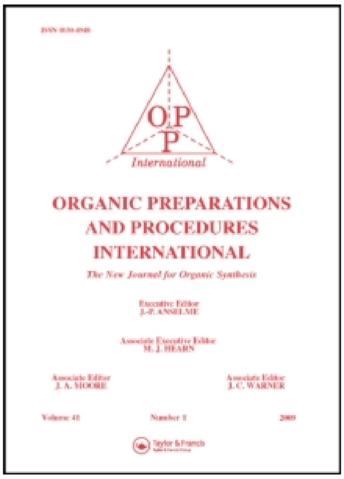

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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

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To cite this Article Liu, Kou-Chang and Howe, Robert K.(1983) 'PHOTOCHEMICAL SYNTHESIS OF 2-(2-ARYL-5-OXAZOLYL) BENZOATES', Organic Preparations and Procedures International, 15: 4, 265 — 268
To link to this Article: DOI: 10.1080/00304948309356652
URL: http://dx.doi.org/10.1080/00304948309356652

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

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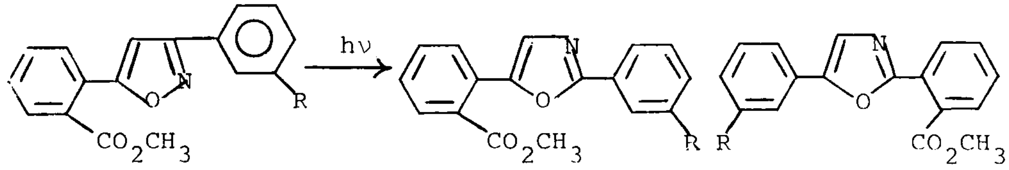
The synthesis of 2-(5-phenyl-2-oxazolyl)benzoates useful as growth regulants[1] and herbicides[2] has been reported; however, the isomeric 2-(2-aryl-5-oxazolyl)benzoates are unknown. We now report the preparation of two derivatives of this latter class of compounds *via* photochemical transformation[3] of the readily accessible[4-6] 2-(3-aryl-5-isoxazolyl)benzoates (1).



1 2 3

a) R = H b) R = CF_3

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 previously[6] 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-oxazolylbenzoate 3a[2] and the new compound 3b were prepared *via* literature methods.[2] The herbicidal and plant growth regulant activities of these two isomeric classes of oxazolylbenzoates were found to be fairly similar.

EXPERIMENTAL SECTION

Methyl 2-(2-phenyl-5-oxazolyl)benzoate (2a).- A solution of 8.0 g of methyl 2-(3-phenyl-5-isoxazolyl)benzoate[6] 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 $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69.
Found: C, 72.91; H, 4.71.

Methyl 2-[2-(3-trifluoromethylphenyl)-5-oxazolyl]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 ($CHCl_3$) 1724 cm^{-1}.

Anal. Calcd for $C_{18}H_{12}F_3NO_3$: 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 acid[2], mp. 185° dec; and methyl 2-(5-phenyl-2-oxazolyl)benzoate, mp. 76-77°, lit.[2] mp. 77-79° [IR ($CHCl_3$) 1720 cm^{-1}; NMR ($CDCl_3$): 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 $C_{17}H_{10}F_3NO_3$: 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 $C_{17}H_{12}F_3NO_4$: 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 ($CDCl_3$): δ 7.45-8.10 (m, 9), 3.90 (s, 3); IR ($CHCl_3$) 1725 cm^{-1}; Anal. Calcd for $C_{18}H_{12}F_3NO_3$: 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