22. [2 + 4]-Cycloadditions under High Pressure: First Realization of a *Diels-Alder* Addition of Furan with Simple 1,4-Benzoquinones[1]

Preliminary Communication

by **Janusz Jurczak, Tomasz Kożluk** and **Stanislaw Filipek**

Institute of Organic Chemistry and Institute of Physical Chemistry, Polish Academy of Sciences,
01-224 Warszawa, Poland

and **Conrad Hans Eugster**

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

(16.XI.82)

Summary

For the first time a successful [2+4]-cycloaddition of furan (**1**) with simple 1,4-benzoquinones **2** has been realized.

Until now no report on a successful [2+4]-cycloaddition of furan (**1**) with simple 1,4-benzoquinones **2** has been published. In contrast, the more active 3,4-dimethoxyfuran reacts smoothly with quinones under normal [2] or high-pressure conditions [1]. These results stimulated us to reinvestigate the reaction between furan and nonactivated 1,4-benzoquinones[2]. According to the literature [4] it could be expected that the *Diels-Alder* reaction would be accelerated by an increase of pressure, whereas the *retro*-reaction would be inhibited. Consequently we expected that under 20–22 kbar and at moderate temperatures (20–60°) the equilibrium of the reaction is shifted to the side of products.

High-pressure experiments on (1:1)- or (2:1)-mixtures of **1** and **2** were performed in ether solutions and in an apparatus of the piston-cylinder type[3] with insertion of two or three *Teflon* ampoules [6], thus permitting simultaneous realization of independent reactions in the same experiment. After reaction at 20 kbar and room temperature during 68 hours, the solvent was evaporated immediately upon decompression, and ^{1}H-NMR. spectra were taken at $-50°$. For results *cf.* the *Scheme* and *Table 1*. In each case beside the signals of starting materials new signals appeared which showed the characteristics of *endo*- and *exo*-cycloadducts **3**

---

[1] Organic Syntheses under High Pressure, Part VI. For Part V see [1].

[2] For reactions of various furans with 'activated' 1,4-benzoquinones see [3]; products of such reactions are always substituted furans.

[3] For the description see [5] [6].

Table 1. *Characteristic ^1H-NMR. data of* exo- *and* endo-*adducts* 3 *and* 4 ($CDCl_3$, –50°, δ [ppm], *Varian FT-80A*)

	H–C(8),H–C(9)	H–C(7),H–C(10)	H–C(1),H–C(6)	H–C(3),H–C(4)	R
3a	6.46 (*m*)	5.40 (*d*, $J = 5$)	3.45 (*m*)	*ca.* 6.4	–
4a	6.56 (*d*, $J = 1.1$)	5.27 (*m*)	2.73 (*s*)	*ca.* 6.4	–
3b	6.38 (br. *s*)	5.45 (*m*)	3.50 (*m*)	*ca.* 6.7	2.10
4b	6.60 (*s*)	5.26 (*s*)	2.78 (*s*)	*ca.* 6.7	1.98
3c	6.44 (*s*)	5.49 (*m*)	3.50 (*m*)	–	4.00 (*s*)
4c	6.59 (*s*)	5.25 (*s*)	2.80	–	4.08 (*s*)

and **4**. In no single case could the signals of the possible rearranged products **5a** or **5b** ($R^3 = H$) be detected[4]).

When the ^1H-NMR. spectrum was recorded with a sample from the high-pressure reaction of **1** and **2a** after storage for 1 hour at –8°, it showed complete disappearance of the signals due to **3a** and simultaneous enhancement of the signals of **1** and **2a**, respectively. The signals of the *exo*-form **4a** had remained practically unchanged at these conditions. After 12 hours at 5°, no more cycloadducts could be detected. We conclude from these facts that both, the *endo*- and *exo*-adducts **3a** and **4a** are unstable at room temperature. This observation explains why adducts **3a** and **4a** could not be obtained under thermal conditions. However, **4a** is more stable than **3a**.

The *endo/exo*-rate of the cycloadducts is markedly affected by either substituents on the quinone or the furan part, see *Table 2* and [1] [2] [8].

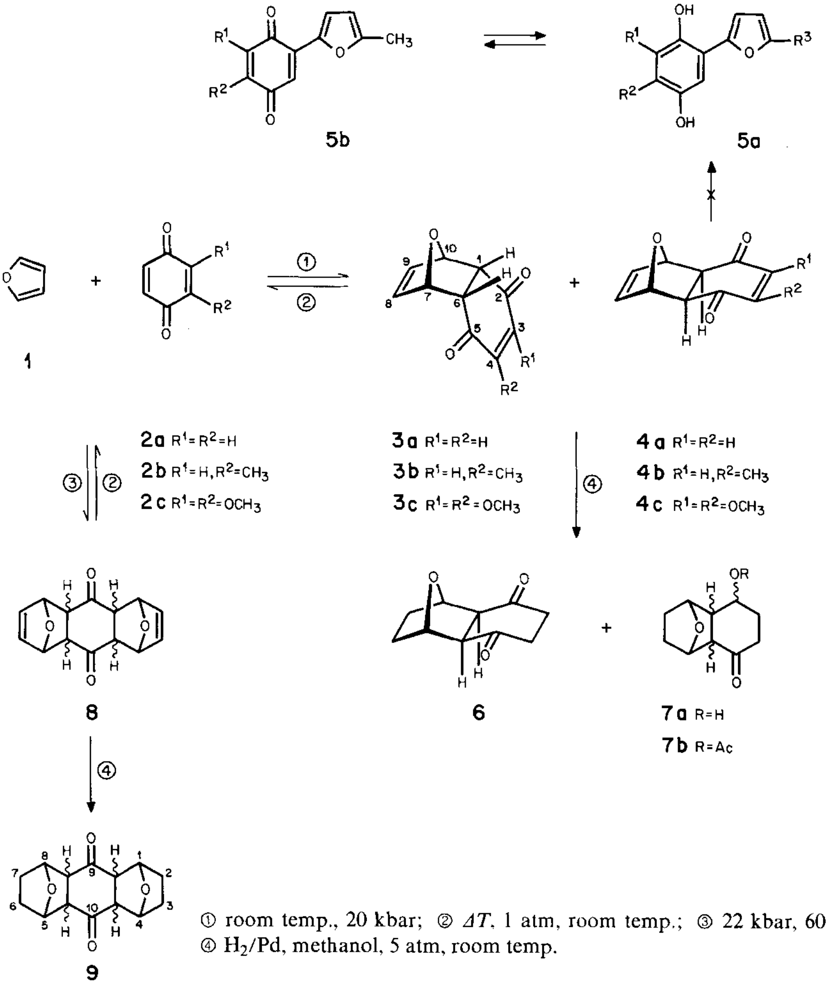
Rapid catalytic hydrogenation of a methanolic solution containing a mixture of **3a**/**4a** with 10% Pd/C at 5 atm, followed by column chromatography on silica gel, afforded *7,10-epoxy-*cis-*1*-cisoid-*1,10*-cis-*10-bicyclo[4.4.0]decane-2,5-dione* (**6**) [Oil, yield 10%. – ^1H-NMR. ($CDCl_3$): 4.73 (*m*, 2 H, H–C(7), H–C(10)); 2.80 (*s*, 2 H, H–C(1), H–C(6)); 2.60 (br. *s*, 4 H, 2 H–C(3), 2 H–C(4)); 1.55 (*m*, 2 H–C(8), 2 H–C(9)). – IR. (film): 1700 (CO), 1200, 1180, 1010 cm^{-1} (C–O–C). – MS.: *m/z* 180] and **7a** (oil, yield 15%). Acylation of the latter with pyridine/acetic anhydride yielded *7,10-epoxy-5-oxobicyclo[4.4.0]dec-2-yl acetate* (**7b**) [Oil. – ^1H-NMR. ($CDCl_3$): 5.10 (*m*, 1 H, H–C(2)); 4.79 (*m*, 2 H, H–C(7), H–C(10)); 2.10 (*s*, 3 H, Ac); 2.7–1.5 (*m*, 10 H). – IR. (film): 1710 (C=O), 1220, 1185, 1115 (C–O–C)].

When **1** and **2a** were reacted at a molar ratio of 2:1 under more drastic conditions (22 kbar, 60°, 8 hours), adduct **8** was formed in yields of *ca.* 50% (calculated from ^1H-NMR. spectra). Similar to **3** and **4**, bis-adduct **8** was also unstable at room temperature. Rapid hydrogenation gave the tetrahydro derivative **9** [M.p. 140°. – ^1H-NMR. ($CDCl_3$): 4.97 (*m*, 4 H, H–C(1), H–C(4), H–C(5), H–C(8)); 2.98 (*s*, 4 H, H–C(4a), H–C(8a), H–C(9a), H–C(10a)); 1.68 (*m*, 8 H, 2 H–C(2), 2 H–C(3), 2 H–C(6), 2 H–C(7)). – IR. (KBr): 1706 (C=O), 1235, 1080, 1120 (C–O–C). Microanalysis: $C_{14}H_{16}O_4$ (248,27), calc. C 67,73 H 6,50%, found C 67,4

---

[4]) Labile cycloadducts of the types 3 and 4 were discussed as possible intermediates in the reaction of furans with activated 1,4-benzoquinones [3a] [3c] [7]. In an acid-catalyzed reaction 1,4-benzoquinone and 2-methylfuran yielded 2-(5-methylfuryl)-1,4-benzoquinone (**5b**, $R^1 = R^2 = H$) through oxidation of **5a** ($R^1 = R^2 = H$, $R^3 = CH_3$)) [3e].

Scheme



① room temp., 20 kbar; ② ΔT, 1 atm, room temp.; ③ 22 kbar, 60°, 8 h; ④ H_2/Pd, methanol, 5 atm, room temp.

Table 2. *Yields of* **3** *and* **4**; endo/exo-*ratio at* – *50°*

	Quinone **2** [%]	*endo*-Adduct **3** [%]	*exo*-Adduct **4** [%]	Ratio *endo*/*exo*
2a	71	14	15	1:1.1
2b	62	10	28	1:2.8
2c	72	10	18	1:1.8

H 6,8%]. Therefore **9** is one of the isomers of *1,4:5,8-diepoxy-perhydroanthracene-9,10-dione*. Based on ^{1}H-NMR. spectra and on the probable course of the cycloaddition step it appears to be the *cis*-1-*cisoid*-1,9a-*cis*-9a-*cisoid*-8a,9a-*cis*-8a-*cisoid*-8,8a-*cis*-5-isomer.

Summing up our results, we have achieved for the first time a successful *Diels-Alder* addition between furan and simple 1,4-benzoquinones.

REFERENCES

[1] *J. Jurczak, T. Kożluk, M. Tkacz & C.H. Eugster*, Helv. Chim. Acta *66*, 218 (1983).
[2] *A.A. Hofmann, I. Wyrsch-Walraf, P.X. Iten & C.H. Eugster*, Helv. Chim. Acta *62*, 2211 (1979).
[3] a) *C.H. Eugster & P. Bosshard*, Chimia *15*, 528 (1961); *iidem*, ibid. *16*, 45 (1962); b) *C.H. Eugster & R. Good*, ibid. *16*, 343 (1962); c) *C.H. Eugster & P. Bosshard*, Helv. Chim. Acta *46*, 815 (1963); d) *P. Bosshard, S. Fumagalli, R. Good, W. Trueb, W. v. Philipsborn & C.H. Eugster*, ibid. *47*, 769 (1964); e) *N. Baumann, S. Fumagalli, G. Weisgerber & C.H. Eugster*, ibid. *49*, 1794 (1966).
[4] *T. Asano & W.J. Le Noble*, Chem. Rev. *78*, 407 (1978).
[5] *J. Jurczak, M. Chmielewski & S. Filipek*, Synthesis *1979*, 41.
[6] *J. Jurczak, T. Kożluk, S. Filipek & C.H. Eugster*, Helv. Chim. Acta *65*, 1021 (1982).
[7] *J. ApSimon, V.S. Srinivasan, M.R. Labbe & R. Sequin*, Heterocycles *15*, 1079 (1981).
[8] *P.X. Iten, A.A. Hofmann & C.H. Eugster*, Helv. Chim. Acta *62*, 2202 (1979).