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Salicylic Acid-Catalyzed Arylation of Enol Acetates with Anilines

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Abstract. *α*-Aryl ketones are both structure moieties commonly found in bioactive compounds and versatile synthetic intermediates for the preparation of drug-like molecules. An operationally simple and scalable protocol has been developed to prepare *α*-aryl ketones from readily available aromatic amines and enol acetates (or silyl enol ethers). This metal-free methodology features the use of salicylic acid as a convenient catalyst to promote the formation of aryl radicals from *in-situ* generated aryl diazonium salts, without demanding thermal or photochemical activation. The mild reaction conditions used are compatible with anilines substituted with diverse functionalities. Structural elaboration of some prepared *α*-aryl ketones was accomplished to illustrate their usefulness as building blocks.

Keywords: *α*-aryl ketone; salicylic acid; aryl radicals; aniline; enol acetates

Introduction

The importance of the *α*-aryl ketone motif is evidenced by its occurrence among natural products and pharmaceuticals. This moiety is an important pharmacophore for a number of bioactive molecules, as illustrated in Figure 1. Moreover, the straightforward transformation of these compounds into a plethora of functionalities facilitates the construction of diverse heterocycles, which, in turn, are common scaffolds of drug molecules.[1]

Intensive investigation on the *α*-arylation of ketones during the last two decades has allowed the development of appealing protocols for the transition-metal catalyzed coupling of enolates with aryl halides,[2] including those with C-H activation.[3] Copper-mediated reaction of lithium enolates with indoles and pyrroles have also been reported.[4] Also recently, important efforts have been devoted to implement transition-metal-free arylation protocols. Among them, those involving diaryliodonium salts provide a good synthetic alternative.[5] Elegant methods based on the triflic acid-mediated hydrative arylation of alkynes,[6] or the reaction of electron-rich aromatic compounds with *in-situ* generated enolonium species (umpolung reactivity),[7] have also been developed.

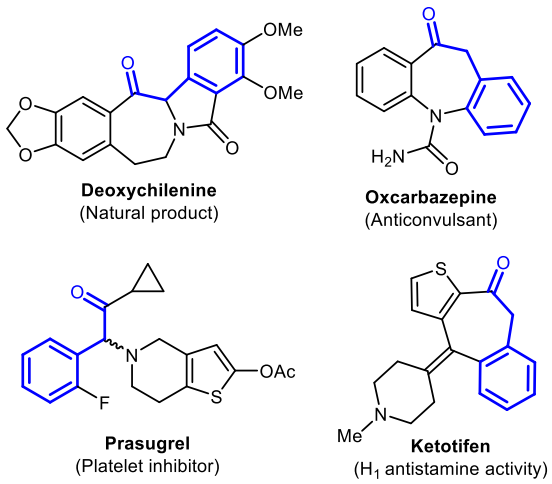
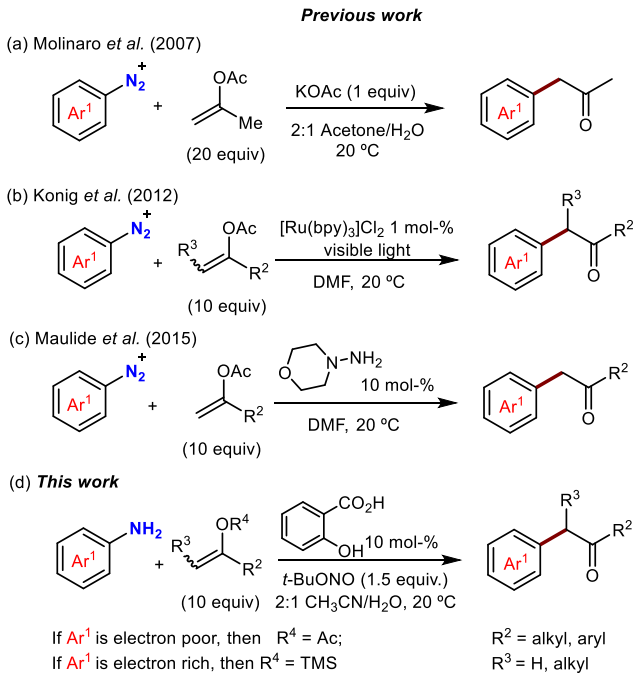


Figure 1. Selected bioactive molecules bearing the *α*-aryl ketone moiety.

Aryldiazonium salts are ideal starting materials in organic synthesis because they can be prepared in one step from cost-effective anilines,[8] and can be easily reduced (E^{o}_{red} ~ + 0 V vs Ag/AgCl)[9] to the corresponding highly reactive aryl radical. This reactivity has been largely exploited in fundamental transformations such as the Sandmeyer reaction,[10] the Meerwein arylation[11] and the intramolecular Pschorr reaction.[12] It is noteworthy that in all these reactions N_2 is released as a traceless and inert by-

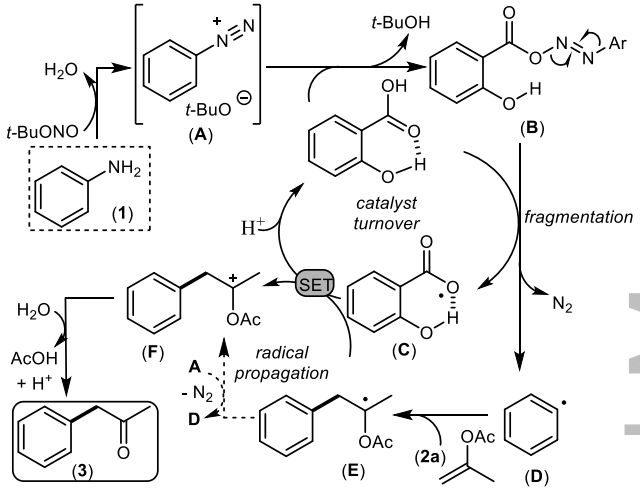
product that does not affect the reactivity of the aryl radical. In particular, aryldiazonium salts have been also used as aryl radical sources which, after interception with enol acetates, have furnished α-aryl ketones. Selected examples illustrating the implementation of this strategy are: (a) the α-arylation of methyl ketones promoted by stoichiometric amounts of KOAc[13] (Scheme 1a); (b) the visible-light induced transformation with $[Ru(bpy)_3]^{2+}$ as photocatalyst[14] (Scheme 1b); and (c) the use of hydrazines as organocatalysts[15] (Scheme 1c). Closely related methods for the oxidative arylation of vinyl arenes with aryl diazonium salts have also been developed, employing stoichiometric amounts of ascorbic acid as promoter [16] or visible-light photoredox catalysis[17]. However, the latter strategy is limited to the synthesis of 2-arylacetophenones, while benzyl alkyl ketones are not accessible. Herein, we describe the *in-situ* generation of aryl diazonium salts from anilines and *tert*-butylnitrite, and their salicylic acid (SA)- catalyzed reaction with enol acetates (or silyl enol ethers) at 20 ºC, to afford the corresponding α-aryl ketones (Scheme 1d).



Scheme 1. α-Arylation of enol acetates with aryl diazonium salts.

Results and Discussion

The group of Carrillo has reported that aryl radicals can be conveniently generated at room temperature, by reduction of the corresponding diazonium ions catalyzed by ascorbic acid[18] or gallic acid[19]. Inspired by their work, we have recently developed the hydrodeamination of *in-situ* formed diazonium salts, catalyzed by salicylic acid (SA) and using THF as the hydrogen donor.[20] Given that SA is inexpensive, harmless and a renewable feedstock, it could be an ideal catalyst to generate aryl radicals; therefore, we decided to elaborate this concept for the α-arylation of enol acetates. In our previous work, we proposed that the *in-situ* formed diazonium salts (**A**) could undergo a nucleophilic addition of salicylic acid to form the aryl diazobenzoate **B** (not isolated),[21] which upon N-O bond homolysis, would generate N_2, the aryl radical (**D**) and the H-bond stabilized salicyloyl radical (**C**). Given the intrinsic electrophilic character of aryl radicals, we envisioned that reaction with nucleophilic enol acetate **2a** would afford α-oxyradical **E**, which after single electron transfer to radical **C** would lead to carbocation **F**, regenerating the SA. Alternatively, the diazonium salt **A** can also act as an oxidant of radical **E** in a typical radical polar crossover to propagate the radical chain reaction. Hydrolysis of cation **F** would lead to the final ketone (**3**), generating acetic acid as by-product (Scheme 2).

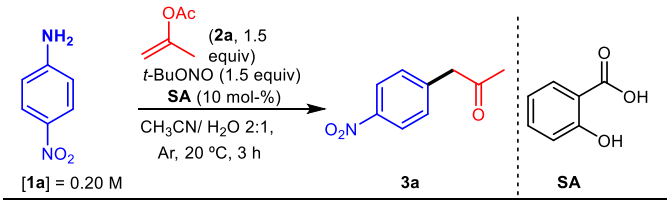


Scheme 2. Plausible mechanism.

In order to validate our proposal, we conducted the reaction of *p*-nitroaniline (**1a**) with isopropenyl acetate (**2a**) in the presence of *tert*-butylnitrite and 10 mol-% of salicylic acid at 20 ºC (Table 1). After screening different solvent systems (entries 1-9), we were pleased to obtain product **3a** in good yield when a 2:1 mixture of CH_3CN / H_2O was used, even with only 1.5 equivalents of **2a** (entry 5). Interestingly, the presence of H_2O as a minor component of the solvent mixture was well tolerated, even affording slightly better results (entries 5 and 9 vs 4). Furthermore, increasing the amount of **2a** up to 10 equivalents (entries 10-12), while keeping the concentration of **1a** in 0.20 M, resulted in an optimal reaction yield (entry 12). Control experiments revealed that the ambient light was not promoting the reaction (entry 13),[22] whereas significantly lower yields of **3a** were obtained in the absence of salicylic acid, even at 60 ºC (entries 14 and 15).[23] It is worth noting that in some related reactions with preformed aryldiazonium salts, slow addition and high temperatures are

required to avoid the attack of the aryl radicals onto unconverted diazonium ions.[24] Our protocol is operationally very simple and easy to reproduce because the reaction is conducted at room temperature (20 ºC of a water bath) and slow addition is not required for any reagent. Presumably, since *tert*-butylnitrite is the last reactant added to the reaction mixture, decomposition of the diazonium salt might occur immediately after its formation, minimizing the concentration of the latter species. This metal-free procedure allows the direct formation of *α*-aryl acetones, from inexpensive and bench stable anilines, without photochemical or thermal activation, under mild acidic conditions (pH ~ 3-4).

Table 1. Optimization of the reaction conditions.

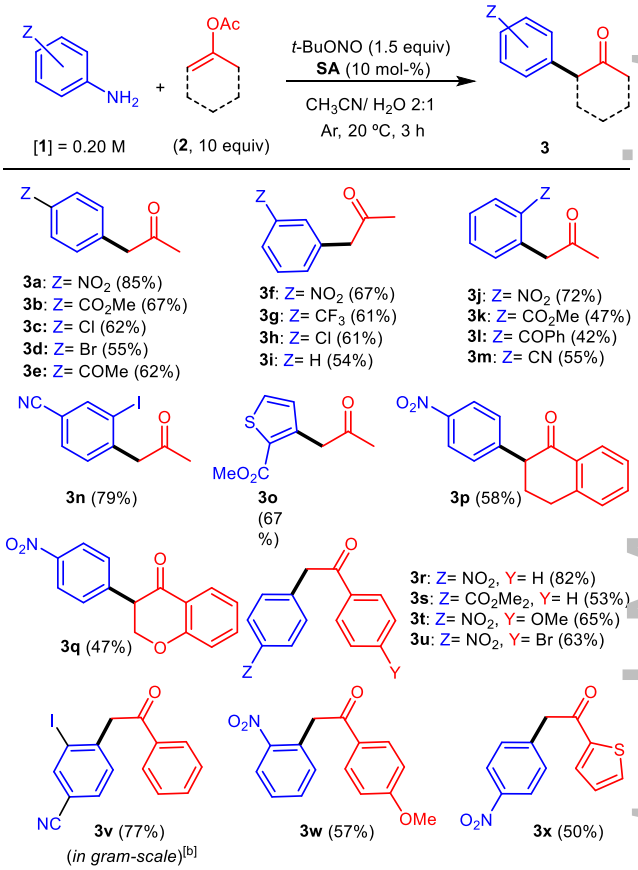


Entry	Deviation from above	Yield (%)[a]
1	in DMF	19
2	in DMSO	21
3	in Acetone	37
4	in CH_3CN	61
5	none	69 (65)
6	in 2:1 Acetone/H_2O	54
7	in 1:1 CH_3CN/H_2O	53
8	in 1:2 CH_3CN/H_2O	51
9	in 5:1 CH_3CN/H_2O	63
10	5 equiv. of **2a**	80
11	[**1a**] = 0.10 M, 10 equiv. of **2a**	56
12	10 equiv. of **2a**	86 (84)
13	10 equiv. of **2a**, protected from light	84
14	Without **S.A.**	16
15	10 equiv. of **2a**, without **SA** and heating to 60 ºC	39

[a] Determined by GC, using adamantane as the internal standard. In parentheses are the yields of isolated pure **3a**.

With suitable reaction conditions in hand (entry 12, Table 1), the scope of the *α*-arylation of different enol acetates was examined for various anilines. As depicted in Table 2, different acceptor substituted anilines reacted with isopropenyl acetate **2a**, affording the corresponding *α*-aryl acetones (**3a** to **3o**) in synthetically useful yields (42-85%). A wide range of functionalities tolerate the mild reaction conditions used, including electron-withdrawing ones at different positions, such as nitro, ester, halogens, ketones, nitriles and the trifluoromethyl group. Remarkably, iodine-bearing anilines were well tolerated and products **3n** and **3v** were obtained in high yields, without significant deiodination.[25] While unsubstituted aniline afforded the expected product (**3i**) in a moderate yield (54%), electron-richer anilines (Me or MeO-substituted) failed to give the desired product in a reasonable yield. Aryl-substituted enol acetates were also found to be good reaction partners, furnishing the desired products (**3p** to **3w**) in moderate-to-good yields. Moreover, the present protocol was also compatible with heteroaromatic enol acetates, as demonstrated by obtaining compound **3x** in a reasonable 50% yield. It is worthwhile mentioning that the standard procedure could be easily extended to a gram scale, as exemplified for the functionalized product **3v**.

Table 2. Substrate scope with enol acetates[a]

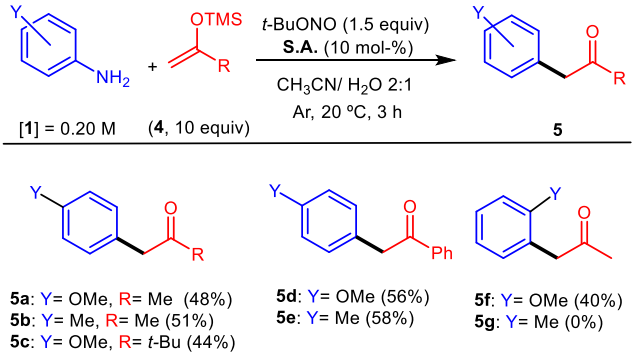


[a] Yields are reported for isolated products in 0.50 mmol scale, unless otherwise indicated. [b] 1.336 g of **3v** were obtained from 5 mmol of **1n**.

The reactions of *p*-anisidine or *p*-toluidine with isopropenyl acetate under the previously optimized conditions were complicated by the formation of several side-products, from which acetanilides and the hydrodeamination products were identified by GC-MS (especially for *p*-anisidine). To avoid the formation of acetanilides and minimizes the hydrodeamination reaction we decided to explore the performance of trimethylsilyl enol ethers in the reaction with electron-richer anilines, under otherwise similar conditions. As shown in Table 3, the corresponding products were obtained in moderate yields. The electron-donating methyl and methoxy groups at the *para*- position of anilines were well tolerated with aliphatic (products **5a-5c**) and aromatic (products **5d** and **5e**) silyl enol ethers. In

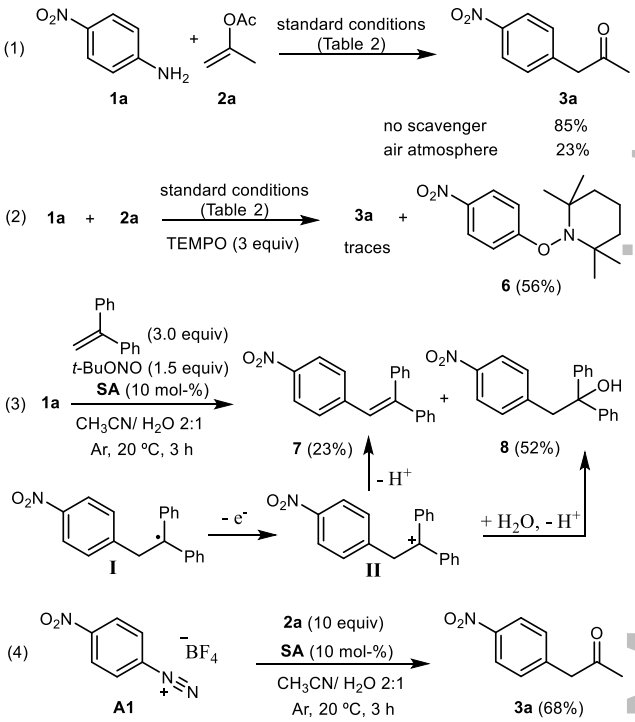
addition, *ortho*-methoxy aniline gave the expected product in a modest 40% yield (**5f**), whereas no reaction took place when introducing a methyl group at *ortho*-position (**5g**), most likely because of the increased steric hindrance.

Table 3. Reaction with trimethylsilyl enol ethers.



In order to support the mechanism proposed in Scheme 2, we conducted some control experiments (Scheme 3). The detrimental effect of O_2 in the reaction yield was evident, increasing from 23% in the presence of air to 85% yield under an Ar atmosphere (eq 1). This result is in accordance with the *in-situ* formation of aryl radicals that can be intercepted by the persistent O_2 diradical. Actually, when 3 equivalents of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) were added to the reaction mixture, the formation of compound **3a** was completely inhibited and *p*-NO_2Ph-TEMPO (**6**) was isolated in 56% yield (eq 2). In addition, when 1,1-diphenylethylene was used as the radical scavenger, instead of **2a**, compounds **7** and **8** were obtained in 75% overall yield (eq 3). The latter result might involve the intermediacy of radical **I** which, after being oxidized to the carbocation **II**, could lose a proton to form compound **7** or undergo water addition from the reaction media to obtain **8**. Moreover, when aryl diazonium salt **A1** was allowed to react with **2a** in the presence of SA, the expected compound **3a** was obtained in good yield after purification (eq 4). All these results support that SA catalyzes the transformation of aryl diazonium salts (*in-situ* formed) into the corresponding aryl radicals, as proposed in Scheme 2.[26]

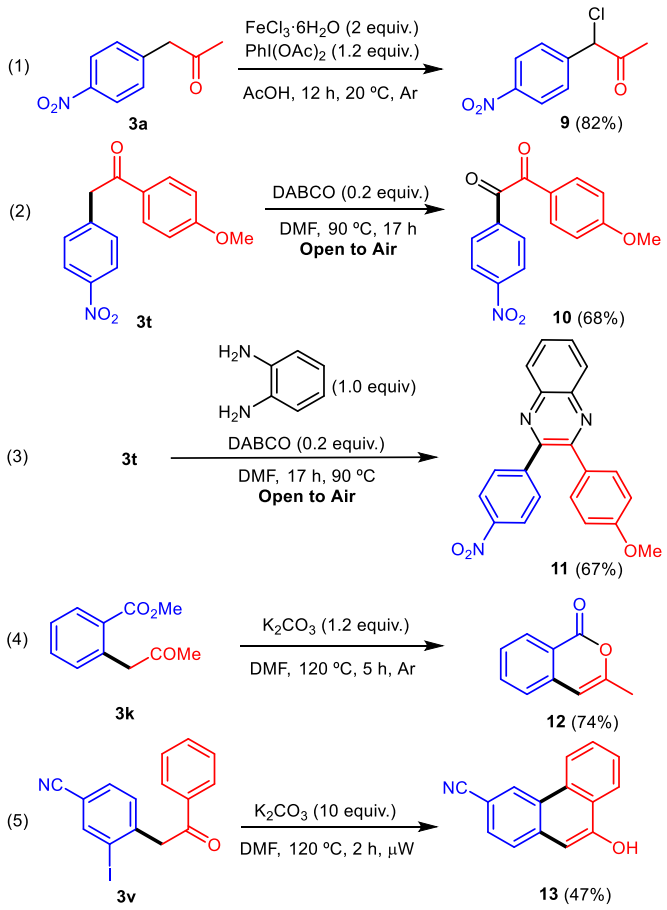
The high tolerance of the method herein described for the preparation of α-aryl ketones to the presence of diverse functionalities, provided a range of useful compounds ready for further structural elaborations, as illustrated for some examples in Scheme 4. Regioselective chlorination at the benzylic position of compound **3a** was easily accomplished using $FeCl_3$ and PIDA, to obtain compound **9** in excellent yield (eq 1).[27] The aerobic oxidation of ketone **3t** was efficiently promoted under the reported reaction conditions to obtain diketone **10** (eq 2) or, in the presence of *o*-phenylenediamine (eq 3), quinoxaline **11**.[28] We must underline that diketone **10** can be also transformed easily into other drug-like aromatic heterocycles. Additionally, when compound **3k** was heated at 120 ºC under mildly basic conditions, isocoumarin **12** was obtained in good yield.[29] Finally, when the iodo derivative **3v** was treated with an excess of K_2CO_3 under microwave activation, the intramolecular biaryl coupling took place, giving rise to the phenanthrene **13** in a non-optimized 47% yield.[30]



Scheme 3. Control experiments.

Conclusion

In summary, α-aryl ketones can be obtained from readily available anilines and enol acetates through the *in-situ* formation of diazonium salts with *tert*-butylnitrite and using salicylic acid as catalyst (10 mol-%), without thermal (20 ºC) or photochemical activation. The mild conditions used enabled the reaction of a wide range of anilines with enol acetates in moderate-to-good yields. It must be highlighted that the protocol is operationally very simple, and the target compounds can be obtained in gram quantities with similar yield. Moreover, the methodology can include anilines with electron-donating groups by using trimethylsilyl enol ethers instead of enol acetates. The utility of the prepared α-aryl ketones as synthetic intermediates was exemplified with five different follow-up reactions. This work demonstrates the potential benefits of the use of salicylic acid as cheap and green catalyst for the generation of aryl radicals from anilines.



Scheme 4. Five follow-up reactions of α-aryl ketones.

Experimental Section

General procedure for the arylation reaction with enol acetates (*GP-A, Table 2***)**: The corresponding aniline (0.50 mmol) and salicylic acid (6.9 mg, 0.05 mmol) were added into an oven dried Schlenck. The system was evacuated and filled with argon (three times), before the corresponding enol acetate (5.0 mmol), and the solvents MeCN (1.65 mL) and H_2O (0.85 mL) were added. The reaction mixture was stirred vigorously until a homogeneous solution was obtained (1-5 min). At this point, *tert*-butylnitrite (100 μL, 86 mg, 0.75 mmol) was added (the solution turned orange after some minutes) and the stirring continued for 3 h, keeping the temperature at 20 ºC with an external water bath. Then, water (10 mL) was added and the mixture was extracted three times with EtOAc (3 x 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and the residue was purified by flash column chromatography on silica gel to give the desired product.

General procedure for the arylation reaction with silyl enol ethers (*GP-B, Table 3***)**: The corresponding aniline (0.50 mmol) and salicylic acid (6.9 mg, 0.05 mmol) were added into an oven dried Schlenck. The system was evacuated and filled with argon (three times), before MeCN (1.65 mL) and H_2O (0.85 mL) were added, and the reaction mixture was stirred vigorously until a homogeneous solution was obtained (1-5 min). Then, *tert*-butylnitrite (100 μL, 86 mg, 0.75 mmol) was added, and immediately after the corresponding silyl enol ether (5.0 mmol) was added under argon atmosphere. The solution turned orange after some minutes, and the reaction mixture was stirred for 3 h, keeping the temperature at 20 ºC with an external water bath. The reaction was quenched by adding water (10 mL) and the mixture was extracted with Et_2O (3 x 15 mL). The organic layers were collected, dried over anhydrous $MgSO_4$ and filtered. The residue was purified by flash column chromatography on silica gel, to give the desired product.

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FULL PAPER

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