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Photochemical O–H Functionalization of Aryldiazoacetates with Phenols via Proton Transfer

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ABSTRACT: In this work, we report a thorough investigation of the reaction of phenols with aryldiazoacetates. Mechanistic studies using different spectroscopic methods and theoretical calculations suggest a hydrogen bond between phenol and aryldiazoacetates, which can be modulated by the phenol acidity. The pK_A of phenol and therefore the hydrogen bond plays an important role in a subsequent photoinduced proton transfer reaction to give the formal O–H functionalization product of phenols.

rganic transformation via photoexcited states is currently an important strategy to conduct highly efficient synthesis by exploiting reaction pathways that are inaccessible in the ground state.^{1,2} In this context, the classic Paterno-Büchi reaction³ and, more lately, photoredox catalysis⁴ are predominant examples, with broad applications in organic synthesis, that rely on the photochemical activation of reaction partners or catalysts. On the contrary, there are rare synthetic applications of photoexcited proton transfer (PPT) reactions to date,⁵⁻⁹ although photoacids^{6,7} or -bases⁸ have been known for interesting usages such as conducting pH jumps or triggering protein folding.⁵ Early examples of PPT reactions reported recently⁶ often rely on the UV-light-mediated photoexcitation of a Brønsted acidic catalyst. The excited state of the catalyst exhibits a lower pK_A value than the ground state and can thus be used to conduct photocatalytic transformations based on a proton transfer reaction. In a similar fashion, the photoexcitation of fluorene-based imine 1 furnishes a representative photobase that is sufficiently basic to deprotonate alcohols to give the ion pair [1·H]⁺EtO⁻ (Scheme $1a^{-}$.

Recently, our group reported on PPT reactions to conduct efficient O–H functionalization reactions of halogenated alcohols with aryldiazoacetates **6** under photochemical conditions (Scheme 1c).^{10,11} This reaction proceeds via photoexcitation of a diazoacetate and enriches the reactivity of diazoalkanes and differentiates from the conventional reactivity in carbene transfer reactions or in the reaction with strong acids.¹² The latter traditionally proceeds via a metalcatalyzed insertion reaction of a carbene intermediate into O– H bonds or via a protonation substitution reaction mechanism in the presence of strong Brønsted acids as reaction partners (Scheme 1b). 13

In our previous report on the reaction of fluorinated alcohols with aryldiazoacetates,¹⁰ we observed a hydrogen bond of an acidic alcohol proton and the ester carbonyl group of the aryldiazoacetate (Scheme 1c). Moreover, the efficiency of the photoinduced proton transfer reaction depends on the fluorine content of the used alcohol, and thus the pK_A of the alcohol may play an important role in this reaction. On the basis of these results, we planned to further investigate the influence of the pK_A to gain deeper insight into the mechanism of such a transformation. In this Letter, we focus on the reaction of phenols with methyl phenyldiazoacetate. Phenols are a particularly suitable class of substrates because the pK_A of the aromatic substituents, and thus the influence of pK_A on the reaction efficiency can be monitored.

In the first step, we studied the interaction of phenol 10a and methyl phenyldiazoacetate 6a by ¹H and ¹³C NMR spectroscopy (Scheme 2). When investigating a solution of a stoichiometric mixture in CDCl₃ (c = 0.1 M for 6a and 10a), we observed a significant chemical shift perturbation for both the 10a O-H proton (0.30 ppm) and the 6a carbonyl carbon (0.26 ppm), which agreed with our previously proposed hydrogen-bond interaction (Scheme 1c). To find further

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Scheme 1. Photoinduced Proton Transfer Reactions and Reactivity of Diazoalkanes





Scheme 2. Formation of Hydrogen Bond Complex 11a and

proton transfer upon

photoexcitation (PPT)

Nuc

unreactive hvdrogen

bonding complex



evidence for this, we performed IR studies, in which we examined a 1:1 mixture of both substrates. We observed a shift of the carbonyl (C=O) and the N=N absorption bands of 22.7 and 5.4 cm⁻¹, respectively, from the original IR spectrum for **6a**, which is also supportive of a hydrogen-bond interaction. To give further insights, we subsequently performed calculations at the MP2/6-311+G(d,p)//B3LYP/6-31G(d) level of theory with basis set superposition error (BSSE) correction.^{14,15} (For details, see the SL) The interaction between phenol **10a** and methyl phenyldiazoacetate **6a** was found to be -8.0 kcal/mol in free energy change. A hydrogen bond length of 1.85 Å was estimated, which indicates a strong intermolecular hydrogen bond in this complex. As a result of

the hydrogen-bond interaction, the O–H bond in phenol 10a and the C=O bond in diazoacetate 6a each lengthen by 0.007 Å, which is consistent with the NMR chemical shift perturbations.

Having solid experimental and theoretical confirmations for the hydrogen-bonding interaction, we subsequently investigated different para-substituted phenols 10b-i to study the influence of the phenol p K_A on the complexation (Table 1).¹⁶

Table 1. Data on Hydrogen-Bonding Complex Formation

	N ₂ C-OMe O 6a	+ * R⊣	0.1 M in CDC	N2 Cl3 11a-j F	COMe [`] H _· O
no.	R	pK_A^{16}	${\Delta E_{ m int}} \left({\Delta E_{ m sol}} ight) \ \left({ m kcal/mol} ight)^a$	$\Delta\delta (O-H) \ (ppm)^b$	$\Delta \delta (C=O) (ppm)^{b}$
11a	Н	9.98	-8.0 (-5.4)	0.30	0.26
11b	4-CN	7.59	-9.5 (-6.2)	0.63	0.49
11c	4-NO ₂	7.15	-9.5 (-6.2)	0.71	0.73
11d	4-F	9.95	-8.4 (-5.6)	0.40	0.33
11e	4-Cl	9.38	-8.6 (-5.8)	0.40	0.39
11f	4-CF ₃		-9.1 (-6.1)	0.43	0.51
11g	4-OMe	10.21	-8.0 (-5.5)	0.25	0.21
11h	4-OCF ₃		-9.1 (-6.0)	0.48	0.42
11i	4-CO ₂ Me		-8.6 (-5.9)	0.32	0.32
11j	2-NO ₂	7.23	-4.5 (-2.8)	0.00	0.00

^{*a*}Interaction energies calculated at the MP2/6-311+G(d,p)//B3LYP/ 6-31G(d) level with BSSE correction. ^{*b*}Determined by ¹H and ¹³C NMR spectroscopy of a 0.1 M solution of a 1:1 mixture of phenol **10** and methyl phenyl diazoacetate **6a** in CDCl₃.

For weakly acidic phenol derivatives, for example, paramethoxy phenol 10g, we observed a smaller perturbation of the chemical shift in the hydrogen-bonding complex 11g as compared with the parent phenol 10a. When studying more acidic phenols, for example, para-cyano phenol 10b, a larger chemical shift perturbation was seen. This dependency of pK_A and the chemical shift perturbation was observed for all parasubstituted phenols (Table 1). Furthermore, we have calculated the single point energy change for the formation of 11 for different para-substituted phenols 10b-i with methyl phenyldiazoacetate 6a upon complex formation. The interaction of acidic phenols of 10 with 6a via a hydrogen bond is energetically more favored compared with less acidic phenols (-9.58 kcal/mol for the complex with *para*-NO₂-phenol 11c vs -8.05 kcal/mol for the complex with para-MeO-phenol 11g), which represents a similar trend, as observed by NMR studies.

We also studied the hydrogen-bonding complexes of metaand ortho-substituted phenols with methyl phenyldiazoacetate **6a**. (For details, see Table S1.) The introduction of substituents in the ortho position opens up the possibility for intramolecular hydrogen bonds of Lewis-basic substituents with the phenol proton. For the 1:1 mixtures of *ortho*-NO₂phenol (**11j**, Table 1) and methyl phenyldiazoacetate **6a**, no perturbation of chemical shifts was observed, which can be attributed to an intramolecular hydrogen bond of the phenolic O-H proton. This is further supported by the calculated interaction energies. IR studies for all hydrogen-bond complexes did not reveal an obvious correlation between differences in the wavenumber and the acidity of the phenol.¹⁵ (For details, see Table S1.)

To study the influence of the hydrogen-bond strength on the reactivity of the O–H moiety, we subjected these phenols to the blue-light-induced PPT reaction with a diazo compound. First, we investigated the reaction of *para*-cyano phenol **10b** with methyl phenyldiazoacetate **6a**, as they form a strong hydrogen-bonding complex (**11b**, $\Delta E_{int} = -9.51$ kcal/mol, Table 1). Gratifyingly, most common organic solvents were compatible with this reaction, and the desired product was obtained in moderate yields (Table 2, entries 1–6). The

Table 2. Optimization of Reaction Conditions

Ph CO ₂ Me	+ NC OH	blue LED (440-460 nm) 1.0 mL solvent	NC Ph
6a	10b		12a
no. ^a	solvent	ratio (6a/10b)	yield (%)
1	1,2-DCE	1:1	50
2	DCM	1:1	53
3	CHCl ₃	1:1	46
4	toluene	1:1	47
5	<i>n</i> -hexane	1:1	17
6	EtOAc	1:1	52
7	MeOH	1:1	no product ^b
8	DCM	2:1	76
9	DCM	1:2	80 ^c
10	1,2-DCE	1:2	75 ^c
11	EtOAc	1:2	61 ^c
12 ^d	DCM	1:2	no reaction
13 ^e	DCM	1:2	traces

^{*a*}Reaction conditions: **6a** and **10b** were dissolved in 1.0 mL of the indicated solvent and irradiated with blue LEDs overnight at ambient temperature (27 °C). Yields were calculated by ¹H NMR spectroscopy using mesitylene as an internal standard. ^{*b*}Product of O–H functionalization of MeOH from crude NMR. ^{*c*}Isolated yield. ^{*d*}Reaction in the dark. ^{*e*}Irradiation with a 23W CFL lamp overnight at ambient temperature (27 °C).

highest reaction yield was obtained using DCM as the solvent. In *n*-hexane, a heterogeneous reaction mixture was observed, which resulted in a reduced reaction efficiency (17% yield). When using MeOH as the solvent, only O-H functionalization of methanol instead of para-cyano phenol was observed by crude NMR of the reaction mixture (Table 2, entry 7). Next, we investigated the reaction stoichiometry, and 2 equiv of phenol was identified as being optimal for the reaction (Table 2, entry 9). The necessity for an excess of phenol can be attributed to the rapid decomposition of diazo compounds under blue-light irradiation conditions to form highly reactive carbene or (in our case) carbocationic intermediates. Thus the use of an excess of the reaction partner is often needed.¹¹ No reaction took place when the reaction was performed in the dark, which underlines the necessity of photoirradiation for the O-H functionalization reaction (Table 2, entry 12).

With the optimized reaction conditions in hand, we investigated the reaction of different aryldiazoacetates in the reaction with *para*-cyano phenol **11b** (Scheme 3). To our delight, different substituted esters were well tolerated under the present reaction conditions, and the corresponding O–H functionalization reaction products were isolated in high yields (12a-e). Moreover, different electron-withdrawing and electron-donating substituents on the aromatic ring and

Scheme 3. Scope of Different Diazoalkanes



polycyclic or heterocyclic aromatic systems are compatible with the PPT reaction. The low yield of 12q can be explained by the lower basicity of the pyridyl-substituted diazo compound. On the contrary, electron-rich heterocyclic systems, such as the 2-thienyl-substituted diazoacetate gave significantly improved yields (12r). (1-diazo-2,2,2trifluoroethyl)benzene gave the O-H functionalization reaction product 13 in 43% yield. When using ethyl diazoacetate 14 (EDA) under irradiation with UV light, only the decomposition of the diazo compound was observed.

We subsequently studied a range of phenols with different electron-donating and electron-withdrawing substituents under the optimized reaction conditions (Scheme 4). On the basis of our studies on the formation of the hydrogen-bonding complex, we expected higher yields for electron-withdrawing substituents as the acidity of the phenol increased. Indeed, this was the case, as we observed higher yields for electron-withdrawing groups compared with electron-donating groups (e.g., *para*-nitro phenol vs *para*-chloro phenol: 85 vs 38% yield; see Scheme 4). Moreover, the yield decreased when changing from para- to meta- or ortho-substituted phenols, which is in good correlation to previously observed trends in the perturbation studies (Table 1). When investigating methyl 2-

Scheme 4. Scope of Different Phenols and N-Heterocyclic Phenols



hydroxybenzoate (10y), no reaction occurred, as the presence of a strong intramolecular hydrogen bond might have interfered with the complexation. Similarly, 4-methoxy phenol (10g) did not give the desired reaction product, which might be related to the weak hydrogen-bond complex (cf. Table 1). It is important to note that in the case of low-yielding O–H functionalization, no byproducts from the undesired C–H insertion into an $C(sp^2)$ –H bond were observed.

For a more general concept of this PPT reaction, we finally studied hydroxy-substituted *N*-heterocycles under the optimized reaction conditions (Scheme 4). When using 2-hydroxy pyridine or 2-hydroxy quinoline, the desired products were isolated in 76 and 70% yield, respectively. The intensely yellow 8-hydroxy quinoline **16** did not react under the blue-light reaction conditions, which might be explained by intermolecular hydrogen bonds of **16**.¹⁷

To further rationalize the relationship between the chemical shift perturbation and the efficiency of the PPT reaction, we plotted the isolated yield against the chemical shift perturbation of the O-H proton of phenols 10 (Figure 1). For para-substituted phenols, a linear trend was observed; when using meta-substituted phenols, a similar trend was obtained, yet with a larger deviation. When investigating orthosubstituted phenols, the opposite trend was obtained. (For details, see Scheme S1.) These observations further emphasize the influence of the intramolecular interactions of the O-H proton.

In summary, we describe detailed studies of photoinduced proton transfer reactions for O–H functionalization reactions of phenols. The hydrogen-bonding interaction of aryldiazoacetates and phenols was investigated by IR and NMR spectroscopy and further supported by computational calculations. This method is applicable to a broad range of



Figure 1. Scope of different phenols and N-heterocyclic phenols.

substrates, including different aryldiazoacetates, phenols, and hydroxyl-substituted N-heterocycles (32 examples, 20-85% yield). The analysis of the studies on the perturbation of chemical shifts against product yields shows a linear correlation, which underlines the importance of the hydrogen-bonding complex in photoinduced proton transfer reactions of aryldiazoacetates.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02564.

Experimental procedures, characterizations, theoretical calculations, and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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