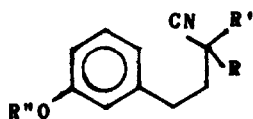
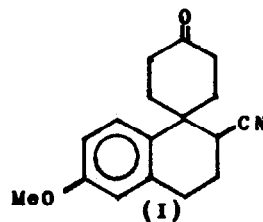
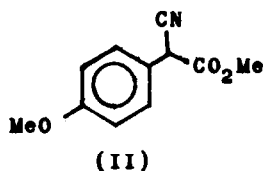


PHOTOCATALYSED INTRAMOLECULAR OXIDATIVE PHENOL COUPLING;
SYNTHESIS OF A SPIRO KETONE RELATED TO DITERPENOIDS

Samir Chatterjee* and Probir Kumar Ghosal
Department of Organic Chemistry, Indian Association for
the Cultivation of Science, Calcutta 700032, India

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Intramolecular oxidative phenol coupling gained its importance¹ through involvement in biosynthesis of various natural products and its synthetic application has also been well documented². Using this as the key step, synthesis of a spiro ketone intermediate (I) is described which represents an advanced relay for elaboration to the newly discovered stemodin³ and aphidicelin⁴ skeleta. The presence of light has been found to accelerate the coupling reaction resulting in a distinct improvement of yield and reaction time as contrasted to the previously known yield² from this reaction.



(III) R = -CO₂Me, R' = *p*-MeOC₆H₄, R'' = -Me

(IV) R = -H, R' = *p*-MeOC₆H₄, R'' = -Me

(V) R = -H, R' = *p*-HOC₆H₄, R'' = -H

Carboxymethylation of *p*-methoxybenzyl cyanide with dimethylcarbonate in presence of NaH afforded the nitrile (II)⁵; b.p. 135-40°/0.3 mm; ν_{\max} (CHCl₃) 2265, 1740, 1600 cm⁻¹; δ (CCl₄) 7.42-6.6 (4H, m), 3.78 (3H, s), 3.72 (3H, s). The nitrile was condensed with *m*-methoxyphenylethyl bromide in presence of NaH to furnish (III) in 89% yield; b.p. 180-85°/0.05 mm; ν_{\max} (CHCl₃) 2270, 1740, 1600 cm⁻¹; δ (CCl₄) 7.42-6.6 (8H, m), 3.72 (6H, s), 3.74 (3H, s). This was decarboxymethylated⁶ by refluxing in a mixture of DMSO and NaCN to yield the nitrile (IV) in 91% yield; b.p. 160-65°/0.05 mm; ν_{\max} (CHCl₃) 2270, 1600 cm⁻¹; δ (CCl₄) 7.3-6.64 (8H, m), 3.6 (1H, t, J = 5 Hz). Demethylation⁷ of (IV) with pyridine hydrochloride at 210-20° furnished almost quantitatively the phenol (V); m.p. 90-92°; ν_{\max} (CHCl₃) 3600, 2270, 1600 cm⁻¹; δ (CDCl₃) 5.2 (2H, vanishes on deuteration). Intramolecular oxidative phenol coupling⁸ of (V) with a 2.5 x 10⁻³(M) solution

of VOCl_3 in ether at -78° for 5 hr led to the formation of a highly viscous oil; $\nu_{\text{max}}(\text{CHCl}_3)$ 3600, 2270, 1665, 1620(w), 1600 cm^{-1} ; $\lambda_{\text{max}}(\text{EtOH})$ 246 nm ($\epsilon = 6143$). This crude coupling product was evidently present as a mixture (t.l.c, i.r and u.v). Although absorption maximum at 246 nm suggested formation of a spiro cyclohexadienone, the poor ϵ value warranted a meagre reaction yield. Use of FeCl_3 -DMF complex² in either solvent, ether or CH_2Cl_2 produced no coupling. The reaction using VOCl_3 under illumination of a tungsten lamp and under above condition afforded after 3 hr a mixture of products (t.l.c) for which ϵ value in u.v. absorption was recorded to be 11,735. This significant rise in ϵ after carrying out the reaction under illumination could result from a photoenergized VO^{3+} species coming down more rapidly to VO^{2+} with a stabler configuration during photoactivation in oxidation process. Fractional sublimation for purification of the phenolic dienone from unreacted (V) was not satisfactory. The coupling product was directly hydrogenated over Pd/C (10%) in ethanol, the resulting tetrahydroderivative was O-methylated with CH_3I in presence of dry K_2CO_3 and chromatographic separation of the product mixture over Al_2O_3 by eluting with pet. ether : benzene (4:2) afforded (I) in 49% overall yield from (V); m.p. 112-13°; $\delta(\text{CDCl}_3)$ 3.72 (3H, s), 3.62 (1H, t, J = 5 Hz); $\nu_{\text{max}}(\text{CHCl}_3)$ 2275, 1705, 1600 cm^{-1} ; m/e 269 (M^+).

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