.833$ mm^{-1}, $d_{calc} = 1.493$ g cm^{-3}. Total 6410 reflections were collected, where 2073 reflections were independent; 154 refined parameters, $\sigma = 1.069$, and final R factor was 0.0522 ($R_{int} = 0.0734$).

Crystal data for **7g**. $C_{18}H_{20}N_4O_4$, $M = 356.38$, orthorhombic, space group $Pna2_1$, $a = 9.9748(5)$, $b = 14.3508(7)$ and $c = 12.6074(6)$ Å, $\beta = 90°$, $V = 1804.70(15)$ Å^3, $Z = 4$. At 99.9(6) K: $\mu = 0.784$ mm^{-1}, $d_{calc} = 1.312$ g cm^{-3}. Total 8561 reflections were collected, where 3056 reflections were independent; 242 refined parameters, $\sigma = 1.036$, and final R factor was 0.0514 ($R_{int} = 0.0459$).

Crystal data for **9b**. $C_{17}H_{12}N_4O_2S$, $M = 336.37$, orthorhombic, space group $Pbca$, $a = 12.2712(2)$, $b = 8.7366(2)$ and $c = 29.4794(6)$ Å, $\beta = 90°$, $V = 3160.44(11)$ Å^3, $Z = 8$. At 99.9(5) K: $\mu = 1.976$ mm^{-1}, $d_{calc} = 1.414$ g cm^{-3}. Total 21106 reflections were collected, where 2996 reflections were independent; 217 refined parameters, $\sigma = 1.101$, and final R factor was 0.0541 ($R_{int} = 0.0556$).

Crystallographic data were collected on an Agilent Technologies SuperNova Atlas diffractometer (CuKα radiation, $\lambda = 1.54184$ Å). The structures were solved and refined by direct methods using a set of SHELX[32] programs. The data were corrected for absorption effects using the multiscan method (SADABS). Non-hydrogen atoms were refined anisotropically using SHELX.[33] All the hydrogen atoms were found *via* Fourier difference maps.

CCDC 2353106–2353108 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* https://www.ccdc.cam.ac.uk.

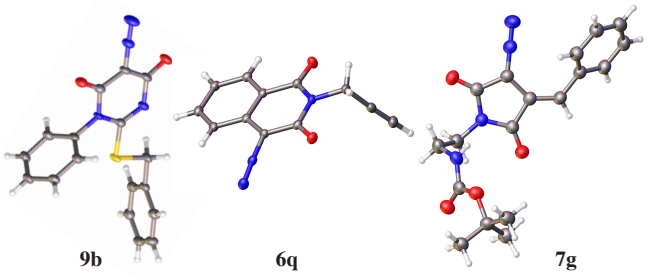


Figure 1 X-ray data of compounds **6q**, **7g** and **9b**.

using halides and alcohols has been compared for a series of diazo heterocyclic substrates. The Mitsunobu reaction-based approach exhibits a wider substrate scope with regard to alcohol and diazo pattern. The undoubted advantages of the method are mild conditions, the use of less hazardous alkylating agents and insertion of important for medicinal chemistry substituents. The developed method allows introduction of menthyl and cholesteryl motifs in a stereoselective manner. The diazo thiobarbituric acid selectively gave *S*-alkylated product under both protocols, providing a hitherto undescribed type of diazo pyrimidine. These synthetic findings are expected to significantly boost the research in the field of diazo chemistry and its application to the synthesis of valuable structures.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7586.

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