

Photo-isomerisation of 1-(2,4-Dimethoxyphenyl)but-2-en-1-one

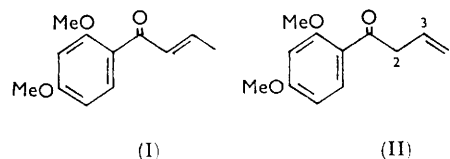
By H. D. Munro and O. C. Musgrave, Chemistry Department, The University, Old Aberdeen

On exposure to light, 1-(2,4-dimethoxyphenyl)but-2-en-1-one undergoes hydrogen migration giving 1-(2,4-dimethoxyphenyl)but-3-en-1-one.

IN the course of the identification of the chromophore of α,β -dehydrocurvularin¹ we synthesised the $\alpha\beta$ -unsaturated ketone 1-(2,4-dimethoxyphenyl)but-2-en-1-one (I) by the acylation of *m*-dimethoxybenzene with crotonoyl chloride. The use of anhydrous stannic chloride as catalyst avoided the partial demethylation which occurs when the reaction is brought about by anhydrous aluminium chloride.² The nuclear magnetic resonance (n.m.r.) spectrum of the product shows the expected multiplets at *ca.* τ 8.1 and 3.15 due to the allylic methyl protons and the olefinic protons, respectively, while the u.v. absorption resembles closely that of 2,4-dimethoxybenzophenone,³ so confirming the presence of the cross-conjugated system.

Exposure of this α,β -unsaturated ketone in dilute ethanolic solution to diffuse sunlight for 7 days resulted in a marked change in its u.v. absorption and we therefore examined the photochemistry of the compound.

Irradiation in ethanolic solution with the unfiltered light from a medium-pressure mercury-vapour lamp gave a mixture which was separated by thin-layer chromatography (t.l.c.) into unchanged starting material and an isomeric compound. The latter shows u.v.



absorption which resembles closely that of 2,4-dimethoxyacetophenone indicating that its olefinic group is no longer conjugated with the aromatic carbonyl group. Its n.m.r. spectrum establishes that it is the β,γ -unsaturated ketone (II). The methylene protons at C-2

¹ H. D. Munro, O. C. Musgrave, and R. Templeton, *J. Chem. Soc. (C)*, 1967, in the press.

² J. Smith and R. H. Thomson, *J. Chem. Soc.*, 1960, 346.

³ J. VanAllan and J. F. Tinker, *J. Org. Chem.*, 1954, **19**, 1243.

Org.

appear as a pair of triplets centred at τ 6.4, being coupled with the proton at C-3 ($J = 6$ c./sec.) and, at long range, with the two protons at C-4 (with identical coupling constants $J = 1.4$ c./sec.). The multiplet found at τ 3.7–4.3 corresponds to the olefinic proton at C-3 which is coupled with the protons at C-2 ($J = 6$ c./sec.) and with those at C-4 ($J = 9$ and 12 c./sec.). The two remaining olefinic protons at C-4 give complex multiplets centred at τ 4.85 and 5.08 which resemble closely those observed for the corresponding protons in safrole.⁴ The signals given by the methoxyl protons (singlets at τ 6.13 and 6.2) and by the aromatic protons (multiplets centred at τ 2.3 and 3.59) resemble closely those obtained from the conjugated isomer (I).

The unconjugated ketone (II) readily reverts to the conjugated isomer (I). Distillation resulted in complete conversion, while keeping for 2 months in subdued artificial light gave a mixture which appeared from its n.m.r. spectrum to contain approximately equal amounts of the ketones (I) and (II).

The behaviour of the α,β -unsaturated ketone (I) on irradiation is similar to that of phorone. The latter also contains a cross-conjugated system and has recently been shown⁵ to give a β,γ -unsaturated ketone on exposure to sunlight or to u.v. light.

EXPERIMENTAL

Ultraviolet absorption spectra were measured for ethanolic solutions using a Hilger "Ultrascan" or a Unicam SP 500 spectrophotometer. I.r. absorption spectra were obtained for liquid films using a Perkin-Elmer "Infracord" model 237 spectrophotometer. N.m.r. spectra were measured in carbon tetrachloride with a Varian Associates A-60 spectrometer (60 Mc.) using tetramethylsilane (τ 10.0) as internal standard.

1-(2,4-Dimethoxyphenyl)but-2-en-1-one.—A solution of anhydrous stannic chloride (26.2 g.) in dry benzene (20 ml.) was added slowly with swirling at 0° to a solution of crotonoyl chloride⁶ (8.4 g.) and *m*-dimethoxybenzene (11.05 g.) in dry benzene (40 ml.). The mixture was kept at 0° for 1.5 hr. and then at room temperature overnight, poured into a mixture of ice and concentrated hydrochloric acid, and extracted with ether. The ethereal solution was washed with water and aqueous sodium hydrogen carbonate, and dried (MgSO_4). Evaporation of the solvent left an oil which on distillation under reduced pressure gave 1-(2,4-di-

methoxyphenyl)but-2-en-1-one (11.4 g.) as an oil, b. p. $130^\circ/0.4$ mm., which solidified on keeping and then had m. p. $44\text{--}46^\circ$ (Found: C, 70.0; H, 6.9. $\text{C}_{12}\text{H}_{14}\text{O}_3$ requires C, 69.9; H, 6.85%), λ_{max} 2390 (log ϵ 4.13, $E_{1\text{cm}}^{1\%}$ 660), 2800 (log ϵ 3.90, $E_{1\text{cm}}^{1\%}$ 383), and 3150 Å (log ϵ 3.92, $E_{1\text{cm}}^{1\%}$ 405); ν_{max} 1660 (aryl alkenyl ketone), 1610 (conjugated aromatic system), and 970 cm^{-1} (*trans* -CH=CH-).

2,4-Dimethoxyacetophenone.—Prepared by the methylation of 2,4-dihydroxyacetophenone this, after repeated distillation, had b. p. $118\text{--}122^\circ/1.0$ mm.; λ_{max} 2280 (log ϵ 4.12), 2665 (log ϵ 4.08), and 3025 Å (log ϵ 3.91), the values of log ϵ being somewhat higher than those previously recorded;⁷ ν_{max} 1648 (aryl alkyl ketone), and 1600 cm^{-1} (conjugated aromatic system).

Irradiation Experiments.—(a) A 0.001% solution of 1-(2,4-dimethoxyphenyl)but-2-en-1-one in ethanol after exposure in a Pyrex vessel to diffuse January sunlight for 7 days had λ_{max} 2305 ($E_{1\text{cm}}^{1\%}$ 557), 2730 ($E_{1\text{cm}}^{1\%}$ 408), and 3070 Å ($E_{1\text{cm}}^{1\%}$ 351).

(b) A solution of 1-(2,4-dimethoxyphenyl)but-2-en-1-one (2.0 g.) in ethanol (150 ml.) was irradiated for 20 hr. under a nitrogen atmosphere in an annular quartz vessel using a "Hanovia" S500 medium-pressure mercury-vapour lamp, filtered to remove gummy material, and then evaporated under reduced pressure. The residual oil was subjected in the dark to t.l.c. on silica gel with a mixture (3:2 by volume) of light petroleum (b. p. $60\text{--}80^\circ$) and ether for development. From visual examination of the chromatogram it appeared that the starting material and the photo-product, although not completely separated, were present in approximately equal quantities. The appropriate part of the chromatogram was extracted with ether and the extract was evaporated, finally at $60^\circ/0.1$ mm., giving 1-(2,4-dimethoxyphenyl)but-3-en-1-one (0.30 g.) as an oil (Found: C, 69.8; H, 6.8%; M (by vapour-pressure osmometry in chloroform), 226. $\text{C}_{12}\text{H}_{14}\text{O}_3$ requires C, 69.9; H, 6.85%; M , 206.25); λ_{max} 2270 (log ϵ 4.17, $E_{1\text{cm}}^{1\%}$ 713), 2680 (log ϵ 4.13, $E_{1\text{cm}}^{1\%}$ 656), and 3025 Å (log ϵ 3.95, $E_{1\text{cm}}^{1\%}$ 434); ν_{max} 1660 (aryl alkyl ketone), and 1600 cm^{-1} (conjugated aromatic system). This distilled at 180° (bath temperature)/0.4 mm. giving 1-(2,4-dimethoxyphenyl)but-2-en-1-one, the i.r. absorption of which was identical with that of the authentic specimen described above.

We are indebted to Dr. D. G. Williamson for determining and discussing the n.m.r. spectra, and to the S.R.C. for the award of a studentship to H. D. M.

[6/1333 Received, October 19th, 1966]

⁵ K. J. Crowley, R. A. Schneider, and J. Meinwald, *J. Chem. Soc. (C)*, 1966, 571.

⁶ H. C. Brown, *J. Amer. Chem. Soc.*, 1938, **60**, 1325.

⁷ O. C. Musgrave, *J. Chem. Soc.*, 1957, 1104.

⁴ N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, *NMR Spectra Catalog* (Varian Associates, Palo Alto, 1962), vol. 1, Spectrum no. 253.