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New deconjugation reaction of (*E*)-1-indanylidene methylarene brought by photolysis with protic acid☆

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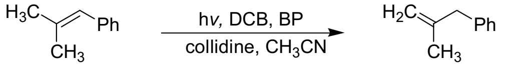
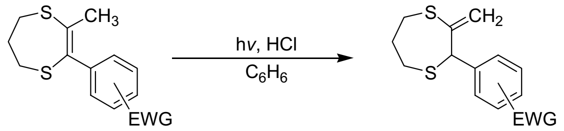
Abstract—A new photodeconjugation reaction of (*E*) indanylidene methylarenes (**1a**–**d**) carried out by photolysis in the presence of protic acid are reported with 80% to >95% yields. The reaction mechanism is through the protonation of the less stable (*Z*) isomer to form stable indanyl cation followed by deprotonation.

Deconjugation reaction is one of the most interesting topics for photochemistry, since it involves the conversion of the more stable reactants to the less stable products. Recently there are several reports on the photodeconjugation reactions. Arnold and Mines have studied the photodeconjugation reaction of 1-phenylpropene[1,2] and 1-arylcyclohexene.[3] The reaction is carried out by photolysis of a mixture of 1,4-dicyanobenzene (DCB), biphenyl (BP), collidine and the reaction (e.g., 2-methyl-1-phenylpropene) in acetonitrile afford 2-methyl-3-phenylpropene in 90% yield (Eq. 1). The reaction is initiated by photosensitized electron transfer from the reactant to the excited state of 1,4-dicyanobenzene and involves reactive intermediates such as the cation radical, anion radical, allyl radical and allyl anion.



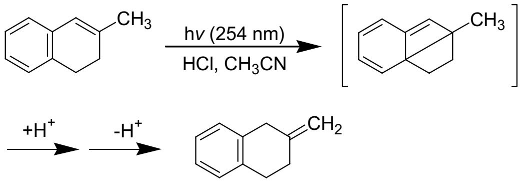
(1)

Another type of photodeconjugation is reported by Kutateladze and co-workers.[4] Their photodeconjugation for 2-aryl-3-methyl-6,7-dihydro-5*H*-[1,4]dithiepine is assisted by protic acids (Eq. 2). This reaction is achieved by the combination of electron donating sulfur and electron-withdrawing phenyl systems.



(2)

Photodeconjugation of an α,β-unsaturated ketone to the less stable β,γ-unsaturated ketone has also been reported through the Norrish-type hydrogen abstraction reaction.[5] Photolysis[6] of 3-methyl-1,2-dihydronaphthalene (3-MDHN) in acidic acetonitrile with 254 nm light at room temperature, the major product is the deconjugated 2-methylene-1,2,3,4-tetrahydronaphthalene (2-MTHN) with the quantum yield of 0.027 (Eq. 3). The deconjugation product is formed via protonation and deprotonation of the ring opening product of an initially formed intramolecular [2 + 2] cycloadduct.



(3)

The course of photochemical reaction is sometimes sensitive to its acidic environments.[7–10] We have prepared a series of (*E*)-1-indanylidene methylarenes **1a**–**g** (Scheme 1) and would like to report a new deconjugation reaction, which is assisted by photolysis in the presence of protic acid. Compounds **1a**–**d** were synthesized by reacting indanyl-(1)-triphenyl-phosphonium bromide with the corresponding aldehydes and sodium amide.[11] Compounds **1a**–**g** show stilbene type of absorption at λ_{max} around 330 nm. When 105 mg of

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Keywords: Deconjugation; Photochemistry; Protic acid.

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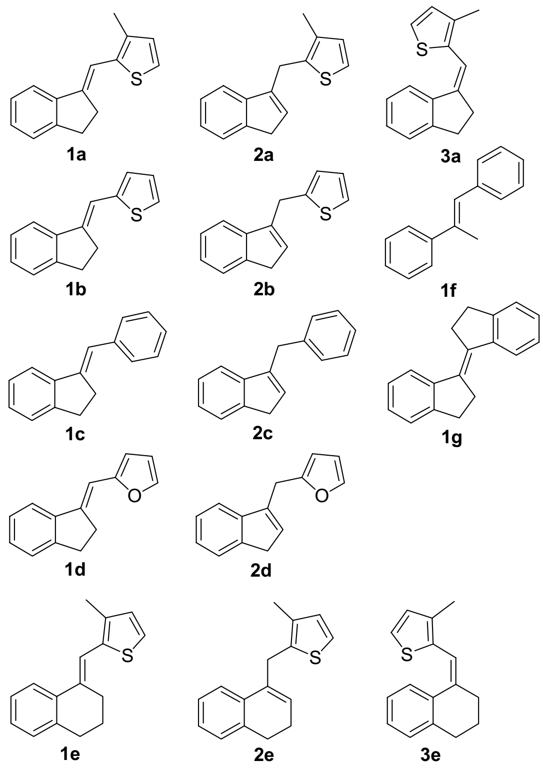
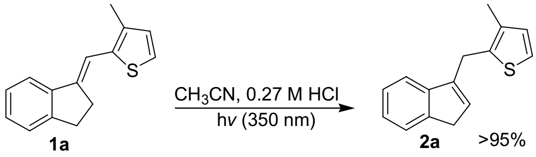


Scheme 1.

(*E*)-2-(1-indanylidenemethyl)-3-methylthiophene **1a** is dissolved in 105 mL of acetonitrile (4.4×10^{-3} M) containing 2.34 mL of hydrochloric acid (0.27 M) and the solution is outgasssed with argon. Then the solution is irradiated at 350 nm for 40 min with a Rayonet reactor. The solution is neutralized with sodium hydroxide solution and the product is extracted with ethyl acetate to afford >95% yield (96.5 mg isolated at conversion of 93%) of 2-(inden-3-ylmethyl)-3-methylthiophene[12] **2a** (Eq. 4).



(4)

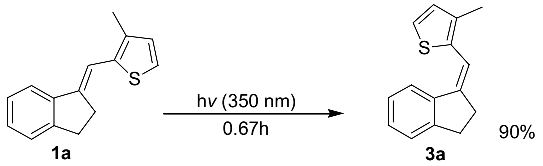
Similarly photolysis of compounds **1b–d** with 0.27 M hydrochloric acid afforded **2b–d**, respectively, in 80–95% yields (Table 1).

Irradiation of 2-(*E*)-(1-(2,3,4-trihydronaphthylidene)-methyl)-3-methylthiophene **1e** in the presence of 0.27 M HCl afford 2-(1-(3,4-dihydronaphthyl)methyl)-3-methylthiophene **2e** in only 8% yield. Photolysis of (*E*)-1,2-diphenyl-propene **1f** with 0.27 M HCl leads to mixture of *E*, *Z* isomers without any deconjugation products. Thus it is clear that only the indanylidene system can undergo efficient photodeconjugation. The six-member ring system (**1e**) afford very few deconjugation product. The open system (**1f**) does not react at all. We can get some insight into the mechanism of this new photodeconjugation system from the fact that photolysis of (*E*)-2,3,2′,3′-tetrahydro-[1,1′]biindenylidene **1g** in the presence of 0.27 M HCl resulted in the isolation of the starting reactant only. It has been reported[13] that the *Z* form of **1g** is not stable due to it's steric hindrance. Thus the *Z* compound formation is essential for the photodeconjugation process for the indanylidene system. When compound **1a** is photolyzed in acetonitrile in the absence of hydrochloric acid, the reaction afford the *Z* compound **3a** in 90% yield (Eq. 5) as compared with the photolysis in the presence of HCl (Eq. 4).

Table 1. The conversion and yields of the photodeconjugation of compounds **1a–g** in the presence of 0.27 M hydrochloric acid using 350 nm light at room temperature (25 °C)

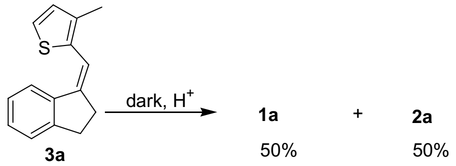
Reactant	Irrad. time (h)	Conversion (%)	Product	Yield (%)
1a	0.67	93	**2a**	>95
1a	0.67	92	**3a**	90[a]
1b	0.67	93	**2b**	90
1c	0.67	94	**2c**	>95
1d	1.33	90	**2d**	80
1e	0.67	75	**2e**	8
1f	0.67	—	$Z+E$	—
1g	2.5	—	No reaction	—

[a] Irradiation without HCl.



(5)

When the *Z* compound **3a** is treated 0.27 M HCl in the dark the reaction products contain one to one mixture of the deconjugation product **2a** and the *E* compound **1a** (Eq. 6).



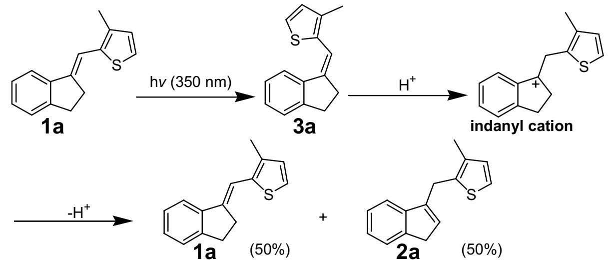
(6)

The product **2a** can also be converted to the starting reactant **1a** by heating **2a** in the presence of hydrochloric acid at 70 °C for 5 h. (Eq. 7).

$$\mathbf{2a} \xrightarrow[70^{\circ}\mathrm{C},\ 5\mathrm{h}]{\mathrm{CH_3CN,\ HCl}} \mathbf{1a}\quad 90\% \qquad (7)$$

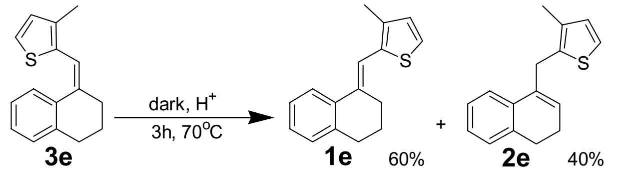
Thus the mechanism for the deconjugation process can be summarized in Scheme 2. Photolysis of **1a** produces the unstable *Z* compound **3a**. The regioselective protonation of the (*Z*)-**3a** produces the 1-indanyl carbocation which can undergo nonselective deprotonation back to the (*E*)-**1a** and to the deconjugated **2a** in one to one ratio. The relatively stable indanyl cation[14] has been proposed as a reactive intermediate.

The high theoretical proton affinity for 1-methylindene has been calculated (209.8 K cal/mol) by density functional theory.[15] And it was predicted that indanyl cation is a persistent carbenium ion. There is one report[16]



Scheme 2. Proposed mechanism for the photodeconjugation of **1a**.

saying that in strong acid environment the indanyl cation is stable than indene. Haw and co-workers[17] have also measured the NMR spectra for indanyl cation. Thus in our hydrochloric acid environment, the indanyl cation is obtained from protonation at the less stable *Z*-alkene, which is derived from *E*-alkene by photoisomerization and undergoes nonselective deprotonation at room temperature. The related six-member ring cation (2,3,4-trihydro-1-naphthyl cation) is less stable and is not easily achievable at room temperature. This accounts for the low yield (8% yield for **2e**). However higher deconjugation product can be achieved for compound **2e** when the **3e** (which is obtain by photolysis of **1e**) is heated at high temperature (Eq. 8).



(8)

The acyclic carbenium ion is even more unstable and no reaction is observed for compound **1f**. The lack of deconjugation for the compound **1g** has been ascribed to the fact that *Z* form of **1g** can not be achieved photochemically, thus the unstable *Z* isomers of indanylidene arenes (**1a–d**) are precursors to the indanyl cations.

In summary, we have presented a new deconjugation reaction of (*E*)-indanylidene methylarene system, which is assisted by photolysis with protic acid. The reaction mechanism is through the regioselective protonation of the *Z* isomer to form relatively stable indanyl cation. Then deprotonation from the indanyl cation can lead to the deconjugation product. Since the deconjugated product can be converted back to the starting material under acidic condition at higher temperature (>70 °C) in high yield (>90%), our system may be developed into a new thermally reversible photochromic system for compounds **1a–d**.

Acknowledgements

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