Anal. Calcd for $C_{15}H_{19}ClO_4$ (298.5): C, 60.30; H, 6.36. Found: C, 60.21; H, 6.31.

Ethyl 2-(ethoxycarbonyl)-4-(*p*-nitrophenyl)butanoate (6g): ^{1}H NMR (300 MHz) δ 1.18 (t, J = 7.5 Hz, 6 H, 2 OCH_2CH_3), 2.14 (m, 2 H, H-3), 2.68 (t, J = 7.5 Hz, 2 H, H-4), 3.24 (t, J = 7.5 Hz, 1 H, H-2), 4.10 (m, 4 H, 2 OCH_2CH_3), 7.30, 8.10 (m, Ar). Anal. Calcd for $C_{15}H_{19}NO_6$ (309.0): C, 58.25; H, 6.15. Found: C, 58.31; H, 6.18.

Acknowledgment. This work was carried out thanks to the generous support by Ministero della Pubblica Istruzione and Consiglio Nazionale delle Ricerche (E.B. and R.R.) and by Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (B.G. and H.F.).

Registry No. **3a**, 637-69-4; **3b**, 622-97-9; **3c**, 100-42-5; **3d**, 1073-67-2; **3e**, 2039-85-2; **3f**, 586-39-0; **3g**, 100-13-0; **4b**, 128752-78-3; **4c**, 109949-87-3; **4d**, 128752-79-4; **4e**, 128752-80-7; **4f**, 128752-81-8; **5b**, 128752-82-9; **5c**, 3709-35-1; **5d**, 128752-83-0; **5e**, 128752-84-1; **5f**, 128752-85-2; **6a**, 118598-43-9; **6b**, 128752-86-3; **6c**, 6628-68-8; **6d**, 85211-00-3; **6g**, 72201-24-2; MeOC(O)CH_2C(O)OMe, 108-59-8; EtOC(O)CH_2C(O)OEt, 14064-10-9; CAN, 15078-94-1; Bu_3SnH, 688-73-3.

Molecular Recognition Phenomena in the Excited State: The Meta Photocycloaddition of *cis*- and *trans*-2,5-Dihydro-2,5-dimethoxyfuran and *cis*-1,4-Dimethoxycyclopent-2-ene to Anisole[1]

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The meta photocycloaddition of *cis*-2,5-dihydro-2,5-dimethoxyfuran (**8**), *trans*-2,5-dihydro-2,5-dimethoxyfuran (**9**), and *cis*-1,4-dimethoxycyclopent-2-ene (**10**) to anisole (**7**) is described. The results are discussed in light of the most recent findings concerning the mechanism of this reaction.

Introduction

Much work has been done to elucidate the characteristics of the meta photocycloaddition of alkenes to arenes since its discovery in 1966.[2] Of the originally proposed reaction pathways, only those depicted in Scheme I are still under discussion:[3-9] (a) A concerted mechanism between the singlet excited arene (benzene or substituted benzene derivative, **1***) and the alkene in its ground state forming the biradical (**4**)[10] or "zwitterionic" intermediate (**4′**).[6] (b) A mechanism similar to a, however, via a polarized transition state (**2**).[6,7] (c) A mechanism involving an exciplex intermediate (**3**) with charge-transfer (CT) character depending on the electronic properties of the starting materials.[3-5] This exciplex is probably formed via a polarized transition state (encounter).[4,11] Within the bicyclic intermediate of the type **4** or **4′**, the third σ-bond is formed either between C1′ and C3′ or between C1′ and C5′, yielding the meta cycloadduct (in Scheme I only one alternative is shown).

Of these mechanisms, currently b and c are most probable and will be considered here. A common feature is that the electronic properties of the starting material (substitution pattern) strongly influence the mode of reaction (ortho or meta cycloaddition),[3,5] the regioselectivity,[4,5] and the stereoselectivity.[4,5] The observed selectivities can be attributed to a polarized transition state such as **2** or, alternatively, an exciplex intermediate **3**, the existence of which has been experimentally proven for certain arene–olefin systems.[12] Furthermore, the regio- and stereoselectivity may be influenced by intermediates of the type **4** or **4′** as well.[4,13-18] The recently reported correlation

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(1) Part 27 of Radical Ions and Photochemical Charge Transfer Phenomena. For part 26, see: Vondenhof, M.; Mattay, J.: Sulfonic Acid Esters Derived from 1,1′-Binaphthalene As New Axially Chiral Photosensitizers. *Tetrahedron Lett.* **1990**, *31*, 985.

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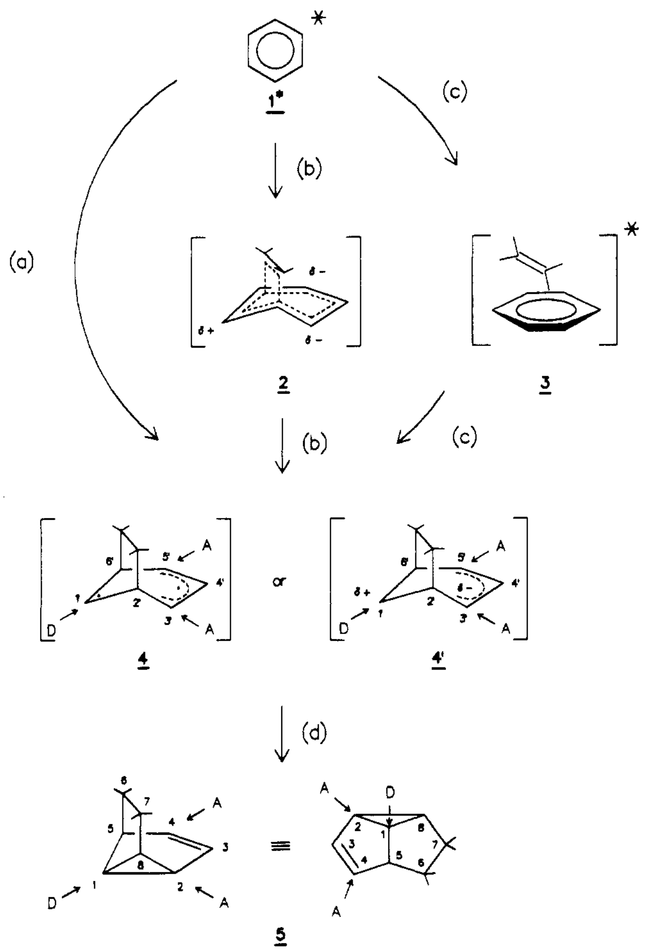
Scheme I



D: electron donor substituents

A: electron acceptor substituents

between the free enthalpies of the photoinduced charge transfer and the modes of reaction as well as the regio- and stereoselectivity for arene–olefin systems,[3-5] based on Weller's theory of photochemical electron transfer,[18] support the exciplex mechanism. However, the final decision cannot be made for all reactions, since exciplex emission measurement as well as the corresponding kinetic analyses have only been carried out for few systems.[7,12]

Summarizing these results: in meta cycloadditions donor substituents are generally found in position 1 whereas acceptor groups are located in positions 2 and 4.[4] Unfunctionalized alkenes (especially cyclic alkenes) show a high preference for the formation of endo cycloadducts. In contrast, with olefins that are substituted by strong electron-donating substituents (e.g. enol and enediol ethers) the stereoselectivity is reversed.[3,4,13-17] These findings support a preorientation of the starting materials in the excited state. This preorientation may be realized by a sandwich-like arrangement of the arene and the olefin. Originally Srinivasan and co-workers[20] postulated this arrangement for an exciplex (**3**), or for a polarized transition state (**2**). Two extremes are shown in Figure 1.[3-5]

In order to get more information about this preorientation in the excited state and its usability for controlling the stereoselectivity of meta cycloadditions (by utilizing molecular recognition phenomena, here: noncovalent interactions in the excited state), we have investigated the photoreactions of anisole (**7**) with five-membered ring olefins, which are substituted in the allylic position (*cis*- and *trans*-2,5-dihydro-2,5-dimethoxyfuran (**8**, **9**) as well as *cis*-1,4-dimethoxycyclopent-2-ene (**10**)).

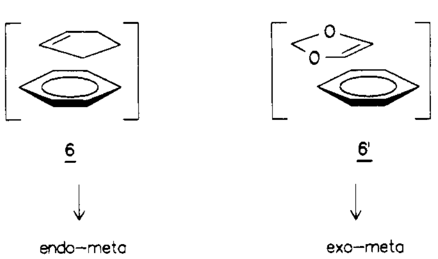


Figure 1.

Results

Upon irradiation of a solution of 0.4 M *cis*-2,5-dihydro-2,5-dimethoxyfuran (**8**) and 1.5 M anisole (**7**) in cyclohexane with a low-pressure mercury lamp in a quartz reaction vessel, a mixture of products is formed, containing two main products: 1,*exo*-4,6-trimethoxy-5-oxa-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (**11**, 66%) and 1,*endo*-4,6-trimethoxy-5-oxa-*exo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (**12**, 14%). In addition, two byproducts of 4% each and several others of less than 2% each were formed. None of these are 1:1 photoproducts.

Under the same conditions, irradiation of *trans*-2,5-dihydro-2,5-dimethoxyfuran (**9**) and anisole (**7**) in cyclohexane resulted in a mixture containing four main products: 1,*exo*-4,*endo*-6-trimethoxy-5-oxa-*exo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (**13**, 27%), 1,*endo*-4,*exo*-6-trimethoxy-5-oxa-*exo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (**14**, 10%), dimeric *trans*-2,5-dihydro-2,5-dimethoxyfuran (**15**, 23%), and an unidentified product (11%) which certainly is no 1:1 photoaddition product according to NMR analysis. Aside from the main products, 14 byproducts are formed, in yields of less than 5% each, an amount which is too small to allow product characterization.

Likewise, irradiation of a solution of 0.5 M *cis*-1,4-dimethoxycyclopent-2-ene (**10**) and 2.2 M anisole (**7**) in cyclohexane results in the formation of 1,*exo*-4,6-trimethoxy-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (**16**, 49%), 1,*endo*-4,6-trimethoxy-*exo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (**17**, 7%), and a third product (9%) which has not been identified.

The product ratios indicated were all determined at low conversion. In the case of **11**–**14** the ratios do not change significantly at higher conversion; in the case of **16** and **17**, however, this ratio changes to 38% (**16**), 14% (**17**), and 15% (unidentified product) at 80% conversion. Such a high conversion, however, is not recommended due to the evidential photolability of the products, an observation which has been made for meta photoadducts by others as well (e.g. Cornelisse[21]).

It is worth mentioning that irradiation of a 1:1 mixture of *cis*- and *trans*-2,5-dihydro-2,5-dimethoxyfuran (**8** and **9**) and anisole (**7**) yields the main products **11** and **13** in a ratio of 65% (**11**) to 14% (**13**) (~5:1), indicating that product formation is more favored in the cis than in the trans case. The most significant differences in reaction rates, however, are to be observed comparing 2,5-di-

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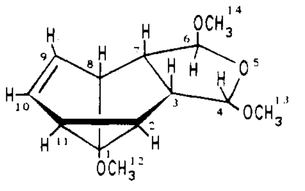
Table I. Chemical Shifts of the Meta Photoadducts



13

	11	12^b	13	14	16	17^b
H-2	1.95^a	1.86	2.83	2.00	2.06	2.19
H-3	3.35	2.23	2.30	2.49	3.13	2.38
H-4	4.75	4.78	5.08	4.95	3.54	3.44
H-5a	–	–	–	–	1.91	2.14
H-5b	–	–	–	–	2.28	1.84
H-6	4.57	5.01^c	5.30	4.94^c	3.33	3.41
H-7	3.54	2.48^c	2.45	2.55^c	3.45	2.30
H-8	3.04	3.11	3.23	3.43	3.04^e	3.36
H-9	5.47	5.48^d	5.36	5.40	5.41^e	5.45
H-10	5.57	5.46^d	5.41	5.44	5.55^e	5.48
H-11	1.95^a	1.99	2.02	1.91	1.98^e	1.87
OCH_3	3.11	3.17	3.16	3.22	3.08	3.17
	3.25	3.18	3.33	3.30	3.15	3.18
	3.30	3.28	3.35	3.35	3.17	3.20

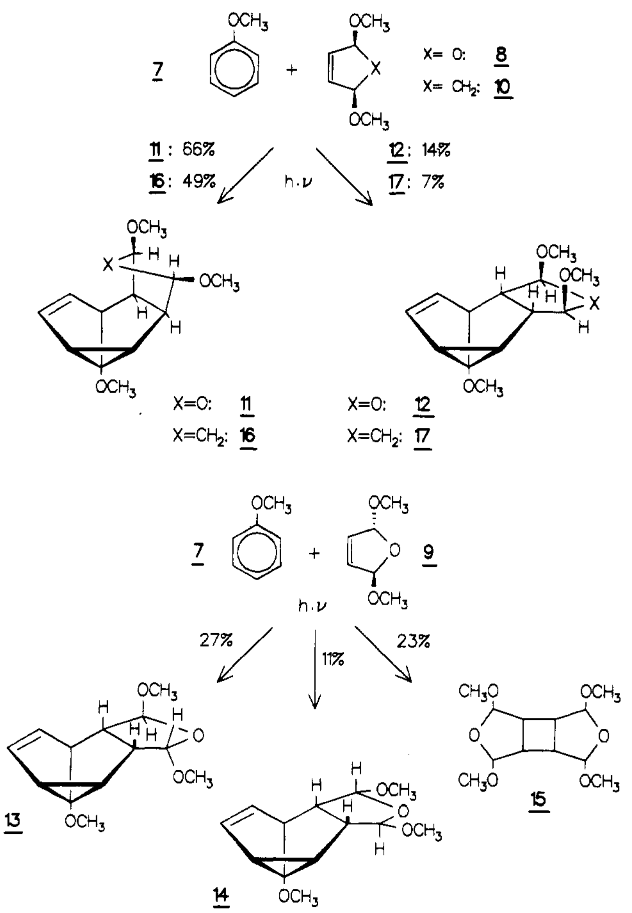
[a] H-2 and H-11 are incidentally isochrone and show a multiplet at 1.93–1.98 ppm. [b] Measured in $C_6D_6 + CS_2$ solution. [c] NOE experiment on H-8 is showing an effect on these H-atoms, the effect on the signals of H-9 and H-10 is ambiguous. [d] On decoupling H-8 the 2.2-Hz coupling within the signal at 5.48 ppm disappears leading to the indicated assignment. [e] On decoupling the 5.4 ppm signal the 2.8-Hz coupling within the signal at 3.04 ppm and a 1.2-Hz coupling at 1.98 ppm ($J_{9,11}$) disappear, on decoupling the 5.6 ppm signal the 2.3-Hz coupling within the signal at 1.98 ppm disappears.

hydro-2,5-dimethoxyfuran and 1,4-dimethoxycyclopent-2-ene: 85% of *cis*- (**8**) and 75% of *trans*-2,5-dihydro-2,5-dimethoxyfuran (**9**) are converted within 18 h of irradiation, whereas only 40% of *cis*-1,4-dimethoxycyclopent-2-ene are converted after 20 h.

The structure of the products was assigned by means of 300-MHz ^1H NMR spectroscopy. The chemical shifts of the meta adducts **11**–**14**, **16**, and **17** are compiled in Table I, and their coupling constants are presented in Table II.

The products **11** and **16** are both endo meta cycloadducts; this can be concluded from the coupling constants $J_{2,3}$ (4 and 6 Hz, respectively) and $J_{7,8}$ (6.8 and 7 Hz, respectively).[22] The coupling constant $J_{6,7}$ in compound **11** is too small to be observable, which implies that the angle between H-6 and H-7 must be nearly 90°. Consequently, the methoxy group at C-6 must have the exo configuration. Under the assumption that no isomerization in the olefin moiety occurs during the photoreaction (as will be shown below), the methoxy group at C-4 must have the exo configuration as well. In the case of **16** this assignment is not entirely certain, since the coupling constant $J_{6,7}$ of 2.3 Hz indicates a slight deviation from a 90° angle. However, this might be neglected since **16** is a highly strained (δ_{5a} and δ_{5b} nearly equal) molecule. The products **12** and **17** are exo meta cycloadducts since the coupling constants $J_{2,3}$ and $J_{7,8}$ are not observed.[22] The coupling between H-3 and H-4 in **12** is small as well, which means that the the angle between these H atoms is nearly 90°. Thus, the methoxy group at carbon 4 has the endo configuration. Taking into account that **12** and **17** are meta adducts of the cis isomers **8** and **10** and that no isomerization from the cis to the trans adduct has taken place (see below) the methoxy group at C-6 must also have endo configuration. Further support of the 4-endo,6-endo assignment is derived from the fact that compound **12** is not found among the products of *trans*-2,5-dihydro-2,5-dimethoxyfuran (and vice versa) as would be the case if cis to trans isomerization were a competing reaction.

Scheme II



The structure assignment of **13** and **14** follows the same reasoning: coupling constants $J_{2,3}$ and $J_{7,8}$ smaller than 0.5 Hz show that these compounds are exo meta adducts.

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[22] Jans, A. W. H. Thesis, Rijksuniversiteit Leiden, 1984.

Table II. Coupling Constants ^3J for the Meta Photoadducts[a]

	11	12	13	14	16	17
$J_{2,3}$	4	<0.5	<0.5	<0.5	6.6	<0.5
$J_{3,4}$	4	<0.5	5	≈0.7	6.8	9.4
$J_{3,7}$	9.8	5.8	6.0	7.3	11.5	6.2
$J_{4,5a}$	–	–	–	–	6.6	6.6
$J_{4,5b}$	–	–	–	–	7.3	10.6
$J_{5a,5b}$	–	–	–	–	14.0	11.3
$J_{6,5a}$	–	–	–	–	5.0	5.8
$J_{6,5b}$	–	–	–	–	6.5	11.3
$J_{6,7}$	<0.5	3.7	4.7	6.4	2.3	6.0
$J_{7,8}$	6.8	<0.5	<0.5	<0.5	7	<0.5
$J_{8,9}$	2.7	2	2.4	2.5	2.8	2.4
$J_{9,10}$	5.7	5.6	5.7	5.5	5.7	5.6
$J_{10,11}$	1.8	2.1	2.4	2.2	2.3	2.2
$J_{2,11}$	–[b]	8.7	8.9	8.7	8.5	8.8

[a] The entry "<0.5 Hz" indicates a coupling too small to be detected. [b] H-2 and H-11 are incidentally isochrone and show a multiplet at 1.93–1.98 ppm.

A coupling constant $J_{3,4} \approx 0.7$ Hz in compound **14** indicates an angle of ≈90° between H-3 and H-4. Thus the methoxy group at carbon-4 has endo configuration. Again assuming that no isomerization in the olefin moiety has taken place during reaction and isolation, the methoxy group at carbon 6 must have exo configuration. Since there are only two possibilities to build exo meta adducts with *trans*-2,5-dihydro-2,5-dimethoxyfuran (**9**) (methoxy group of anisole always in position 1, cf. ref 3), compound **13** must have the opposite configuration at the carbon atoms 4 and 6. The equivalence of the coupling constants $J_{3,4}$ and $J_{6,7}$ does not contradict this assignment since the conformation of the side-bonded five-membered ring is highly deformed by the high strain in the tetracyclic product.

The configuration assignments of the methoxy groups at C-4 and C-6 of all meta adducts are based on the supposition that isomerization of the olefin moiety does not take place during irradiation and workup procedure. To prove this assumption, compound **11**, dissolved in a mixture of hexane and ethyl acetate (60 + 40), was treated with acidic catalysts. Using weakly acidic ion exchangers with carboxyl groups as active groups, no reaction was observed. Using a strongly acidic ion exchanger with sulfonic acid groups as active centers, compound **11** was fully converted to a mixture of new products within 3 weeks. Although the structure of these products has not yet been clarified, it can be said that they are certainly no meta adducts, particularly none of the compounds **13** and **14**, which would be expected if the isomerization from the cis to the trans meta adduct were an important competing reaction.

Discussion

Since the early 1970s, it has been postulated that the meta photocycloaddition involves an exciplex or exciplex-like intermediate.[20,23,24] While there are only few examples of direct (spectroscopic) evidence,[12] Cornelisse has recently emphasized that an exciplex need not necessarily be involved. Nevertheless, the kinetic analysis of the Leiden group does not allow a definite decision for or against the existence of such an intermediate.[7] On the other hand, our investigation of the steric influence of allylic substitution on the stereochemical course gives further information about the reaction mechanism.[25]

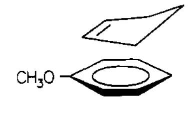

Figure 2.

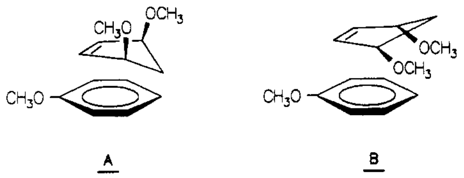

Figure 3.

The examples of intermolecular meta cycloaddition described in the literature exhibit the best efficiencies with five-membered ring olefins. In the case of carbocyclic alkenes the endo addition mode (cf. Figure 1) is always favored over the exo addition mode.[4] This effect has been attributed to "secondary interactions" of the H atom or certain orbitals of the C–H bond in the allyl position with the excited arene.[27,28] A simultaneous interaction of the alkene moiety and the allyl moiety with the arene is possible only when the olefin and the arene are arranged almost coplanarily, i.e. a sandwich-like arrangement of the reactants should be most favorable for the endo meta cycloaddition. In the case of cyclopentene this orientation is not hindered. Assuming an envelope conformation of the cyclopentene, a planar arrangement of the double bond and the allyl groups in regard to the S_1-arene[29] is not disturbed (Figure 2).[30]

Assuming an envelope conformation as the most favored for the dimethoxycyclopentene (**10**), too, the two possi-

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(23) Ferree, W.; Grutzner, G. B.; Morrison, H. *J. Am. Chem. Soc.* **1971**, *93*, 5502.

(24) Srinivasan, R.; Ors, J. A. *Chem. Phys. Lett.* **1976**, *42*, 506.

(25) Aside from two examples, the addition of 3-methylcyclopentene and 3,5-dimethylcyclopentene to anisole (ref 26), no allylic substituted alkenes have been used in meta photocycloaddition. The stereochemistry of this reaction type has never been reported on.

(26) Ors, J. A.; Srinivasan, R. *J. Org. Chem.* **1977**, *42*, 1321.

(27) Houk, K. N. *Pure Appl. Chem.* **1982**, *54*, 1633.

(28) Bryce-Smith, D.; Drew, M. G. B.; Fenton, G. A.; Gilbert, A. *J. Chem. Soc., Chem. Commun.* **1985**, 607.

(29) The meta photocycloaddition is generally assumed to proceed from the S_1 state of the arene, though this assumption has only been proven in a few cases (ref 12c, cf. introductory part of ref 7). Although, in the reaction of **7** and **9** the dimer **15** is formed, indicating that here the triplet state of anisole is involved, one should not conclude that triplet arene may also be involved in the meta additon. On the contrary, in the reaction where indications for triplet anisole is found, meta addition is least effective. Another example for this observation is the reaction of 1,3-dioxoles and benzene: unsubstituted 1,3-dioxole yields 60% cycloaddition products and less than 1% dimers, whereas 2,2-dimethyldioxole yields only 45% cycloadducts and about 2% dimers (ref 12b). This finding can be regarded as a confirmation that meta addition neccessarily proceeds from S_1, while only in cases where where meta addition is hindered, other reaction pathways proceeding via T_1 state are to be considered.

(30) The S_1 anisole is assumed to be planar similar to benzene and phenol for which calculations and experimental results are available: Padma Malar, E. J.; Jug, K. *J. Phys. Chem.* **1984**, *88*, 3508.

bilities of an arrangement of the reactants in the encounter complex shown in Figure 3 are to be considered for the endo addition mode. The arrangement B, with the methoxy groups directed toward the arene, evidently suppresses the reaction. Consequently no products are formed with an endo configuration of both the cyclopentene ring and the substituents. The only way to accomplish the endo cycloaddition is the encounter complex A with the methoxy groups directed away from the arene. But in this case a coplanar arrangement of the allylic C atoms and the C atoms of the double bond on one hand and the arene on the other is disturbed to some extent by the CH_2 group. Thus the cyclopentene ring must adopt a planarized conformation before the allylic secondary interactions mentioned above can come to effect. As a consequence the yield of the endo product **16** of dimethoxycyclopentene (4%) is much lower than the yield of the addition of the unsubstituted cyclopentene to anisole (>80%). The second consequence is a reduction of the endo:exo ratio from 9:1 for the unsubstituted cyclopentene to 7:1 for the dimethoxycyclopentene.

In general, the dihydrofuran **8** shows the same behavior. The even smaller endo:exo ratio of 4.7:1 is probably caused by electronic interactions between the lone pairs of the oxygen and the polarized arene. For a detailed discussion of photoinduced charge transfer and stereoselectivity cf. ref 4.

In the case of the trans-substituted compounds **9** the endo orientation of the five membered ring without endo orientation of a substituent is impossible. Correspondingly, the only meta cycloadducts to be found are exo adducts. Since exo orientation is not so favorable as described above, a different reaction pathway, that is the dimerization of **9**, becomes important.

In conclusion one can say: though the existence of an exciplex is not conclusively proven in most cases of meta photocycloadditions, the assumption of an exciplex-like arrangement of the reactants as an necessary step is the best model to predict the stereochemistry of the products.

Experimental Section

Apparatus. NMR spectra: Varian VXR 300 (300 MHz) with TMS as internal standard. Mass spectra: Varian MAT 212 (70 eV). GC: Carlo Erba Fractovap 2200 with FID and a packed column (length: 3 m, ϕ 3 mm, 5% OV 101 on Chromosorb WAW DMCS 80–100 mesh) for the reaction monitoring; all other gas chromatograms Siemens Sichromat 3 with FID, a capillary column Hewlett-Packard Ultra 1 (length 25 m, ϕ 0.2 mm, 0.33 μm thickness of the film) and an integrator of the Spectra Physics Co. HPLC: Gilson type 803, UV detector Gilson Spektrochrom M. differential refractometer type Bischoff, column Dynamax Si 60. Flash chromatography: glass column of about 1 m length and 80 mm diameter packed with silica gel 60 Machery-Nagel ordering no. 815 38 (0.04–0.063 mm, 230–400 mesh ASTM). TLC: aluminum foils (50 × 75 mm) coated with 0.2 mm silica gel 60 F_{254}, Merck ordering no. 5549. Irradiation experiments: photo reactor Gräntzel (Karlsruhe, Germany) type 400 with low-pressure mercury lamps surrounding a water-cooled reaction vessel of about 120 mL contents made of quartz glass.

Reagents. Anisole (a gift of the Bayer Co., Germany) was distilled prior to use. A mixture of the cis and trans isomers of 2,5-dihydro-2,5-dimethoxyfuran (Merck-Schuchardt ordering no. 803509) was separated into the isomers by distillation according to the literature.[31] The boiling points found are as follows. **8**: 62.5 °C (27 mbar) (lit.[31] 54 °C (13 Torr)). **9**: 65.4 °C (27 mbar) (lit.[31] 56 °C (13 Torr)). The cyclohexane used as solvent was of technical grade and was first distilled over phosphorus pentoxide followed by distillation over potassium carbonate. The ethyl acetate and the hexane (technical grade) used for chromatography were purified by distillation. The ethyl acetate was further purified by filtration over basic aluminum oxide.

***cis*-1,4-Dimethoxycyclopent-2-ene (10).**[32] To a solution of 9 g (90 mmol) of *cis*-1,4-dihydroxycyclopent-2-ene[33] and 57 g (400 mmol) of methyl iodide in 100 mL of dry *N*,*N*-dimethylformamide in a 1-L flask which is equipped with two effective reflux condensors on top of each other is added 38 g (250 mmol) of barium oxide.[34] After magnetic stirring during 30–60 min while heating with a water bath of 40 °C, a violent reaction suddenly takes place(!). After 2 min, the reaction has ceased and again 15 g (106 mmol) of methyl iodide is added. The mixture is refluxed for 5 h. The product slurry is then poured into water, and the product is extracted with a 1:1 mixture of ether and benzene, washed with brine until no DMF is detectable in the organic layer by means of GC, dried 24 h over $MgSO_4$, and distilled. The yield is 5.5 g (48%) of a colorless liquid of >99% (GC) purity. ^1H NMR (300 MHz, $CDCl_3$): δ 1.64 (1 H, dt, J = 13, J = 5, H-5), 2.67 (1 H, dt, J = 13, J = 7, H-5′), 3.47 (6 H, s, OCH_3), 4.37 (2 H, dd, J = 7, J = 5, H-1/4), 6.16 (2 H, s, H-2/3).

Irradiation Experiments. A 16-g (0.15-mol) portion of anisole and 5 g (0.04 mol) of the respective 2,5-dihydro-2,5-dimethoxyfuran isomer in 100 mL of cyclohexane are irradiated under a nitrogen atmosphere for 18 h. The experiment is repeated once to get enough material for the workup procedure. The solvent and most of the excessing anisole are removed under reduced pressure at 50 °C. The residue (≈3 g) is distilled at less than 1 Torr in a small-scale distillation apparatus. The temperature of the heating bath must not exceed 160 °C. The separation of the constituents of the distillate is accomplished in two steps: first by flash chromatography (ethyl acetate + hexane: (1) 15 + 85, (2) 40 + 60), then by HPLC (ethyl acetate + hexane, 25 + 75 to 40 + 60).

With 1,4-dimethoxycyclopent-2-ene the irradiations are performed accordingly with two exceptions: The optimum yield of meta adducts is reached after 40 h of irradiation (40% conversion) and the separation of products may be effected in one step by means of HPLC (eluant: 25% ethyl acetate + 75% hexane).

Isomerization Experiments. Compound **11** (40 mg) in 10 mL of a mixture of ethyl acetate and hexane (40 + 60) and 200 mg of the catalyst are allowed to stand at room temperature for 3 weeks with occassional shaking. The reaction is monitored by means of GLC every day. Four catalysts have been tested: Bayer CNO and CNP 80 (weakly acidic with carboxyl groups). Bayer Lewatit SC 104 H (strongly acidic with sulfonic acid groups), and *p*-toluenesulfonic acid. In the last case a mixture of eight products is obtained. With CNO and CNP 80 no reaction was observed. With SC 104 H a new product was formed aside from 1.5% of byproducts.

The purities (GC) of the compounds obtained were: **11**, >99%; **12**, >99%; **13**, 97%; **14**, 89%; **16**, >95%; **17**, >95%.

Elemental analysis for **11**–**14**: $C_{13}H_{18}O_4$ (238.3) Calcd C, 65.53; H, 7.61. Found **11**: C, 65.41; H, 7.63. **12**: C, 65.25; H, 7.78. **13**: C, 65.35; H, 7.72. **14**: C, 64.11; H, 7.74. **16**, **17**: $C_{14}H_{20}O_3$ (236.3) Calcd C, 71.16; H, 8.53. Found **16**: C, 67.90; H, 8.36. **17**: C, 70.31; H, 8.62.

Mol. mass **11**–**14**: 238 (MS). **16**, **17**: 236 (MS).

Mass spectra: **11**: m/z (%) 238 (2, M^+), 207 (3, $M^+ - CH_3O$), 179 (1), 178 (1), 177 (1), 175 (2), 163 (5), 147 (11), 135 (3), 131 (5), 130 (5), 115 (8), 109 (14), 108 (100, anisole), 103 (8), 101 (1), 99 (1), 91 (7), 78 (10, anisole − CH_2O), 77 (6, 78 − $H^\bullet$),[35] 75 (4), 71 (3), 65 (5), 45 (5), 41 (4).

12: m/z (%) 238 (0.1, M^+), 207 (14, $M^+ - OCH_3$), 179 (1), 178 (1), 177 (1), 175 (2), 163 (4), 147 (15), 135 (4), 131 (12), 130 (100), 115 (34), 109 (52), 108 (45, anisole), 103 (11), 101 (17), 99 (12), 94 (12), 91 (12), 78 (15, anisole − CH_2O), 77 (13, 78 − $H^\bullet$),[35] 75 (18), 71 (13), 65 (8), 45 (9), 41 (7).

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(32) Alkylation of *cis*-1,4-dimethoxycyclopentene using NaH/THF/CH_3I gives poor yields. Other methods of alkylation were not successful. Even the controlled addition of CH_3I to the system described did not result in weighable amounts of **10**.

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13: *m/z* (%) 238 (0.3, M^+), 207 (5, $M^+ - OCH_3$), 179 (2), 178 (7), 177 (9), 175 (1), 163 (5), 147 (20), 139 (5), 135 (4), 131 (11), 130 (26), 115 (10), 109 (18), 108 (100, anisole), 103 (9), 101 (17), 99 (17), 91 (10), 78 (16, anisole - CH_2O), 77 (9, 78 - $H^\bullet$),[35] 75 (23), 71 (12), 65 (8), 45 (10), 41 (8).

14: *m/z* (%) 238 (0.9, M^+), 207 (8, $M^+ - OCH_3$), 179 (2), 178 (8), 177 (9), 175 (1), 163 (5), 147 (20), 139 (5), 135 (4), 131 (11), 130 (29), 115 (9), 109 (18), 108 (100, anisole), 103 (9), 101 (16), 99 (20), 91 (10), 78 (15, anisole - CH_2O), 77 (9, 78 - $H^\bullet$),[35] 75 (23), 71 (13), 65 (8), 45 (10), 41 (8).

15: *m/z* (%) 260 (0.3, M^+), 259 (2, M^+ - H), 229 (21, $M^+ - CH_3O$), 197 (19), 168 (11), 140 (52), 139 (28), 137 (15), 125 (14), 109 (33), 101 (12), 99 (11), 97 (11), 75 (100), 45 (18), 41 (17).

16: *m/z* (%) 236 (0.4, M^+), 163 (2), 147 (3), 131 (3), 128 (1), 127 (6), 115 (3), 109 (9), 108 (100, anisole), 103 (5), 101 (5), 95 (4), 91 (5), 79 (3), 78 (11, anisole - CH_2O), 77 (5), 75 (3), 65 (5), 45 (5), 41 (4), 39 (4).

17: *m/z* (%) 236 (4, M^+), 172 (1), 163 (1), 147 (2), 146 (1), 131 (2), 129 (1), 128 (1), 127 (1), 117 (1), 115 (2), 109 (8), 108 (100, anisole), 103 (4), 101 (2), 97 (2), 95 (1), 93 (2), 91 (4), 79 (3), 78 (11, anisole - CH_2O), 77 (3), 75 (2), 65 (4), 45 (3), 41 (3), 39 (3).

^{13}C NMR data (C_6D_6, TMS, **15**: $C_6D_6 + CS_2$). **11**: 35.1, 37.5, 52.6, 52.7, 53.9, 55.4, 56.0, 69.3, 94.8, 105.7, 111.5, 128.8, 133.6. **12**: 35.5, 38.8, 50.2, 54.0, 54.2, 55.9, 56.2, 61.6, 89.0, 109.4, 111.0, 127.2, 134.0. **13**: 35.2, 35.5, 46.6, 53.5, 56.1, 57.0, 62.0, 89.2, 105.8, 107.6, 127.6, 133.0 (two C isochrone). **14**: 36.0, 40.3, 50.2, 51.6, 54.5, 56.5, 56.7, 58.0, 89.5, 106.2, 108.6, 127.1, 135.0. **15**: 39.1, 40.4, 53.8, 57.1, 105.8, 107.6. **16**: 37.3, 38.0, 42.1, 53.8, 53.9, 55.9, 56.1, 56.7, 67.9, 81.5, 85.9, 95.3, 130.8, 134.3. **17**: 35.4, 37.0, 37.3, 45.7, 51.1, 56.0, 56.4, 56.8, 57.4, 79.1, 79.2, 88.8, 127.4, 135.4.

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Registry No. **8**, 5143-07-7; **9**, 5143-08-8; **10**, 59415-72-4; **11**, 129215-89-0; **12**, 129263-09-8; **13**, 129263-11-2; **14**, 129263-12-3; **15**, 129215-91-4; **16**, 129215-90-3; **17**, 129263-10-1; DMF, 68-12-2; PhOMe, 100-66-3; MeI, 74-88-4; BaO, 1304-28-5; *cis*-1,4-dihydroxycyclopent-2-ene, 29783-26-4.

Through-Bond Interactions of β-Carbonyl and β-Imine Lone Pairs with Cationic 2p Orbital. Quantum Calculations on Bicyclo[2.2.2]oct-1-yl Cation and Derivatives[†]

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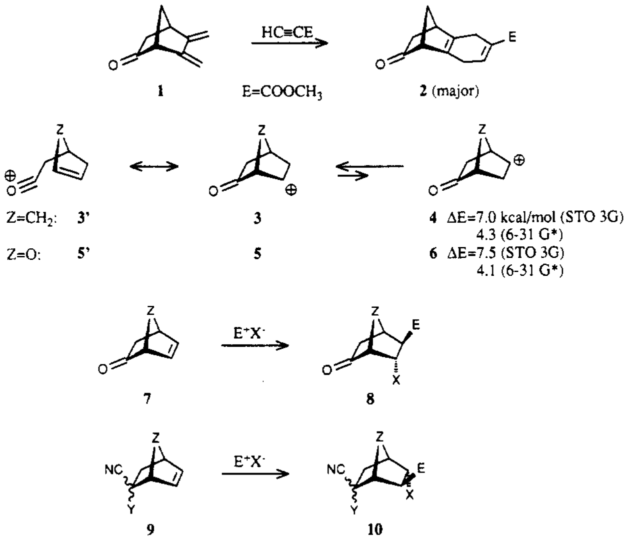
Semiempirical AM1 and ab initio STO 3G quantum calculations on bicyclo[2.2.2]oct-1-yl cation (**11**) and derivatives (**12–25**) substituted at C(2) or C(3) with electron-withdrawing groups such as Z = O, NH, CH_2, $C(CN)_2$ or X = CN and NO_2 suggested that the 3-oxobicyclo[2.2.2]oct-1-yl cation (**13**) and 3-(*E*)-iminobicyclo[2.2.2]oct-1-yl cation (**15**) are more stable than expected on the basis of the inductive effect of their oxo and imino substituents, respectively. This phenomenon has been attributed to favorable through-bond n(CO) ↔ σC(2),C(3) ↔ $p(C(1))^+$ and n((*E*)-NH=C) ↔ σC(2),C(3) ↔ $p(C(1))^+$ interactions. This electron-releasing effect of the imino substituents is less important in the 3-(*Z*)-iminobicyclo[2.2.2]oct-1-yl cation (**17**).

In a recent publication in this journal on the solvolysis of 3-oxobicyclo[2.2.2]oct-1-yl triflate and derivatives, Takeuchi and Yoshida[1] claimed to have discovered the first example of the through-bond interaction of the β-carbonyl lone pair with cationic p orbital. Already in 1978, we reported that 5,6-dimethylidenebicyclo[2.2.1]heptan-2-one (**1**) added to methyl propynoate with a relatively good "para" regioselectivity, giving **2** as major adduct.[2] The results were in agreement with predictions based on the FMO theory[3] which considers the HOMO(diene)-LUMO-(dienophile) orbital interaction to control the regioselectivity of the cycloaddition.[2,4] The shape of the HOMO of **1** suggested the intervention of a through-bond interaction of type n(CO) ↔ σ(C(1),C(2)) ↔ π(C(5),C(6)) making the p atomic coefficients at C(6)=CH_2 significantly larger than those at C(5)=CH_2.[4,5] Semiempirical MO calculations, first,[6] and than ab initio MO calculations[7,8] predicted that the 6-oxobicyclo[2.2.1]hept-2-yl cations **3**, **5** are more stable than their 5-oxo isomers **4**, **6** due to favorable n(CO) ↔ σ(C(1),C(6)) ↔ $pC(2)^+$ interactions that render the carbonyl group electron-releasing in the former carbocations. These predictions were supported by the regioselectivity observed for the electrophilic additions of enones **7** and of their synthetic precursors **9** which led to adducts **8** and **10**, respectively,[9,10] under conditions of kinetic control. We also found that an acyl group has a



[†] Dedicated to Dr. Paul von Ragué Schleyer on the occasion of his 60th birthday.

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