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PHOTOCYCLOADDITION OF ETHYLVINYLETHER AND CYCLOPENTENE TO 3,5-DIMETHYLANISOLE

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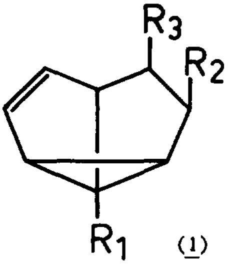
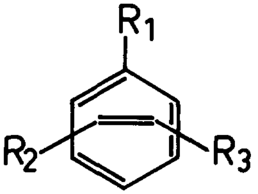
Abstract: Photocycloaddition of ethylvinylether and cyclopentene to 3,5-dimethylanisole yields derivatives of 1-methoxy-2,4-dimethyltricyclo[3.3.0.0^{2,8}]oct-3-ene in which the substituents at positions 6 and/or 7 are *endo*. Structural proofs are based on 250 MHz ^{1}H and 62.9 MHz ^{13}C NMR spectra.

The photocycloaddition of anisole and toluene to ethylvinylether [1] and to cyclopentene [2] yields *meta* photoadducts of type (1). The olefin adds to positions 2 and 6 of the arene and the substituent is at position 1 of the photoproduct. An "open sandwich exciplex" (2) has been postulated as an intermediate in these reactions [2,3].

In the photoadducts of cyclopentene to methyl substituted anisoles [4,5,6] the methoxy group is always at position 1, indicating that this group exerts an *ortho* directing influence. We are still investigating whether this effect is related to the directing influence of the methoxy group in the nucleophilic photosubstitution of anisoles [7]. The origin of the *ortho* directing effect in the photoaddition is not yet known.



(1)



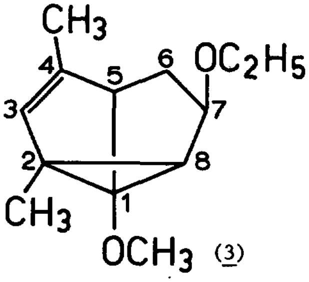
(2)

$R_1 = OCH_3$ or CH_3
a) $R_2 = H$; $R_3 = OC_2H_5$
b) $R_2 = OC_2H_5$; $R_3 = H$
c) $R_2\text{-}R_3 = CH_2\text{-}CH_2\text{-}CH_2$

As part of our studies on the directing effect of substituents in these reactions and of the possible relationships with nucleophilic photosubstitution, we investigated the photoaddition of 3,5-dimethylanisole to ethylvinylether and cyclopentene.

After irradiation of a solution of 3,5-dimethylanisole (1 M) in ethylvinylether with light of 254 nm, two products could be detected by GLC. The product with the shortest retention time, isolated by means of preparative GLC, was identified on the basis of its

NMR spectra (250 MHz ^{1}H and 62.9 MHz ^{13}C) as *endo*-7-ethoxy-1-methoxy-2,4-dimethyltricyclo-[3.3.0.0^{2,8}]oct-3-ene (3). Chemical shifts, multiplicities and coupling constants of the ^{1}H NMR spectrum are presented in Table 1. Determination of coupling constants was made possible by selective decoupling.



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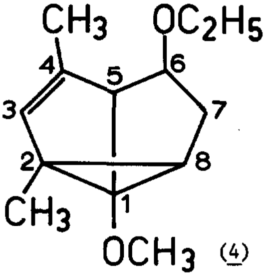

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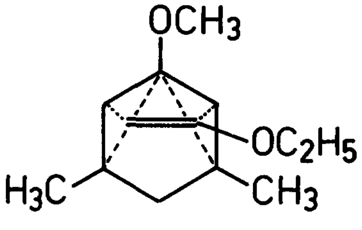


(5)

	Photoadduct (3)				Photoadduct (4)			
	δ in ppm	Multiplicity; Number of protons; Coupling constant (Hz)			δ in ppm	Multiplicity; Number of protons; Coupling constant (Hz)		
OCH_3	3.38	s	3H		3.34	s	3H	
$O\underline{CH_2}CH_3$	3.23-3.4	m	2H		3.26-3.5	m	2H	
$OCH_2\underline{CH_3}$	1.09	t	3H		1.13	t	3H	
2-CH_3	1.27	s	3H		1.25	s	3H	
4-CH_3	1.65	s	3H		1.73	s	3H	
H-3	5.15	s	1H		5.23	s	1H	
H-5	2.95	d	1H	$J_{5,6'}$ = 6.4	3.17	d	1H	$J_{5,6'}$ = 5.2
H-6(*endo*)	1.82	d	1H	$J_{6,6'}$ = 13.4				
H-6'(*exo*)	2.29	m	1H	$J_{5,6'}$ = 6.4 $J_{6,6'}$ = 13.4 $J_{6',7'}$ = 8.0	4.06	dd	1H	$J_{5,6'}$ = 5.2 $J_{6',7'}$ = 8.0
H-7(*endo*)					1.65	d	1H	$J_{7,7'}$ = 13.5
H-7'(*exo*)	4.42	dd	1H	$J_{6',7'}$ = 8.0 $J_{7',8}$ = 5.8	2.08	m	1H	$J_{6',7'}$ = 8.0 $J_{7,7'}$ = 13.5 $J_{7',8}$ = 6.4
H-8	1.77	d	1H	$J_{7',8}$ = 5.8	1.34	d	1H	$J_{7',8}$ = 6.4

Table 1. 250 MHz ^{1}H NMR spectral data of *endo*-7-ethoxy-1-methoxy-2,4-dimethyltricyclo[3.3.0.0^{2,8}]oct-3-ene (3) and *endo*-6-ethoxy-1-methoxy-2,4-dimethyltricyclo[3.3.0.0^{2,8}]oct-3-ene (4) in $CDCl_3$.

The signals at δ = 1.82 and δ = 2.29 are from two geminally coupled protons (J = 13.4 Hz). One of them (δ = 2.29) is coupled (J = 8.0 Hz) to the proton with δ = 4.42 which obviously must be situated at the carbon atom bearing the ethoxy group. The coupling disappears upon saturation of the signal at δ = 4.42. It can be concluded that these three protons derive from the vinyl group in ethylvinylether.

Decoupling of the low field proton at $\delta = 4.42$ also changes the doublet at $\delta = 1.77$ (J = 5.8 Hz): it becomes a singlet. Decoupling of the proton at $\delta = 2.29$ transforms the doublets at $\delta = 1.82$ and $\delta = 2.95$ into singlets. The signals at $\delta = 1.77$ and $\delta = 2.95$ can now be assigned to H-8 and H-5, respectively; the signal at high field must belong to the cyclopropane proton. Because H-8 is coupled to the proton next to the ethoxy group, it can be concluded that this group is at C-7. The ethoxy group is in the *endo* configuration: the magnitude of the coupling constant between H-7 and H-8 (5.8 Hz) shows that H-7 must be *exo*.

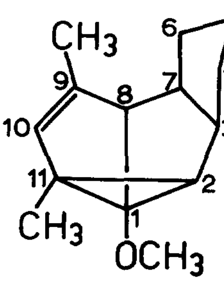
The methyl group at $\delta = 1.65$ is located on the double bond. In agreement with this, the 62.9 MHz ^{13}C NMR spectrum shows an olefinic carbon atom at $\delta = 127.8$ with $^1J_{C,H} = 161.5$ Hz. In the ^{13}C spectrum one cyclopropane carbon atom with the typical coupling constant $^1J_{C,H}$ = 157.2 Hz can be observed. It can therefore be concluded that two substituents (CH_3 and OCH_3) are located on the three membered ring.

A NOE difference experiment on the high field methyl group ($\delta = 1.27$) shows that this group is close to the olefinic proton at $\delta = 5.15$ and to H-8 at $\delta = 1.77$. This methyl group must therefore be situated at C-2, while the other methyl group is at C-4. This leaves position 1 for the methoxy group, a conclusion which is confirmed by a NOE difference experiment on this group. It shows short distances to H-8 and to H-5. The magnitude of these Nuclear Overhauser Effects is ca. 10 %.

The GLC peak with the longer retention time appears to correspond to a mixture of two products. The major product has been identified as *endo*-6-ethoxy-1-methoxy-2,4-dimethyltricyclo[3.3.0.0^{2,8}]oct-3-ene (4). The structural proof, based on NMR data, is similar to that of compound (3). Upon decoupling of the multiplet at $\delta = 4.06$ (H-6) the doublet at $\delta = 3.17$ (H-5) becomes a singlet. The magnitude of the coupling constant $J_{5,6}$ = 5.2 Hz agrees with an angle between H-5 and H-6 which can only be obtained if H-6 is *exo*. The ethoxy group must therefore be in the *endo* position at C-6. The ^1H NMR data of adduct (4) are presented in Table 1. The hitherto unidentified component of the mixture appears to be a thermal product of photoadduct (4).

An exciplex (5), similar to the one postulated by Srinivasan et al.[2,3], agrees with the formation of the photoadducts (3) and (4). Each of the isomers is formed in 30 % yield, based on the amount of starting material converted.

After irradiation of a solution of 3,5-dimethylanisole (0.1 M) and cyclopentene (0.3 M) in cyclohexane with light of 254 nm, the photoadduct (6) can be isolated in 70 % yield. The NMR data of compound (6) are as follows:



(6)

62.9 MHz ^{13}C ($CDCl_3$) (δ in ppm): 99.8 (s, C-1); 46.5 (d, C-2); 48.9 (d, C-3); 29.7/28.1 (t, C-4); 26.7 (t, C-5); 28.1/29.7 (t, C-6); 60.4 (d, C-7); 58.1 (d, C-8); 142.9 (s, C-9); 130.2 (d, C-10); 42.0 (s, C-11); 56.5 (q, OCH_3); 17.6 (q, 9-CH_3); 15.9 (q, 11-CH_3).

250 MHz ^1H ($CDCl_3$) (δ in ppm): 1.18 (s, 3H, 11-CH_3); 1.23-1.7 (m, 6H, H-4,4',5,5',6,6'); 1.7 (d, 1H, H-2); 1.75 (s, 3H, 9-CH_3); 2.8 (d, 1H, H-8, $J_{7,8}$ = 6.7 Hz); 2.85-3.0 (broad q, 1H, H-3); 3.1-3.26 (m, 1H, H-7); 3.31 (s, 3H, OCH_3); 5.15 (s, 1H, H-10).

The 62.9 MHz ^{13}C NMR spectrum shows the 14 signals which one would expect to see. Comparison of this spectrum to that of the anisole-cyclopentene adduct [8] shows that the doublets of C-9 and C-11 are reduced to singlets and that there are two methyl groups and one hydrogen-substituted cyclopropane carbon atom. It can be concluded that the substituents are at positions 1, 9 and 11.

In the 250 MHz ^{1}H NMR spectrum the methyl groups have their signals at $\delta = 1.75$ and $\delta = 1.18$. The low field signal obviously belongs to a methyl group situated at position 9. A NOE difference experiment on the methyl group at $\delta = 1.18$ shows that this group is close to the olefinic proton (H-10) at $\delta = 5.15$ and to the cyclopropane proton at $\delta = 1.7$. This methyl group must therefore be at position 11. Evidently, adduct (6) is a 1-methoxy-9,11-dimethyl derivative.

From the magnitude of the coupling constant $J_{7,8} = 6.7$ Hz it can be concluded that the cyclopentene ring is in the *endo* configuration. The value of J corresponds to a dihedral angle between H-7 and H-8 of 35°, in agreement with an *endo* linkage for the cyclopentene ring [8].

It follows that adduct (6) must be 1-methoxy-9,11-dimethyl-*endo*-tetracyclo-$[6.3.0.0^{2,11}.0^{3,7}]$undec-9-ene, formed by addition of cyclopentene at the positions *ortho* to the methoxy group in 3,5-dimethylanisole.

Our results show that also in *meta*-photocycloaddition of ethylvinylether and cyclopentene to 3,5-dimethylanisole the methoxy group exerts a stronger directing effect than the methyl groups. Further investigations aimed at clarification of the origin of this effect are in progress.

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