Tetrahedron Letters,Vol.23,No.37,pp 3827-3830,1982 0040-4039/82/373827-04$03.00/0
Printed in Great Britain

THE *meta*-PHOTOCYCLOADDITION OF ETHYLVINYLETHER TO 3-METHYLANISOLE AND 3-FLUOROANISOLE

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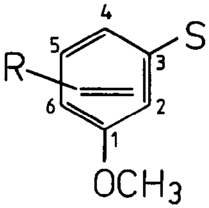
Summary: Photoaddition of ethylvinylether to 3-methylanisole yields six derivatives of 1-methoxytricyclo[3.3.0.0^{2,8}]oct-3-ene. Four of the adducts have the ethoxy group in an *endo* position. Products in which the methyl group is at position 4 are favoured. Photoaddition of ethylvinylether to 3-fluoroanisole yields three isomeric adducts, two *endo* and one *exo*.

The *meta*-photocycloaddition of olefins to anisole [1] and to methyl substituted anisoles [2-6] yields derivatives of tricyclo[3.3.0.0^{2,8}]oct-3-ene in which the methoxy group is invariably located at position 1. An open sandwich exciplex (I) has been postulated as an intermediate in this type of reaction [7]. Bond formation takes place between the termini of the olefinic double bond and the positions 2 and 6 of the anisole. A three membered ring is made by formation of a bond between atoms 1 and 3 or 5. Neither the origin of the *ortho* directing effect nor the factors determining the direction of the cyclopropane ring formation are known.

In order to get more insight into the effects of substituents on the *meta*-photocycloaddition, we have investigated the addition of ethylvinylether (ionization potential 8.6 eV) to 3-methylanisole (I.P. 8.38 eV) and to 3-fluoroanisole (I.P. 8.72 eV).



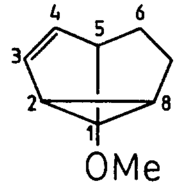
(I)

$R = OC_2H_5$
$S = CH_3$ or F

With an asymmetrically substituted olefin and a *meta* substituted anisole, there are four different orientations in the exciplex and for each of those there are two different possibilities for formation of a three membered ring. Therefore, eight isomeric cycloadducts are theoretically possible.

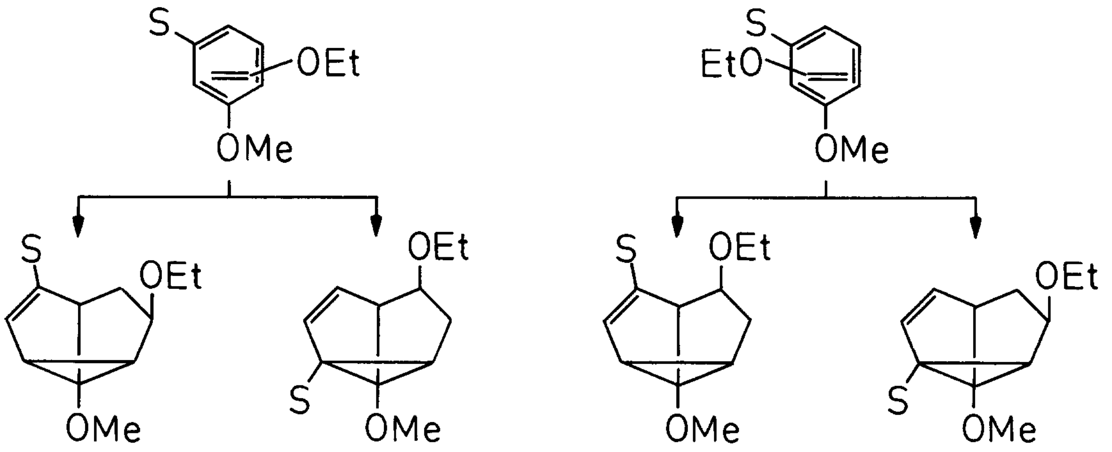
After irradiation (254 nm) of a solution of 3-methylanisole (1 M) in ethylvinylether, GLC analysis (10 % SE-30) showed three new peaks. The three fractions were separated by preparative GLC under the same experimental conditions. Preliminary analysis by NMR and by capillary GLC (dynamically coated Carbowax, v = 6 cm/s) showed that the first fraction consisted of one photo-adduct, while the second and third fractions were mixtures of three and two photo-adducts, respectively. These were further separated by means of HPLC (Partisil 5; 15 cm x 46 mm; ethyl acetate : n-hexane 1 : 30; detection at 233 nm).

Thus, six of the eight theoretically possible isomeric adducts were isolated and identified. They are all derivatives of 1-methoxytricyclo[3.3.0.0^{2,8}]oct-3-ene (II): *endo*-7-ethoxy-4-methyl-II (1); *endo*-6-ethoxy-2-methyl-II (2); *endo*-6-ethoxy-4-methyl-II (3); *endo*-7-ethoxy-2-methyl-II (4); *exo*-6-ethoxy-4-methyl-II (5) and *exo*-7-ethoxy-2-methyl-II (6).



(II)

Adducts 1, 2, 3, 4, 5 and 6 were formed in the ratio 1.4 : 1.0 : 1.9 : 1.0 : 1.7 : 0.75.

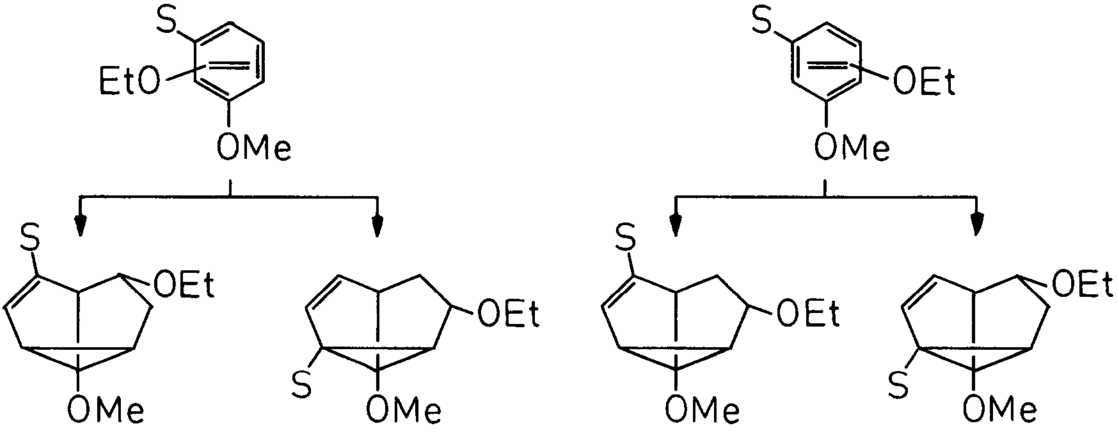


(1) S = CH_3
(1a) S = F

(2) S = CH_3
(2a) S = F

(3) S = CH_3
(3a) S = F

(4) S = CH_3
(4a) S = F



(5) S = CH_3
(5a) S = F

(6) S = CH_3
(6a) S = F

(7) S = CH_3
(7a) S = F

(8) S = CH_3
(8a) S = F

Structure elucidation was based on 300 MHz ^1H NMR spectroscopy. The chemical shift values are presented in Table 1. All NMR spectra were measured in $CDCl_3$.

	(1) δ (ppm)	(2) δ (ppm)	(3) δ (ppm)	(4) δ (ppm)	(5) δ (ppm)	(6) δ (ppm)
OCH_3	3.38	3.41	3.34	3.31	3.38	3.48
$O\underline{CH_2}CH_3$	3.35	3.43	3.46	3.28	3.45	3.50
$OCH_2\underline{CH_3}$	1.16	1.20	1.15	1.05	1.20	1.25
$2\text{-}CH_3$		1.36		1.23		1.38
$4\text{-}CH_3$	1.68		1.76		1.73	
H-2	2.16		2.03		2.17	
H-3	5.28	5.46	5.29	5.48	5.18	5.50
H-4		5.46		5.48		
H-5	2.92	2.83	3.16	3.10	3.07	3.33
H-6 *(endo)*	1.85			1.63	3.68	
H-6' *(exo)*	2.35	4.36	4.16	2.25		2.04
H-7 *(endo)*		1.29	1.26		1.62	3.72
H-7' *(exo)*	4.42	2.00	2.11	4.31	1.98	
H-8	2.16	2.21	1.73	1.72	2.08	1.85

Table 1. 300 MHz ^1H NMR spectral data of photo-adducts 1, 2, 3, 4, 5 and 6.

In all adducts, the nuclear Overhauser effect shows the proximity of the methoxy group to the cyclopropane proton(s) and to H-5.

The presence of a proton H-6' (*exo*) can be shown by its coupling with H-5 ($J_{5,6'}$ = ca. 6 Hz), in agreement with a dihedral angle of 35°. There is zero coupling between H-5 and H-6 (*endo*), in accordance with the dihedral angle of 85° that is found from model studies.

In all adducts except 6 the W-relationship between protons H-5 and H-7' (*exo*) is responsible for coupling with a coupling constant $J_{5,7'}$ = 1.5 Hz [8,9].

The position of the ethoxy group could be established by irradiating the low field proton that is located on the carbon atom bearing this group.

Other assignments were made by using homonuclear decoupling techniques in the same way as described elsewhere [5].

The total yield of isolated photo-adducts, based on the amount of starting material converted, was 70 %.

It is remarkable that no traces could be found of the adducts *exo*-7-ethoxy-4-methyl-II (7) and *exo*-6-ethoxy-2-methyl-II (8). We do not yet have a satisfactory explanation for their absence. From the ratio in which the six adducts are formed it can be seen that there is some preference for formation of a three membered ring between the carbon atom bearing the methoxy group and the unsubstituted *meta* position.

After irradiation of 3-fluoroanisole (1 M) in ethylvinylether with light of 254 nm, the three photo-adducts (1a), (2a) and (5a) could be isolated by HPLC in the ratio 2.5 : 3 : 1. The structural analysis by means of 300 MHz ^1H NMR spectroscopy was performed similarly as with the methyl substituted compounds. The absence of adducts (3a) and (4a) may be rationalized by assuming electronic repulsion between the ethoxy group and the fluorine atom in the corresponding exciplex. The NMR spectral data of photo-adducts (1a), (2a) and (5a) are presented in Table 2. The spectra were measured in $CDCl_3$.

	(1a) δ in ppm; (multiplicity); J in Hz	(2a) δ in ppm; (multiplicity); J in Hz	(5a) δ in ppm; (multiplicity); J in Hz
OCH_3	3.50 (s)	3.48 (s)	3.41 (s)
$O\underline{CH_2}CH_3$	3.41 (m)	3.35 (m)	3.48 (m)
$OCH_2\underline{CH_3}$	1.21 (t)	1.15 (t)	1.19 (t)
H-2	1.6 (m)		2.10 (m)
H-3	5.86 (d) $J_{3,F}$ = 6	5.63 (m)	4.89 (d) $J_{3,F}$ = 6
H-4		6.00 (d) $J_{3,4}$ = 6.9	
H-5	2.45 (dd) $J_{5,F}$ = 26 $J_{5,6}$ = 6.3	2.63 (dd) $J_{5,F}$ = 19.8 $J_{5,6}$ = 6.2	3.22 (dd) $J_{5,F}$ = 26 $J_{5,7'}$ = 1.5
H-6 (*endo*)	1.65 (dd)		3.95 (d) $J_{6,7}$ = 8
H-6' (*exo*)	2.13 (m)	4.55 (m)	
H-7 (*endo*)		1.64 (dd) $J_{7,F}$ = 3.6 $J_{7,7'}$ = 13.2	1.81 (dd) $J_{7,7'}$ = ca. 12.5
H-7' (*exo*)	5.45 (m)	2.26 (m)	2.05 (m)
H-8	1.6 (m)	1.21 (d) $J_{8,F}$ = 26	2.00 (m)

Table 2. 300 MHz ^1H NMR spectral data of photo-adducts 1a, 2a and 5a.

Acknowledgement

The authors wish to express their gratitude to Mr. C. Erkelens for his assistance in recording the 300 MHz ^1H NMR spectra on the Bruker WM 300 NMR spectrometer and to Mr. B.E. Parera for his help with the GLC separations.

This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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(Received in UK 24 June 1982)