

Photochemical Synthesis. 32

THE SYNTHESIS OF METHYL ISOMARASMATE

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We describe a synthesis directed towards methyl marasmate², (11) but which so far has only yielded the isomer (10). Since the synthesis contains several photochemical steps we believe that there remains a kernel of chemical interest.

Spiro (2.4) heptadiene was hydrogenated over W2 Raney nickel and the mixture of hydrocarbons, containing 60% of the 5-ene, was fractionated. A solution of cyclopentane-1,2-dione (2g) enol acetate in the spiro[2.4]hept-5-ene (16.2 g) and ether (15 ml) was irradiated through Pyrex to give the adduct (1), m.p. 76-77^{o3}. Hydrogenation in acetic acid (PtO₂) followed by oxidation (CrO₃) gave the ketone (2). Bromination (pyridinium bromide perbromide) gave the α -bromoketone, m.p. 86^{o3} which was dehydrobrominated with 1,5-diazabicyclo [4.3.0]-5-nonene to give (3) as an oil³. Rearrangement with 1% aqueous methanolic sodium hydroxide at room temperature gave the ketol (4), m.p. 89-90^{o3}. Cleavage with lead tetraacetate followed by esterification (CH₂N₂) gave the ketoester (5), m.p. 70-71^{o3,4}. Elimination of methanol using *p*-toluenesulphonic acid in refluxing benzene (1 min.) gave the crude conjugated ester which was oxidised by irradiation in the presence of Rose Bengal and oxygen to the hydroperoxide

(6, R = O₂H)⁵: the latter was reduced to the alcohol m.p. 111°³ (6, R = OH) with triphenylphosphine. Irradiation through Pyrex of (6, R = OH) in the presence of excess vinylene carbonate gave the crude unstable carbonate which was hydrogenated over platinum-rhodium catalyst to the diol (7, R = H), m.p. 185-185.5°³. This was converted into the pivalate (7, R = COC₄H₉) and the crude ester dehydrated with phosphorus oxychloride in pyridine (50°; 4 hr) to give the unsaturated ester (8), m.p. 183.5 - 185°^{3,6}. Diazomethane converted this to the pyrazoline, m.p. 158-165°³, which on irradiation gave (9) which was hydrolysed to give the glycol, m.p. 126-128°³. Cleavage with sodium periodate, followed by heating with triethylamine in benzene (75°; 20 min) gave (10) as an oil^{3,7} $\nu_{\text{max}}^{\text{CCl}_4}$ ca. 1740 (shoulder), 1718, 1690, 1641, 1267, 1142 cm⁻¹; $\lambda_{\text{max}}^{\text{MeOH}}$ 237 nm (ϵ 6, 100); δ^{CDCl_3} 9.62 (1H, s), 9.47 (1H, s), 6.85 (1H, d, J ~ 2Hz), 3.68 (3H, s), 2.53 (1H, d, J ~ 5Hz), 1.06 (3H, s), 1.08 (3H, s) and 0.88 (1H, d, J ~ 5Hz).

Footnotes and References

- (1) Present addresses: M.N., University of Guelph, Ontario; L.W. Swedish Forest Products Research Laboratory, Stockholm, Sweden; R.B.Y., Bishop's University, Quebec.
- (2) J. J. Dugan, P. de Mayo, M. Nisbet and M. Anchel. J. Am. Chem. Soc., **87**, 2768 (1965).
- (3) Compounds so designated had adequate analyses, and full spectral analyses in accord with the assigned structures.
- (4) A model series, using cyclopentene, was first used and the carbon skeleton proven by conversion to the phenol in the indane series.
- (5) This oxidation proceeds by singlet oxygen addition to the small amount of dienol in equilibrium with the ketone. We thank Mr. J. A. Siddiqui for his help in elucidating the mechanism.

(6) A very large number of possible routes from **8** to **11**, methyl marasmate, were explored without success. We thank Dr. K. Maheshwari for his persistent efforts.

(7) **10** was very similar to **11** in UV and IR and indistinguishable on thin layer chromatography. Both were in the stable configuration at the allylic position. The nmr data while supporting structure **10** is different from that of **11**.

