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1,3-Dipolar cycloaddition reactions of carbonyl ylides with 1,2-diones: synthesis of novel spiro oxabicycles

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This paper is dedicated with best wishes to Professor Dr Lutz F. Tietze on the occation of his 60th birthday

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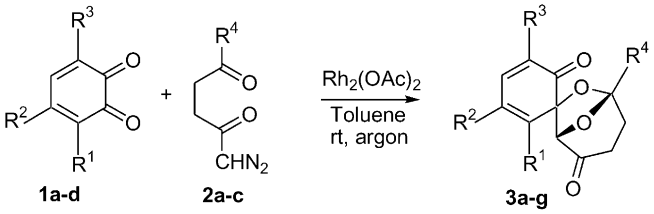
Abstract—1,3-Dipolar cycloaddition reaction of carbonyl ylides with various *o*-quinones afforded highly oxygenated spiro oxabicycles.

1. Introduction

Ever since the pioneering work of Huisgen,[1] 1,3-dipolar cycloadditions have been the most well-studied and well-established reactions for the construction of 5-membered heterocycles. A wide variety of dipolar species,[2] including carbonyl ylides have been employed in these reactions. Most of the dipolar cycloadditions, however, have involved addition across carbon–carbon multiple bonds. In contrast, much less attention has been paid to the carbonyl group, especially that of *o*-quinones[3] as a dipolarophile. In the context of our general fascination for the reactivity of 1,2-dicarbonyl compounds as dienophiles[4] and dipolarophiles,[5] it was of interest to investigate their reaction with carbonyl ylides.[6] Recently we have shown that aryl nitrile *N*-oxides[7] and zwitterionic species[8] undergo facile cycloaddition to the carbonyl group of *o*-benzoquinones.

A survey of the literature revealed that except for isolated reports, there has been no systematic investigation of the



1a-d **2a-c** **3a-g**

o-Quinones	Diazo ketones	Products	Yield(%)
1a: R_1=H, R_2=R_3=CMe_3	**2a**: R_4=Ph	**3a**	76
1a: R_1=H, R_2=R_3=CMe_3	**2b**: R_4=CH_3	**3b**	53
1a: R_1=H, R_2=R_3=CMe_3	**2c**: R_4=$(C_5H_5)_2Fe$	**3c**	42
1b: R_1=OCH_3, R_2=R_3=CMe_3	**2a**: R_4=Ph	**3d**	63
1b: R_1=OCH_3, R_2=R_3=CMe_3	**2b**: R_4=CH_3	**3e**	48
1c: R_1=OCH_3, R_2=CMe_3, R_3=H	**2a**: R_4=Ph	**3f**	48
1d: R_1=H, R_2=CMe_3, R_3=H	**2a**: R_4=Ph	**3g**	55

Scheme 1.

Keywords: carbonyl ylides; cycloaddition; oxabicycles.
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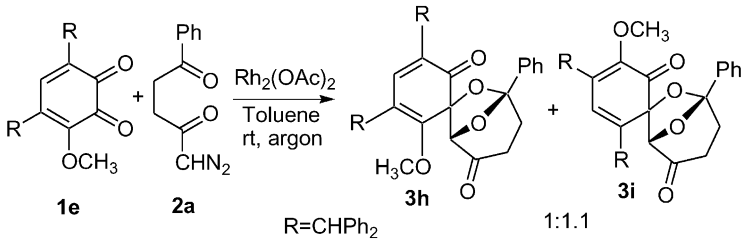
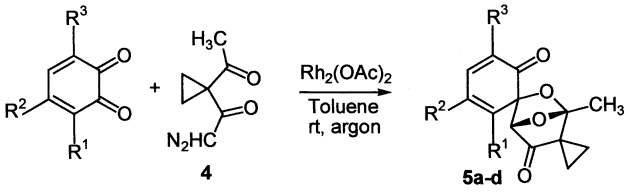


Scheme 2.



o-Quinone	Diazoketone	Product	Yield(%)
1a: R_1=H, R_2=R_3=CMe_3	**4**	**5a**	72
1b: R_1=OCH_3, R_2=R_3=CMe_3	**4**	**5b**	86
1c: R_1=OCH_3, R_2=CMe_3, R_3=H	**4**	**5c**	75
1e: R_1=H, R_2=CMe_3, R_3=$CH(C_6H_5)_2$	**4**	**5d**	62

Scheme 3.

reaction of carbonyl ylides with carbonyl compounds, 1,2-dicarbonyl systems being completely ignored. Intrigued by the possibility that such reactions will lead to novel heterocycles, we have undertaken some investigations in this area and our preliminary results have been published.[9] Details of our extended studies are presented in this paper.

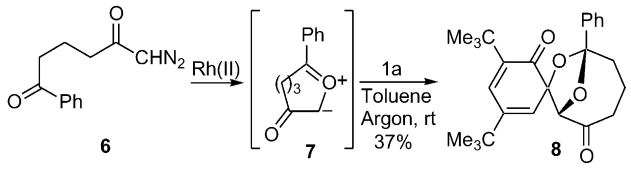
2. Results and discussion

Our studies were initiated by exposing a solution of 3,5-di-*tert*-butyl-1,2-benzoquinone **1a** and 1-diazo-5-phenyl-2,5-pentanedione **2a** to Rh(II)acetate. The carbonyl ylide[9] generated, in situ, underwent cycloaddition with **1a** to afford a crystalline product **3a** in 76% yield. The product was characterized by spectroscopic methods and its structure confirmed by single crystal X-ray analysis.[9] The experiment was repeated with three other substituted 1,2-benzoquinones and in these cases also the reaction proceeded smoothly to afford the products **3** (**a**–**g**), (Scheme 1).

Not surprisingly 3-methoxy-4,6-bis(1,1-diphenylmethyl)-1,2-benzoquinone **1e** on treatment with the diazoketone **2a** in the presence of Rh(II)acetate afforded a mixture of regioisomers **3h** and **3i** in 77% yield (Scheme 2). These were separated by silica gel column chromatography and characterized by spectroscopic analysis.

Following this, we investigated the cycloaddition of *o*-quinones with a five membered carbonyl ylide. The dipole generated by the Rh(II)acetate catalyzed reaction of cyclopropyl substituted diazoketone **4**[6] with 3,5-di-*tert*-butyl-1,2-benzoquinone in dry toluene afforded the expected cycloadduct **5a** in 72% yield. (Scheme 3). The scope of the reaction was examined with different substituted 1,2-benzoquinones and the results are summarized below (Scheme 3).

The seven membered carbonyl ylide **7** generated in situ, by the Rh(II) acetate mediated decomposition of diazoketone **6**,[6] on reaction with 3,5-di-*tert*-butyl-1,2-benzoquinone **1a** resulted in the formation of **8** as a yellow solid in 37% yield.



Scheme 4.

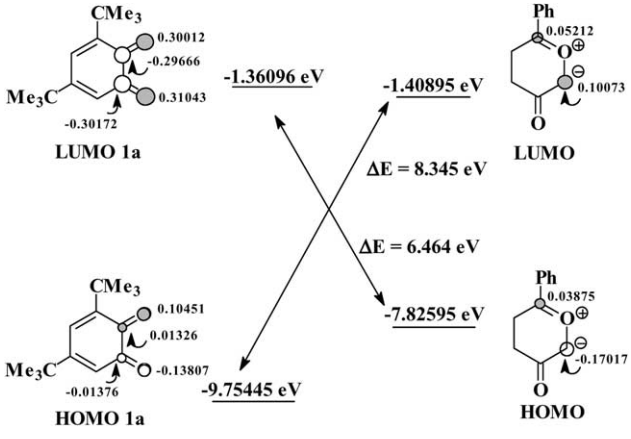
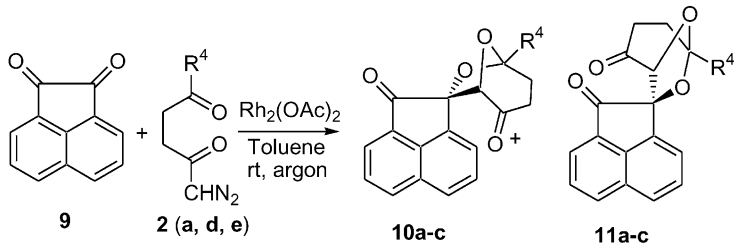


Figure 1.



Diazoketone	Products	Yield %	Ratio
2a	**10a:11a**	67	1.3:1
2d: R^4=*P*-CH_3 C_6H_4	**10b:11b**	68	2.8:1
2e: R^4=*P*-CH_3O- C_6H_4	**10c:11c**	61	1:1.6

Scheme 5.

A small amount of 3,5-di-*tert*-butyl-catechol was also observed in the reaction mixture (Scheme 4).

In order to explain the observed mode of cycloaddition and regioselectivity in the above reactions, we have carried out some AM1 calculations using PC SPARTAN Graphical Interface Package for Molecular Mechanics and Molecular Orbital Models. The correlation diagram for the reaction of 3,5-di-*tert*-butyl-1,2-benzoquinone **1a** with the carbonyl ylide derived from **2a** is illustrated as an example in Fig. 1.

Frontier molecular orbital theory correctly rationalizes the regiochemistry of the product in this 1,3-dipolar cycloaddition. The most favorable FMO interaction is between HOMO of the dipole and LUMO of the dipolarophile. The HOMO (dipolarophile)–LUMO (dipole) interaction is unimportant due to the large energy gap.

In continuation of our investigations, cycloaddition of carbonyl ylides with acenaphthenequinone **9** was undertaken. The latter, on treatment with the diazoketone **2a**, **2d** and **2e** in the presence of a catalytic amount of Rh(II)acetate at room temperature in an atmosphere of argon, underwent

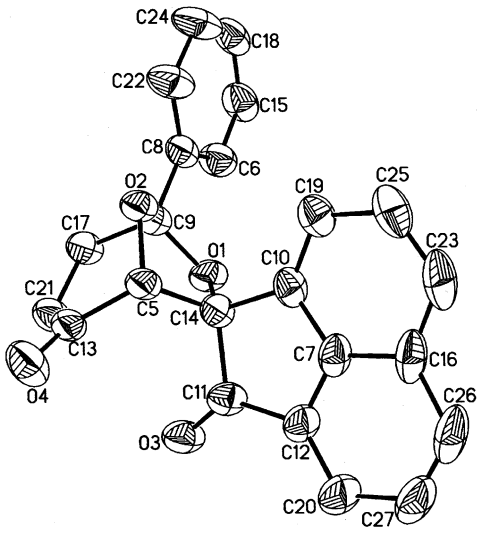


Figure 2. X-Ray structure of **10a**.

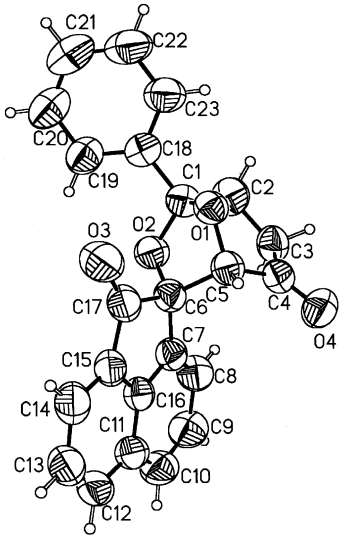


Figure 3. X-Ray structure of **11a**.

facile cycloaddition to afford a mixture of stereoisomers **10** and **11** in the ratio 1.3:1 (Scheme 5). The products were characterized by spectroscopic methods and the stereochemistry confirmed by X-ray crystallography (Figs. 2 and 3).

In conclusion, it has been shown that carbonyl ylides undergo facile cycloaddition to 1,2-diones thus offering an efficient method for the synthesis of novel spiro oxabicyclic derivatives. In the case of 1,2-benzoquinones, the ylide preferentially adds to the more electron deficient of the two carbonyls of the quinone. Such a preference has precedent in the reactivity of dicarbonyl compounds towards 1,3 dipoles. In the case of 1,2-benzoquinone **1e**, a mixture of regioisomers is obtained. The reaction of carbonyl ylides with acenaphthenequinone also afforded a mixture of stereoisomers.

3. Experimental

All the reactions were carried out in oven-dried glassware

under an atmosphere of argon. Melting points were recorded on a Büchi-530 melting point apparatus and are uncorrected. The IR spectra were recorded on Bomem MB series FT-IR spectrophotometer, using potassium bromide pellets. NMR spectra were recorded on Bruker-300 MHz FT NMR spectrometer using chloroform-*d* as the solvent unless otherwise specified. The chemical shifts are given in the δ scale with tetramethylsilane as internal standard. Elemental analyses were carried out using Perkin–Elmer 2400 CHN analyzer. High-resolution mass spectra were done using a Kratos MS50 instrument.

3.1. General procedure for the rhodium(II)-catalyzed cycloaddition reaction of 1-diazo alkanediones with various dipolarophiles

A 5 mL toluene solution containing 1.2 equiv. of the appropriate diazo alkanedione was purged with argon. To this was added a catalytic amount (2 mg) of $Rh_2(OAc)_4$ and stirred under argon atmosphere at room temperature for 3 min. One equivalent of the appropriate dipolarophile was added to it and the reaction mixture was allowed to stir at room temperature until nitrogen evolution ceased (30 min). The solvent was removed under reduced pressure and the residue subjected to silica gel column chromatography using hexane–ethyl acetate mixture, (95:5 and 90:10), as eluent to give the pure cycloadducts. The products were characterized on the basis of their spectral data.

3.1.1. 3,5-Bis(1,1-dimethylethyl)-5′-phenylspiro[3,5-cyclohexadiene-1,7′-[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (3a). Treatment of 1-diazo-5-phenyl-2,5-pentanedione **2a** (0.243 g, 1.2 mmol) with 3,5-di-*tert*-butyl-1,2-benzoquinone **1a** (0.220 g, 1 mmol) in the presence of a catalytic amount of rhodium(II) acetate at room temperature for 30 min followed by purification of the residue using a Chromatotron® (5% ethylacetate in hexane) afforded the cycloadduct **3a** (76%, 0.298 g). Yellow crystalline solid; recrystallized from hexane–dichloromethane mixture. Mp: 207–209°C; IR (KBr) ν_{max}: 2555, 1735, 1708, 1640, 1276, 1128, 1074, 946, 778, 703 cm^{-1}; ^1H NMR: δ 7.72–7.42 (m, 5H), 6.76 (d, 1H, J=2.1 Hz), 5.85 (d, 1H, J=2.1 Hz), 4.58 (s, 1H), 2.66–2.42 (m, 4H), 1.18 (s, 9H), 1.11 (s, 9H); ^{13}C NMR: δ 201.85, 199.33, 147.49, 144.75, 138.72, 133.69, 128.70, 128.20, 125.29, 122.54, 110.51, 87.90, 82.08, 35.67, 34.56, 33.26, 29.25, 28.37; Anal. calcd for $C_{25}H_{30}O_4$: C, 76.11; H, 7.66, Found: C, 75.84; H, 7.95.

3.1.2. 3,5-Bis(1,1-dimethylethyl)-5′-methylspiro[3,5-cyclohexadiene-1,7′-[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (3b). Rhodium(II) acetate catalyzed reaction of 1-diazohexane-2,5-dione **2b** (0.168 g, 1.2 mmol) with 3,5-di-*tert*-butyl-1,2-benzoquinone **1a** (0.220 g, 1 mmol) in 5 mL of toluene at room temperature for 30 min according to the general procedure followed by silica gel column chromatography using 5% ethylacetate in hexane as the eluent afforded the cycloadduct **3b** (0.178 g) in 54% yield. Yellow crystals; recrystallized from hexane–dichloromethane mixture. Mp: 166–168°C; IR (KBr) ν_{max}: 2974, 2881, 1732, 1679, 1487, 1367, 1277, 1167, 1101, 1067, 988, 922, 893 cm^{-1}; ^1H NMR: δ 6.76 (s, 1H), 5.70 (s, 1H), 4.32 (s, 1H), 2.49–2.38 (m, 2H), 2.26–2.14 (m, 2H), 1.85 (s, 3H), 1.23 (s, 9H), 1.09 (s, 9H); ^{13}C NMR: δ 201.81, 199.84, 151.47, 146.94, 144.49, 133.81, 123.10, 110.45, 87.75, 81.90, 34.66, 34.57, 34.00, 32.81, 29.31, 28.43, 23.13; Anal. calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49, Found: C, 72.41; H, 8.62.

3.1.3. 3,5-Bis(1,1-dimethylethyl)-5′-ferrocenylspiro[3,5-cyclohexadiene-1,7′-[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (3c). 3,5-Di-*tert*-butyl-1,2-benzoquinone **1a** (0.050 g, 0.23 mmol) was added to a solution of 1-diazo-5-ferrocenyl-2,5-pentanedione **2c** (0.845 g, 0.27 mmol) and Rh(II) acetate in dry toluene (3 mL) under the standard conditions. Purification of the residue on a silica gel column using 5% ethylacetate in hexane gave **3c** (0.048 g, 42%). Yellow crystals; recrystallized from hexane–dichloromethane mixture. Mp: 181–183°C; IR (KBr) ν_{max}: 2962, 1742, 1701, 1485, 1378, 1276, 1142, 1094, 1027, 926, 791 cm^{-1}; ^1H NMR: δ 6.74 (s, 1H), 5.74 (s, 1H), 4.84 (s, 1H), 4.67 (s, 1H), 4.47 (s, 1H), 4.27 (s, 2H), 4.19 (s, 5H), 2.78–2.52 (m, 4H), 1.23 (s, 9H), 1.09 (s, 9H); ^{13}C NMR: δ 202.10, 199.71, 146.71, 144.54, 133.49, 123.61, 111.08, 96.23, 87.35, 84.40, 82.08, 69.03, 68.76, 68.00, 67.96, 34.58, 32.89, 32.81, 29.32, 28.35; HRMS calcd for $C_{29}H_{34}O_4Fe$: 502.1806, Found: 502.1854.

3.1.4. 3,5-Bis(1,1-dimethylethyl)-6-methoxy-5′-phenylspiro[3,5-cyclohexadiene-1,7′-[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (3d). Rhodium(II) acetate catalyzed reaction of the diazo ketone **2a** (0.145 g, 0.72 mmol) and 3-methoxy-4,6-di-*tert*-butyl-1,2-benzoquinone **1b** (0.150 g, 0.6 mmol) in toluene (5 mL) under the standard conditions afforded the cycloadduct **3d** (0.160 g) in 63% yield. Yellow crystals; recrystallized from hexane–ethyl acetate. Mp: 168–170°C; IR (KBr) ν_{max}: 2962, 1735, 1688, 1627, 1445, 1303, 1270, 1135, 1067, 939, 892, 757 cm^{-1}; ^1H NMR: δ 7.74–7.40 (m, 5H), 6.92 (s, 1H), 4.59 (s, 1H), 3.88 (s, 3H), 2.69–2.50 (m, 4H), 1.23 (s, 9H), 1.17 (s, 9H); ^{13}C NMR: δ 203.51, 197.57, 151.73, 141.38, 139.46, 136.97, 132.02, 128.69, 128.21, 125.21, 110.77, 93.39, 82.03, 62.54, 35.31, 34.89, 33.90, 32.95, 30.16, 29.18; Anal. calcd for $C_{26}H_{32}O_5$: C, 73.56; H, 7.60, Found: C, 73.30; H, 7.66.

3.1.5. 3,5-Bis(1,1-dimethy(lethyl)-6-methoxy-5′-methylspiro[3,5-cyclohexadiene-1,7′-[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (3e). Rhodium(II) acetate catalyzed reaction of 0.168 g (1.2 mmol) of α-diazo ketone **2b** with 0.250 g (1 mmol) of 3-methoxy-4,6-di-*tert*-butyl-1,2-benzoquinone **1b** in toluene (5 mL) under the standard conditions afforded the cycloadduct **3e** (0.174 g, 48%). Yellow crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 156–158°C; IR (KBr) ν_{max}: 2962, 1732, 1685, 1645, 1569, 1481, 1379, 1298, 1173, 1053, 989, 839 cm^{-1}; ^1H NMR: δ 6.92 (s, 1H), 4.33 (s, 1H), 3.78 (s, 3H), 2.56–2.44 (m, 2H), 2.26–2.24 (m, 2H), 1.88 (s, 3H), 1.21 (s, 18H); ^{13}C NMR: δ 203.26, 198.21, 152.24, 141.23, 137.21, 131.79, 110.91, 93.39, 82.00, 62.36, 34.91, 34.56, 32.49, 30.29, 29.32, 24.13; Anal. calcd for $C_{21}H_{30}O_5$: C, 69.59; H, 8.34, Found: C, 70.05; H, 8.50.

3.1.6. 5-(1,1-Dimethylethyl)-6-methoxy-5′-phenylspiro-[3,5-cyclohexadiene-1,7′-[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (3f). Treatment of 1-diazo-5-phenylpentane-2,5-dione **2a** (0.242 g, 1.2 mmol) with 3-methoxy-4-*tert*-butyl-1,2-benzoquinone **1c** (0.194 g,1 mmol) under the standard

conditions according to the standard procedure afforded the cycloadduct **3f** (0.177 g, 48%). Yellow crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 164–166°C; IR (KBr) ν_{max}: 2956, 1732, 1682, 1645, 1574, 1384, 1260, 1084, 992, 887, 760 cm^{-1}; ^1H NMR: δ 7.78–7.40 (m, 5H), 6.79 (d, 1H, J=7.3 Hz), 5.33 (d, 1H, J=7.3 Hz), 4.48 (s, 1H), 3.60 (s, 3H), 2.69–2.53 (m, 4H), 1.16 (s, 9H); ^{13}C NMR: δ 205.92, 195.81, 158.57, 139.71, 138.49, 135.36, 129.12, 128.62, 125.77, 111.52, 88.98, 82.20, 55.99, 34.30, 33.54, 29.60; Anal. calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57, Found: C, 71.81; H,6.61

3.1.7. 5-(1,1-Dimethylethyl)-5′-phenylspiro[3,5-cyclohexadiene-1,7′-[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (3g). Rhodium(II) acetate catalyzed reaction of 0.221 g (1.09 mmol) of the α-diazo ketone **2a** with 0.150 g (0.91 mmol) of 4-*tert*-butyl-1,2-benzoquinone **1d** in toluene (5 mL) under the standard conditions afforded the cycloadduct **3g** (0.186 g, 55%). Yellow crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 112–113°C; IR (KBr) ν_{max}: 2977, 1735, 1691, 1450, 1367, 1279, 1114, 1025, 937, 772 cm^{-1}; ^1H NMR: δ 7.71–7.37 (m, 5H), 7.05 (dd, 1H, J=2.3 and 10.2 Hz), 6.02 (d, 1H, J=10.2 Hz), 5.90 (d, 1H, J=2.0 Hz), 4.57 (s, 1H), 2.68–2.44 (m, 4H), 1.12 (s, 9H); ^{13}C NMR: δ 201.69, 198.69, 147.50, 141.17, 138.58, 128.76, 128.16, 125.49, 125.28, 124.79, 111.00, 86.20, 83.04, 35.16, 34.56, 33.26, 28.34; Anal. calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55, Found: C, 74.79; H, 6.65%.

3.2. Cycloadducts 3h and 3i

Treatment of 1-diazo-5-phenylpentane-2,5-dione **2a** (0.103 g, 0.51 mmol) with the quinone **1e** (0.200 g, 0.42 mmol) in the presence of a catalytic amount of rhodium(II) acetate afforded a mixture of two products. Chromatography of the mixture on silica gel using 3% ethyl acetate in hexane as the eluent afforded **3h** (0.099 g) in 36% yield and further elution using 5% ethylacetate in hexane afforded the cycloadduct **3i** (0.112 g, 29%).

3.2.1. 3,5-Bis(diphenylmethyl)-6-methoxy-5′-phenylspiro-[3,5-cyclohexadiene-1,7′-[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (3h). Yellow crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 161–163°C; IR (KBr) ν_{max}: 3030, 2924, 1732, 1675, 1495, 1452, 1065, 980, 762, 707 cm^{-1}; ^1H NMR: δ 7.66–6.83 (m, 25H), 6.42 (s, 1H), 5.47 (s, 1H), 5.24 (s, 1H), 4.70 (s, 1H), 3.13 (s, 3H), 2.82–2.80 (m, 1H), 2.54–2.41 (m, 3H); ^{13}C NMR: δ 204.78, 196.58, 159.88, 144.05, 141.54, 141.34, 141.19, 140.05, 137.41, 129.10, 128.71, 128.53, 128.45, 128.29, 128.07, 126.65, 126.35, 126.20, 124.53, 123.32, 112.09, 90.77, 90.10, 62.31, 49.01, 47.61, 33.92, 33.24; HRMS calcd for $C_{44}H_{36}O_5$: 644.2562, Found: 644.2565.

3.2.2. Cycloadduct 3i. Yellow crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 92–94°C; IR (KBr) ν_{max}: 3030, 2943, 1739, 1695, 1494, 1446, 1305, 1128, 1072, 1029, 789, 699 cm^{-1}; ^1H NMR: δ 7.70–6.75 (m, 25H), 6.29 (s, 1H), 5.59 (s, 1H), 5.41 (s, 1H), 4.38 (s, 1H), 3.67 (s, 3H), 2.71–2.58 (m, 4H); ^{13}C NMR: δ 203.82, 195.99, 152.81, 142.48, 142.22, 141.44, 141.18, 140.74, 139.17, 136.26, 129.27, 128.77, 128.71, 128.57, 128.42, 128.19, 127.60, 126.81, 126.64, 126.31, 125.31, 124.81, 111.19, 90.70, 82.67, 62.73, 48.33, 47.56, 33.14, 32.82; Anal. calcd for $C_{44}H_{36}O_5$: C, 81.97; H, 5.63, Found: C, 81.94; H, 5.75.

3.2.3. Cycloadduct 5a. Treatment of the *o*-benzoquinone **1a** (50 mg, 0.23 mmol) with diazoketone **4** (41 mg, 0.027 mmol) in presence of $Rh_2(OAc)_4$, according to the standard procedure afforded the product **5a** (56 mg, 72%). Pale yellow crystals; recrystallized from hexane–ethyl acetate mixture mixture. Mp: 140–142°C; IR (KBr) ν_{max}: 2962, 2868, 1763, 1695, 1401, 1364, 1333, 1145, 1014, 964, 914, 814 cm^{-1}; ^1H NMR: δ 5.62 (d, 1H, J=2.32 Hz), 4.60 (s, 1H), 1.52 (s, 3H), 1.25 (s, 9H), 1.10 (s, 9H), 0.829–1.19 (m, 4H); ^{13}C NMR: δ 206.28, 198.37, 146.15, 144.78, 134.06, 125.89, 113.27, 104.82, 84.60, 83.40, 78.19, 39.61, 34.71, 34.63, 29.44, 28.54, 14.63, 14.48, 12.25; Anal. cacld for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19, Found: C, 73.11; H, 7.99.

3.2.4. Cycloadduct 5b. Treatment of the *o*-benzoquinone **1b** (50 mg, 0.20 mmol) with diazoketone **4** (36 mg, 0.24 mmol) in presence of $Rh_2(OAc)_4$, according to the standard procedure afforded the product **5b** (65 mg, 86%). Pale yellow crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 154–156°C; IR (KBr) ν_{max}: 2957, 1767, 1696, 1541, 1400, 1258, 1141, 965, 827, 654 cm^{-1}; ^1H NMR: δ 6.98 (s, 1H), 4.58 (s, 1H), 3.78 (s, 3H), 1.26 (s, 9H), 1.22 (s, 9H), 1.11–1.29 (m, 4H); ^{13}C NMR: δ 205.01, 197.08, 153.54, 141.69, 136.76, 131.57, 114.17, 91.12, 83.85, 61.97, 39.68, 34.63, 30.37, 29.41, 14.79, 14.32, 12.02; HRMS calcd for $C_{22}H_{30}O_5$: 374. 2093, Found: 374.2093.

3.2.5. Cycloadduct 5c. Treatment of the *o*-benzoquinone **1c** (50 mg, 0.25 mmol) with diazoketone **4** (47 mg, 0.30 mmol) in presence of $Rh_2(OAc)_4$, according to the standard procedure afforded the product **5c** (61 mg, 75%). Pale yellow crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 179–180°C; IR (KBr) ν_{max}: 2919, 1677, 1632, 1563, 1457, 1258, 1145, 1064, 827 cm^{-1}; ^1H NMR: δ 6.81 (d, 1H, J=7.32 Hz), 5.27 (d, 1H, J=7.32 Hz), 4.55 (s, 1H), 3.56 (s, 3H), 1.22 (s, 3H), 1.10–1.19 (m, 4H); ^{13}C NMR: δ 206.18, 194.97, 159.53, 138.42, 134.84, 134.81, 114.45, 86.81, 83.53, 55.58, 40.12, 34.05, 29.41, 14.87, 14.58, 12.70; HRMS calcd for $C_{18}H_{22}O_5$: 318.1467, Found: 318.1466.

3.2.6. Cycloadduct 5d. Treatment of the *o*-benzoquinone **1e** (66 mg, 0.20 mmol) with diazoketone **4** (36 mg, 0.24 mmol) in presence of $Rh_2(OAc)_4$, according to the standard procedure afforded the product **5d** (58 mg, 62%). Pale yellow crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 182°C; IR (KBr) ν_{max}: 2962, 1757, 1675, 1601, 1489, 1307, 1189, 1126, 1033, 666 cm^{-1}; ^1H NMR: 7.02–7.34 (m, 10H), 6.57 (s, 1H), 5.64 (s, 1H), 5.54 (s, 1H), 4.45 (s, 1H), 0.980 (s, 3H), 0.917–1.25 (m, 4H); ^{13}C NMR: δ 206.13, 196.82, 146.03, 141.64, 140.95, 139.71, 139.00, 128.92, 128.72, 128.46, 126.96, 126.63, 126.46, 113.54, 84.56, 83.56, 49.49, 39.73, 34.57, 28.34, 14.61, 14.55, 12.34; HRMS calcd for $C_{30}H_{30}O_4$: 454.2144, Found: 454.2143.

3.2.7. 3,5-Bis(1,1-dimethylethyl)-5′-phenylspiro[3,5-cyclohexadiene-1,8′-[6,8]dioxabicyclo[4.2.1]nonane]-2,2′-dione (8). 3,5-Di-*tert*-butyl-1,2-benzoquinone **1a** (0.025 g,

0.11 mmol) was added to a solution of the diazo ketone **6** (0.030 g, 0.14 mmol) and a catalytic amount of Rh(II) acetate in dry toluene (2 mL) at room temperature under an atmosphere of argon and stirred for 60 min. The solvent was removed in vacuo and the residue on silica gel column chromatography afforded 8 (0.017 g, 37%). Pale yellow crystalline solid: recrystallized from hexane–dichloromethane mixture. Mp: 200–202°C; IR (KBr) ν_{max}: 2968, 1708, 1695, 1663, 1466, 1370, 1274, 1134, 970, 889, 754 cm^{-1}; ^1H NMR: δ 7.54–7.32 (m, 5H), 6.70 (d, 1H, J=2.0 Hz), 5.69 (d, 1H, J=2.0 Hz), 4.53 (s, 1H), 2.97–2.89 (m, 1H), 2.46–2.27 (m, 2H), 2.11–1.84 (m, 3H), 1.13 (s, 9H), 1.10 (s, 9H); ^{13}C NMR: δ 210.89, 198.89, 146.50, 143.96, 142.95, 133.46, 127.73, 124.76, 122.98, 115.86, 89.41, 81.85, 42.58, 42.32, 34.73, 34.45, 29.30, 28.37, 18.16; Anal. calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90; C, 76.37; H, 8.21.

3.3. Cycloadducts 10a and 11a

To a solution of 1-diazo-5-phenylpentane-2,5-dione **2a** (0.242 g, 1.2 mmol) and a catalytic amount of $Rh_2(OAc)_4$ in toluene (3 mL) was added 0.182 g (1 mmol) of acenaphthenequinone **9** under argon atmosphere and resulting solution was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue purified by silica gel column chromatography (hexane–ethyl acetate) to give **10a** (0.134 g, 38%) and **11a** (0.104 g, 29%) in 67% overall yield in 1.3:1 ratio.

3.3.1. 5-Phenylspiro[acenaphthylene-1-(2*H*),7′[6,8]dioxabicyclo[3.2.1]octane]-2,2′-dione (10a). Colorless crystals; recrystallized from hexane–dichloromethane mixture. Mp: 194–196°C; IR (KBr) ν_{max}: 3065, 2930, 1730, 1606, 1494, 1278, 1131, 1031, 935, 788, 704 cm^{-1}; ^1H NMR: δ 8.11–7.30 (m, 11H), 4.54 (s, 1H), 3.50–3.37 (m, 1H), 2.78–2.69 (m, 2H), 2.62–2.51 (m, 1H); ^{13}C NMR: δ 202.34, 198.25, 140.77, 139.60, 138.32, 132.19, 131.06, 130.30, 128.93, 128.70, 128.31, 125.66, 124.88, 122.28, 120.79, 111.22, 87.60, 86.79, 35.70, 33.87; Anal. calcd for $C_{23}H_{16}O_4$: C, 77.52; H, 4.53, Found: C, 77.60; H, 4.37.

X-Ray data[10] for **10a**: $C_{23}H_{16}O_4$. M 356.36, Triclinic, space group $P1$, unit cell dimensions a=5.6933 (2) Å, α=86.06°; b=10.6985 (4) Å, β=88.908 (3)°; c=14.0918 (6) Å, γ=78.55 (3)°, R indices (all data) $R1$=0.0721, $wR2$=0.2651, volume, Z=839.26 (6) $Å^3$, 2, D calc=1.410 Mg/m^3, absorption coefficient=0.096 mm^{-1}, reflections collected=10049.

3.3.2. Cycloadduct 11a. Colorless crystals; recrystallized from hexane–dichloromethane mixture. Mp: 172–174°C; IR (KBr) ν_{max}: 3071, 2970, 1730, 1605, 1502, 1312, 1138, 1068, 910, 785 cm^{-1}; ^1H NMR: δ 8.20–7.28 (m, 11H), 4.63 (s, 1H), 2.88–2.83 (m, 2H), 2.73–2.68 (m, 2H); ^{13}C NMR: δ 202.72, 199.36, 141.98, 138.93, 134.98, 133.18, 132.32, 131.77, 130.47, 128.81, 128.43, 128.18, 126.48, 125.43, 122.33, 121.72, 110.51, 98.12, 85.25, 33.90, 33.56; Anal. calcd for $C_{23}H_{16}O_4$: C, 77.52; H, 4.53, Found: C, 77.12; H, 4.47.

X-Ray data[10] for **11a**: $C_{23}H_{16}O_4$. M 356.36, monoclinic, space group $P2(1)/c$, unit cell dimensions a=14.1914 (5) Å, α=90°; b=14.2803 (5) Å, β=104.410 (3)°; c=8.7367 (3) Å, γ=90°, R indices (all data) $R1$=0.0864, $wR2$=0.1984, volume, Z=1714.85 (10) $Å^3$, 4, D calc=1.380 Mg/m^3, absorption coefficient=0.094 mm^{-1}, reflections collected=28171.

3.4. Cycloadduct 10b and 11b

Treatment of the diazo ketone **2d** (0.106 g, 0.49 mmol) with acenaphthenequinone **9** (0.075 g, 0.41 mmol) according to the general procedure afforded **10b** (0.076 g, 50%) and **11b** (0.027 g, 18%) in 68% yield in the ratio 2.8:1.

3.4.1. Cycloadduct 10b. Colorless crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 230–231°C; IR (KBr) ν_{max}: 3068, 2924, 1718, 1716, 1603, 1491, 1351, 1288, 1130, 1050, 922, 812, 770 cm^{-1}; ^1H NMR: δ 8.12–7.21 (m, 10H), 4.54 (s, 1H), 3.49–3.37 (m, 1H), 2.78–2.68 (m, 2H), 2.61–2.51 (m, 1H), 2.39 (s, 3H); ^{13}C NMR: δ 202.64, 198.47, 140.86, 138.50, 136.82, 132.29, 131.17, 130.38, 129.08, 128.33, 125.74, 124.94, 122.36, 120.94, 111.45, 87.70, 86.89, 35.78, 34.00, 21.29; Anal. calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90, Found: C, 77.78; H, 4.88.

3.4.2. Cycloadduct 11b. Colorless crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 201–203°C; IR (KBr) ν_{max}: 3043, 2912, 1735, 1710, 1604, 1430, 1398, 1262, 1128, 1073, 930, 786 cm^{-1}; ^1H NMR: δ 8.62–7.23 (m, 10H), 4.70 (s, 1H), 2.94–2.90 (m, 2H), 2.80–2.76 (m, 2H), 2.39 (s, 3H); ^{13}C NMR: δ 203.00, 199.50, 142.23, 138.73, 136.32, 135.17, 133.41, 132.52, 131.95, 130.72, 129.08, 128.64, 128.41, 127.54, 126.66, 125.67, 122.52, 121.94, 110.85, 96.50, 85.51, 34.07, 33.82, 21.42; Anal. calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90, Found: C, 77.83; H, 4.87.

3.5. Cycloadducts 10c and 11c

Rhodium(II) acetate catalyzed reaction of diazoketone **2e** (0.278 g, 1.2 mmol) and acenaphthenequinone **9** (0.182 g, 1 mmol) in dry toluene (5 mL) under the standard conditions afforded a mixture of cycloadducts (1:1.6 ratio) **10c** (0.091 g, 24%) and **11c** (0.144 g, 37%).

3.5.1. Cycloadduct 10c. Colorless crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 190–191°C; IR (KBr) ν_{max}: 3061, 2930, 1731, 1718, 1611, 1517, 1437, 1254, 1174, 1032, 925, 837, 770 cm^{-1}; ^1H NMR: δ 8.13–7.35 (m, 8H), 6.93 (d, 2H, J=8.6 Hz), 4.53 (s, 1H), 3.84 (s, 3H), 3.43–3.40 (m, 1H), 2.75–2.68 (m, 2H), 2.59–2.57 (m, 1H); ^{13}C NMR: δ 202.54, 198.38, 159.85, 140.80, 138.46, 132.20, 131.93, 131.13, 130.35, 128.96, 128.26, 126.32, 125.67, 122.28, 121.88, 120.87, 113.65, 111.31, 87.70, 86.85, 55.12, 35.70, 33.93; Anal. calcd for $C_{24}H_{18}O_5$: C, 74.60; H, 4.70, Found: C, 74.75; H, 4.64.

3.5.2. Cycloadduct 11c. Colorless crystals; recrystallized from hexane–ethyl acetate mixture. Mp: 166–168°C; IR (KBr) ν_{max}: 3030, 2930, 1730, 1717, 1608, 1519, 1252, 1050, 827, 770 cm^{-1}; ^1H NMR: δ 8.12–7.40 (m, 8H), 6.96 (d, 2H, J=8.7 Hz), 4.70 (s, 1H), 3.83 (s, 3H), 2.75–2.68 (m, 2H), 2.94–2.90 (m, 2H), 2.83–2.79 (m, 2H); ^{13}C NMR: δ 203.04, 199.74, 160.02, 142.03, 131.85, 131.13,

130.52, 129.38, 128.48, 128.22, 127.13, 126.50, 122.39, 121.73, 113.57, 110.58, 85.35, 85.22, 55.16, 33.58, 33.53; Anal. calcd for $C_{24}H_{18}O_5$: C, 74.60; H, 4.70, Found: C, 74.91; H, 4.88.

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10. All X-ray data pertaining to the adducts **10a** and **11a** have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 178638 and 178639 for **10a** and **11a**, respectively.