

A CIS-PHOTODIMER OF 2-METHOXYNAPHTHALENE

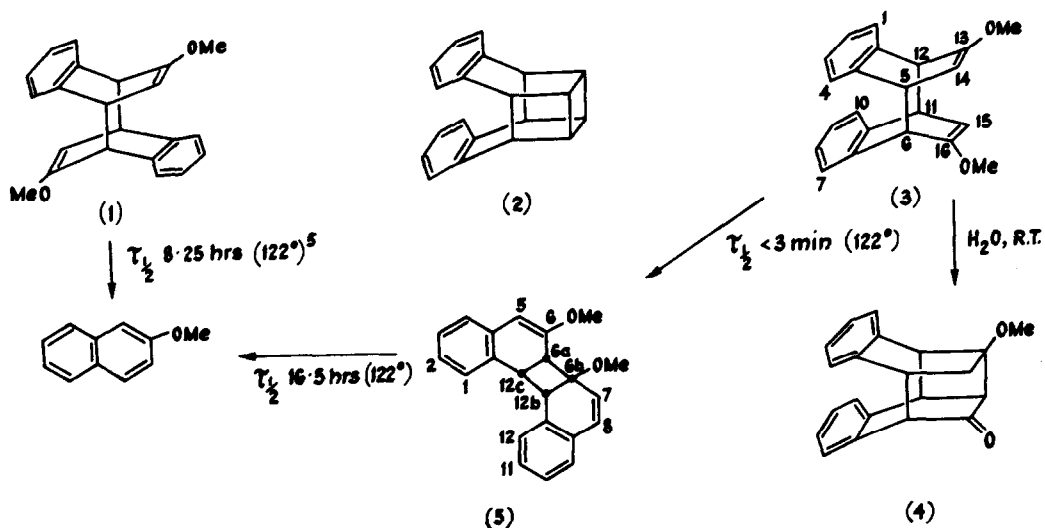
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On irradiation with Pyrex-filtered ultraviolet light solutions of 2-methoxynaphthalene deposit a photodimer¹ for which the *trans*-structure has been established by X-ray structure analysis² but other naphthalene derivatives form *cis*-photodimers that are based on the ring system (2).^{3,4,5} We now report that u.v. irradiation of 2-methoxynaphthalene in benzene produces besides the *trans*-dimer (1) a second photodimer for which we propose the *cis*-structure (3) on the basis of its spectroscopic and chemical properties.



The formation of a *cis*-photodimer of 2-methoxynaphthalene during irradiation in benzene was first suggested by the isolation of the ketone (4) from this reaction⁶, and we now report that this ketone is in fact formed by hydrolysis of the *cis*-dimer (3). As described below this reaction is relatively fast even at ambient temperatures, and in the absence of added acid catalysts, and an analogous *trans*-annular reaction in methanol proceeds equally readily. This reactivity of (3) together with its thermal instability above *ca.* 50° determine the conditions under which it can be isolated.

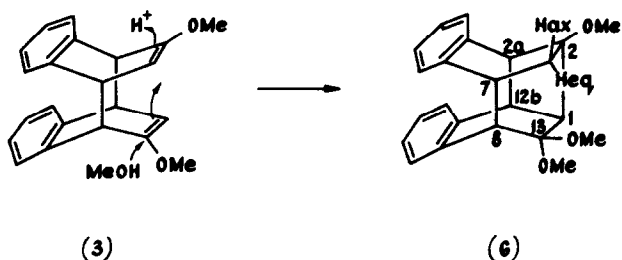
A degassed solution of 2-methoxynaphthalene (10g; sublimed) in anhydrous benzene (50 ml) was irradiated in a Pyrex photoreactor for four days at 10° with a Philips HPK 125 W lamp. The precipitated *trans*-dimer (1) (3.0 g) was filtered off and washed with cold acetone. The filtrate was freed of solvents below 40° and extracted with petrol.⁷ The soluble part was chromatographed on silica gel to give 2-methoxynaphthalene (5.1 g) and ketone (4) (0.63g), m.p. 185-186°.⁶ Rapid crystallisation of the petrol-insoluble part (1.0 g) from benzene-petrol⁷ (2:1) gave colourless crystals (up to 0.5 g) of (3), m.p. 130-136° (decomp.)⁸. According to its mass spectrum [molecular ion peak at m/e 316 (relative abundance 4%); base peak at m/e 158] the new compound is a dimer of methoxynaphthalene. We propose structure (3) mainly on the basis of the p.m.r. spectrum⁹ in which a slightly broadened singlet at δ 6.68 accounts for eight aromatic protons and a singlet at δ 3.58 for two methoxy groups. The six remaining protons give rise to three doublet-of-doublets, each corresponding to two protons [at δ 3.60 ($J_{6,15}=J_{12,14}=\pm 2.4$ Hz; $J_{5,6}=J_{11,12}=10.4$ Hz; H-6 and H-12); δ 3.74 ($J_{5,14}=J_{11,15}=7.4$ Hz; $J_{5,6}=J_{11,12}=10.4$ Hz; H-5 and H-11); δ 5.27 ($J_{5,14}=J_{11,15}=7.4$ Hz; $J_{6,15}=J_{12,14}=\pm 2.4$ Hz; H-14 and H-15)]; these parameters, which were obtained by computer analysis⁹, reproduce the experimental spectrum irrespective of the sign of $J_{6,15}$. The u.v. spectrum of the new dimer [isooctane λ_{\max} (ϵ) at 268 (1000) and at 289 nm (1260); shoulders at 235 (6400), 260 (1110), and at 282 nm (1070); no significant absorption above 300 nm] is consistent with structure (3) and reveals considerable interaction between the two vinyl ether moieties.¹⁰

In keeping with the proposed structure^{10,11} the *cis*-dimer (3) rearranges on heating [half-life 11 min. at 80°; < 3 min. at 122°] to give an isomer for which we propose the structure (5) mainly on spectroscopic grounds. This dimer was isolated from the mother liquors of the crystallisation of (3) in up to 35% yield by removal of the solvents (below 40°) and crystallisation from ethanol which gave colourless crystals of (5), m.p. 124-126°.⁸ Its mass spectrum is virtually identical with that of (3) but its ultraviolet spectrum [$\lambda_{\max}^{\text{EtOH}}$ at

266 nm (17000) extending to ca. 330 nm (ϵ 9100, 1900, and 350 at 285, 310 and 325 nm, respectively)] indicates additional conjugation and its p.m.r. spectrum reveals the presence of two non-equivalent methoxy groups (3-proton singlets at δ 3.07 and 3.71). Other signals (δ) and their assignments on the basis of structure (5) are as follows: dd, 3.62 (1H; $J_{6a,12c}$ 11.3 Hz; $J_{6a,12b}$ 0.4 Hz; H-6a); dd^{*}, 4.06 (1H; $J_{6a,12c}$ 11.3 Hz; $J_{12c,12b}$ 10.0 Hz; H-12c); ddd^{*}, 4.26 (1H; $J_{12b,12c}$ 10.0 Hz; $J_{12b,7}$ 1.5 Hz; $J_{6a,12b}$ 0.4 Hz; H-12b); s^{*}, 5.42 (1H; H-5); dd, 5.61 (1H; $J_{7,8}$ 10.0 Hz; $J_{7,12b}$ 1.5 Hz; H-7); d, 6.31 (1H; $J_{7,8}$ 10.0 Hz; H-8); these parameters were obtained by computer analysis.⁹ Two further signals [d^* , 6.03 (7.5 Hz) and ddd, 6.43 (7.5 Hz; 7.0 Hz; 2.0 Hz)] correspond to two shielded aromatic protons whose assignment depends on the conformation adopted by (5);³ with 6b-OMe in the equatorial position H-1 and H-2 are shielded by the second aromatic ring; in the other conformation (6b-OMe axial) H-12 and H-11 are shielded. Six other aromatic protons resonate as a multiplet between δ 6.6 and 7.3. In agreement with structure (5) this dimer reverts quantitatively to 2-methoxynaphthalene on heating (half-life at 122° 16.5 hrs).

The conversion of the photodimer (3) to the ketone (4)⁶ was monitored using a 10% solution of (3) in benzene, which had previously been equilibrated with water; 50% conversion to (4) occurred after 4 days at 18-20° but when this experiment was carried out in the presence of a trace of *p*-toluenesulphonic acid (4) was formed instantaneously and quantitatively.

Analogous transannular acid-catalysed additions occurred equally fast with alcohols. For instance, treatment of (3) in benzene with methanol and *p*-toluenesulphonic acid (all anhydrous) gave a quantitative yield of the dimethylketal (6), which separated from benzene-petrol⁷ as colourless crystals, m.p. 148-150°.⁸ The structure proposed for this compound rests on its quantitative conversion to (4) by treatment with *p*-toluenesulphonic acid in boiling benzene, or by chromatography on silica gel, and on its spectroscopic properties [molecular ion at m/e 348 (4%), base peak at 158. δ (CDCl₃)⁹: dd, 1.45 (1H; $J_{14ax,14eq}$ -11.7 Hz; $J_{7,14ax}$ 1.9 Hz; H-14ax); dd, 2.63 (1H; $J_{14ax,14eq}$ -11.7 Hz; $J_{7,14eq}$ 4.1 Hz; H-14eq); s, 2.88 (3H; CH₃-O-13_{ax}); ddd, 3.15 (1H; $J_{1,12b}$ 10.2 Hz; $J_{1,8}$ 2.3 Hz; $J_{1,2a}$ 1.3 Hz; H-1); s, 3.30 (3H; CH₃-O-2(?)); s, 3.36 (3H; CH₃-O-13eq(?)); dd, 3.47 (1H; $J_{7,8}$ 10.4 Hz; $J_{1,8}$ 2.3 Hz; H-8); ddd, 3.56 (1H; $J_{7,8}$ 10.4 Hz; $J_{7,14eq}$ 4.1 Hz; $J_{7,14ax}$ 1.9 Hz; H-7); dd, 3.83 (1H; $J_{2a,12b}$ 10.9 Hz; $J_{1,2a}$ 1.3 Hz; H-2a); dd, 3.98 (1H; $J_{2a,12b}$ 10.9 Hz; $J_{1,12b}$ 10.2 Hz; H-12b); m, 6.5-7.0 (8H; ArH)].



Irradiation of (3) in benzene with Pyrex-filtered u.v. light with and without benzophenone or xanthone (3) gave 2-methoxynaphthalene and traces of (1); the corresponding dimethoxy derivative of (2) was not detected.

The detection of a second photodimer of 2-methoxynaphthalene may be relevant in connection with unsuccessful attempts to correlate the kinetics of the formation of (1) with the excimer fluorescence of 2-methoxynaphthalene.¹²

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7. Petroleum Spirit, b.p. 60-80°, containing less than 1% aromatics.
8. Satisfactory microanalytical data have been obtained for this compound.
9. Recorded in CDCl₃ against TMS as internal standard with a Varian HA-100 spectrometer. Calculations were performed using the LAOCOON III program. s, singlet; d, doublet; m, multiplet. An asterisk (*) refers to a broadened signal.
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