Photochemical reactions of diazodihydronaphthalenones† in cyclic ethers

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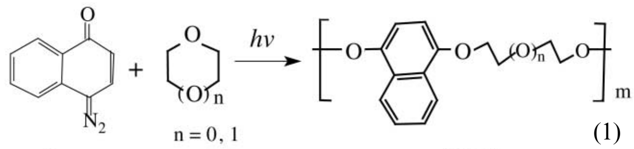
Photolysis of 4-diazonaphthalen-1(4*H*)-one (**1a**), 2-methyl-4-diazonaphthalen-1(4*H*)-one (**1b**) and 4-diazo-2-nitronaphthalen-1(4*H*)-one (**1c**) in neat THF and 1,4-dioxane produced a variety of products depending on the 2-substituent and the solvent. While **1a** and **1c** produced predominantly insoluble copolymers in both solvents, **1b** produced, besides small amounts of copolymers, a novel polyether bridged naphthalene, 2,3:11,12-bis(2-methyl-1,4-naphthylene)-18-crown-6 (**2b**), 1,4-dioxa-3′-methyl-4′-oxo-1′,4′-dihydronaphthalene-1′-spiro-5-cycloheptane (**3b**), 2-methyl-4-(1,4-dioxan-2-yl)naphthol (**4b**) and 2-methylnaphthol (**5b**) in dioxane, and 3′-methyl-4′-oxo-1′,4′-dihydronaphthalene-1′-spiro-2-pyrane (**3b′**), 2-methyl-4-(tetrahydrofuran-2-yl)naphthol (**4b′**) and **5b** in THF. Compound **2b** is characterised by X-ray crystallography.

Introduction

Compounds where an oxo group is replaced by a diazo group in arenoquinones are convenient precursors of conjugated ketocarbenes which are active intermediates and can react readily with alkanes, alcohols, olefins and cyclic ethers interchangeably as carbenes, biradicals and/or zwitterions.[1–10] Earlier works on photolysis of 4-diazocyclohexa-2,5-dien-1-one in cyclic ethers reported exclusive formation of 1 : 1 copolymers of the ketocarbene with the solvent,[6,7] while thermal decomposition of 3,5-di-*tert*-butyl-4-diazocyclohexa-2,5-dien-1-one in cyclic ethers at high temperatures was reported to give 1 : 1 spirocyclic compounds in good yields.[8] On the other hand, thermal decomposition of 2,6-diphenyl-4-diazocyclohexa-2,5-dien-1-one in dioxane produced a 1 : 1 cyclic polyether compound,[4] and photolysis of cyano-substituted 2-diazoazulen-4(2*H*)-one in tetrahydrofuran, tetrahydropyran and dioxane produced 1 : 2, 1 : 3 and 1 : 4 polyether-bridged azulenes.[9,10] These diversity of activities motivated us to explore the reaction of diazodihydronaphthalenones in cyclic ethers. Here we report the photolysis of 4-diazonaphthalen-1(4*H*)-one (**1a**), 2-methyl-4-diazonaphthalen-1(4*H*)-one (**1b**) and 2-nitro-4-diazonaphthalen-1(4*H*)-one (**1c**) in neat THF and dioxane.

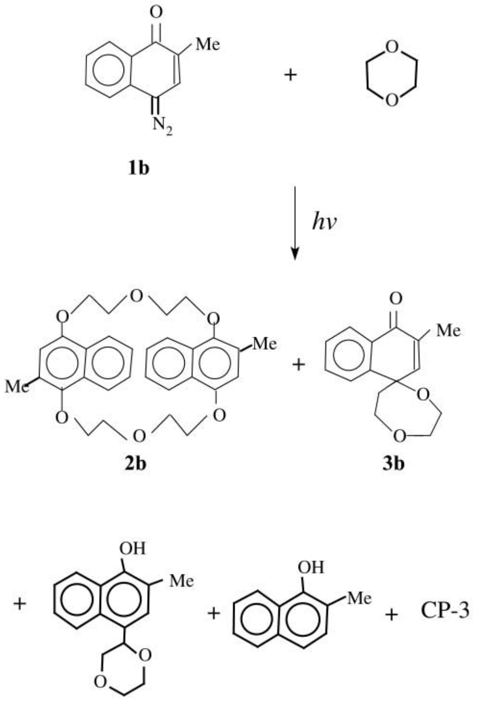
Results

Photolysis of **1** in anhydrous THF or dioxane with a 250 watt high pressure mercury lamp in a Pyrex bottle ($\lambda > 300$ nm) under an argon atmosphere produced a diversity of products depending on the substituent and the solvent. Compound **1a** produced exclusively insoluble polymers which adhered to the wall of the bottle in both solvents. Similar to the reaction of 4-diazocyclohexa-2,5-dien-1-one reported previously,[6,7] the polymers should be the 1 : 1 copolymers (CPs) of the corresponding ketocarbene with the solvents [eqn. (1)].



1a CP-1,2 (1)

Photolysis of **1b** in dioxane produced a novel 2 : 2 polyether bridged naphthalene, 2,3:11,12-bis(2-methyl-1,4-naphthylene)-18-crown-6 (**2b**), 1,4-dioxa-3′-methyl-4′-oxo-1′,4′-dihydronaphthalene-1′-spiro-5-cycloheptane (**3b**), 2-methyl-4-(1,4-dioxan-2-yl)naphthol (**4b**) and 2-methylnaphthol (**5b**) [eqn. (2)].



1b **2b** **3b** **4b** **5b** (2)

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† These compounds are often referred to as naphthoquinone diazides in the literature.
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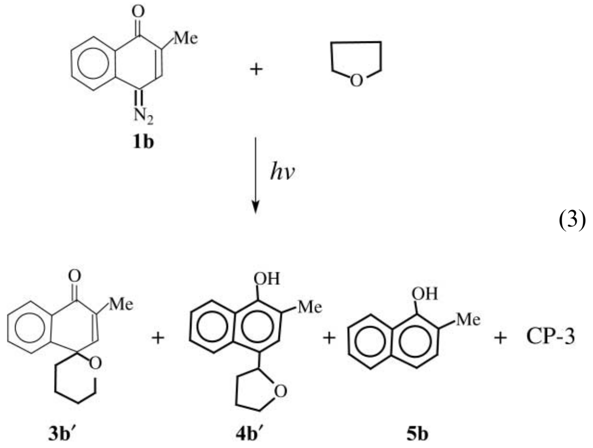
Photolysis of **1b** in THF produced similar spirocyclic compounds 3′-methyl-4′-oxo-1′,4′-dihydronaphthalene-1′-spiro-2-pyrane (**3b′**), 2-methyl-4-(tetrahydrofuran-2-yl)naphthol (**4b′**) and **5b**, but no polyether-bridged 2-methylnaphthalene (**2b** analogues) was obtained [eqn. (3)]. Structures of these compounds



(3)

were characterized by spectroscopic data including 2D NMR, and in the case of **2b**, also confirmed by single crystal X-ray analysis (Fig. 1). As shown in the figure, **2b** possesses a symmetric center with the two naphthalene rings located on both sides of the crown ether ring. The two naphthalene rings are parallel and are almost perpendicular to the crown ether ring (the dihedral angle of C14–O1–C7–C8 is 72.8°).

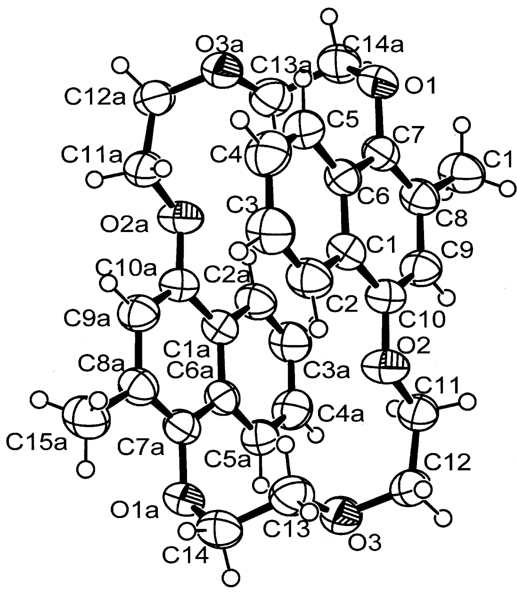
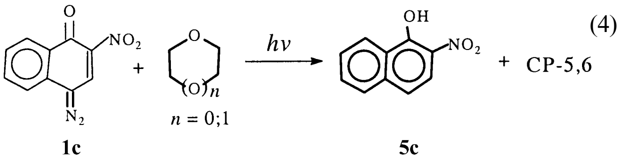


Fig. 1 X-Ray structure (ORTEP drawing) of **2b**.§

Photolysis of **1c** in both solvents produced a small amount of 2-nitro-1-naphthol (**5c**) together with a large amount of copolymer [eqn. (4)]. The results are summarized in Table 1.



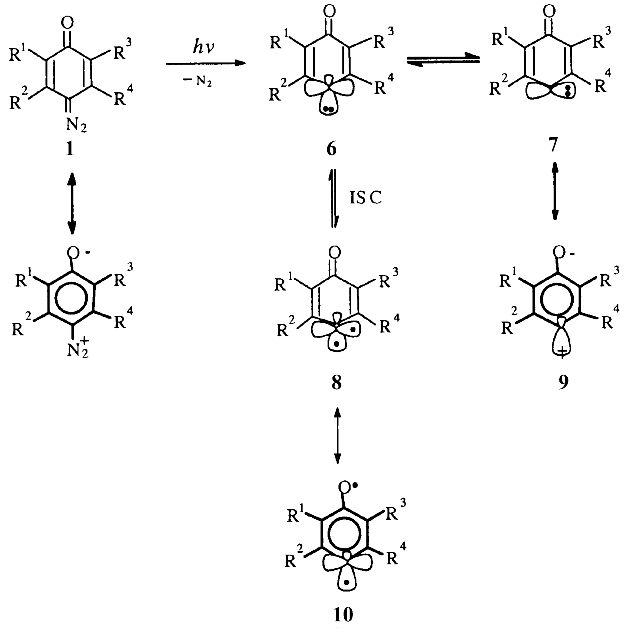
(4)

Table 1 Photolysis of diazodihydronaphthalenones in THF and dioxane

Substrate	Solvent	Product and isolated yield (%)	
1a	Dioxane		**CP-1** (85)
1a	THF		**CP-2** (90)
1b	Dioxane	**2b** (30), **3b** (22), **4b** (7), **5b** (15)	**CP-3** (14)
1b	THF	**3b′** (32), **4b′** (8), **5b** (14)	**CP-4** (35)
1c	Dioxane	**5c** (7)	**CP-5** (80)
1c	THF	**5c** (5)	**CP-6** (85)

Discussion

It is well-known that the thermal or photolytic decomposition of diazo-ketones (**1**) produces doubly conjugated transient ketocarbenes that can react interchangeably as singlet carbene (**6** and/or **7**), triplet carbene (**8**), zwitterion (**9**) and/or biradical (**10**) (Scheme 1).[1–5] A number of such diazo-ketones have been photolysed in argon matrices to generate the matrix isolated ketocarbenes that have been characterized by IR, EPR and UV spectroscopy.[11–14] It was concluded that the energy of the triplet ground state of the conjugated ketocarbene is lower than that of the singlet ground state, but the energy gap between the triplet and singlet states is very small, especially for the σ,p-triplet state (**8**) and the p^2-singlet state (**7**).[1,2,10,15] Therefore, both triplet and singlet reactions can take place and the reactivity is significantly influenced by the structure of the substrate, and in some cases singlet reactions are dominant.[3–5,10] Ether formation from alcohols,[1–5] ylide formation with pyridine[16] and stereospecific cyclopropanation of olefins[5] are commonly attributed to the singlet state reaction, while the reaction with oxygen,[1–2] hydrogen atom abstraction[2–5,10] and nonstereospecific cyclopropanation of olefins[2] are believed to be characteristic reactions of the carbenes in their triplet states.



Scheme 1

In the present case formation of polymers from the photolysis of **1** is similar to the photolysis of diazocyclohexadienone and 4-diazo-2,6-dimethylcyclohexa-2,5-dien-1-one in THF which gave exclusively 1 : 1 copolymers.[6,7] The reaction may be rationalized by a zwitterion reaction as shown in Scheme 2. The relatively polar solvent cyclic ether stabilizes the zwitterion and makes it easy to incorporate with the solvent to form an ylide. Successive nucleophilic attack of the zwitterion on the oxonium ion of the ylide resulted in the ring-opening of the cyclic ether

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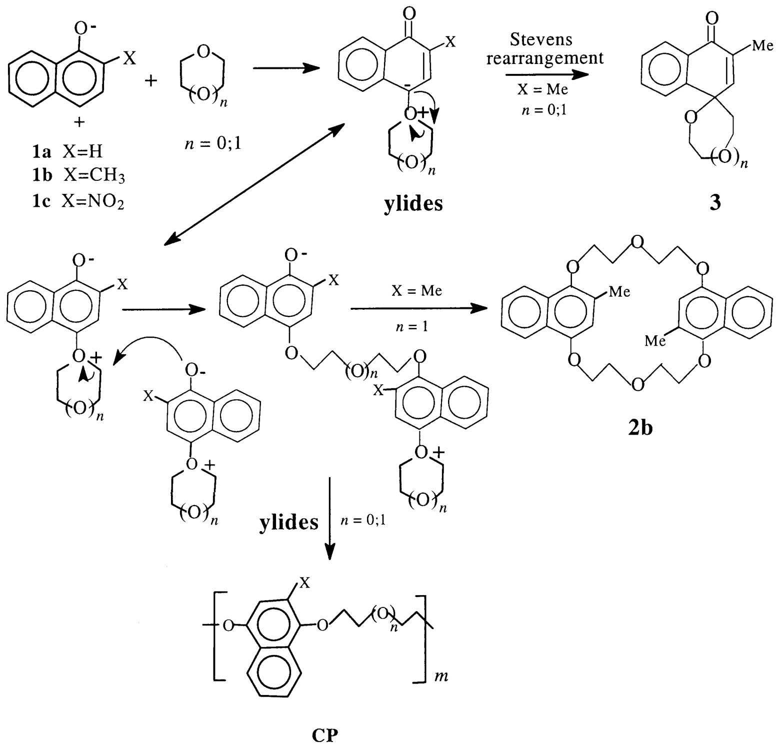
§ Crystal data. $C_{30}H_{32}O_6$, M = 488.56, monoclinic, a = 20.549(4), b = 7.456(1), c = 16.856(3) Å^3, U = 2491.0(7) Å^3, T = 293 K, space group $C2/c$, Z = 4, μ (Mo-Kα) = 0.090 mm^{-1}, 1573 reflections measured, 1106 unique (Rint = 0.0706) which were used in all calculations. The final $wR(F2)$ was 0.0726 (all data). CCDC reference number 175319. See http://www.rsc.org/suppdata/p2/b1/b106968n/ for crystallographic files in .cif or other electronic format.



Scheme 2

and formation of the 1 : 1 copolymer. The ylide may also be the precursor of **2b**, **3b** and **3b′**. Compound **2b** may be formed by a mutual nucleophilic substitution of two ylides and **3** should be the Stevens rearrangement product of the ylide (Scheme 2). Compounds **4b** and **4b′** must be α-C–H bond insertion products of the singlet carbene to the cyclic ether. On the other hand, **5b** and **5c** are certainly the H-abstraction products of the triplet carbene.

The significantly different reaction behaviour of **1a**, **1b** and **1c** demonstrates the subtle influence of the substituent on the reaction of the ketocarbenes. Methyl substitution may decrease the electrophilicity of the zwitterion, and the steric hindrance may decrease the reactivity of the phenoxide anion in the ylide, hence the yield of polymers decreases and the competitive ylide reaction products **2** and **3** become predominant, and the triplet reaction product **5** appears. The strong electron-withdrawing nitro group in **1c** increases the electrophilicity of its zwitterion and facilitates formation of the ylide with the cyclic ether, making the formation of the copolymer predominant.

Experimental

General

NMR spectra were recorded on a BRUKER AM-400 NMR spectrometer in $CDCl_3$ with TMS as an internal standard. HR-SIMS and EIMS spectra were obtained with a Bruker APEXII FT-MS and a HP 5988A mass spectrometer, respectively. The X-ray diffraction data were collected on an ENRAF-NOINUS CAD diffractometer with Mo-Kα radiation. Melting points were uncorrected.

4-Diazonaphthalen-1(4*H*)-one (**1a**), 2-methyl-4-diazonaphthalen-1(4*H*)-one (**1b**) and 2-nitro-4-diazonaphthalen-1(4*H*)-one (**1c**) were prepared according to the available procedures.[17–19] THF and 1,4-dioxane were dried with sodium sulfate and distilled over sodium benzophenone ketyl under nitrogen.

Photolysis was carried out in a Pyrex bottle. A dilute solution of **1a**, **1b** or **1c** (5 mmol) in 100 ml of dry THF or dioxane was purged with argon for 20 min and irradiated with a 250 W high pressure Hg lamp for 12–18 h at 0 °C under stirring. The reactions were followed by TLC until the disappearance of the substrate and the crude products were separated by column chromatography with silica gel and eluted with petroleum ether–benzene–chloroform (20 : 10 : 1 v/v/v).

2,3:11,12-Bis(2-methyl-1,4-naphthylene)-18-crown-6 (2b). Colourless needles, mp: 187–188 °C. HR-SIMS: 488.2190 ($C_{30}H_{32}O_4$, calc. 488.2193). EIMS: (*m*/*z*, %) 488 (M^+, 100), 244 (48), 201 (62), 199 (60), 173 (65), 128 (69), 115 (44), 104 (20). ^{1}H NMR ($CDCl_3$) δ: 2.26 (2 × 3H, s), 3.49 (2 × 2H, dd, $J = 3.6$, 4.0 Hz), 3.73 (2 × 2H, dd, $J = 3.6$, 4.0 Hz), 3.83 (2 × 2H, dd, $J = 4.2$, 4.5 Hz), 4.31 (2 × 2H, dd, $J = 4.2$, 4.4 Hz), 5.88 (2 × 1H, s), 7.28 (2 × 1H, dd, $J = 7.2$, 8.4 Hz), 7.41 (2 × 1H, dd, $J = 7.2$, 8.4 Hz), 7.81 (2 × 1H, d, $J = 8.8$ Hz), 8.09 (2 × 1H, d, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$) δ: 17.17, 68.48, 69.85, 71.07, 72.16, 108.01, 121.79, 122.59, 123.66, 124.71, 125.30, 129.09, 145.37, 149.75. H,H COSY, HMQC and HMBC spectra suggested the presence of –O–CH_2–CH_2–O–CH_2–CH_2–O– moiety. The NOESY correlation of the methyl protons with the 5-H in the naphthalene ring suggested that the two naphthalene rings must stay parallel on each side of the crown ether ring. The significant high-field shift of the chemical shift of C-3 (δ 108.1) and H-3 (δ 5.88) also suggested that this C and H are shielded by another naphthalene ring.

1,4-Dioxa-3′-methyl-4′-oxo-1′,4′-dihydronaphthalene-1′-spiro-5-cycloheptane (3b). Colourless needles, mp: 111–112 °C. HR-SIMS: 245.1171 ($C_{15}H_{16}O_3$ + H, calc. 245.1172). EIMS (*m*/*z*, %): 244 (M^+, 16), 201 (100), 174 (23), 160 (31), 141 (36), 128 (43), 115 (48), 104 (20). ^{1}H NMR ($CDCl_3$) δ: 2.01 (3H, s), 2.07 (1H, ddd, $J = 1.2$, 7.3, 13.2 Hz) 2.36 (1H, ddd, $J = 1.8$, 8.7, 13.2 Hz), 3.80 (1H, ddd, $J = 1.6$, 5.4, 13.2 Hz), 3.94–4.03 (4H, m), 4.02 (1H, ddd, $J = 3.2$, 7.6, 14.4 Hz), 7.09 (1H, s), 7.42 (1H, dd, $J = 7.6$, 8.0 Hz), 7.58 (1H, dd, $J = 7.6$, 7.4 Hz), 7.85 (1H, d, $J = 7.4$ Hz), 8.09 (1H, d, $J = 8.0$ Hz). ^{13}C NMR ($CDCl_3$) δ: 16.03, 45.97, 65.97, 67.55, 72.71, 74.37, 125.61, 127.09, 127.79, 129.35, 132.33, 133.36, 144.61, 147.77, 184.91.

2-Methyl-4-(1,4-dioxan-2-yl)naphthol (4b). Colourless needles, mp: 147–148 °C. HR-SIMS: 245.1176 ($C_{15}H_{16}O_3$ + H, calc. 245.1172). EIMS (*m*/*z*, %): 244 (M^+, 58), 186 (100), 185

(55), 158 (24), 141 (36), 128 (29), 115 (15). ^{1}H NMR ($CDCl_3$) δ: 2.42 (3H, s), 3.59 (1H, dd, J = 10.1, 11.4 Hz), 3.81–3.90 (2H, m), 4.04–4.08 (2H, m), 5.25 (1H, br), 5.32 (1H, dd, J = 2.4, 10.0 Hz), 7.44 (1H, s), 7.49 (2H, d, J = 9.6 Hz), 8.02 (1H, d, J = 9.6 Hz), 8.20 (1H, d, J = 9.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.64, 66.61, 67.60, 72.34, 74.67, 115.71, 121.82, 122.60, 124.38, 125.03, 125.78, 127.19, 130.96, 131.58, 148.62.

3′-Methyl-4′-oxo-1′,4′-dihydronaphthalene-1′-spiro-2-pyrane (3b′). Colourless needles, mp: 88–89 °C. HR-SIMS: 229.1229 ($C_{15}H_{16}O_2$ + H, calc. 229.1223). EIMS (m/z, %): 228 (M^+, 100), 213 (50), 185 (78), 172 (29), 173 (29), 144 (48), 141 (31), 128 (35), 115 (98), 104 (45). ^{1}H NMR ($CDCl_3$) δ: 1.63 (1H, dd, J = 2.2, 13.4 Hz), 1.74–1.78 (1H, m), 1.82–1.86 (1H, m), 1.85 (2H, dd, J = 2.2, 8.4 Hz), 2.02–2.06 (1H, m), 2.06 (3H, s), 4.01 (1H, dd, J = 3.6, 12.1 Hz), 4.10 (1H, dd, J = 2.2, 12.1 Hz), 7.41 (1H, dd, J = 7.0, 7.6 Hz), 7.54 (1H, s), 7.60 (1H, dd, J = 7.0, 7.6 Hz), 7.79 (1H, d, J = 7.6 Hz), 8.08 (1H, d, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 16.69, 20.37, 25.58, 40.22, 62.33, 70.80, 126.27, 127.72, 129.70, 132.78, 134.23, 129.70, 140.41, 147.66, 184.85.

2-Methyl-4-(tetrahydrofuran-2-yl)naphthol (4b′). Colourless needles, mp: 126–127 °C. HR-SIMS: 229.1224 ($C_{15}H_{16}O_2$ + H, calc. 229.1223). EIMS (m/z, %): 228 (M^+, 100), 213 (48), 185 (78), 171 (26), 172 (29), 158 (71), 128 (54), 115 (28). ^{1}H NMR ($CDCl_3$) δ: 1.86–1.93 (1H, m), 2.03–2.10 (1H, m), 2.17 (3H, s), 2.44–2.53 (2H, m), 4.01 (1H, dd, J = 7.6, 14.0 Hz), 4.25 (1H, dd, J = 7.6, 14.0 Hz), 5.25 (1H, br), 5.53 (1H, dd, J = 6.8, 6.9 Hz), 7.38 (1H, s), 7.45–7.48 (2H, m), 7.89–7.92 (1H, dd, J = 1.2, 9.7 Hz), 8.18 (1H, d, J = 10.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.73, 25.97, 33.71, 68.54, 77.64, 115.50, 121.70, 123.80, 124.62, 124.85, 125.18, 125.29, 130.16, 130.97, 147.54.

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