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INTRAMOLECULAR REACTIVITY OF 1-ALKOXYANTHRONYLIDENES. DISPROPORTIONATION (SET) OF CARBENE-DERIVED 1,5-BIRADICALS

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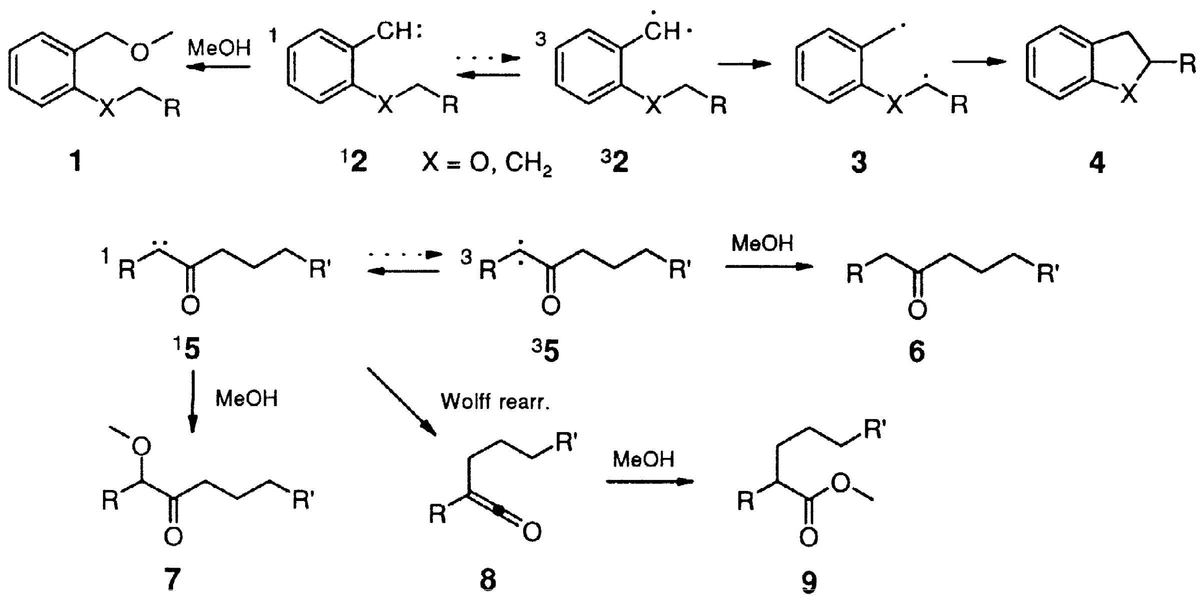
Abstract: Photolyses of 1-alkoxy-9-diazoanthrones **12** in benzene induce abstraction of hydrogen from the side chain, followed by cyclization (→ **15** → **16**) or disproportionation (→ **17** + **18**) of the intervening biradicals **20**. In alcohols, reduction of triplet anthronylidenes (^{3}**14** → **21** → **22**) competes with the formation of **20**, and intramolecular electron transfer of **20** leads eventually to the acetals **24**.

Keywords: Carbenes, Cyclisation, Electron transfer, Diazo compounds

Triplet arylcarbenes with *ortho* side chains produce five-membered rings by an abstraction-recombination mechanism, ^{3}**2** → **3** → **4**.[1] Although the triplet is the ground state of **1**, T → S crossing is competitive ($k_{TS} \sim k_T$). Scavenging of ^{1}**2** with methanol leads to the benzyl ether **1**. In some contrast, triplet carbonylcarbenes abstract hydrogen from the solvent methanol rather than from δ-C-H bonds, ^{3}**5** → **6**.[2] However, spin inversion prevails ($k_{TS} \sim 3k_T$). Singlet **5** undergoes the Wolff rearrangement, ^{1}**5** → **8** → **9**, in addition to O-H insertion with methanol, ^{1}**5** → **7**.



The divergent behavior of ^{3}**1** and ^{3}**5** can be attributed to conformational effects and/or to the electron-withdrawing carbonyl group of **5**. We felt that a study of 1-alkoxyanthronylidenes **14** might provide further insight. The geometrical constraints of **14** are similar to those of **1** while the carbonyl group should confer some features of **5**. The chemical and spectroscopic properties of the parent anthronylidene are characteristic of a ground-state triplet carbene where intersystem crossing to the singlet is slow ($\Delta G_{ST} \sim 5$ kcal/mol).[3]

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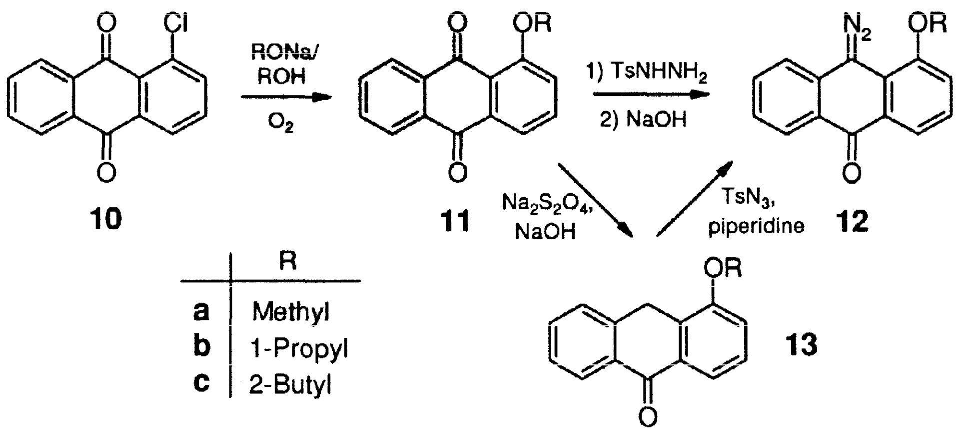
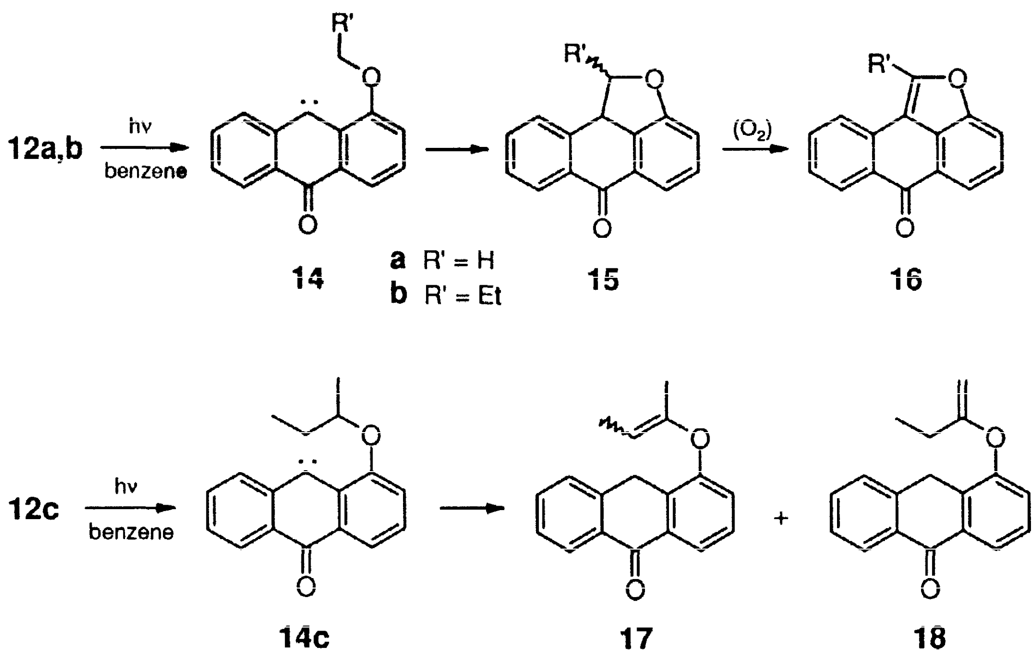
As precursors for the desired carbenes, 1-alkoxy-9-diazoanthrones **12** were prepared from 1-chloroanthraquinone **10**. The nucleophilic displacement **10** → **11** proceeded smoothly with methanol[4] whereas low and erratic yields were obtained with higher alcohols.[5] The yields were improved substantially (from 16 to 79% for **11b**) when we passed oxygen through the reacting mixture. Reduction of **11** with sodium dithionite[4,6] led to the 1-alkoxyanthrones **13a**[4] and **13b** (96%) which gave **12a** (68%) and **12b** (83%), respectively, on diazo transfer with tosyl azide.[7] Alternatively, treatment of **11c** with tosylhydrazine, followed by NaOH, afforded **12c** (26%).



	R
a	Methyl
b	1-Propyl
c	2-Butyl

When **12a,b** were photolyzed in degassed benzene, only the products of formal C-H insertion, **15a,b** were detected by NMR (C_6D_6). Two diastereomers of **15b** (10:1) were observed but could not be assigned. On workup, rapid dehydrogenation of **15a,b** occurred to give **16a,b**.[8] In an attempt to avoid dehydrogenation and to establish the stereochemistry of the insertion process, **12c** was employed. Photolysis of **12c** in benzene, however, gave rise to **17** (two stereoisomers, 92:8) and **18** in the ratio of 27:73. These findings suggest that intramolecular hydrogen abstraction by triplet **14** generates biradicals which cyclize in the case of **14a,b** but disproportionate in the case of the sterically more congested **14c**.



The major products arising from direct photolyses of **12** in methanol were the 1-alkoxy-9-methoxyanthrones **19** (R = Me)[9]; i.e., scavenging of ^{1}**14** prevails over intersystem crossing. On sensitization with benzophenone, **22** and **24**[10] were found to increase at the expense of **19** (Table 1). The triplet carbene ^{3}**14** abstracts hydrogen from the solvent to give **22** by way of **23**, in analogy with the reaction of carbonylcarbenes ^{3}**5** leading to **6**. Formation of the acetals **24** is, to our knowledge, without precedent in the chemistry of triplet carbenes. We suggest that electron tranfer, promoted by a polar solvent, converts the biradical **20** into the dipolar species **21**.

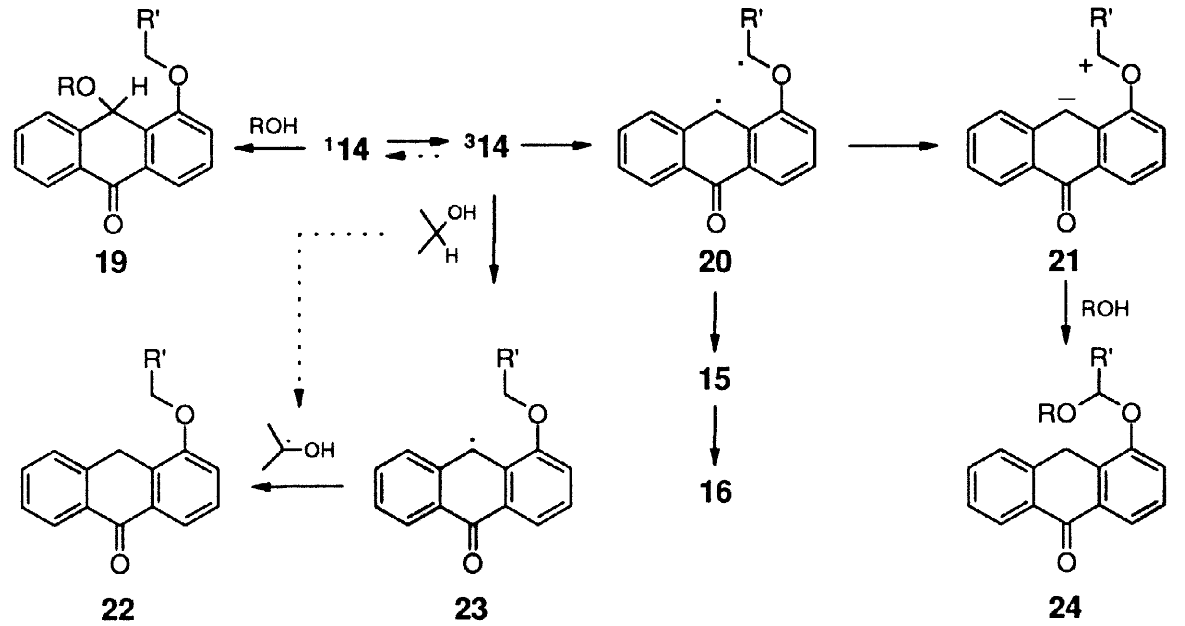
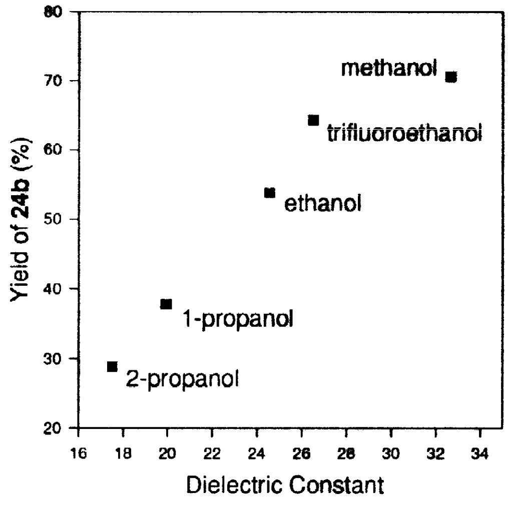


Table 1. Product distributions (%) obtained by photolyses of **12** in methanol

precursor	[Ph_2CO], M	**16**	**19**	**22**	**24**
12a	0.00	9.9	57.9	32.2	-
	0.25	12.7	26.3	61.0	-
12b	0.00	2.2	93.4	0.8	3.6
	0.25	4.9	2.2	22.3	70.6
12c	0.00	-	87.8	5.7	6.5
	0.25	-	0.8	47.1	52.1

This notion is consistent with the effects of structure and solvent on the behavior of **20**. The hydrocarbon **16a** is the only product arising from **20a** in methanol; the acetal **24a** is not obtained. Conversely, **20c** favors acetal formation (→ **24c**) to the virtual exclusion of **17** and **18**. Ranging intermediate between these extremes, **20b** produces **16b** and **24b** competitively (Table 1). The data are readily understood in terms of increasing stabilization of **21**, as the positively charged carbon atom is varied from primary (**21a**) to secondary (**21b**) to tertiary (**21c**). Moreover, the yield of **24b** was found to increase with the polarity of the solvent (Fig. 1).

In summary, triplet 1-alkoxyanthronylidenes ^{3}**14** behave like triplet arylcarbenes ^{3}**2** with regard to intramolecular abstraction of hydrogen. Hence the failure of carbonylcarbenes ^{3}**5** to attack δ-C-H



bonds is most likely due to conformational factors. However, conjugation with carbonyl groups facilitates the "reduction" of both ^{3}**5** ($\rightarrow$ **6**) and ^{3}**14** ($\rightarrow$ **22**) by alcohols. The crucial step of the reaction sequence appears to be electron transfer from "electron-rich" oxyalkyl radicals to "electron-poor" carbon radicals, **23** $\rightarrow$ **22**. An intramolecular version of this process accounts for "oxidation" of the side chain, with formation of the acetals **24**.

Figure 1. Yields of **24b** in various alcohols

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8. Anthra[1,9-*bc*]furan-6-one (**16a**): ^{1}H NMR ($CDCl_3$): δ 7.52 (td, J = 8.0/1.2 Hz), 7.58 (t, J = 8.0 Hz), 7.66 (td, J = 7.5/1.5 Hz), 7.75 (dd, J = 8.0/0.5 Hz), 7.85 (ddd, J = 8.0/1.2/0.5 Hz), 8.13 (dd, J = 7.5/0.5 Hz), 8.22 (s), 8.50 (ddd, J = 8.0/1.5/0.5 Hz). 1-Ethylanthra[1,9-*bc*]furan-6-one (**16b**), m.p. 174 °C, ^{1}H NMR ($CDCl_3$): δ 1.52 (t, J = 7.6 Hz, 3 H), 3.31 (q, J = 7.6 Hz, 2 H), 7.52 (t, J = 8.0 Hz, and td, J = 8.0/1.5 Hz), 7.68 (dd, J = 8.0/0.6 Hz), 7.70 (td, J = 8.0/1.5 Hz), 7.93 (d, br, J = 8.0 Hz), 8,12 (dd, J = 8.0/0.6 Hz), 8.56 (dd, br, J = 8.0/1.5 Hz).
9. 4,10-Dimethoxy-10*H*-anthracen-9-one (**19**, R=Me, R`=H): $^1$H NMR ($CDCl_3$): $\delta$ 2.96 (s, 3 H), 3.98 (s, 3 H), 5.94 (s, 1 H), 7.1-8.3 (m, 7 H). 10-Methoxy-4-propoxy-10*H*-anthracen-9-one (**19**, R=Me, R`=Et): ^{1}H NMR ($CDCl_3$): δ 1.12 (t, J = 7.5 Hz, 3 H), 1.95 (qt, J = 7.5/6.5 Hz, 2 H), 3.06 (s, 3 H), 4.03 and 4.14 (dt, J = 9.5/6.5 Hz, 1 H), 5.87 (s, 1 H), 7.16-8.23 (m, 7 H).
10. 10-Methoxy-4-(1-methoxypropoxy)-10*H*-anthracen-9-one (**24**, R=Me, R'=Et): ^{1}H NMR ($CDCl_3$): δ 1.05 (t, J = 7.5 Hz, 3 H), 1.95 (qd, J = 7.5/5.5 Hz, 2 H), 3.40 (s, 3 H), 4.26 (s, 2 H), 5.25 (t, J = 5.5 Hz, 1 H), 7.32 (d, br, J = 8 Hz), 7.41 (t, br, J = 8 Hz) 7.46 (t, br, J = 8 Hz), 7.52 (d, br, J = 8 Hz), 7.60 (t, br, J = 8 Hz), 8.02 (d, br, J = 8 Hz), 8.34 (d, br, J = 8 Hz).