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PHOTOCHEMICAL SYNTHESIS OF 2-(2-ARYL-5-OXAZOLYL) BENZOATES

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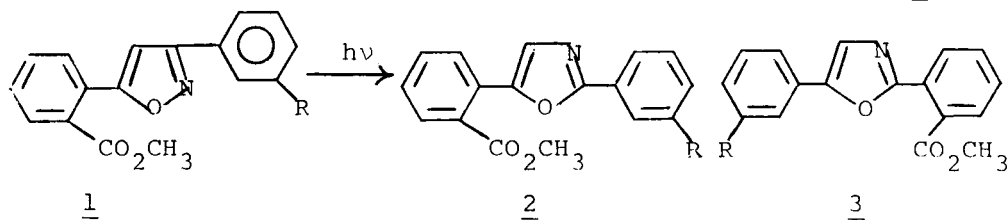
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PHOTOCHEMICAL SYNTHESIS OF
2-(2-ARYL-5-OXAZOLYL)BENZOATES

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(12/10/82)

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The synthesis of 2-(5-phenyl-2-oxazolyl)benzoates useful as growth regulants¹ and herbicides² has been reported; however, the isomeric 2-(2-aryl-5-oxazolyl)benzoates are unknown. We now report the preparation of two derivatives of this latter class of compounds via photochemical transformation³ of the readily accessible⁴⁻⁶ 2-(3-aryl-5-isoxazolyl)benzoates (1).



a) R = H b) R = CF₃

Irradiation of methyl 2-(3-phenyl-5-isoxazolyl)benzoate (1a) at 254 nm produced methyl 2-(2-phenyl-5-oxazolyl)benzoate (2a) in 74% yield; similarly, irradiation of 1b produced methyl 2-[2-(3-trifluoromethylphenyl)-5-oxazolyl]benzoate (2b). The successful general route to compounds 1 reported previously⁶ in combination with the results of photochemical transformations reported here show that this sequence provides a good, convenient synthetic route to 2-(2-aryl-5-oxazolyl)benzoates.

The known 2-oxazolybenzoate 3a² and the new compound 3b were prepared via literature methods.² The herbicidal and plant growth regulant activities of these two isomeric classes of oxazolybenzoates were found to be fairly similar.

EXPERIMENTAL SECTION

Methyl 2-(2-phenyl-5-oxazoly)benzoate (2a).- A solution of 8.0 g of methyl 2-(3-phenyl-5-isoxazoly)benzoate⁶ in 260 mL of acetonitrile was irradiated with low pressure mercury lamps in a Rayonet photochemical reactor, using a quartz vessel. A slow stream of nitrogen was bubbled through the solution to provide mixing. GC analyses on a 2-ft by 0.25 inch column of 2% XE-60 at 225° at various times indicated 99% conversion of 1a to 2a after 53 hrs (the product eluted faster than the starting material). Removal of the solvent gave 8.2 g of oil. Chromatography of the oil by HPLC on an EM LOBAR size "C" silica gel column with 30% ethyl acetate in cyclohexane at 20 mL/min gave a center cut of 5.88 g (74% yield) of product (one spot on TLC, 99% pure by GC) as an oil, n_D^{25} 1.6337; IR (film) 1722 cm^{-1} ; NMR (CDCl_3): δ 8.0 (m, 2), 7.8-7.32 (m, 7), 7.35 (s, 1, H-4), 3.80 (s, 3, OCH_3).

Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_3$: C, 73.11; H, 4.69.

Found: C, 72.91; H, 4.71.

Methyl 2-[2-(3-trifluoromethylphenyl)-5-oxazoly]benzoate (2b).- Ester 2b was prepared in similar fashion from 4.12 g of 1b.⁶ Chromatography of the crude product gave 3.48 g of crystals, mp 63-72°. Recrystallization of the crystals once from toluene-hexane and once from hexane yielded 2.22 g (54%) of pure product as white crystals, mp. 84.5-86°; NMR (CDCl_3): δ 8.12

(m, 2), 7.75-7.30 (m, 6), 7.38 (s, 1, H-4), 3.77 (s, 3); IR (CHCl₃) 1724 cm⁻¹.

Anal. Calcd for C₁₈H₁₂F₃NO₃: C, 62.25; H, 3.48.

Found: C, 62.11; H, 3.49.

Methyl 2-(5-phenyl-2-oxazolyl)benzoate (3a).- N-phenacylphthalimide, mp. 166-168°, lit.⁷ mp. 167°; N-phenacylphthalamic acid, mp. 160°, lit.⁷ mp. 160°; 2-(5-phenyl-2-oxazolyl)benzoic acid², mp. 185° dec; and methyl 2-(5-phenyl-2-oxazolyl)benzoate, mp. 76-77°, lit.² mp. 77-79° [IR (CHCl₃) 1720 cm⁻¹; NMR (CDCl₃): δ 7.94 (m, 1), 7.75-7.10 (m, 9), 3.77 (s, 3)] were prepared by literature procedures.^{2,8}

Methyl 2-[5-(3-trifluoromethylphenyl)-2-oxazolyl]benzoate (3b).-

In similar manner were prepared N-(3-trifluoromethylphenacyl)-phthalimide, mp. 145-148°, 77% yield (Anal. Calcd for C₁₇H₁₀F₃NO₃: C, 61.27; H, 3.02. Found: C, 61.10; H, 3.06); N-(3-trifluoromethylphenacyl)phthalamic acid, mp. 162-164°, 92% yield (Anal. Calcd for C₁₇H₁₂F₃NO₄: C, 58.13; H, 3.44; N, 3.99. Found: C, 58.02; H, 3.38; N, 4.00); 2-[5-(3-trifluoromethylphenyl)-2-oxazolyl]benzoic acid, mp. 165-166°, 87% crude yield; and methyl 2-[5-(3-trifluoromethylphenyl)-2-oxazolyl]benzoate, mp. 92.5-94°, 61% yield [NMR (CDCl₃): δ 7.45-8.10 (m, 9), 3.90 (s, 3); IR (CHCl₃) 1725 cm⁻¹; Anal. Calcd for C₁₈H₁₂F₃NO₃: C, 62.25; H, 3.48. Found: C, 62.37; 3.54].

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NEW HYDRAZONOYL BROMIDES AND AZOMETHYLENE PHOSPHORANES

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Highly crystalline, stable azomethylene triphenylphosphoranes II (Table 2) are obtained from the reaction of equimolar amounts of hydrazonoyl bromide (I) and triphenylphosphine in the presence of a slight excess of triethylamine in benzene or