Photochemical Cycloadditions of 1,3-Dioxoles to Anisole †

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Anisole yields both *ortho*- and *meta*-cycloadducts upon irradiation in the presence of 1,3-dioxole and 2,2-dimethyl-1,3-dioxole. The mode and the regio- and stereo-selectivities of these cycloadditions are rationalized on the basis of the exciplex–zwitterion mechanism.

Although the photoadditions of aromatic compounds to alkenes have a long history of investigation,[1] different mechanisms having been proposed at least for the *meta*-cycloaddition,[1-6] only the 'exciplex-mechanism' provides a rationalization which fits all the experimental evidence.[7] In addition to the exciplex (3), dipolar intermediates of the type (4) have been proposed on various occasions[5,6,8-10] in order to explain the high regioselectivities of photocycloadditions with donor- and acceptor-substituted benzenes (1) (Scheme 1).

According to this hypothesis donor (D) substituents are preferentially located at position 1 of the *meta*-adduct (5) and (6), respectively, whereas acceptor (A) substituents are generally placed at position 2 or 4.

Here we describe the photoreactions of 1,3-dioxole (9) and 2,2-dimethyl-1,3-dioxole (8) with anisole (7) which complement already published results on the stereochemical aspects of *meta*-cycloaddition with 2-methyl-1,3-dioxole.[11]

Results and Discussion

Products.—The preparative irradiations ($\lambda = 254$ nm) of solutions which contain anisole (7) (1M) and 2,2-dimethyl-1,3-dioxole (8) or 1,3-dioxole (9) (both 2M), respectively, in 1,4-dioxane result in formation of the cycloadducts (10)—(17) (60—70% yield) (Scheme 2).

The products were isolated by h.p.l.c. and identified spectroscopically by ^{1}H and [13]C n.m.r. and by g.c.–m.s. The spectroscopic data of these new compounds were similar to those of the arene-1,3-dioxole adducts which have already been described.[8,11-13] The product ratio is very sensitive to the irradiation time and intensity. As shown in Table 1 high yields of the *ortho*-adducts (14)—(17) could be obtained only at very low conversions.

ortho-Cycloaddition is the main reaction with compound (8), and even with (9) the *ortho*-adducts are formed in 32% yield. However, the product ratios change in favour of the *meta*-adducts (10)—(13) at higher conversions. This photochemical behaviour of the *ortho*-cycloadducts has already been observed in other systems.[13] It should be noted that the *exo-meta–endo-meta* ratio is independent of the irradiation time, owing to the photochemical stability of these products.

There is no significant dependence on the solvent polarity for the formation of product. The quantum yields are independent within the experimental error (max. $\pm 15\%$) in cyclohexane ($\varepsilon = 2.02$), 1,4-dioxane ($\varepsilon = 2.21$), dibutyl ether ($\varepsilon = 3.08$), tetrahydrofuran ($\varepsilon = 7.58$), dichloromethane ($\varepsilon = 8.93$), propiononitrile ($\varepsilon = 27.2$), and acetonitrile ($\varepsilon = 37.5$) [for
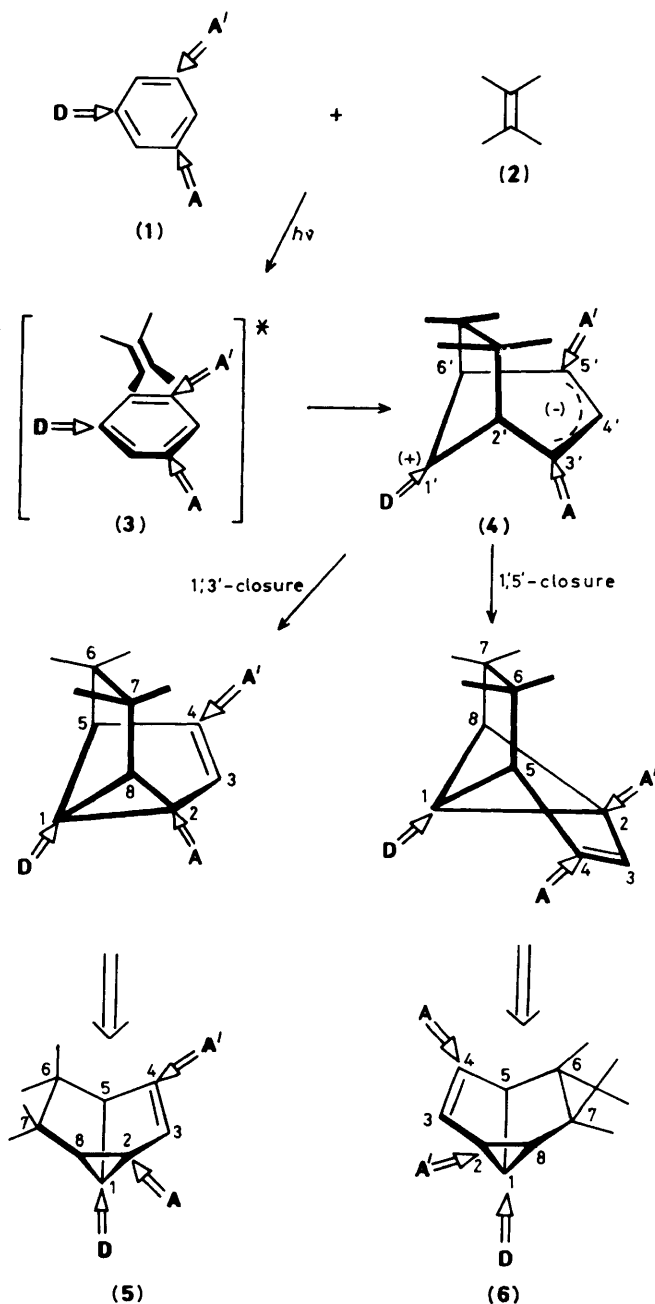
Scheme 1. Regioselectivity in *meta*-photocycloadditions of alkenes to substituted benzenes (**A** = electron acceptor substituent; **D** = electron donor substituent).
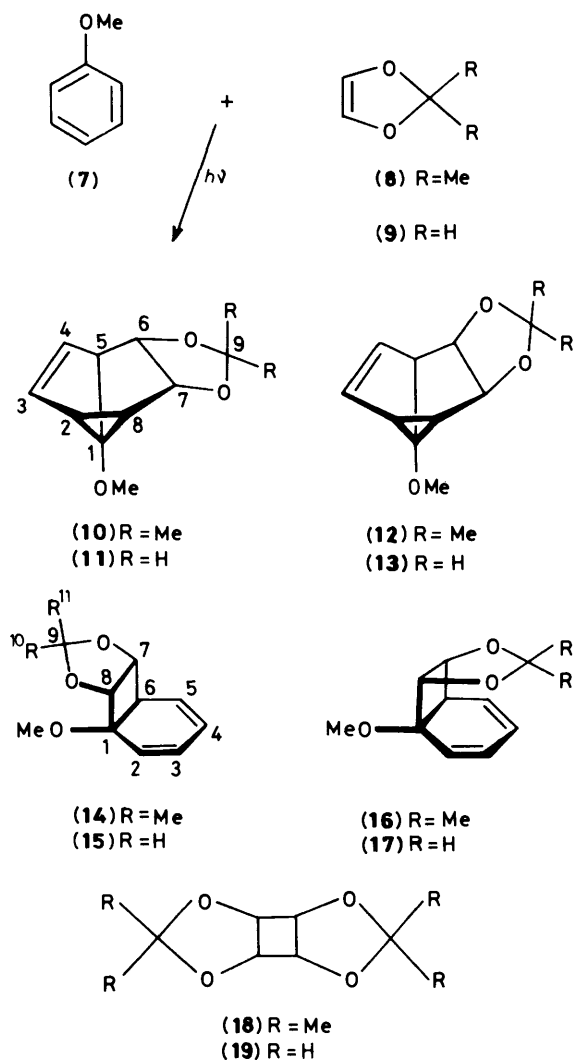
Scheme 2. Products of the photoreaction of anisole (7) with 1,3-dioxole (9) and 2,2-dimethyl-1,3-dioxole (8).
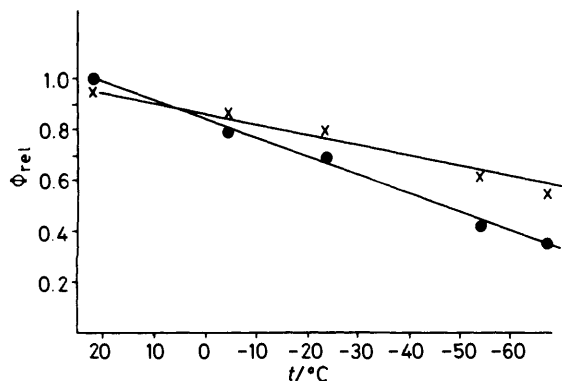

Figure. Temperature dependence of the relative quantum yields of product formation in the photoreaction of anisole (7) with 2,2-dimethyl-1,3-dioxole (8) in hexane (conversion 3%). × *exo-meta* (10); ● *ortho* (14) + (16)

dielectric constants (ε) see Reichardt].[14] Furthermore the formation of both the *meta*- and the *ortho*-adducts show similar deviations from the average (see Table 1) in a variety of solvents.

In contrast the *meta*- and *ortho*-cycloaddition adducts exhibit

Table 1. Product ratio in photoreactions of anisole (7) with 1,3-dioxoles (8) and (9)[a]

Conversion (%)	Products from (7) + (8)			Products from (7) + (9)		
	(10)	(12)	(14)[b] (16)	(11)	(13)	(15)[c] (17)
5	38	12	50	46	22	32
70	56	18	26	57	28	15

[a] The product ratio is given in percent referring to (10) + (12) + (14) + (16) = 100% or (11) + (13) + (15) + (17) = 100%, respectively. [b] The ratio of the *ortho*-adducts depends on the temperature and the reaction time due to a thermal rearrangement (see text). At room temperature (14):(16) = (4:1) according to analytical h.p.l.c. analysis of the reaction mixture. [c] This ratio is constant at room temperature: (15):(17) = (7:1).

Table 2. ^{1}H N.m.r. spectroscopic data [δ_H and J(Hz)] of (10)—(13)

H	(10) [^{2}H$_6$]-Acetone	(10) CS$_2$	(12) CS$_2$	(11) CS$_2$	(11) CDCl$_3$	(13) CDCl$_3$
2	2.21	2.10	2.07	2.15	2.31	2.31
3	5.64	5.57	5.63	5.59	5.67	5.83
4	5.51	5.40	5.51	5.43	5.50	5.72
5	3.40	3.32	3.24	3.37	3.55	3.47
6	4.29	4.14	4.85	3.93	4.09	5.07
7	4.10	4.02	4.96	4.06	4.20	4.94
8	2.10	2.03	1.89	1.99[b]	2.16	2.17
10[g]	1.47	1.42	1.46	4.70	4.86	4.96
11[g]	1.23	1.18	1.16[a]	5.06	5.23[c]	5.15[d]
OMe	3.34	3.28	3.23	3.25	3.37	3.36
$J_{2,3}$	2.1		2.0	2.2		2.3
$J_{2,4}$	1.2		1.0	1.2		0.7
$J_{2,5}$			0.5			
$J_{2,6}$	0.4			0.4		
$J_{2,8}$	9.0		8.6	8.9		8.6
$J_{3,4}$	5.7		5.7	5.6		5.7
$J_{4,5}$	2.6		2.6	2.6		2.8
$J_{4,8}$	0.7		0.6	0.7		
$J_{5,6}$	0.8		6.3	0.9		6.6
$J_{5,7}$	0.5		2.2			1.5
$J_{6,7}$	4.5		8.1	4.4		7.8
$J_{6,8}$	0.4		0.8	0.7		
$J_{7,8}$	e		5.0	f		5.8
$J_{10,11}$	0.6		0.6	0.7		

[a] N.O.e. [11-H] to 6-H, 7-H. [b] N.O.e. [8-H] to 7-H. [c] N.O.e. [11-H] to 6-H. [d] N.O.e. [11-H] to 6-H, 7-H. [e] $J_{7,10}$ 0.3 Hz. [f] $J_{7,11}$ 0.5 Hz. [g] 10,11 Indicate substituents R at C-9. (10) and (12): $R^{10,11}$ = Me; (11) and (13): $R^{10,11}$ = H.

different temperature dependence. This is shown for the reaction with (8) in the Figure, where both cycloaddition modes show negative temperature effects. However, the product formation decreases more in the *ortho*-mode at lower temperatures. These effects have been observed in both polar and non-polar solvents (hexane and tetrahydrofuran).

In addition to the cycloadducts (10)—(17) some minor products were detected by g.c. and h.p.l.c. At least 2 products in a *ca.* 1:2 ratio are formed for compounds (7) and (8), and at least 3 products are formed in a *ca.* 3:1:1 ratio from compounds (7) + (9). In the photoreactions with (9) the formation of by-products increases with longer irradiation times. The total yields of such by-products do not exceed 5% at low conversion.

All the products are [1:1] adducts of anisole and the corresponding 1,3-dioxole according to g.c.–m.s. analysis (some of them exhibiting unusually strong molecular peaks).

Table 3. ^{13}C N.m.r. spectroscopic data [δ_C (p.p.m.) and J(Hz)^b] of (10)—(13)

C	(10) [^{2}H$_6$]Acetone	(12) C$_6$D$_6$	(11) CDCl$_3{}^a$	(13) CDCl$_3{}^a$
1	88.92	92.84	87.49	91.83
2	36.52	37.32	35.07	36.45
3	129.78	129.58	128.93	129.84
4	130.14	134.85	128.71	132.47
5	55.07	54.88	53.61	54.10
6	88.65	89.60	87.83	89.23
7	81.70	83.55	80.14	83.49
8	41.39	33.78	38.89	33.28
9	110.95	113.82	95.12	99.43
10^c	27.59	25.58		
11^c	25.73	25.32		
OMe	56.73	56.16	56.04	56.02
2	168 (t,10)	168 (t,11)	168 (t,10)	167 (t,10)
3	164 (m,17)	169 (m,16)	167 (m,16)	167 (m,11)
4	164 (m,17)	169 (m,16)	167 (m,16)	169 (m,16)
5	143 (t,7)	140 (m,20)	142 (t,7)	142 (m,12)
6	154 (m,12)	152 (m,12)	157 (m,4)	154 (m,6)
7	156 (d,8)	151 (d,7)	158 (m,9)	152 (m,14)
8	166 (d,5)	166 (m,4)	170 (d,5)	168 (s)
9			167 (d,3)	167 (d,4)
10^c	127 (q,3)	126 (q,3)		
11^c	127 (q,3)	126 (q,3)		
OMe	143 (s)	142 (s)	143 (s)	143 (s)

^{a} Reference CDCl$_3$ δ = 77.00 p.p.m. ^{b} For long-range coupling constants the multiplicities and J-values are given in parentheses. For 'm' the sum of all J-values are given. ^{c} See note g of Table 2.

Table 4. ^{1}H N.m.r. spectroscopic data [δ_H and J(Hz)] of (14)—(17) in C$_6$D$_6$

H	(14)	(16)	(15)	(17)
2			5.37^b	
3	5.4	5.4	5.84	5.4
4	6.1^a	6.1^a	5.63	6.1^a
5			5.63	
6	2.93	2.59	2.72	2.07
7	3.94	4.44	4.10	4.51
8	4.39	4.67	4.30	4.78
10^c	1.63	1.52	5.12	5.05
11^c	1.23	1.13	5.22	5.28
OMe	2.99	3.00	2.93	2.93
$J_{6.7}$	3.9	6.4	3.6	6.9
$J_{6.8}$	1.2	2.1	1.2	2.5
$J_{7.8}$	5.1	5.7	5.0	5.7
$J_{10.11}$	0.6	0.6	0	0.7

^{a} Multiplet. ^{b} J_{26} 1.0 Hz, $J_{56} + J_{46}$ 3.0 Hz, $J_{35} + J_{34}$ 6.9 Hz, $J_{25} + J_{24}$ 2.0 Hz, and J_{23} 9.6 Hz. ^{c} See note g of Table 2.

The dimerization products (18) and (19) are formed in a *ca.* 10% yield. It is assumed that this process results from sensitization by the anisole triplet analogous to the photoreactions with benzene.[13]

N.m.r. Analysis of the Products.—The ^{1}H and ^{13}C n.m.r. spectroscopic data of compounds (10)—(13) are summarized in Tables 2 and 3. Both show typical chemical shifts and coupling constants expected for *exo-* and *endo-meta*-cycloadducts with a methoxy substituent at position 1.[6,8,11—13] The coupling between 5-H and 6-H and between 7-H and 8-H, respectively, is small ($J < 1$ Hz) for the *exo*-adducts (10) and (11) but large (J 5.0—6.6 Hz) for the *endo*-isomers (12) and (13). Recently, by the use of molecular models, the differences in the vicinal coupling J_{56} and J_{78} of the *meta*-adducts between benzene and

Table 5. ^{13}C N.m.r. spectroscopic data [δ_C (p.p.m.)] of (14)—(17) in C$_6$D$_6$.

| C	(14)^a	(16)^a	(15)^b	(17)^b
1	83.79^c	78.67^c	72.09	72.96
2^d	122.18	122.64	122.19	^{e}
3^d	124.37	124.37	123.75	123.34
4^d	126.51	124.83	125.53	123.91
5^d	127.84	128.59	127.44	128.51
6	48.77	39.33	44.59	41.78
7	78.67	75.18	80.13	77.30
8	83.86	85.94	84.00	84.04
9	113.81	114.44	95.70	99.20
10^f	27.61	26.25		
11^f	26.89	26.17		
OMe	50.21	50.78	50.29	50.47

^{a} Mixture of (14):(16) (1.4:1). ^{b} Mixture of (15):(17) (7:1). ^{c} Assignment of the C-1 resonances of (14) and (16) may be reversed. ^{d} Olefinic signals not assigned. ^{e} One of the olefinic signals is hidden by signals of the solvent or of (15). ^{f} Assignment of CH$_3$ resonances may be reversed. See also note g of Table 2.

1,3-dioxole have been interpreted as being due to different dihedral angles.[8] The assignment of the 6-H and 7-H resonances in the *exo*-isomer was unclear. However the assignments of the 6-H and 7-H resonances of the *endo*-isomer (12) have been confirmed by n.O.e. experimentation. The 7-H signal shows a 10% increased integration upon irradiation of 8-H due to the small distance between 8-H and *exo*-7-H. The ^{13}C n.m.r. spectra of the isomers (11) and (13) are assigned using a ^{13}C–^{1}H 2D n.m.r. spectrum of the main isomer (11). The assignment of the structures (10) and (12) have been performed similarly.

Tables 4 and 5 show the ^{1}H and ^{13}C n.m.r. data of compounds (14)—(17). Here the methoxy group is also located at position 1, and all products show three cyclobutane and four olefinic proton signals. The *exo–endo* assignment has been performed as follows. (*i*) The coupling constant J_{67} are larger for the *endo*-adducts (16) and (17) (measured 6.4 and 6.9 Hz) compared to the corresponding parameters of the *exo*-isomers (14) and (15) (measured 3.9 and 3.6 Hz) as a result of smaller dihedral angles in the *endo*-structure; (*ii*) the cyclobutane protons 7-H and 8-H of (14) and (15) are shifted upfield in comparison to those of (16) and (17). This may be caused by the anisotropy effect of the diene group.[12b]

Thermal Rearrangement of the ortho-*Adducts* (14) *and* (16).— At first sight the formation of both the *exo*- and the *endo-ortho*-adducts (14) and (16) is surprising, since in all other reactions with 1,3-dioxoles only the products with an *exo*-configuration have been observed.[8,10—13] The situation seems to be even more complicated because (9) yields almost exclusively the *exo-ortho*-adduct (15). This apparent contradiction is simply explained by a thermal rearrangement between (14) and (16) (Scheme 3). The *endo*-isomer (16) is formed only in small amounts as evidenced by h.p.l.c. analysis of the crude reaction mixture. After work-up *via* chromatography or distillation the (14):(16) ratio is 1.2:1 in hexachlorobuta-1,3-diene. It was further shown by quantitative ^{1}H n.m.r. analysis that this rearrangement is totally reversible up to 80 °C. Thus when this mixture was heated in a sealed n.m.r. tube at 80 °C for 20 min the ratio increased to 1.4:1. When left at room temperature overnight the ratio again levels off to the starting value. This procedure is repeatable with the same result.

Two alternative mechanisms may explain the observed thermal isomerism. (*i*) In addition to the regioselectivity a rearrangement *via* a zwitterionic intermediate of the type (20) would explain the formation of the *endo-ortho*-adducts at the start of the photoreaction (Scheme 4). This process is supported
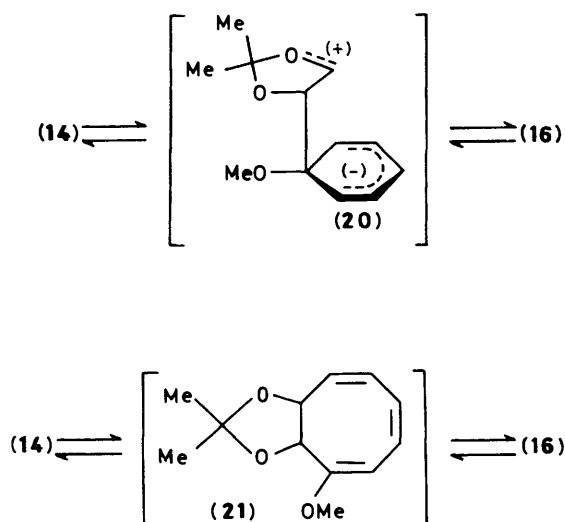
Scheme 3. Alternative mechanisms of the thermal equilibrium between the *exo-* and *endo-ortho*-adducts (14) and (16)
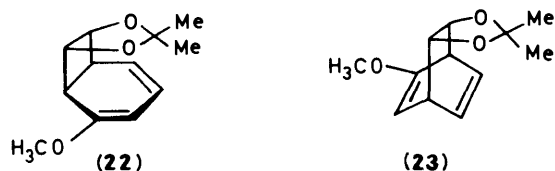

A further stepwise rearrangment *via* diradical type intermediates or a rearrangement by an [1,5] sigmatropic shift should also yield regioisomeric *ortho*-adducts of the type (22) and eventually *para*-adducts, *e.g.* (23). However, the latter products have not been observed.

(*ii*) Rearrangement *via* a cyclo-octatriene intermediate (21) may provide an alternative explanation for the high regioselectivity. Experimental criteria to distinguish between these two possibilities is so far not forthcoming.

The Exciplex–Zwitterion Mechanism.—The selectivities of the photocycloadditions are in accordance with those of other photoreactions between arenes and alkenes and may be explained on the basis of a correlation with the free enthalpy of electron transfer.[7] According to the empirical ΔG rule both *ortho-* and *meta*-cycloaddition are observed in photoreactions of anisole with electron-rich alkenes. Furthermore, the *ortho*-reaction mode should increase with increasing CT character of the exciplex intermediates. This effect is actually observed in the reaction with the stronger donor (8) (see Table 1).

The preferred formation of cycloadducts of *exo*-configuration can also be rationalized on the basis of the exciplex-mechanism depending on the direction of the photo induced charge transfer.[7] According to this model, excited anisole acts as the acceptor leading to an intermediate of the type (24) with a negative charge in the arene portion. The electronic repulsion between the negatively charged arene and the n-orbitals of the oxygens in the dioxole ring causes the *endo*-approach to be less favoured. The same interactions should be effective in dipolar intermediates of the type (20) and (25).
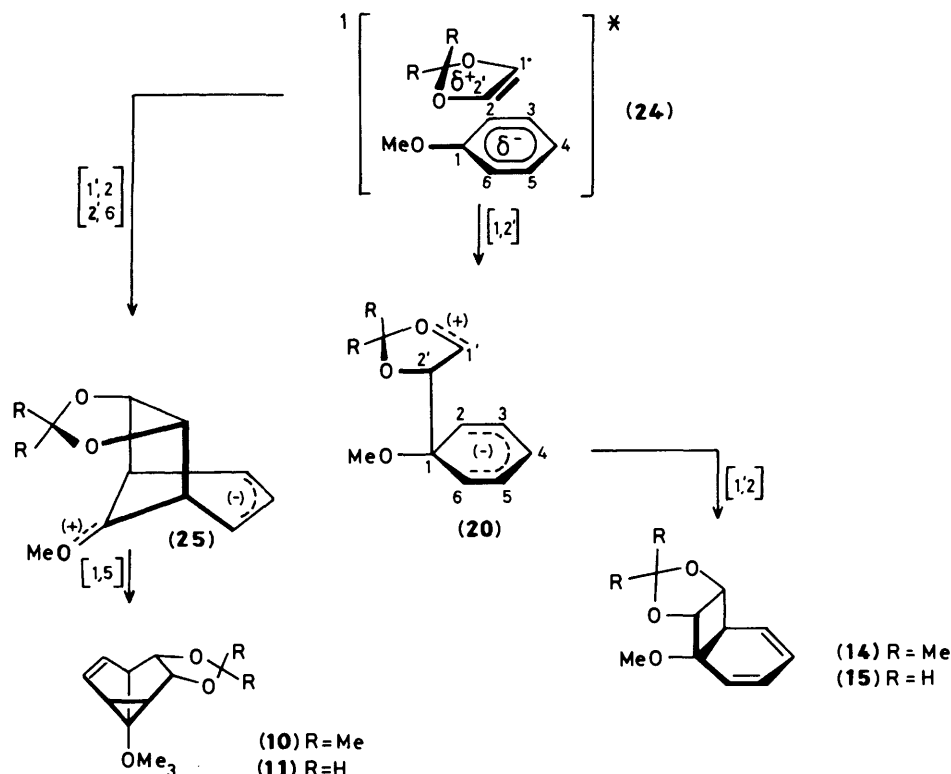
Scheme 4. Exciplex–zwitterion mechanism of *ortho-* and *meta*-cycloaddition of 1,3-dioxoles to anisole

by (8) indicating a pronounced degree of charge separation within the intermediate (20). This may also be reflected in the increased charge transfer (CT) between the starting materials (7) and (8) compared to (7) and (9) which can easily be derived by applying the Weller theory of electron transfer.[7,15]

The origin of the high regioselectivity of both the *meta-* and *ortho*-cycloadditions can be easily understood by assuming the involvement of dipolar intermediates which, can be represented as the zwitterions (20) and (25) (Scheme 4). The assumption of dipolar intermediates is in accord with the exciplex-mechanism,

since we could show in our kinetic studies that an exciplex [here (24)] is a necessary, but not a direct precursor of the products. The methoxy substituent can stabilize the positive charge in position 1 of (25). The exclusive formation of 1-substituted *ortho*-adducts may be interpreted by assuming various mechanisms. One possibility is presented in Scheme 4 where stepwise C–C bond formation leads to the dipolar intermediate (20) which mainly forms the *exo-ortho*-adduct. Rotation around the C(1)–C(2') bond plays a minor role since the *endo*-isomer is formed in only small amounts at the beginning of the reaction [see above for the thermal rearrangement between (14) and (16)]. Alternative single-bond formation between C(1') and C(2) may be excluded since the methoxy group would destabilize the negative charge at position 1.

The more complex mechanism of the *ortho*-cycloaddition[7b] may be reflected in its temperature dependence indicating a higher free enthalpy of activation (Figure).

The absence of a significant dependence of both the product quantum yields and the product ratios on the solvent polarity is not clear since Cornelisse[6,9] and we ourselves[5,12] have found such effects in other systems. This may serve to highlight the complexity of the mechanism with compensating effects of the individual elementary steps.

Experimental

Commerically available anisole was purified by distillation. The 1,3-dioxoles were synthesized according to Field.[16] Spectrophotometric grade solvents (from Fluka) were used for quantitative measurements. For preparative procedures the solvents were purified by standard methods; peroxides were removed from ethers and methylene dichloride was distilled over potassium carbonate.

I.r. spectra were recorded on a Perkin-Elmer–377 Spectrometer. ^{1}H And ^{13}C n.m.r. spectra were measured using a Varian EM 390 (90 MHz), a Varian CFT 20 (20 MHz) and a Bruker WM 300 (300 MHz) spectrometer, respectively. For n.m.r. data see Tables 2—5. Gas chromatographic analyses were performed on a Carlo Erba Fractovap 2101 using OV 17, OV 101 and NPGS glass columns, all 5—10% on Chromosorb WAW DMCS 80—100 mesh. A Perkin-Elmer-Ser 3-LC-65 T and a Gilson-303-Chromatograph were used for analytical and preparative liquid chromatographic separations, respectively. In both cases Lichrosorb Si60 columns (Merck) and mixtures of ethyl acetate (a maximum of 5%) in hexane as eluants were used.

All products were pure after h.p.l.c. isolation. Only the *ortho*-adducts needed to be chromatographed again in order to obtain at least 95% purity.

Irradiation Conditions.—Preparative irradiations were carried out in a photoreactor from Grāntzel (160 W low-pressure mercury lamp, quartz filter) containing 100 ml of a solution of 1M anisole and 2M 1,3-dioxole under a nitrogen atmosphere. In some cases a photoreactor fitted with a quartz immersion well and a low-pressure mercury lamp TNN 15 W (from Heraeus) was also used. The reaction mixture was checked by analytical g.c. After *ca.* 10 h (160 W lamp) or *ca.* 2 days (15 W lamp) the reaction was stopped (*ca.* 50% conversion). In order to isolate the *ortho*-adducts only the 15 W lamp was used owing to the photochemical lability of these products. In such cases the conversion did not exceed 20%. Irradiations for analytical purposes were performed in a 'merry-go-round' apparatus (from H. Mangels, Bornheim-Roisdorf) which was fitted with a TNN 15 W lamp. The concentration of the starting materials and the products were determined by means of g.c. using dibenzyl as internal standard. Analytical h.p.l.c. measurements were also performed in order to check the peak assignment and to eliminate thermal rearrangement reactions of the products. The

h.p.l.c. technique provided efficient separation of the *endo-* and *exo-ortho*-adducts.

Product Isolation.—After the solvents had been distilled off at room temperature, the product mixtures were either distilled at *ca.* 60—70 °C/0.1 Torr or were purified by filtration over silica gel (Woelm 32—100 mesh). The latter method was used especially to isolate enriched samples of the labile *exo-ortho*-adduct (14). The crude product mixtures were then separated by means of semi-preparative h.p.l.c. (Si 60).

Products* *from Compounds* (7) *and* (8).—The dimerization product of (8) started to crystallize in the reaction mixture. Further product was isolated during the h.p.l.c. procedure. The product was identified as trans-1,2,3,4-*bis(isopropylidenedioxy)-cyclobutane* (18) by comparison with an authentic sample.[13a]

exo-6,7-*Isopropylidenedioxy-1-methoxytricyclo*[3.3.0.0^{2,8}]-*oct-3-ene* (10). Colourless oil (Found: C, 69.05; H, 7.6. Calc. for C$_{12}$H$_{16}$O$_3$: C, 69.21; H, 7.75%) *m/z* 208 (0.1% *M*$^+$), 193 (2.2 *M*$^+$ – CH$_3$), 151 (7.8), 150 (3.4, *M*$^+$ – acetone), 135 (2.5, *M*$^+$ – acetone – CH$_3$), 133 (6.8), 121 (62.2, C$_8$H$_9$O$^+$), 119 (7.5), 108 [18.1, (7)$^+$], 107 (12.3), 101 (11.7), 100 [100, (8)$^+$], 91 (26.3), 86 (13.7), 85 [100, (8)$^+$ – CH$_3$], 79 (12.1), 78 (18.6), 77 (22.0), 65 (17.8), 60 (35.3), 51 (10.7), 43 (49.7), and 41 (18.3).

endo-6,7-*Isopropylidenedioxy-1-methoxytricyclo*[3.3.0.0^{2,8}]-*oct-3-ene* (12). Colourless oil (Found: C, 68.95; H, 7.65%) *m/z* 208 (0.1%, *M*$^+$), 193 (0.7, *M*$^+$ – CH$_3$), 151 (1.9), 150, (2.5, *M*$^+$ – acetone), 135 (2.0, *M*$^+$ – acetone – CH$_3$), 133 (1.7), 121 (15.6, C$_8$H$_8$O$^+$), 119. (5.3), 108 [6.5, (7)$^+$], 107 (7.6), 101 (4.5), 100 [75.6, (8)$^+$], 96 (4.5), 91 (10.4), 86 (4.7), 85 [100, (8)$^+$ – CH$_3$], 79 (6.7), 78 (7.4), 77 (10.5), 65 (7.2), 60 (9.3), 51 (3.9), 43 (12.7), and 41 (5.4).

exo-7,8-*Isopropylidenedioxy-1-methoxybicyclo*[4.2.0]*octa-2,4-diene* (14). Colourless oil (Found: C, 68.9; H, 7.7%) compound (14) contains *ca.* 24—40% of the *endo*-isomer (16) according to h.p.l.c. analysis; *m/z* 208 (0.1%, *M*$^+$), 193 (0.5, *M*$^+$ – CH$_3$), 151 (1.4), 150 (1.2, *M*$^+$ – acetone), 135 (0.6, *M*$^+$ – acetone – CH$_3$), 133 (1.3), 121 (13.3, C$_8$H$_9$O$^+$), 119 (4.5), 111 (2.3), 108 [6.2, (7)$^+$], 107 (3.3), 101 (3.5), 100 [67.0, (8)$^+$], 91 (13.7), 86 (4.1), 85 [100 (8)$^+$ – CH$_3$], 79 (6.2), 78 (9.5), 77 (10.8), 73 (14.0), 65 (11.4), 60 (17.3), 51 (6.5), 43 (26.5), and 41 (14.8).

endo-7,8-*Isopropylidenedioxy-1-methoxybicyclo*[4.2.0]*octa-2,4-diene* (16). This compound was only obtained in a mixture with the *exo*-isomer (14) as a colourless oil. Since gas chromatographic separation was not possible the g.c.–m.s. data are recorded together with (14).

At least two minor products in a *ca.* 1:2 ratio are also formed (yield <5%). The mass spectra are similar to those of compounds (10), (12), and (14). One compound exhibits an unusual strong molecular peak (34.5% compared with 0.1—0.5% of the other identified products.).

Products* *from Compounds* (7) *and* (9).—Here the dimerization products of (9) were isolated by h.p.l.c. and were identified as trans- and cis-1,2;3,4-bis(methylenedioxy)cyclobutane (19a) and (19b) by comparison with an authentic sample.[13a]

1-*Methoxy*-exo-6,7-*methylenedioxytricyclo*[3.3.0.0^{2,8}]*oct-3-ene* (11). Colourless oil (Found: C, 66.55; H, 6.6. Calc. for C$_{10}$H$_{12}$O$_3$: C, 66.65; H, 6.7%) *m/z* 180 (0.1% *M*$^+$), 150 (0.2, *M*$^+$ – CH$_2$O), 135 (0.5, 150 – CH$_3$), 121 (3.7, C$_8$H$_9$O$^+$), 109 (10.3), 108 [100, (7)$^+$], 107 (3.5), 93 [8.1, (7)$^+$ – CH$_3$], 91 (10.7), 79 (12.4), 78 (45.6), 77 (15.4), 73 (5.1), 72 [100, (9)$^+$], 71

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* The *meta*-adducts may also be described as derivatives of 1-methoxy-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-enes.[6] However, we have chosen the tricyclo as the basic molecular framework for reasons of simplicity. Analogous arguments count for the description of the *ortho*-adducts.

(35.7), 65 (23.6), 63 (4.4), 55 (2.2), 53 (5.2), 52 (5.6), 51 (10.8), 50 (3.8), 45 (2.5), 43 (2.7), and 41 (4.7).

1-*Methoxy*-endo-6,7-*methylenedioxytricyclo*[3.3.0.0^{2,8}]*oct*-3-*ene* (**13**). Colourless oil (Found: C, 66.5; H, 6.5%) m/z 180 (0.1% M^+), 150 (0.2, $M^+ - CH_2O$), 135 (0.6, 150 $- CH_3$), 121 (4.3, $C_8H_9O^+$), 109 (11.2), 108 [100, (7)$^+$], 107 (3.9), 93 [9.2, (7)$^+ - CH_3$], 91 (11.9), 79 (13.9), 78 (51.1), 77 (17.6), 73 (5.5), 72 [100, (9)$^+$], 71 (40.5), 65 (27.2), 63 (5.2), 55 (2.6), 53 (5.6), 52 (7.3), 51 (12.7), 50 (4.5), 45 (3.2), and 43 (3.1), and 41 (5.5).

1-*Methoxy*-exo-7,8-*methylenedioxybicyclo*[4.2.0]*octa*-2,4-*diene* (**15**). Colourless oil (Found: C, 66.5; H, 6.6%) compound (**15**) contains *ca.* 13% of the *endo*-isomer (**17**) according to h.p.l.c. analysis; m/z 180 (0.2%, M^+), 150 (0.6, $M^+ - CH_2O$), 135 (0.8, 150 $- CH_3$), 121 (6.3, $C_8H_9O^+$), 109 (8.7), 108 [100, (7)$^+$], 107 (3.7), 93 [6.9, (7)$^+ - CH_3$], 91 (10.6), 79 (10.9), 78 (39.5), 77 (14.3), 73 (4.5), 72 [100, (9)$^+$], 71 (28.9), 65 (22.9), 63 (4.6), 55 (2.2), 53 (4.5), 52 (5.3), 51 (10.6), 50 (4.0), 45 (3.4), 43 (2.6), and 41 (4.3).

1-*Methoxy*-endo-7,8-*methylenedioxybicyclo*[4.2.0]*octa*-2,4-*diene* (**17**).—This compound was only obtained in a mixture with the *exo*-isomer (**15**) as a colourless oil. Since gas chromatographic separation was not possible, the g.c.–m.s. data are recorded together with (**15**).

At least three minor products were formed (yield $<5\%$), which have been assigned as 1:1 adducts from compounds (**7**) and (**9**) according to their g.c.–m.s. spectra. The main compound exhibits an unusual strong molecular peak (23.0% compared to maximal 0.2% of the other identified products).

Acknowledgements

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