Pergamon

Tetrahedron Letters, Vol. 37, No. 13, pp. 2121-2124, 1996

0040-4039/96 $15.00 + 0.00

S0040-4039(96)00231-6

UNUSUAL PHOTOREARRANGEMENTS OF 9,10-DISUBSTITUTED TRIPTYCENE-1,4-QUINONE DERIVATIVES

Bozena Borecka, Janet N. Gamlin, Anna D. Gudmundsdottir, Gunnar Olovsson,
John R. Scheffer* and James Trotter
Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1Z1

Abstract. In contrast to triptycene-1,4-quinone (**1a**), which forms exclusively a di-π-methane type product when irradiated in acetonitrile, photolysis of the 9,10-dialkyl-substituted triptycene quinones **1b** and **1c** leads to carbene-derived as well as hydrogen atom abstraction-derived photoproducts. Mechanistic schemes that are capable of rationalizing the results on stereoelectronic grounds are presented and discussed.

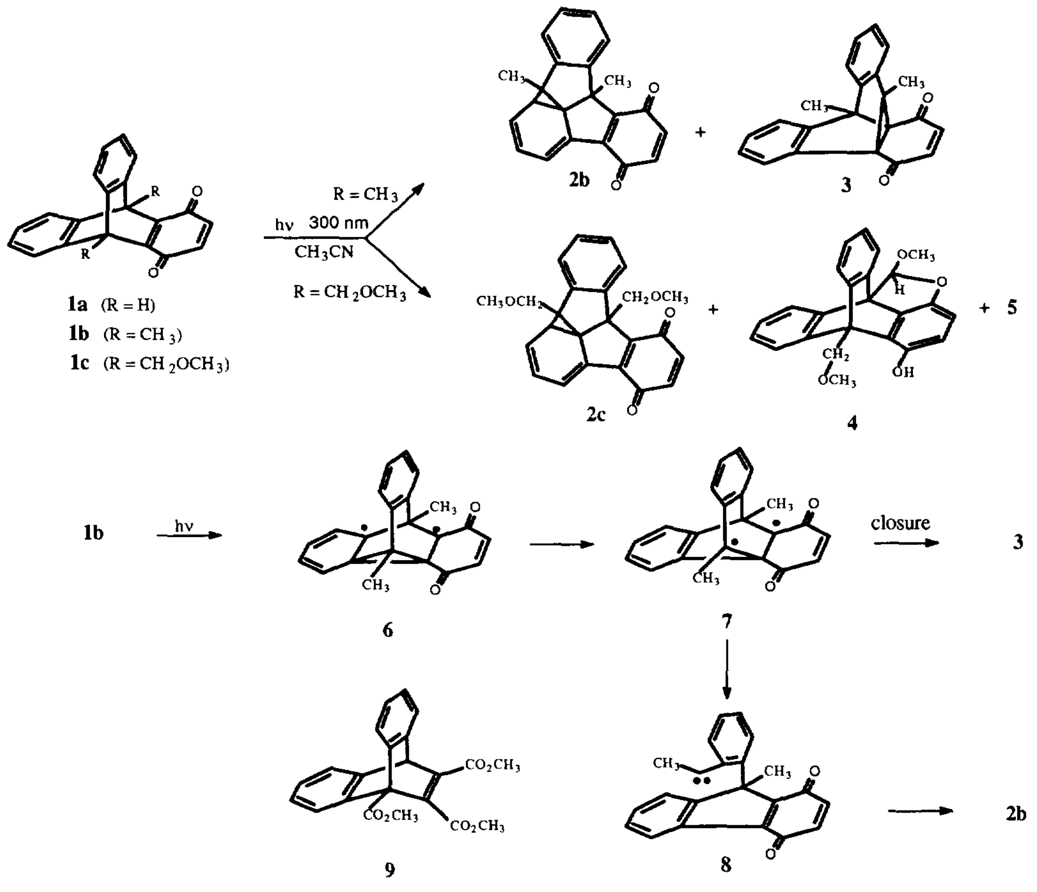
We recently reported the novel solution phase photochemical behavior of triptycene-1,4-quinone (**1a**, Scheme 3),[1] and these findings encouraged us to extend this work to derivatives of **1a**, specifically the 9,10-dimethyl and 9,10-bis(methoxymethyl) derivatives **1b** and **1c**. We report here that these substituents lead to the formation of additional photoproducts not found in the photolysis of the parent system **1a**, photoproducts whose unusual structure and color have allowed us to solve a long-standing mystery in our laboratory regarding the apparent solid state photochromism of certain 9,10-ethenoanthracene derivatives.

Results. Quinone **1b**, a known compound,[2] was synthesized by oxidation of the corresponding hydroquinone with potassium bromate. The hydroquinone was prepared according to the literature procedure through the Diels-Alder addition of p-benzoquinone to 9,10-dimethylanthracene followed by base-catalyzed aromatization.[3] Quinone **1c**, a new compound (mp 249-251 °C), was prepared analogously by substituting 9,10-bis(methoxymethyl)anthracene[4] for 9,10-dimethylanthracene. The structure of quinone **1c** was established unambiguously through an X-ray crystal structure determination.[5] Compounds **1b** and **1c** (10^{-3} M) were irradiated (300 nm, Rayonet photoreactor) in deoxygenated acetonitrile for 1-3 hours. In the case of quinone **1b**, two products were formed: the expected di-π-methane photoproduct **3** (yellow needles, mp 130-132 °C, 28% isolated yield) and the norcaradiene-containing derivative **2b** (blue-black prisms, mp 172-173 °C, 23% isolated yield). The structure of photoproduct **3** was assigned on the basis of its spectroscopic data,[6] and the structure of **2b** was established by means of a single crystal X-ray diffraction study.[5] Significantly different results were obtained in the case of quinone **1c**. Here, photolysis produced only a small amount (3% isolated yield) of the dark-blue norcaradiene compound **2c**, mp 125-128 °C, and 19% of the dihydrobenzofuran derivative **4**, mp 252-254 °C. The structures of compounds **2c** and **4** were assigned on the basis of their spectra.[7] A third dark orange and as yet unidentified photoproduct **5** (mp 236-238 °C) could also be isolated in 18% yield from photolysis of quinone **1c**.[8]

Discussion. Our previous work showed that irradiation of quinone **1a** in acetonitrile led exclusively to a di-π-methane product analogous to **3** (80% isolated yield).[1] The methyl and methoxymethyl substituents thus have a profound effect on the photochemistry of quinones **1b** and **1c**.[9] The formation of photoproducts **2b** and **2c** from these quinones finds close analogy in the photochemistry of triptycene, which forms a similar norcaradiene derivative upon irradiation in solution.[10,11] Subsequent work by

Iwamura and co-workers established that this reaction occurs through a carbene mechanism,[12] and application of this mechanism (Scheme) to quinones **1b** and **1c** rationalizes the formation of photoproducts **2b** and **2c**. In the case of quinone **1b**, a plausible common intermediate leading to both norcaradiene **2b** and di-π-methane photoproduct **3** is biradical **7**, the familar 1,3-biradical of the Zimmerman mechanism for the di-π-methane photorearrangement.[13] This scheme allows a reasonable explanation of the finding that norcaradiene derivatives are formed from quinones **1b** and **1c**, but not from **1a**: alkyl substitution has the effect of stabilizing carbene **8** (thereby facilitating its formation from biradical **7**) while at the same time sterically retarding the closure of **7** to **3**. A second possibility is that carbene **8** is the common intermediate, leading to both **2b** and **3**. This is ruled out on the basis of trapping studies, which showed that the yield of **2b** is greatly diminished in methanol (4%), whereas the amount of di-π-methane product **3** actually increases (40%). Control experiments also established that **2b** and **3** do not interconvert under the photolysis conditions.

Scheme



In the case of the methoxymethyl-substituted quinone **1c**, the proportion of the reaction proceeding through the carbene pathway is considerably diminished, the likely reason being that γ-hydrogen atom abstraction of one of the methylene hydrogens becomes favored by virtue of the radical-stabilizing effect of the methoxy group. Wagner and co-workers have clearly demonstrated the efficacy of alkoxy groups in promoting hydrogen abstraction in the Norrish type II photoreactions of aralkyl ketones.[14] Following hydrogen atom abstraction, the resulting biradical goes on to form photoproduct **4** through a mechanism analagous to that proposed by Orlando *et al.* for the photochemical conversion of *tert*-butylbenzoquinone into the corresponding dihydrobenzofuran derivative.[15] The X-ray crystal structure of quinone **1c** shows that the postulated hydrogen atom abstraction leading to **4** is geometrically favorable, with two abstractable hydrogens at C=O...H distances of 2.44 and 2.53 Å and ω angles (the degree to which the γ-hydrogen lies outside the mean plane of the carbonyl group) of 13.0 and 24.7°. Abstraction of activated hydrogens involving such geometries is virtually certain.[16]

As far as we are aware, quinones **1b** and **1c** are the first 9,10-ethenoanthracene derivatives to be shown to form norcaradiene type products upon photolysis, all previous examples of this reaction having been found in triptycene derivatives.[10-12,17] The triptycene photoproduct is reported as being yellow,[10] and so the midnight blue color of photoproducts **2b** and **2c** is quite unusual. This color is due to a very broad absorption centered around 570 nm that we assign to a charge-transfer interaction between the norcaradiene and quinone chromophores. We observed similar *transient* colors in the crystalline state photochemistry of a number of 9,10-ethenoanthracene derivatives bearing electron-withdrawing ester or carboxylic acid substituents on the bridging double bond - colors that we could never explain satisfactorily until now. Significantly, these transient colorations were invariably associated with either 9- or 9,10-disubstitution. As an example, crystals of triester **9** (Scheme)[18] turn dark blue on photolysis and gradually lose their color upon standing for several hours at room temperature in the dark. Heating the crystals accelerates the decoloration, and dissolving them causes instant loss of color. The diffuse reflectance UV/VIS absorption spectrum of the irradiated crystals is very similar to the corresponding spectra of photoproducts **2b** and **2c**, and we propose that small amounts of an analogous norcaradiene derivative are formed, which break down to form colorless product(s). Attempts to detect and isolate such products were, however, unsuccessful. Interestingly, the coloration of triester **9** and other such compounds is unique to the crystalline state, but quinones **1b** and **1c** proved to be photostable under these conditions. An understanding of these medium effects is lacking at the present time.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the Natural Sciences and Engineering Research Council of Canada is also gratefully acknowledged.

References and Footnotes

1. Fu, T.Y.; Gamlin, J.N., Olovsson, G.; Scheffer, J.R.; Trotter, J. and Young, D.T. *Tetrahedron Lett.* **1995**, *36*, 2025.
2. Mylorie, V.L.; Stenberg, J.F. *Ann. N.Y. Acad. Sci.* **1973**, *214*, 255.
3. Theilacker, W.; Berger-Brose, U.; Beyer, K-H. *Chem. Ber.* **1960**, *93*, 1658.
4. Miller, M.W.; Amidon, R.W.; Tawney, P.O. *J. Am. Chem. Soc.* **1955**, *77*, 2845.
5. Quinone **1c**: space group C2/c, a = 15.772(1) Å, b = 8.000(1) Å, c = 14.7883(9) Å, β = 98.430(6)°, Z = 4, R = 4.0%; photoproduct **2b**: space group $P2_1/n$, a = 8.114(3) Å, b = 11.966(3) Å, c = 16.694 Å, Z = 4, R = 3.7%. Full crystallographic details will be published separately.
6. Photoproduct **3**: IR (KBr) ν_{max} 2927 (C-H), 1668 (C=O), 1283 (C-O) cm^{-1}; EI MS m/e (rel intensity) 313 (M+1, 22), 312 (M^+, 94), 284 (18), 269 (44), 242 (31), 239 (32), 215 (100); HRMS calcd for

$C_{22}H_{16}O_2$ 312.1150, found 312.1152; ^{1}H NMR (400 MHz , $CDCl_3$) δ 7.80 (m,1H, Ar-H), 7.20-7.02 (m, 7H, Ar-H), 6.74 (ABq, 2H, J = 10 Hz, vinyls), 2.13 (s, 3H, CH_3), 1.98 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.00 (C=O), 191.87 (C=O), 153.06 (quaternary Ar), 152.68 (quaternary Ar), 142.67 (vinyl), 140.38 (vinyl), 137.45, 132.95 (quaternary Ar), 128.66, 127.71, 127.15, 126.85, 125.01,124.51, 119.06, 118.96 (Ar C-H), 73.06, 61.03, 60.48, 59.08 (pentalene ring), 14.96 (CH_3), 13.99 (CH_3); Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59, H, 5.16. Found: C, 84.19; H, 5.13.

7. Photoproduct **2c**: IR (KBr) ν_{max} 2926 (C-H), 1665, 1625 (C=O), 1261 (C-O) cm^{-1}; EI MS m/e (rel intensity) 373 (M+1, 27), 372 (M^+, 100), 343 (16), 327 (11), 311 (10), 297 (15); HRMS calcd for $C_{24}H_{20}O_4$ 372.1362, found 372.1364; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, 1H, J = 7 Hz, Ar-H), 7.58 (d, 1H, J = 7 Hz, Ar-H), 7.28-7.19 (m, 2H, Ar-H), 6.90 (d, 1H, J = 6 Hz, vinyl), 6.64 (AB q, 2H, J = 8 Hz, quinone vinyls), 6.31 (dd, 1H, J = 9 & 6 Hz, vinyl), 6.16 (dd, 1H, J = 9 & 5 Hz, vinyl), 4.05 (d, 1H, J = 9 Hz, CH_2), 3.30 (d, 1H, J = 9 Hz, CH_2), 3.28 (AB q, 2H, J = 9 Hz, CH_2), 3.21 (s, 3H, CH_3), 3.17 (s, 3H, CH_3), 2.85 (d, 1H, J = 5 Hz, cyclopropyl H). Additional spectroscopic data were not obtained owing to lack of material. Photoproduct **4**: IR (KBr) ν_{max} 3270 (O-H), 2922 (C-H) cm^{-1}; EI MS m/e (rel intensity) 373 (M+1, 27), 372 (M+, 100), 310 (13), 281 (11), 258 (18); HRMS calcd for $C_{24}H_{20}O_4$ 372.1362, found 372.1365; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H, OH), 8.14 (m, 1H, Ar-H), 7.40 (d, 1H, J = 7 Hz, Ar-H), 7.19 (m, 2H, Ar-H), 7.08-6.97 (m, 4H, Ar-H), 6.87 (s, 1H, acetal methine), 6.48 (AB q, 2H, J = 8Hz, Ar-H), 4.96 (s, 2H, CH_2OMe), 3.98 & 3.91 (s, 3H each, OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.17, 146.15, 145.96, 145.62, 145.36, 145.03,138.24, 126.00 (Ar C), 125.16, 124.97, 124.82, 124.81, 124.59, 121.82, 121.31, 120.48, 116.61 (Ar C-H), 112.06 (acetal C-H), 107.83 (Ar C-H), 71.43 (CH_2OMe), 59.60 & 58.22 (OMe), 57.60, 53.91 (bridgehead C); Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.28; H, 5.25.
8. Our best guess is that this material is a phenolic aldehyde having the benz[a]aceanthrylene carbon skeleton. Benz[a]aceanthrylene derivatives are commonly observed byproducts in the photochemistry of triptycenes. See, for example, Kawada, Y.; Tukada, H.; Iwamura, H. *Tetrahedron Lett.* **1980**, *21*, 181 and references cited therein.
9. For additional examples of the strong effect that bridgehead substitution has on the photochemistry of 9,10-ethenoanthracene derivatives, see Scheffer, J.R.; Trotter, J.; Yang, J. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W.M.; Song, P-S. Eds.; CRC Press: Boca Raton, Florida, 1995, Chapter 16.
10. Walsh, T.D. *J. Am. Chem. Soc.* **1969**, *91*, 515.
11. Turro, N.J.; Tobin, M; Friedman, L.; Hamilton, J.B. *J. Am. Chem. Soc.* **1969**, *91*, 516.
12. (a) Iwamura, H.; Yoshimura, K. *J. Am. Chem. Soc.* **1974**, *96*, 2652; (b) Iwamura, M.; Tukada, H.; Iwamura, H. *Tetrahedron Lett.* **1980**, *21*, 4865.
13. For reviews of the di-π-methane rearrangement, see (a) Zimmerman, H.E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Chapter 16; (b) Zimmerman, H.E. In *Organic Photochemistry*, Padwa, A., Ed.; Marcel Dekker: New York, 1991; Volume 11, Chapter 1. The preference for initial benzo-quino bridging as opposed to benzo-benzo bridging is the same as that observed for quinone **1a** (see reference 1) and is in accord with formation of the more stable biradical intermediate in which aromaticity has been lost in only one of the two benzenoid rings and the second odd electron is stabilized by being next to a carbonyl group.
14. For a recent review of the Norrish/Yang type II photoreaction, see Wagner, P.J.; Park, B-S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Volume 11, Chapter 4.
15. Orlando, C.M.; Mark, H.; Bose, A.K.; Manhas, M.S. *J. Am. Chem. Soc.* **1967**, *89*, 6527.
16. Scheffer, J.R. In *Organic Solid State Chemistry*; Desiraju, G.R., Ed.; Elsevier: New York, 1987; Chapter 1.
17. (a) Iwamura, H.; Tukada, H. *J. Chem. Soc., Chem. Commun.* **1975**, 969; (b) Day, R.O.; Day, V.W.; Fuerniss, S.J.; Hohman, J.R.; Wheeler, D.M.S. *J. Chem. Soc., Chem. Commun.*, **1976**, 853; (c) Iwamura, M.; Mori, E.; Koike, A.; Kitagawa, T.; Koga, N.; Iwamura, H. *Chem. Lett.* **1992**, 2051 and references cited therein.
18. Prepared by standard procedures, mp 174-176 °C. Gudmundsdottir, A.D.; Scheffer, J.R. unpublished results.

(*Received in USA* 3 *November* 1995; *revised* 23 *January* 1996; *accepted* 30 *January* 1996)