

PHOTOCHEMICAL CYCLOADDITION OF OLEFINS TO AROMATIC COMPOUNDS -IV.<sup>1)</sup>  
 ON THE MECHANISM OF THE PHOTOCHEMICAL META-CYCLOADDITION

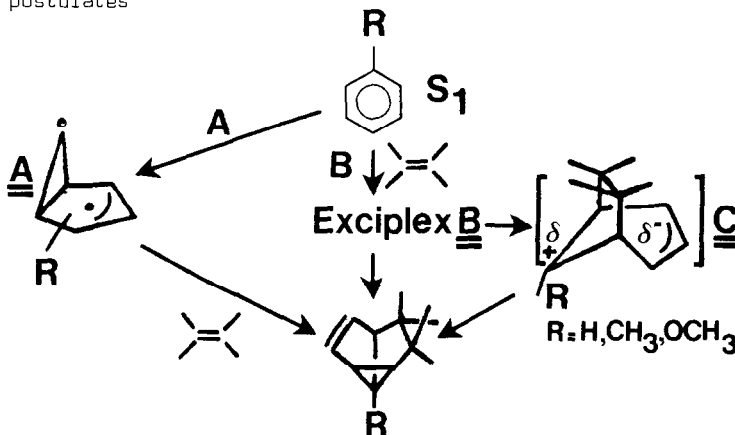
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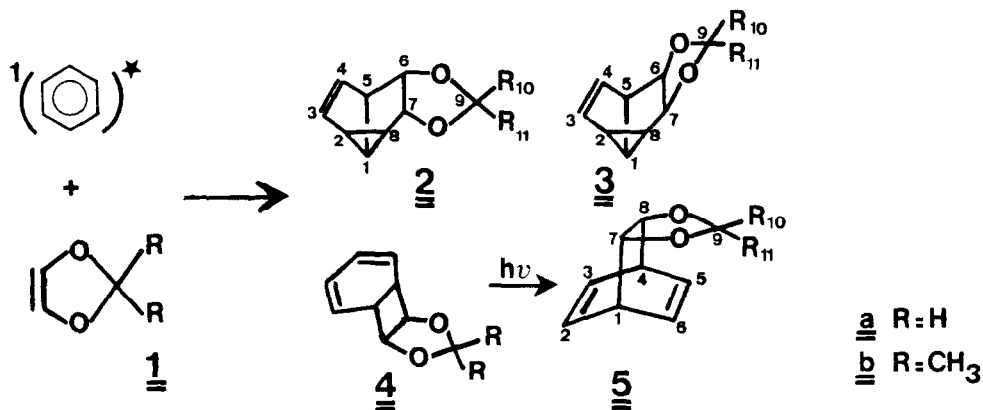
Abstract The meta-photoadditions of 1,3-dioxoles to benzene are shown to yield predominantly exo-configured products. The mechanism is considered in the light of these new results.

Introduction

The 1,3- or meta-addition of olefins to singlet excited benzene derivatives has generated much interest, both from a purely mechanistic point of view and as a synthetic route to natural products (1-6). Despite extensive investigations, there are still open questions concerning the underlying mechanism. Bryce-Smith and Longuet-Higgins made the early suggestion that the reaction began with 1,3-closure of excited singlet benzene to give a biradical A (7). Gilbert presented experimental support for this hypothesis (8) but Sheridan corrected these results and thus weakened the assumption of a biradical A as an intermediate in the meta-photoadditions in general (6). In a very recent publication Bryce-Smith and Gilbert (2c) presented investigations which could support their favourite mechanism but still uncertainties remain. However, in our investigations we found experimental evidence of an exciplex intermediate B (a) by detecting its long wavelength emission for the first time (1b,c) and (b) by measuring identical quenching constants of both exciplex emission and product formation (1b), i.e. a direct pathway leads from the fluorescent exciplex to the meta-adduct. Our results are in accordance with Morrisons' (9) and Srinivasans' (10) early postulates.



As reported earlier (1a,b) photoexcited benzene adds to 1,3-dioxole 1a and 2,2-dimethyl-1,3-dioxole 1b under formation of a mixture of ortho-, meta-, and para-cycloadducts 2 - 5.



2 and 4 are the main products and their ratio depends on both the ionization potential of the olefin (1a,b) and the solvent polarity (11), whereas 5 is formed in a photochemical subsequent reaction from 4 (1a,b,12). The ortho- and meta-additions are very efficient as indicated by high quantum yields of the exciplex (13) and product formation (0.50-0.63)(1b). Our structural assignment of the meta-adducts originally based on the chemical conversion of the endo-meta-adduct of vinylene carbonate/benzene (14) to the dimethylketal (1a). We now wish to report a detailed <sup>1</sup>H- and <sup>13</sup>C-NMR-analysis of 2 and 3 which leads to the following results.

**Results** The <sup>13</sup>C-NMR-spectra (table 2) of 2a, 2b and 3a confirm the meta-adduct structure, i.e. three cyclopropane carbons ( $\delta=30-40$ ,  $^1J_{13-C-1H} \approx 170$ Hz), two olefinic carbons ( $\delta \approx 130$ ,  $^1J_{13-C-1H} \approx 165$ Hz), and three saturated tertiary carbons. As shown by Cornelisse et al. (3) the coupling constant  $J_{56}$  in the <sup>1</sup>H-NMR-spectra (table 1) should be large for the endo- and nearly zero for the exo-isomer because of the different dihedral angles found in models of these isomers. The same reasoning holds for  $J_{78}$ . So the isomer with  $J_{56}=0.7$  and  $J_{78} \leq 0.1$  Hz must be the exo- and the other isomer with the large coupling constants must be the endo-isomer. Although it was not possible to determine the individual coupling constants  $J_{56}$ ,  $J_{57}$ ,  $J_{68}$  and  $J_{78}$  for 3a, because of the chemical equivalence of H-6 and H-7, it is clear from the large sum  $^3J_{56} + ^4J_{57}$  and  $^3J_{78} + ^4J_{68}$  that the three bond coupling constants must be large, as is confirmed by the coupling constants of endo-1,3-vinylene carbonate - benzene adduct (table 1) where these sums are comparable. The large value  $^4J_{57}=1.7$  Hz for the carbonate adduct is also in accordance with the structure since there is only a favourable W-pathway for H-5 and H-7 in the endo-isomer. The large chemical shift differences in 2a and 3a for H-6 and H-7 confirm the assignment of the structure since in the exo-isomer the protons H-6 and H-7 are lying above the double bond C3=C4, and thus their signals are shielded (15) with respect to the protons in the exo-position of the endo-isomer. The steric hindrance in the endo-isomer is reflected by the increase of  $J_{67}$  since models show that the strain can be released by decreasing the dihedral angle and hence increasing  $J_{67}$ . In the <sup>13</sup>C- and <sup>1</sup>H-NMR-spectra of the crude reaction mixture of 1b and benzene there are signals indicating that 3b is present (2b:3b=96:4). The <sup>13</sup>C-NMR (C6D6) shows  $\delta=39.46$ ,  $35.95$  and  $32.97$  for C-1, C-2 and C-8,  $\delta=51.52$  for C-5,  $\delta=84.08$  for C-7 and  $\delta=92.14$  for C-6. In the <sup>1</sup>H-NMR-spectrum (CS<sub>2</sub>) there are the signals of H-7 at  $\delta=5.02$  and of H-6 at  $\delta=4.80$  with  $J_{67}=8.1$ ,  $J_{56}=6.2$ ,  $J_{78}=5.9$  and  $J_{57}=1.8$  Hz. The other signals

are covered by the much more intensive signals of the other isomers. Because of its thermal lability 3b could not be isolated. Our chemical structure-proof failed because of the geometrical strain in 3b, so only 2b could be formed without complication and thus we detected it qualitatively in the GLC (1a).

#### Discussion

Summarizing the presented results: singlet excited benzene adds to 1,3-dioxoles predominantly exo in both ortho- and meta-cycloadditions. This is contrary to the meta-addition of alkenes (e.g. cyclopentene) to benzene and its simple derivatives (2,3,10). However the stereoselectivity seems to be weakened for enol ethers (16). These striking effects can be satisfactorily rationalized in terms of a type (B) mechanism involving an exciplex intermediate B with product-like structure (1b). Electron-rich cis-enediol ethers destabilize the endo-configuration by repulsive effects between the oxygen atoms and the partly negatively charged arene as a consequence of the CT-character of the exciplex-formation (1b,c). Even vinylene carbonate as an acceptor olefin (IP=10.08 eV)(14) fits into this concept. It can induce a reverse charge transfer resulting in a partly positively charged arene which then will stabilize an endo-configuration. Electron donating substituents in position 1 of the arene degenerate the intermediate to a zwitterionic species and thus the stereoselectivity should be the same as for benzene. Indeed photoaddition of 1,3-dioxoles to anisoles yields predominantly exo-meta-products (17).

#### Acknowledgement

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Dedicated to H. Stetter on the occasion of his 65th birthday.

- 1)(a) Part I: J. Mattay, H. Leismann, and H.-D. Scharf, Chem. Ber. **112**, 577 (1979), (b) Part II: J. Mattay, H. Leismann, and H.-D. Scharf, Molecular Photochemistry **9** (2), 119 (1979), (c) Part III: H. Leismann and J. Mattay, Tetrahedron Lett. **1978**, 4285.
- 2)(a) A. Gilbert, Pure Appl. Chem. **52**, 2663 (1980), (b) A. Gilbert and P. Yianni, Tetrahedron Lett. **1982**, 2697, (c) D. Bryce-Smith, G. A. Fenton, and A. Gilbert, Tetrahedron Lett. **1982**, 2697.
- 3)(a) A. W. H. Jans and J. Cornelisse, Recl. Trav. Chim. Pays-Bas **100**, 213 (1981), (b) A. W. H. Jans, J. J. van Dijk-Knepper, and J. Cornelisse, Tetrahedron Lett. **1982**, 1111, (c) A. W. H. Jans, J. Lugtenburg, J. Cornelisse, and C. Kruk, Org. Magn. Res. **19**, 58 (1982).
- 4) P. A. Wender and G. B. Dreyer, Tetrahedron **37**, 4445 (1981).
- 5) T. R. Hoye, Tetrahedron Lett. **1981**, 2523.
- 6) R. S. Sheridan, Tetrahedron Lett. **1982**, 267.
- 7) D. Bryce-Smith and H. Longuet-Higgins, Chem. Commun. **1966**, 593.
- 8) M. Dodson, A. Gilbert, and P. Heath, J. Chem. Soc. Perkin I, **1960**, 1314.
- 9) W. Ferree, G. B. Grutzner, and H. Morrison, J. Amer. Chem. Soc. **93**, 5502 (1971).
- 10) J. Cornelisse, V. Y. Merrit, and R. Srinivasan, J. Amer. Chem. Soc. **95**, 6197, 8250 (1973), J. Cornelisse and R. Srinivasan, Chem. Phys. Lett. **20**, 278 (1973), J. Ors and R. Srinivasan, J. Org. Chem. **42**, 1321 (1977).
- 11) The total quantum yield enhances by turning from solvents of high polarity to those of low polarity whereas the ratio of the quantum yields of the formation of 2, 3, 4 decreases (8 IUPAC-Symposium on Photochemistry, Seefeld, Austria, July 13-19, 1980, Contributed Paper No. 97, Abstracts p. 216-217).

- 12) NMR-Data of 5b in C6D6 are  $^1\text{H}$   $\delta=1.28(\text{s}), 3\text{H}, \text{H}-11, \delta=1.58(\text{s}), 3\text{H}, \text{H}-10, \delta=3.60(\text{m}), 2\text{H}, \text{H}-1, \text{H}-4, \delta=4.02(\text{m}), 2\text{H}, \text{H}-7, \text{H}-8, \delta=5.93(\text{m}), 2\text{H}, \text{H}-2, \text{H}-3, \delta=6.25(\text{m}), 2\text{H}, \text{H}-5, \text{H}-6, ^{13}\text{C}$   $\delta=26.45$  and  $25.73$ , C-10 and C-11,  $\delta=42.57$ , C-1, C-4,  $\delta=78.95$ , C-7, C-8,  $\delta=110.63$ , C-9,  $\delta=132.16$  and  $133.81$ , C-2, C-3 and C-5, C-6.
- 13) The efficiency of exciplex-formation is ca 0.8-1.0 indicating that fluorescence ( $\phi \approx 0.0001$ ) and radiationless deactivation are the minor processes. These results will be published soon.
- 14) H.G. Heine and W. Hartmann, Angew. Chem. **87**, 708 (1975).
- 15) W. Gunther, NMR-Spektroskopie, Georg Thieme Verlag, Stuttgart 1973.
- 16) J. Cornelisse, private communication.
- 17) Cooperative publication with Corelisses' group (University of Leiden, NL) is in progress.

Table 1  $^1\text{H}$ -NMR-spectroscopic data of 2a, 2b and 3a

$\delta^{\text{a}}$	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8</sub>	H <sub>10</sub>	H <sub>11</sub>
<u>2a</u>	2.48	1.91	5.57	5.32	3.30	3.92	4.26	1.69	4.70	5.07
<u>3a</u>	2.62	1.90	5.67	5.47	3.11	4.83	4.83	1.59	4.86	5.03
<u>2b</u>	2.49	1.83	5.53	5.29	3.22	4.11	4.20	1.71	1.17	1.39

J (Hz)	$^3J_{12}$	$^3J_{15}$	$^3J_{18}$	$^3J_{23}$	$^3J_{28}$	$^3J_{34}$	$^3J_{45}$	$^3J_{56}$	$^4J_{57}$	$^3J_{67}$	$^4J_{68}$	$^3J_{78}$	$^4J_{14}$	$^4J_{24}$	$^5J_{26}$	$^5J_{48}$	$^2J_{1011}$
<u>2a</u>	6.5	5.4	6.4	2.3	7.8	5.5	2.4	0.7	0.6	4.0	0.5	<0.1	0.7	0.7	0.7	0.9	0.8
<u>3a</u> <sup>b)</sup>	6.8	5.7	6.6	2.1	7.4	5.4	2.4	$\Sigma=7.8^{\text{c)}$		$8.4^{\text{e)}$		$\Sigma=5.2^{\text{d)}$	0.7	0.6	<0.2	0.8	1.3
<u>2b</u>	6.6	5.5	6.3	2.2	7.8	5.4	2.4	0.7	0.7	5.0	0.6	<0.2	0.7	0.7	0.7	0.7	0.6

(a)  $\delta$ (ppm), solvent  $\text{CS}_2$  90 MHz (Varian EM-390)

(b) coupling constants are determined using C6D6 as solvent (c) since H-6 and H-7 are chemical equivalent only the sum of  $J_{56}$  and  $J_{57}$  could be measured. In case of the 1,3-endo-benzene vinylene carbonate adduct these values are  $J_{56} = 6.5$  and  $J_{57} = 1.7$  Hz ( $\Sigma = 8.2$  Hz); (d) sum of  $J_{68}$  and  $J_{78}$  (see note c) for the carbonate (see note c) these values are  $J_{68} = 0.5$  and  $J_{78} = 6.0$  Hz ( $\Sigma = 6.5$  Hz); (e)  $J_{67} = 8.6$  Hz for the carbonate (see note c)

Table 2  $^{13}\text{C}$ -NMR-spectroscopic data of 2a, 2b and 3a<sup>a)</sup>

	<u>2a</u>		<u>3a</u>		<u>2b</u>	
	$\delta$ (ppm)	$^1J_{^{13}\text{C}-^1\text{H}}$ (Hz)	$\delta$ (ppm)	$^1J_{^{13}\text{C}-^1\text{H}}$ (Hz)	$\delta$ (ppm)	$^1J_{^{13}\text{C}-^1\text{H}}$ (Hz)
1	34.84	176	39.62	180	34.87	180
2	30.72	169	32.94	170	31.29	168
3 <sup>b)</sup>	129.87	166	131.03	165	129.62	165
4 <sup>b)</sup>	130.44	166	133.76	165	129.91	165
5	52.72	144	51.95	144	52.67	146
6	90.76	154	92.89	155	90.51	152
7	80.94	157	84.88	150	81.29	156
8	34.51	169	27.56	170	35.98	168
9	95.50	165	101.25	166	110.14	-
10					25.92	126
11					27.87	126

a) solvent  $\text{CS}_2/\text{C6D6}=5/1$  (V/V) 20 MHz (Varian CFT-20)

b) the assignment of C-3 and C-4 may be reversed