

INTRAMOLECULAR REACTIVITY OF FUNCTIONALIZED ARYLCARBENES: 1-(HYDROXYMETHYL)-9-FLUORENYLIDENE

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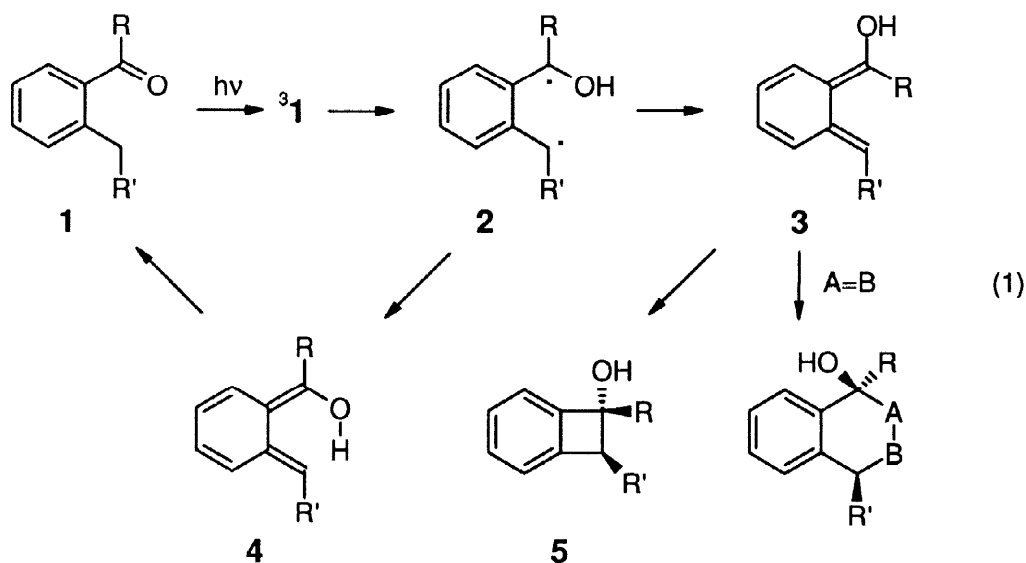
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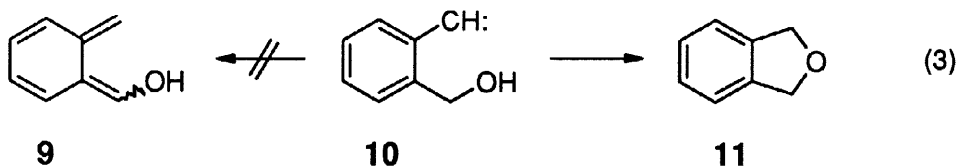
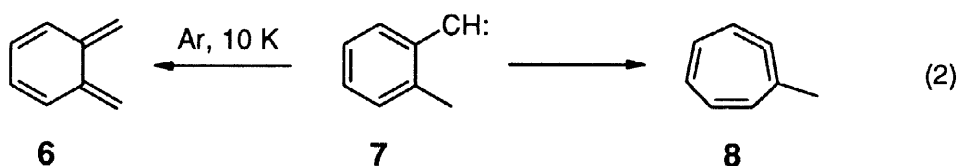
Abstract: Photolyses of 9-diazo-1-fluorenylmethanol (**22**) in benzene or MeCN afford $\geq 95\%$ of fluorene-1-carbaldehyde (**14**). In methanol, **14** and 9-methoxy-1-fluorenylmethanol (**24**) are formed competitively from **22**. Intramolecular hydrogen transfer of triplet 1-(hydroxymethyl)-9-fluorenylidene (**12**) appears to be the major reaction path leading to **14**. The photoenol **13** is suggested as an intermediate.

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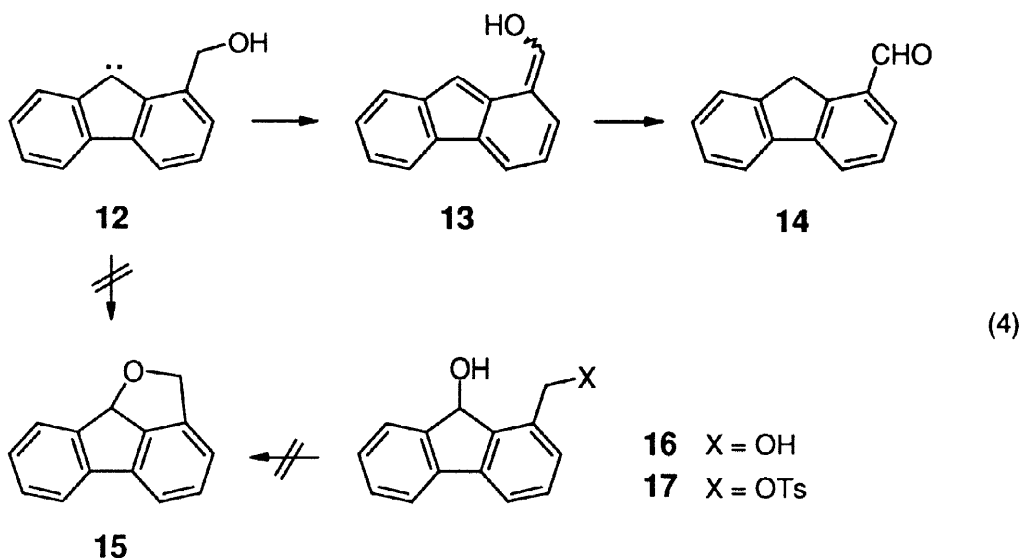
Irradiation of *ortho*-alkyl aryl carbonyl compounds **1** induces hydrogen shifts commonly known as photoenolization, Eq.(1).^{1,2} The triplet state of the carbonyl abstracts hydrogen, giving rise to a rotationally equilibrated diradical **2** which decays to both *E* (**3**) and *Z* enol (**4**). The latter undergoes a very rapid 1,5-sigmatropic H shift to regenerate **1**, while the long-lived *E* enol can be trapped by dienophiles or rearranges to a benzocyclobutenol (**5**).³



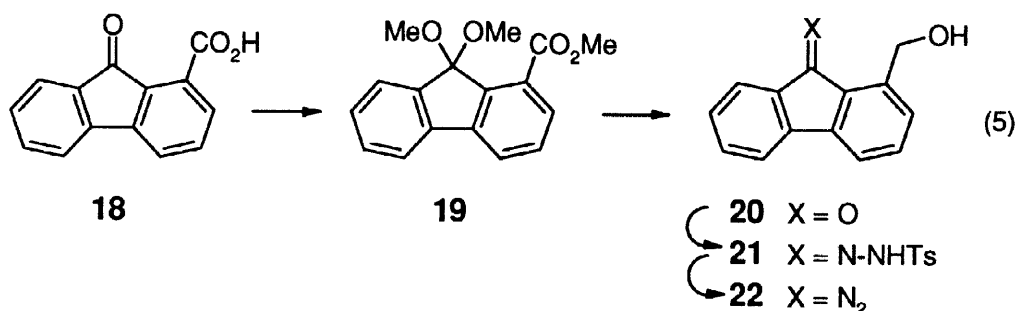
Photoenols are a subgroup of quinodimethanes, some of which are accessible from 2-alkyl-arylcabenenes. Thus, studies of matrix-isolated *o*-tolylcarbene (**7**) revealed the 1,4-hydrogen shift to form *o*-xyllylene (**6**), along with ring expansion leading to 1-methylcycloheptatetraene (**8**), Eq. (2).⁴ In solution, however, intermolecular reactions of *o*-tolylcarbene predominate.⁵ Not surprisingly, 2-(hydroxymethyl)phenylcarbene (**10**) undergoes intramolecular O-H insertion (**10** → **11**) rather than 1,4-H shift to give a photoenol (**10** → **9**), Eq. (3).⁶



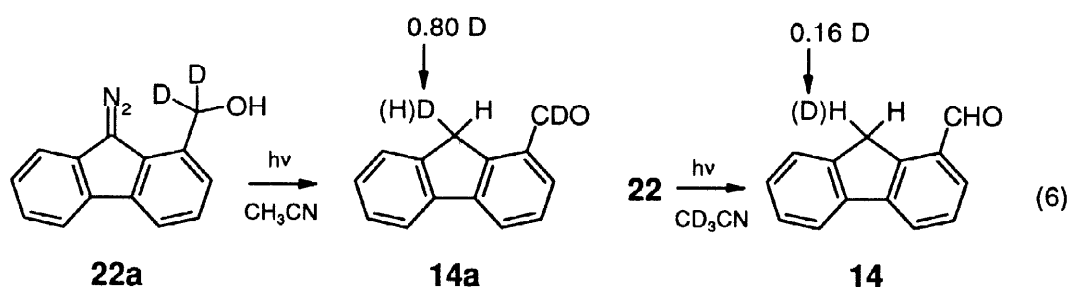
In an effort to reverse the reactivity of **10**, we studied 1-(hydroxymethyl)-9-fluorenylidene (**12**). We found that **12** affords fluorene-1-carbaldehyde (**14**), presumably by way of the photoenol **13**, Eq. (4). The highly strained ether **15** is not formed. According to force field calculations (MMX), the strain energy of **15** exceeds that of **11** by 34 kcal/mol and that of **14** by 19 kcal/mol. Accordingly, we failed to obtain **15** by conventional ether syntheses, such as Mitsunobu reaction of the diol **16** and base-induced cyclization of the tosylate **17**.



The carbene **12** was generated from the diazo compound **22**. The synthesis of **22** started from 9-oxofluorene-1-carboxylic acid (**18**) and proceeded by way of **19-21**,⁷ as outlined in Eq. (5). The deuterated precursor **22a** was prepared analogously, using LiAlD₄ for the reduction of **19**. Photolyses of **22** in benzene or acetonitrile afforded **14**^{7f} as the only product with ≥95% yield. The photolysis of **22a** in CH₃CN gave **14a** with 0.80±0.02 D in position 9 (²H NMR). Conversely, 0.16±0.01 9-D was incorporated on photolysis of **22** in CD₃CN, Eq. (6). These data indicate that the H transfer leading to **14** is mostly intramolecular. A minor fraction of the hydrogen shift appears to be mediated by solvent molecules, according to the mechanism shown in Eq. (7).



(a) HC(OMe)₃, MeOH, H₂SO₄, reflux, 10 h, 98%. (b) LiAlH₄, THF, reflux, 1 h, 87%. (c) conc. H₂SO₄, Et₂O, reflux, 30 min, 67%. (d) TsNHNH₂, MeOH, 2 h reflux, 73%. (e) 30% NaOH, dioxane, 60 °C, 1.5 h, 24%.



Photolyses of **22** in methanol gave 9-methoxy-1-fluorenylmethanol (**24**) as the major product, along with **14** and 1-fluorenylmethanol (**26**) (Table). Controls revealed that **26** (but not **14**) is formed on photolysis of **24** in methanol.⁸ Since O-H insertion is characteristic of singlet carbenes,⁹ the origin of **14** was probed by photolyzing **22** in the presence of benzophenone or isoprene. The ratio of **14** : (**24** + **26**) was found to increase on triplet sensitization and to decrease on triplet scavenging (Table).¹⁰ Therefore, the hydrogen transfer is thought to proceed from the triplet carbene, ³**12**, to give a triplet diradical, ³**23**, which relaxes to **13** and, eventually, **14**, Eq. (7). To our knowledge, **12** is the first arylcarbene that undergoes an efficient 1,4-H shift *in solution*.¹¹

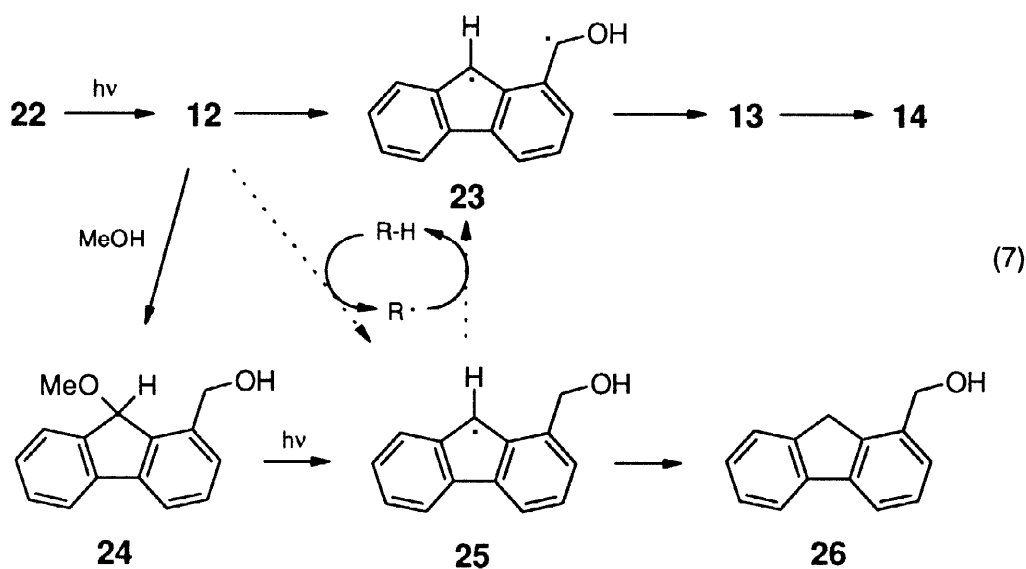


Table. Product distributions (%) obtained on photolysis of **22** (4.4 mM) in methanol (20 °C)

Additive	14	24	26	14 : (24 + 26)
-	18.7	75.8	2.8	0.24
benzophenone, 0.05 M	22.1	70.4	3.8	0.30
benzophenone, 0.2 M	31.0	58.2	4.5	0.49
isoprene, 0.05 M	18.2	80.2	1.6	0.22
isoprene, 0.1 M	15.8	77.0	3.5	0.20
isoprene, 0.2 M	14.7	82.5	1.5	0.18

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- (a) **19**: X. M. Cherian, S. A. Van Arman, A. W. Czarnik, *J. Am. Chem. Soc.* **1990**, *112*, 4490-4498. (b) **20**: m.p. 123 °C; ¹H NMR (CDCl₃): δ = 4.16 (t, *J* = 7 Hz, OH), 4.82 (d, *J* = 7 Hz, CH₂), 7.1-7.7 (m, Ar-H). (c) **21**: m.p. 193-194 °C (dec.); ¹H NMR (acetone-*d*₆): δ = 2.41 (s, CH₃), 3.15 (br. s, OH), 4.73 (s, CH₂), 7.3-8.2 (m, Ar-H), 10.3 (br. s, NH). (d) **22**: m.p. 122 °C (dec.); IR (KBr): ν = 2073 cm⁻¹ (CN₂); ¹H NMR (CDCl₃): δ = 1.76 (t, *J* = 6 Hz, OH), 2.89 (d, *J* = 6 Hz, CH₂), 7.2-8.0 (m, Ar-H). (e) **24**: m.p. 87 °C; ¹H NMR (CDCl₃): δ = 3.08 (s, OCH₃), 4.71 and 4.98 (d, *J* = 12 Hz, CH₂), 5.78 (s, 9-H), 7.2-7.7 (m, Ar-H). (f) **14**, **26**: E. H. Jensen, P. H. Nielsen, R. Hohlweg, *Heterocycles* **1995**, *11*, 2441-2458.
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