Pergamon

Tetrahedron Letters 39 (1998) 799–802

TETRAHEDRON
LETTERS

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

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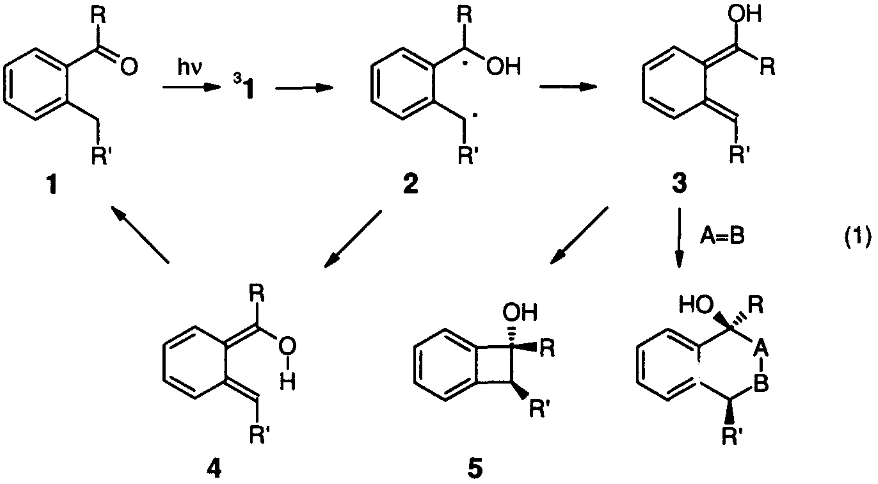
Received 12 November 1997; accepted 26 November 1997

Abstract: Photolyses of 9-diazo-1-fluorenylmethanol (**22**) in benzene or MeCN afford ≥95% of fluorene-1-carbaldehyde (**14**). In methanol, **14** and 9-methoxy1-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.

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-alkylarylcarbenes. Thus, studies of matrix-isolated *o*-tolylcarbene (**7**) revealed the 1,4-hydrogen shift to form *o*-xylylene (**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]

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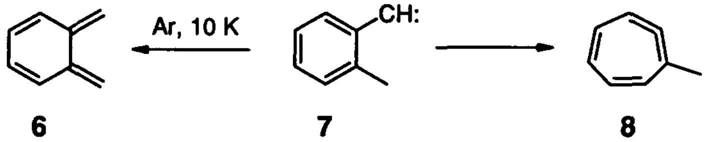
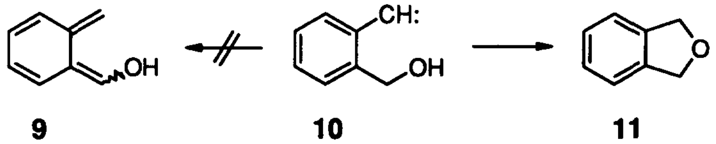
PII: S0040-4039(97)10741-9

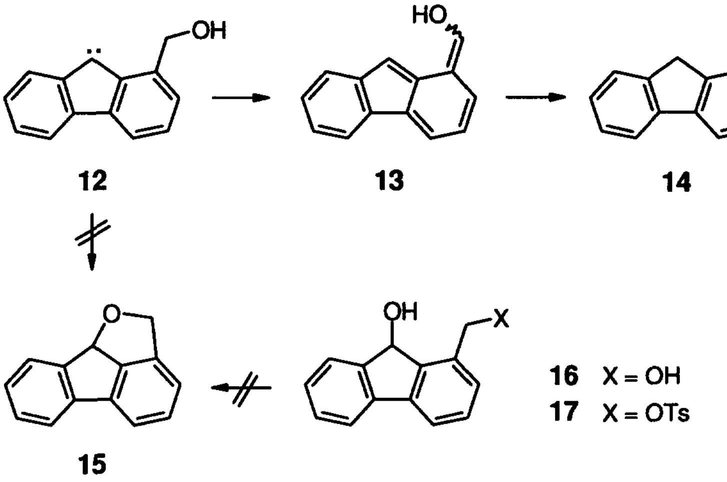


(2)



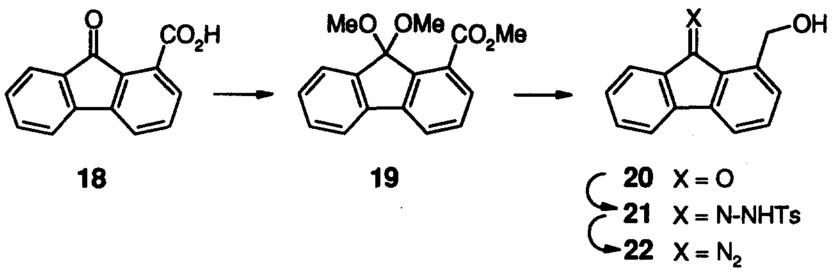
(3)

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**.



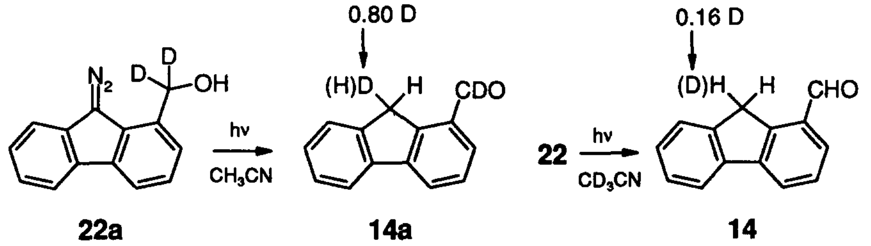
(4)

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 $LiAlD_4$ for the reduction of **19**. Photolyses of **22** in benzene or acetonitrile afforded **14**[7l] as the only product with ≥95% yield. The photolysis of **22a** in CH_3CN 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 CD_3CN, 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).



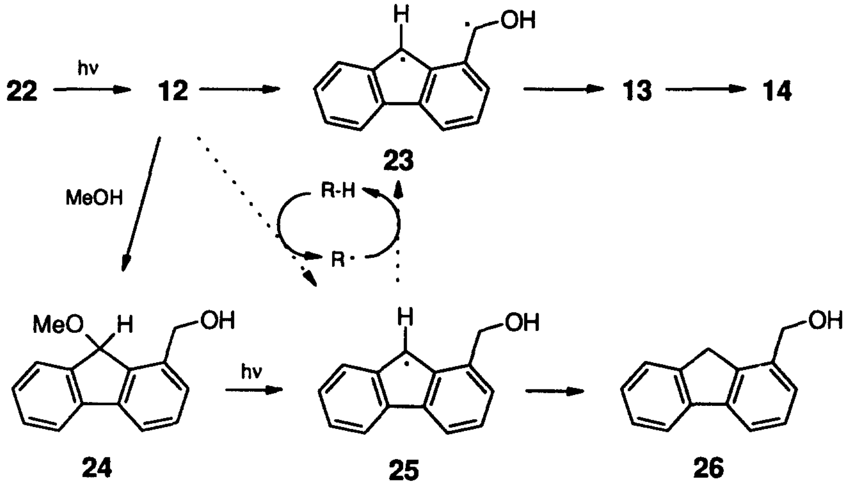
(5)

(a) $HC(OMe)_3$, MeOH, H_2SO_4, reflux, 10 h, 98%. (b) $LiAlH_4$, THF, reflux, 1 h, 87%. (c) conc.H_2SO_4, Et_2O, reflux, 30 min, 67%. (d) $TsNHNH_2$, MeOH, 2 h reflux, 73%. (e) 30% NaOH, dioxane, 60 °C, 1.5 h, 24%.



(6)

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]



(7)

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

REFERENCES AND NOTES

1. For reviews, see: (a) P. G. Sammes, *Tetrahedron* **1976**, *32*, 405-422. (b) R. M. Wilson, *Organic Photochemistry* **1985**, *7*, 373-387.
2. For recent references, see: (a) J. C. Netto-Ferreira, J. C. Scaiano, *J. Am. Chem. Soc.* **1991**, *113*, 5800-5803. (b) H. Hopf, T. Laue, M. Zander, *Angew. Chem.* **1991**, *103*, 441-442; *Angew. Chem.Int. Ed. Engl.* **1991**, *30*, 432-433; Chem. Ber. **1994**, *127*, 965-966. (c) R. M. Wilson, K. A. Schnapp, W. S. Patterson, *J. Am. Chem. Soc.* **1992**, *114*, 10987-10989. (d) J. C. Scaiano, V. Wintgens, J. C. Netto-Ferreira, *Tetrahedron Lett.* **1992**, *33*, 5905-5908; *Can. J. Chem.* **1994**, *72*, 1565-1569. (e) A. G. Griesbeck, S. Stadtmüller, *Chem. Ber.* **1993**, *126*, 2149-2150. (f) M. A. Garcia-Garibay, A. Gamarnik, R. Bise, L. Pang, W. S. Jenks, *J. Am. Chem. Soc.* **1995**, *117*, 10264-10275.
3. P. J. Wagner, D. Subrahmanyam, B.-S. Park, *J. Am. Chem. Soc.* **1991**, *113*, 709-710, and references cited therein.
4. (a) R. J. McMahon, C. J. Abelt, O. L. Chapman, J. W. Johnson, C. L. Kreil, J.-P. LeRoux, A. M. Mooring, P. R. West, *J. Am. Chem. Soc.* **1987**, *109*, 2456-2469. (b) O. L. Chapman, J. W. Johnson, R. J. McMahon, P. R. West, *J. Am. Chem. Soc.* **1988**, *110*, 501-509.
5. W. Kirmse, W. Konrad, D. Schnitzler, *J. Org. Chem.* **1994**, *59*, 3821-3829, and references cited therein.
6. W. Kirmse, K. Kund, *J. Org. Chem.* **1990**, *55*, 2325-2332.
7. (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; ^{1}H NMR ($CDCl_3$): $\delta = 4.16$ (t, $J = 7$ Hz, OH), 4.82 (d, $J = 7$ Hz, CH_2), 7.1-7.7 (m, Ar-H). (c) **21**: m.p. 193-194 °C (dec.); ^{1}H NMR (acetone-d_6): $\delta = 2.41$ (s, CH_3), 3.15 (br. s, OH), 4.73 (s, CH_2), 7.3-8.2 (m, Ar-H), 10.3 (br. s, NH). (d) **22**: m.p. 122 °C (dec.); IR (KBr): $\nu = 2073$ cm^{-1} (CN_2); ^{1}H NMR ($CDCl_3$): $\delta = 1.76$ (t, $J = 6$ Hz, OH), 2.89 (d, $J = 6$ Hz, CH_2), 7.2-8.0 (m, Ar-H). (e) **24**: m.p. 87 °C; ^{1}H NMR ($CDCl_3$): $\delta = 3.08$ (s, OCH_3), 4.71 and 4.98 (d, $J = 12$ Hz, CH_2), 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.
8. The photoreduction of 9-methoxyfluorene proceeds by C-O homolysis, followed by disproportionation of the 9-Fl· ·OMe radical pair: P. Wan, E. Krogh, *J. Am. Chem. Soc.* **1989**, *111*, 4887-4895.
9. For a review, see: W. Kirmse, *Adv. Carbene Chem.* **1994**, *1*, 1-57.
10. Small to moderate effects are anticipated, in view of the narrow S-T gap and rapid S-T interconversion of 9-fluorenylidene: G. B. Schuster, *Adv. Phys. Org. Chem.* **1986**, *22*, 311-361.
11. 1,4-H shifts were not observed with 1-alkyl-9-fluorenylidenes: H. Tomioka, H. Kawasaki, N. Kobayashi, K. Hirai, *J. Am. Chem. Soc.* **1995**, *117*, 4483-4498.