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THE *META* PHOTOCYCLOADDITION OF ANISOLE TO OXA- AND DIOXA-CYCLOPENTENES AND TO ETHYL VINYL ETHER

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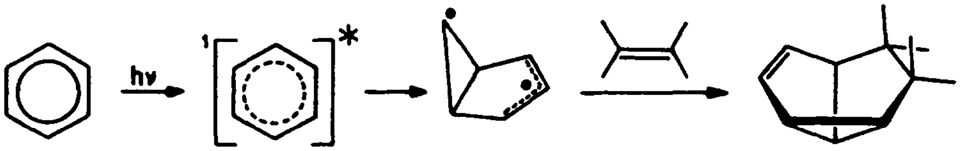
Abstract. The *meta* photocycloaddition of anisole to 2,3- and 2,5-dihydrofuran, 1,3-dioxole and ethyl vinyl ether is described. The NMR data of the adducts are presented. The reaction yields mixtures of *endo* and *exo* adducts. The *endo*/*exo* ratio is strongly influenced by the presence of one or two oxygen atoms next to the double bond of the alkene. A mechanism is presented in which a zwitterionic intermediate is formed from the excited anisole and the alkene.

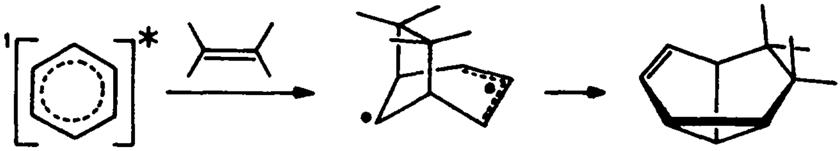
INTRODUCTION

Several mechanisms have been proposed for the intriguing *meta* photocycloaddition of benzene derivatives to alkenes.[1,2,3,4]

Prefulvene, which is also supposed to play a role in the formation of benzvalene from singlet excited benzene, has been invoked as an intermediate.[1,5]



In an alternative pathway the primary chemical step consists of bond formation between the termini of the olefinic bond and two *meta* carbon atoms of the excited benzene.[3,6,7]



Closure of the three membered ring occurs in the second step. The intermediate might be a diradical or a zwitterion.[7]

A fully concerted reaction has been considered unlikely because it cannot be reconciled with the observed regio- and stereoselectivity of the *meta* photocycloaddition reaction.[3,8]

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Prior to the formation of the diradical or the zwitterion an exciplex might be formed from excited benzene and the alkene.[9]

Neither prefulvene, nor the biradical or the zwitterion have ever been detected as an intermediate in the reaction. Exciplex emission has only been observed in a few cases.[10,11]

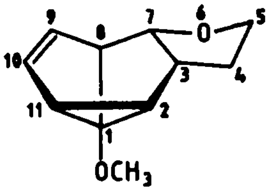
We have investigated the *meta* photocycloaddition of anisole to oxa- and dioxa-cyclopentenes and to ethyl vinyl ether and we have compared the results with those obtained for anisole and cyclopentene that were reported earlier.[12,13]

RESULTS

Anisole and 2,3-dihydrofuran

A solution of anisole (1 M) and 2,3-dihydrofuran (3.5 M) in methanol was irradiated for 80 hours with light of 254 nm. The presence of two photoproducts in the ratio of 1 : 1 was detected by analytical GLC (2 m, 10 % SE 30). These products were separated by preparative GLC (6 m, 20 % SE 30). A preliminary 300 MHz ^1H NMR study showed that the fraction with the shortest retention time was still a mixture of two products in the ratio of 2 : 1, while the second fraction consisted of only one product. The first fraction was separated on a different column with DEGS material into its two components.

The three products could be identified as *meta* photoadducts of anisole to 2,3-dihydrofuran by means of NMR spectroscopy.



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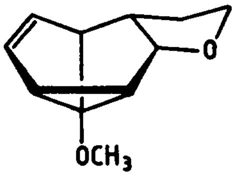

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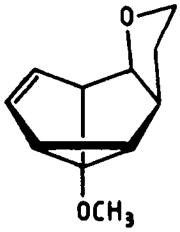

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In Figure 1 a spin echo shift correlated spectrum (SECSY) of compound 1 is represented as a contour plot. A 300 MHz ^1H NMR spectrum is displayed along the top of the plot. The horizontal axis of the contour plot is the chemical shift scale from 1 to 6 ppm (relative to TMS), the vertical axis spans the largest $\Delta\delta$ value, in this case 4 ppm. The diagonal lines represent the chemical shift connectivities: they indicate which protons are coupled with each other.

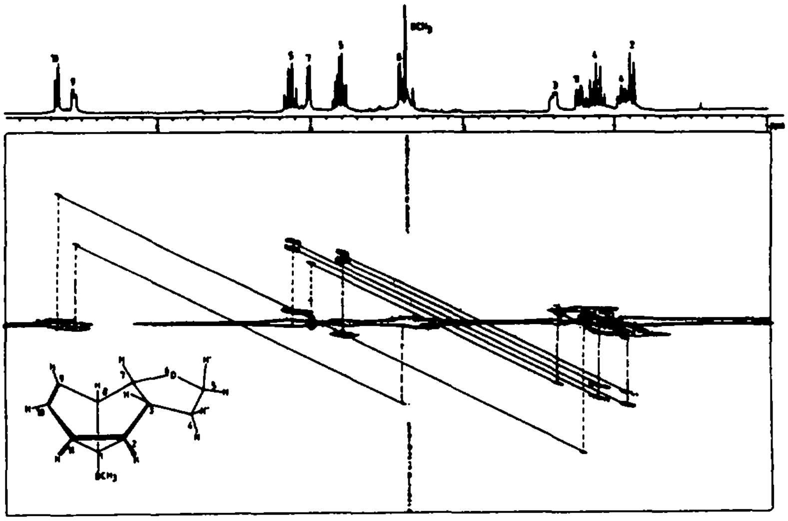


Fig. 1. Contour plot of a 300 MHz SECSY experiment of compound 1 in $CDCl_3$ at 298 K.

Compound 1, 1-methoxy-6-oxa-*exo*-tetracyclo[6.3.0.$0^{2,11}$.$0^{3,7}$]undec-9-ene, is the major component of the fraction with the shortest retention time on SE 30. A comparison of its NMR spectrum with that of the adduct formed from anisole and cyclopentene[14] shows that the compound must be a *meta* photoadduct.

The signals at 5.55 and 5.64 ppm can be assigned to the olefinic protons. The singlet at 3.36 ppm must be ascribed to the methoxy group. A NOE difference experiment on this group shows an effect on the doublet at 1.87 ppm and on the double doublet at 2.23 ppm. The latter proton couples with the former and also with one of the olefinic protons (5.64 ppm) as can be seen from the SECSY plot. The methoxy group is not situated at position 8 or 11 since there is no NOE on the olefinic protons. Therefore, the methoxy group must be either at position 1 or at position 2. This implies that carbon atoms 8 and 11 must bear a hydrogen atom. Each of the olefinic protons will therefore couple with the other olefinic proton and with one other proton. The olefinic proton at 5.55 ppm couples with the proton at 3.40 ppm. A NOE difference experiment on this proton shows that it is close to the olefinic proton and to the proton resonating at 4.00 ppm. The latter proton must be H-3 or H-7, *i.e.* at a carbon atom next to oxygen, It can now be concluded that the proton at 3.40 ppm is H-8 because this is the only proton in the vicinity of the low field proton at 4.00 ppm that is coupled with an olefinic H. This implies that H-7 is at 4.00 ppm and that the oxygen atom occupies position 6. The proton resonating at 5.55 ppm must be H-9 and the one at 5.64 ppm is thus H-10. The latter couples with the one at 2.23 ppm which must therefore be H-11. The signal at 1.87 ppm is that of one of the cyclopropane protons because it couples with H-11. The NOE difference experiment on H-8 (3.40 ppm) does not change the doublet at 1.87 ppm. Thus, this doublet cannot originate from H-1, but must belong to H-2. The methoxy group is situated at position 1.

Neither H-8 nor H-2 shows any coupling with a bridgehead proton (H-7 and H-3, respectively). This shows that the adduct has the *exo* configuration.[13]

Compound 2, the minor component of the fraction with the shortest retention time, could be shown to be 1-methoxy-4-oxa-*exo*-tetracyclo[6.3.0.$0^{2,11}$.$0^{3,7}$]undec-9-ene. Assignment of the NMR signals was performed as in the case of compound 1, on the basis of NOE difference experiments and the two dimensional shift correlated spectrum (SECSY). In this compound the oxygen atom is at position 4, as is evident from the shift to low field of H-3 (4.06 ppm). The absence of coupling between H-7 and H-8 and between H-2 and H-3 shows that this molecule has the *exo* configuration.

Compound 3, the product with the longest retention time, was identified as 1-methoxy-6-oxa-*endo*-tetracyclo[6.3.0.$0^{2,11}$.$0^{3,7}$]undec-9-ene. The NMR spectrum was analyzed in a similar way as that of compound 1. A NOE difference experiment on the methoxy group showed increased intensity of the signals of protons H-2 (2.04 ppm) and H-11 (2.16 ppm). The SECSY plot shows the couplings between H-7 and H-8 and between H-2 and H-3, characteristic of the *endo* configuration.

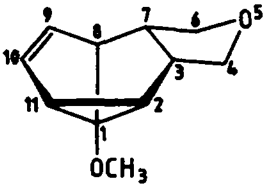
The chemical shifts and coupling constants of compounds 1, 2 and 3 are presented in Table 1.

Table 1. Chemical shifts (ppm) and coupling constants (Hz) of compounds 1, 2 and 3 in $CDCl_3$ (300 MHz) at 298 K.

proton	1	2	3
OCH_3	3.36(s)	3.32(s)	3.35(s)
H-2	1.87(d); $J_{2,11}$ = 8.2	2.15(d); $J_{2,11}$ = 9.1	2.04(dd); $J_{2,3}$ = 7.2; $J_{2,11}$ = 8.7
H-3	2.40(m); $J_{3,7}$ = 4.3	4.06(d); $J_{3,7}$ = 6.0	3.25(m); $J_{3,7}$ = 8.6
H-4,4'	1.92(m)/2.12(m)		1.70(m)/1.80(m)
H-5,5'	3.78(m)/4.11(q)	3.70(m)/4.01(m)	3.88(q)/4.08(dt)
H-6,6'		1.95 - 2.05 (2m)	
H-7	4.00(m)	2.58(m)	5.14(dd); $J_{7,8}$ = 6.9
H-8	3.40(d); $J_{8,9}$ = 2.7	3.22(d); $J_{8,9}$ = 2.2	3.36(d)
H-9	5.55(dd); $J_{9,10}$ = 5.7	5.55(m)	5.73(m)
H-10	5.64(dd); $J_{10,11}$ = 2.4		
H-11	2.23(dd)	2.25(dd); $J_{11,10}$ = 2.4	2.16(dd); $J_{11,10}$ = 2.4

Anisole and 2,5-dihydrofuran

After irradiation of a solution of anisole (1 M) and 2,5-dihydrofuran (3.5 M) in methanol with light of 254 nm for 80 hours, two products could be detected by means of analytical GLC (DEGS) in the ratio of 1 : 16. These products were separated by preparative GLC on the same column material. The product with the shortest retention time, compound 4, could be identified by means of 300 MHz ^1H NMR spectroscopy as 1-methoxy-5-oxa-*exo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene and the major product, compound 5, as 1-methoxy-5-oxa-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene.



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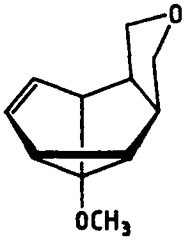

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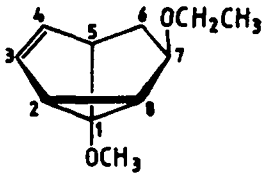
The chemical shifts and coupling constants of compounds 4 and 5 are presented in Table 2.

Table 2. Chemical shifts (ppm) and coupling constants (Hz) of compounds 4 and 5 in $CDCl_3$ (300 MHz) at 298 K.

proton	4	5
OCH_3	3.34(s)	3.40(s)
H-2	1.94(d); $J_{2,11}$ = 8.7	2.08(t); $J_{2,3}$ = 7.4
H-3	2.41(dt)	3.28(m)
H-4,4'	3.83(dd)/3.98(t)	3.42(m), 3.68(m)
H-6,6'	3.75(t)/3.94(dd)	3.52(m), 3.64(m)
H-7	2.56(q)	3.57(m); $J_{7,8}$ = 6.8
H-8	3.40(d); $J_{8,9}$ = 2.3	3.31(dd); $J_{8,9}$ = 2.6
H-9	5.64(m)	5.68(dd); $J_{9,10}$ = 5.7
H-10		5.78(dd); $J_{10,11}$ = 2.3
H-11	2.18(dd); $J_{10,11}$ = 2.1	2.16(dd); $J_{11,2}$ = 8.4

Anisole and ethyl vinyl ether

A solution of anisole (1 M) in ethyl vinyl ether was irradiated for 72 hours with light of 254 nm. The presence of three products in the ratio of 1.5 : 2 : 1 was detected by means of analytical GLC (capillar OV 101). These products were separated by preparative GLC (6 m, 20 % SE 30).



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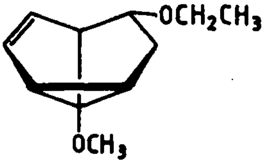

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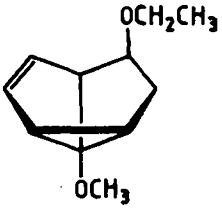

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The first product (which has the shortest retention time) could be identified as 1-methoxy-*endo*-7-ethoxytricyclo[3.3.0.0^{2,8}]oct-3-ene (compound 6) on the basis of the following NMR data.

The 500 MHz ^1H NMR spectrum (Figure 2) shows the resonance of two olefinic protons at 5.76 and 5.67 ppm. The sharp singlet at 3.39 ppm must be due to the methoxy group; the two multiplets at 3.46 and 3.32 ppm belong to the OCH_2 group in the ethoxy substituent, while the CH_3 part of that

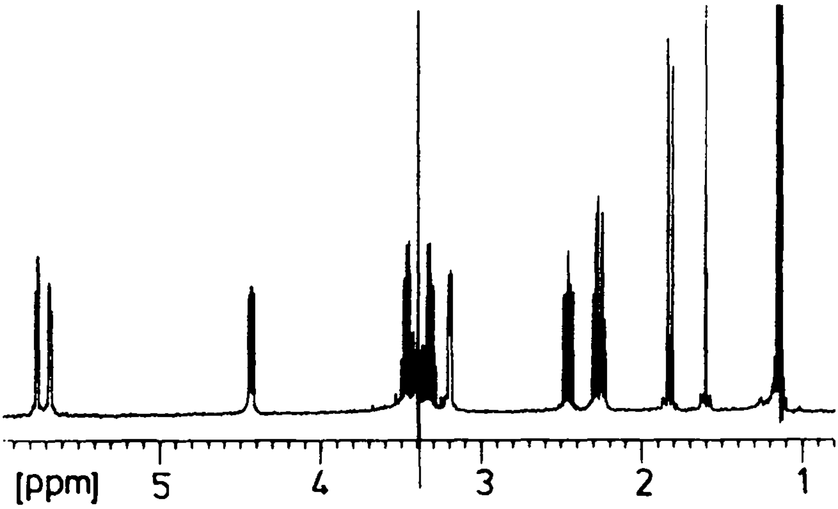


Fig. 2. 500 MHz ^{1}H NMR spectrum of compound 6 in $CDCl_3$ at 298 K.

group gives rise to a triplet at 1.14 ppm. The multiplet at 4.43 ppm must be due to the proton located at the carbon atom with the ethoxy substituent. When this multiplet is decoupled, the following couplings disappear: an 8.5 Hz coupling from the multiplet at 2.45 ppm, a 5.6 Hz coupling from the multiplet at 2.28 ppm and a 1.5 Hz coupling from the double doublet at 3.19 ppm. This last coupling is either $J_{5,7}$ or $J_{6,8}$, long range couplings which are usually found in *meta* photocycloadducts.[15,16,17]

Irradiation experiments indicate that the proton with the signal at 3.19 ppm has a coupling of 2.4 Hz with an olefinic proton (5.67 ppm) and one of 6.5 Hz with a proton with a multiplet at 2.45 ppm. The signal at 3.19 ppm must be due to H-5 since this is the only proton having a coupling with an olefinic proton and a W-relationship, which must be with H-7. The double doublet at 2.45 ppm is from H-6 ($J_{5,6}$ = 6.5 Hz), which also has a 13.5 Hz coupling with H-6' at 1.82 ppm.

On the basis of its coupling of 5.6 Hz with the multiplet at 4.43 ppm (H-7), the double doublet at 2.28 ppm can be ascribed to H-8. The other coupling (8.4 Hz) of this proton is with the double doublet at 2.23 ppm. This proton, which must be H-2, has a 2.0 Hz coupling with the olefinic proton at 5.76 ppm (H-3).

The position of the methoxy group can be deduced from the following two facts: the existence of a cyclopropane proton (H-2) with a coupling with an olefinic proton and the existence of another cyclopropane proton with a 5.6 Hz coupling with a proton originating from the ethyl vinyl ether. The only remaining position for the methoxy group is therefore at C-1.

Similar decoupling experiments at 300 MHz show that the second product, compound 7, is 1-methoxy-*exo*-6-ethoxytricyclo[3.3.0.0^{2,8}]oct-3-ene.

Also on the basis of 300 MHz ^{1}H NMR spectroscopy the third product could be identified as 1-methoxy-*endo*-6-ethoxytricyclo[3.3.0.0^{2,8}]oct-3-ene (compound 8).

The chemical shifts and coupling constants of compounds 6, 7 and 8 are presented in Table 3.

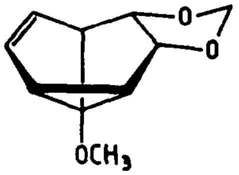
Anisole and 1,3-dioxole

After irradiation of a solution of anisole (1 M) and 1,3-dioxole (3 M) in cyclohexane with a low pressure mercury arc (Hanau TNN 15/32) for 24 hours, GLC analysis (10 % SE 30) of the crude mixture showed the presence of two photoproducts in the ratio of 3 : 1. The products were separated by preparative GLC. Their structures could be elucidated by 300 MHz ^{1}H NMR spectroscopy. The major product (compound 9) was identified as 1-methoxy-4,6-dioxa-*exo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene and the minor product (compound 10) as 1-methoxy-4,6-dioxa-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene. The NMR data of these compounds will be published elsewhere.

Table 3. Chemical shifts (ppm) and coupling constants (Hz) of compounds 6, 7 and 8 in $CDCl_3$ at 298 K. (H-6 and H-7 are *exo*; H-6' and H-7' are *endo*).

compound	OCH_3	$OC\underline{H}_2CH_3$	$OCH_2C\underline{H}_3$	H-2	H-3	H-4	H-5	H-6	H-6'	H-7	H-7'	H-8
6	3.39	3.46/3.32	1.14	2.23	5.76	5.67	3.19	2.45	1.82	4.43		2.28
7	3.40	3.45	1.20	2.26	5.58	5.49	3.28		3.63	1.98	1.62	2.19
8	3.34	3.48	1.18	2.15	5.73	5.66	3.40	4.18		2.15	1.32	1.84

compound	$J_{2,3}$	$J_{2,4}$	$J_{2,8}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,7}$	$J_{6,6'}$	$J_{6,7}$	$J_{6,7'}$	$J_{6',7'}$	$J_{7,7'}$	$J_{7,8}$	$J_{7',8}$
6	2.0		8.4	5.5	2.4	6.5	1.5	13.5	8.5				5.6	
7	2.3	1.4	8.3	5.7	2.6		2.5				4.4	14.6	6.0	
8	2.3	1.4	8.2	5.8	2.4	5.5			7.9	9.5		13.0	6.6	1.5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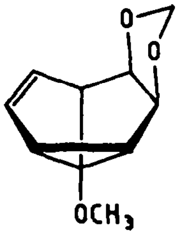
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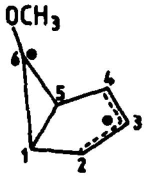
DISCUSSION

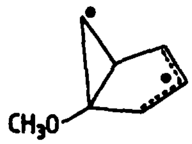
The *meta* photocycloaddition of anisole to cyclopentene yields the *endo* and *exo* adducts[13] in the ratio of 9 : 1. In both adducts the methoxy group is at position 1. The results reported in this paper show that the presence of one or two oxygen atoms next to the double bond in the alkene has a pronounced influence on the *endo*/*exo* ratio. The results are summarized below.

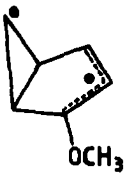
	% *endo*	% *exo*
cyclopentene	90	10
2,3-dihydrofuran	50	50
ethyl vinyl ether	55	45
1,3-dioxole	25	75
2,5-dihydrofuran	94	6

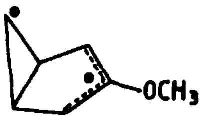
A similar trend is found in the photocycloaddition of benzene to cyclopentene and 1,3-dioxole. Bryce-Smith and Gilbert et al.[7] reported an *endo*/*exo* ratio of 89 : 11 for benzene with cyclopentene, whereas for benzene with 1,3-dioxole Mattay et al.[4] have found that the *exo* isomer is the major *meta* photoadduct.

With anisole, all olefins show similar regioselectivity. The methoxy group is invariably found at position 1 in the adduct. The results are difficult te reconcile with a mechanism in which prefulvene plays a role. From anisole, four methoxyprefulvenes are possible:





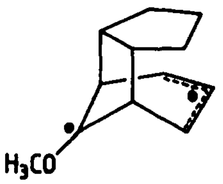


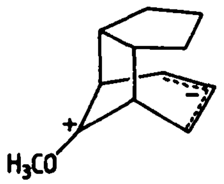


Only 1-methoxyprefulvene would, upon reaction with the alkene, give rise to a 1-methoxy-substituted adduct. To explain the exclusive formation of *meta* photoadduct with methoxy at position 1 one would have to assume either that only one methoxyprefulvene is formed from excited anisole or that only one of the methoxyprefulvenes can react with the olefin. Neither of these two possibilities seems likely. 1-Methoxyprefulvene, with the methoxy group at a bridgehead carbon, is not expected to be the most stable isomer. This fact is in itself not sufficient to discard the prefulvene mechanism. The supposed intermediates are formed from an excited species and it is not uncommon in photochemistry that the thermodynamically least stable isomers are preferentially formed. If 1-methoxyprefulvene would be the predominant intermediate one would, however, expect the species to be able to react with the olefin in two different ways, *viz.* at the positions 2 and 6 or at the positions 4 and 6. These processes would lead to the 1-methoxy- or the 11-methoxy-substituted adduct, respectively. However, the 1-methoxy isomer is found exclusively. If steric factors were to play a role, one would not expect the exclusive formation of this isomer.

The prefulvene can react with the alkene to give the *endo* and the *exo* adduct. Model studies show that there is little difference in steric requirements for formation of the two types of adduct. If steric factors are involved at all, they are expected to favour the formation of *exo* adduct. The *endo*/*exo* ratio in the anisole-cyclopentene system is, however, 9 : 1. That this ratio changes in favour of the *exo* adduct in going from cyclopentene to 1,3-dioxole cannot be the result of steric factors.

In the other possible mechanism the bonds between cyclopentene and anisole are supposed to be formed first. Products that would derive from an intermediate in which only one of these bonds has been formed have never been detected. Furthermore, the addition of open chain alkenes to benzene derivatives always takes place with retention of the stereochemistry in the alkene.[18,19,20] It may therefore be assumed that the bonds are formed simultaneously. This mode of addition would create a diradical or a zwitterion:





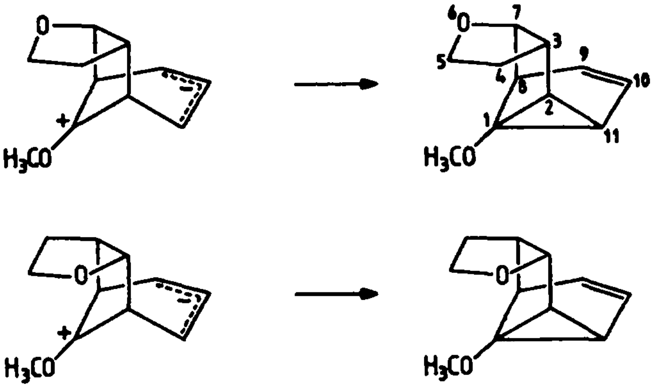
The possible intermediacy of such species has also been mentioned by Bryce-Smith and Gilbert.[3,6] The stabilizing influence of the methoxy group on the carbonium ion or the radical centre nicely explains the activating and directing effect of this group on the photoaddition. The intermediate has a plane of symmetry and the two modes of formation of the three membered ring are degenerate. Thus, by assuming the intermediacy of the diradical or the zwitterion, it follows naturally that only one product will be found in the case of anisole with a symmetric alkene.

The formation of such an intermediate may be preceded by an exciplex between the excited aromatic molecule and the olefin. Such an exciplex has been proposed by Srinivasan and co-workers[9] to explain the predominancy of the *endo* isomer, *e.g.* in the *meta* photocycloaddition of toluene to cyclobutene. In the exciplex leading to *exo* adduct there would be severe steric interaction between the substituent and the methylene groups of the cyclic olefin.

Bond formation between carbon atoms 2 and 6 of anisole and carbon atoms 1 and 2 of cyclopentene (either directly from the excited state or via the exciplex) yields a species which in our view can best be represented as a zwitterion.

The results obtained with the oxa- and dioxa-cyclopentenes demonstrate that the presence of one or two oxygen atoms in the five membered ring has a pronounced effect on the *endo*/*exo* ratio. Replacement of a methylene group next to the double bond by an oxygen atom causes the *endo*/*exo* ratio to drop from 90/10 to 50/50. When the second allylic methylene group is also replaced by oxygen the ratio becomes 25/75 and is almost inverted compared to cyclopentene. We attribute this strong effect to an electronic interaction between the oxygen atom(s) and the negatively charged allylic moiety in the *endo* zwitterion. Repulsion between the lone pair electrons on oxygen and the electrons of the allyl anion will render this zwitterion less stable than the *endo* zwitterion obtained from cyclopentene. The *exo* zwitterion does not suffer from this effect.

The isomer distribution in the case of anisole and 2,3-dihydrofuran may be rationalized as follows. Due to the presence of the oxygen atom, the charge distribution in the allyl anion will be asymmetric in such a way that most negative charge will be concentrated on the carbon atom that is farthest away from the oxygen. The ring closure is expected to take place preferentially to this atom. This yields the 6-oxa-*endo* isomer which is in fact the only one of the two possible *endo* adducts that has been found. In contrast, both possible *exo* adducts have been isolated. They are formed in the ratio of 2 : 1, with the 6-oxa-*exo* isomer predominating. The major isomer is formed by ring closure between the carbon atom bearing the methoxy group and the negatively charged carbon atom that is farthest away from the oxygen atom.



The oxygen atom in the *exo* zwitterion is sufficiently far away from the allylic anion for direct repulsive interaction to be negligible. The zwitterion is, however, asymmetric and the dipole of the C-O bond may be responsible for an asymmetric distortion of the distribution of charge in the allylic anion. The expected charge distribution is in agreement with formation of the 6-oxa-*exo* isomer as the major *exo* adduct.

Ethyl vinyl ether is electronically similar to 2,3-dihydrofuran. The *endo/exo* ratios of the two compounds are almost equal. From ethyl vinyl ether and anisole only one *exo* adduct has been found. The position of the oxygen atom in this adduct is the same as that of the oxygen atom in the major *exo* adduct from 2,3-dihydrofuran, *i.e.* farthest away from the three membered ring. Thus, the similarity of the two compounds is reflected in their behaviour in the addition reaction. There is, however, one difference. From 2,3-dihydrofuran only one *endo* adduct is formed and it was argued that this compound arises from the zwitterion by ring closure to the carbon atom farthest away from the oxygen. Ethyl vinyl ether and anisole, however, give rise to two *endo* adducts in the ratio of 1.5 : 1 and the major isomer is formed by ring closure to the carbon atom nearest to oxygen. At present we do not have a satisfactory explanation for this discrepancy. The greater flexibility of the open chain alkene and of the resulting zwitterion might play a role.

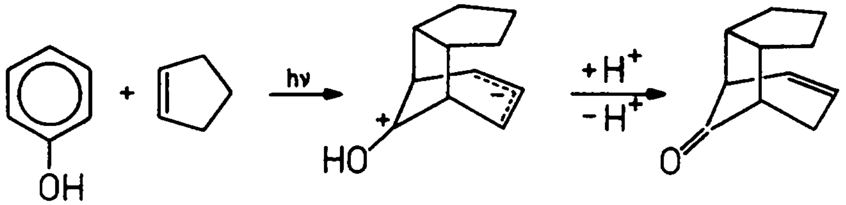
The photoreaction of ethyl vinyl ether with anisole has also been studied by Gilbert et al.[21] The formation of four derivatives of tricyclo[3.3.0.0^{2,8}]oct-3-ene is reported, all with the OCH_3 group at position 1 and the ethoxy group at one of the positions 6 or 7. Qualitatively the results reported by us are very similar to those of Gilbert et al. A quantitative comparison is impossible because these authors have not separately identified the four photoproducts: three products were obtained as a mixture.

Interestingly, Gilbert et al.[21] have found a solvent effect on the *meta* photocycloaddition of anisole to ethyl vinyl ether. The quantum yield increases markedly in the series cyclohexane (Φ=0.2) < methanol < ethyl acetate < acetonitrile (Φ=0.4). The authors propose that this effect may be explained in terms of the polarity of an intermediate formed by 2,6-bonding of the ethyl vinyl ether to excited anisole. This is now corroborated by the results presented in this paper.

In the zwitterion formed from anisole and 2,5-dihydrofuran, the oxygen atom is not only farther away from the allyl anion, but, perhaps more important, it now faces the central carbon atom which bears much less negative charge than the carbon atoms at either end. As a result, the *endo/exo* ratio is almost equal to that in the case of anisole with cyclopentene and the oxygen atom appears to have no effect.

In this paper we report only about photocycloadditions of anisole and our conclusions regarding the mechanism are therefore only valid for this molecule. However, as has been pointed out by Mattay et al.[4], the fact that benzene, like anisole, yields more *exo* than *endo* adduct in its reaction with 1,3-dioxole indicates that a zwitterionic species may also play a role in this case.

The zwitterionic mechanism would also give an explanation for the formation of a tricyclic ketone from phenol and cyclopentene. Srinivasan et al.[12] have reported that the photochemical addition of these two compounds yields tricyclo[5.3.1.0.^{2,6}]undec-8-en-11-one instead of the expected 1-hydroxy-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene. They explained this result by assuming that the 1-hydroxy-substituted adduct undergoes ring opening in the acidic (phenol) medium. If our mechanism is correct, one does not have to assume that the tetracyclic adduct is first formed and then destroyed. The positively charged moiety of the zwitterion formed from phenol is in fact a protonated ketone. It will easily lose a proton, whereas the allylic anion will pick up a proton from the medium:



In conclusion, we can say that our experiments with oxygen-containing alkenes have provided strong indications for the occurrence of a zwitterionic intermediate in the *meta* photocycloaddition to anisole.

EXPERIMENTAL

Chemicals

Anisole, 2,3-dihydrofuran, ethyl vinyl ether and $CDCl_3$ were products of Aldrich Europe. Cyclopentene was a product of Merck-Schuchardt. 1,3-Dioxole was prepared by Dr. J. Mattay of the Rheinisch Westfälische Technische Hochschule, Aachen, Germany, via a method described in the literature.[22] 2,5-Dihydrofuran was prepared by dehydration of but-2-en-1,4-diol.[23]

Irradiation Conditions and Work-Up

The irradiations (except the one with 1,3-dioxole) were carried out in a quartz tube (30 × 3.5 cm) containing 200 - 300 ml of a solution of 1 M anisole and 3.5 M alkene. For the addition of anisole to ethyl vinyl ether, the latter compound was used as the solvent. The tube was placed in a Rayonet RPR 200 Photochemical Reactor, fitted with eight 254 nm lamps.

The irradiation mixture was checked by analytical GLC every 20 hours. After irradiation for 72 - 80 hours the reaction mixture was analyzed by analytical GLC. After removing the solvent and the starting materials by distillation, a 20 - 30 % solution in cyclohexane or in a mixture of ethyl acetate and hexane (1 : 19) was prepared from the crude mixture and then separated by preparative GLC. Only those products were separated that were likely to be *meta* photoadducts on the basis of their GC-MS data or by comparison of their GC retention times with those of the anisole-cyclopentene photoadducts.

Gas-Liquid Chromatography

The following instruments were used for analytical GLC: Hewlett Packard F & M 5750 Scientific Research Chromatograph; Column 1: 10 % SE 30 on Chromosorb WAW 80 - 100 mesh, glass, 2 m × 3.2 mm; Column 2: 10 % DEGS on Chromosorb WAW 80 - 100 mesh, glass, 2 m × 4 mm. The injection port temperature was 190° and the oven temperature was in the range 135 - 150°. Hewlett Packard 5700 A Gas Chromatograph. Column: Capillar OV 101, film thickness 0.3 µm, glass, 50 m × 0.35 mm. The temperature of the injection port was 180°, the oven temperature was 130°.

For the preparative GC separations we used: Varian Aerograph Model 90-P. Column 1: 20 % DEGS on Chromosorb WAW 40 - 60 mesh, glass, 6 m × 8 mm; Column 2: 20 % SE 30 on Chromosorb WAW 40 - 60 mesh, glass, 6 m × 8 mm. The temperature of the injection port was 190°, the oven temperature 150°.

NMR Spectroscopy

The 300 MHz NMR spectra were recorded at 298 K in $CDCl_3$ on a Bruker WM 300 spectrometer. The acquisition parameters were: sweep widths of 2400 Hz, 4.8 s acquisition time and a pulse width of 4 µs, where a 90° flip angle corresponds to 6 µs.

The 500 MHz spectrum (compound 6) was recorded on a Bruker AM 500 spectrometer (Free University of Brussels, Belgium) at 298 K in $CDCl_3$. The acquisition parameters were: sweep widths of 4000 Hz, 4 s acquisition time and a pulse width of 2 µs, where a 90° flip angle corresponds to 12 µs.

Both instruments were interfaced with an Aspect 2000 computer, fitted with a CDC disk drive (96 M bytes).

The SECSY experiments on compounds 1, 2 and 3 were recorded on the Bruker WM 300 spectrometer in $CDCl_3$ at 298 K. Typical parameters: $F_1 = \pm 1000$ Hz, $F_2 = 2000$ Hz, NS = 16, NE = 128, SI = 16 K, 1.5 s recycle delay, $\Delta t_{\frac{1}{2}} = 0.00025$ s, zero filling in F_1 to 512 w, sine bell shifted in both dimensions.

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