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PHOTOCHEMICAL REARRANGEMENT OF 1-METHOXYTRIPTYCENE. AN EFFICIENT RADICAL FRAGMENTATION OF A METHOXYCARBENE

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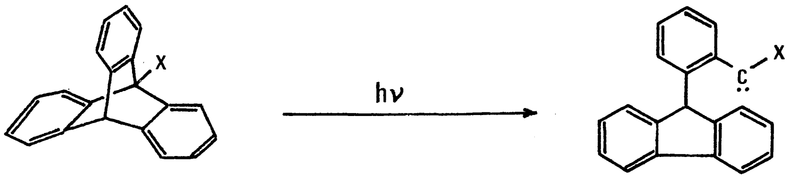
Irradiation of 1-methoxytriptycene 1(X = OCH_3) in alcohols gives 2-(9-fluorenyl)benzaldehyde acetals 3 in good yield, showing the formation of 2-(9-fluorenyl)phenylmethoxycarbene 2(X = OCH_3). In cyclohexane the expected internal adduct 4 is not obtained, but the photoproduct is 2-(9-fluorenyl)benzaldehyde 5. A novel homolysis of the O-CH_3 bond in less electrophilic methoxycarbene 2 has been demonstrated.

Chemistry of methoxycarbenes has been rather unexplored in view of a large number of literature covering a variety of carbenes.1) A primary reason for this scarcity appears to be the lack of suitable precursors which can produce methoxycarbenes efficiently under moderate conditions. Thus, for example, dimethoxycarbene is generated only at high temperature.2) Elimination of nitrogen from the salts of methyl N-tosylbenzohydrazonate is incomplete.3) Free methoxycarbenes are not considered to be liberated from the transition metal-methoxycarbene complexes.4)

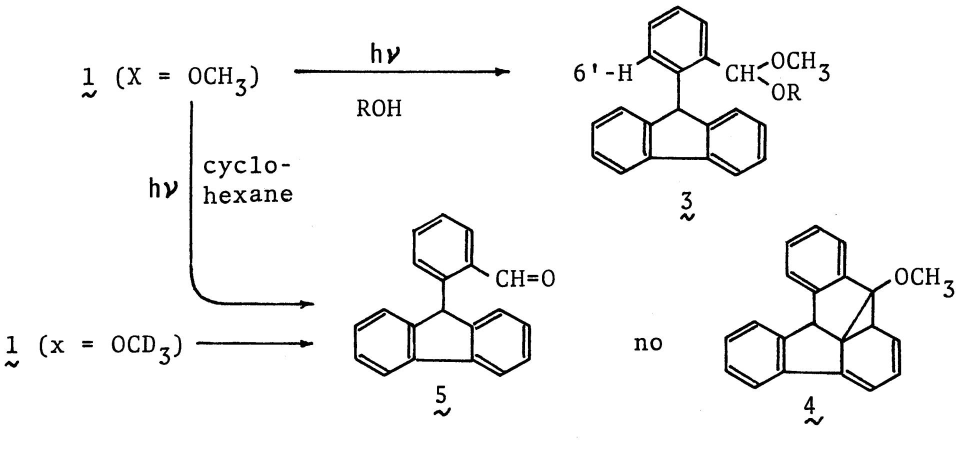
Our recent finding that the triptycene skeleton rearranges under uv irradiation smoothly to 2-(9-fluorenyl)phenylcarbene (Eq. 1)5) prompted us to generate alkoxyarylcarbenes 2(X = OR) by photolysis of 1-alkoxytriptycenes 1(X = OR).



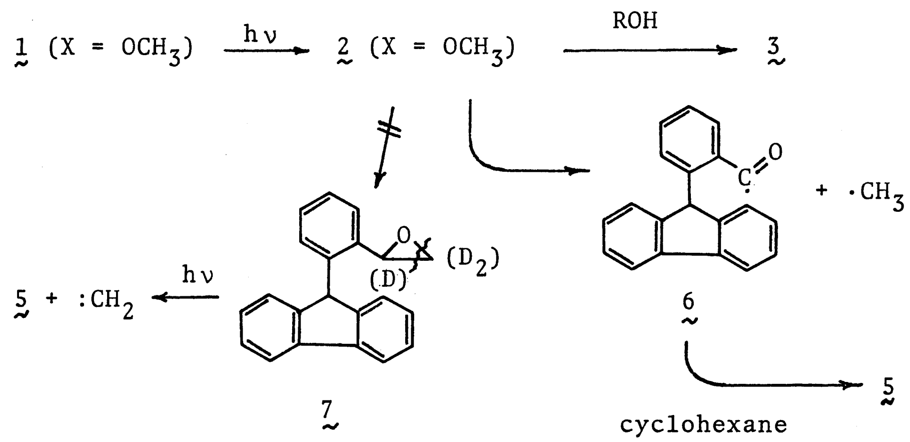
(1)

1 2

When a 4 mM solution of 1(X = OCH_3) in methanol was irradiated for 1.5 hr with a Vycor filtered Ushio UM-452 mercury source in an immersion apparatus, a smooth conversion to acetal 3(R = CH_3), mp 101°C [NMR($CDCl_3$) δ 2.40 (1.45 H, s, OCH_3), 3.48 (4.55 H, s, OCH_3), 3.76 (0.24 H, s, $-CH{<}^{O}_{O}$), 5.03 (0.24 H, s, $\geqslant$CH), 5.72 (0.76 H, s, $\geqslant$CH), 5.82 (0.76 H, s, $-CH{<}^{O}_{O}$), 6.37 (0.76 H, dd, H-6') and 6.9-7.9 (11.24 H, m, aromatic)] was achieved (62% isolated yield). The NMR is characteristic of a 9-(o-substituted phenyl)fluorene[5,6] in which two conformers are present in a ratio of 0.76 to 0.24. Irradiation of 1(X = OCH_3) in tert-butyl alcohol gave acetal 3(R = t-Bu) in 43% yield: NMR($CDCl_3$) δ 0.61 (1.48 H, s, t-Bu), 1.40 (7.52 H, s, t-Bu), 2.25 (0.49 H, s, OCH_3), 3.39 (2.51 H, s, OCH_3), 4.19 (0.16 H, s, $-CH{<}^{O}_{O}$), 5.05 (0.16 H, s, $\geqslant$CH), 5.91 (0.84 H, s, $\geqslant$CH), 6.02 (0.84 H, s, $-CH{<}^{O}_{O}$), 6.35 (0.84 H, dd, H-6') and 6.9 - 7.9 (11.16 H, m, aromatic). In cyclohexane, the reaction was just as efficient as in methanol. However, the product obtained in 73% yield was not the expected photoisomer 4, but aldehyde 5, mp 64 - 65°C, was the main reaction product [NMR($CDCl_3$) δ 5.01 (0.25 H, s, $\geqslant$CH), 6.44 (0.75 H, s, $\geqslant$CH), 6.52 (0.75 H, dd, H-6') 7.0 - 8.0 (11.25 H, m, aromatic), 8.74 (0.25 H, s, -CH=O) and 10.52 (0.75 H, s, -CH=O); IR (CCl_4) 1700 cm^{-1}]. The structure 5 was identified by comparison with the authentic sample prepared from the corresponding 9-(o-iodomethylphenyl)fluorene[5] by the Kornblum oxidation.[7] There was no evidence for the formation of 4 even at the earlier stage of the reaction.[8] Irradiation of 1-(methoxy-d_3)triptycene 1(X = OCD_3)[9] in cyclohexane led to 5 in which no deuterium was incorporated in the formyl group.



The above results show that, while methoxycarbene 2(X = OCH_3) is trapped by insertion into the O-H bond of alcohols to give 3,[10] it cannot be intercepted internally by the aromatic C=C bonds. An explanation for the latter result may be obtained by considering the reactivity of a methoxycarbene. Since the lone pair of electrons on the oxygen atom can delocalize to the vacant orbital of the divalent carbon, the electrophilic reactivity of a methoxycarbene towards C=C bonds is expected to be diminished to a certain extent. While methoxycarbene generated by the reaction of CH_3OCH_2Cl with <u>tert</u>-BuLi11) is successfully added to cyclohexene, methoxyphenylcarbene3) and some oxacarbenes10a) are often reluctant to the addition reaction to olefins.



Thus the homolysis of the O-CH_3 bond to give benzoyl radical **6** followed by abstraction of the hydrogen atom from solvent cyclohexane is an alternative fate of **2**(X = OCH_3). Although we have not confirmed the formation of methane, a broad signal in the δ 1.5 region of the ^1H NMR of the crude photolysate indicates the formation of products derived from cyclohexyl radicals. A second mechanism in which **5** might be formed from the methoxycarbene <u>via</u> epoxy intermediate **7** can be ruled out by the lack of a deuterium atom at the formyl position in product **5** from the methoxy-d_3 compound of **1**.

Homolysis of methoxycarbenes is not without precedents. Dimethoxycarbene generated by pyrolysis of 7,7-dimethoxynorbornadiene is cleaved to the methyl and methoxycarbonyl radicals.2) The reactions are, however, limited to gas phase in which the carbene can be in vibrationally excited states. In solution photochemistry, it is usually the case that reactions go in opposite directions; the α-cleavage of small ring ketones leading to oxacarbenes takes place.10a)

Experiments are underway in our laboratories which will further delineate the driving force for the cleavage of the O-CH_3 bond found in this study.

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7) Independent synthesis of **3**(R = CH_3) was performed by Pyrex-filtered irradiation of **5** in methanol.

8) Formation of **4** would have been easily detected by the characteristic ^{1}H NMR signals at δ 2.6 and 6 for cyclopropyl and vinyl protons, respectively[5] (T. D. Walsh, J. Amer. Chem. Soc., 91, 515 (1969); N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, ibid., 91, 516 (1969), in addition to the methoxyl signal at δ 3.5.

9) **1**(X = OCD_3) was prepared by methylation of anthrone with dimethyl-d_6 sulfate in the presence of sodium hydroxide to give 9-(methoxy-d_3)anthracene followed by the addition of benzyne from anthranilic acid. The anthracene is very susceptible to air when kept in solution and anthraquinone precipitates out. It is recommended to keep the anthracene in a crystalline state or to submit it to the subsequent reactions without delay. All new compounds in this communication gave satisfactory analytical data.

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