

SHORT COMMUNICATIONS

SYNTHESIS OF 4,6-DIMETHYL-3,7-DIARYL-2,8-DIOXO-2H,8H-BENZO [1,2-b:5,4-b'] DIPYRANS AS POTENTIAL INSECTICIDES

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Earlier¹ five title compounds were synthesized by heating 2,4-dihydroxy-5-acetyl acetophenone and substituted sodium phenyl acetates and acetic anhydride. Due to the high temperature required in the above method, the yields were low. Further, the insecticidal and antifeedant activity of the above class of compounds does not seem to have been studied so far. As such, the synthesis of some new 4,6-dimethyl-3,7-diaryl-2,8-dioxo-2H,8H-benzo [1,2-b:5,4-b']-dipyrans has now been taken up with a view to evaluate their fish toxicity and antifeedant activities.

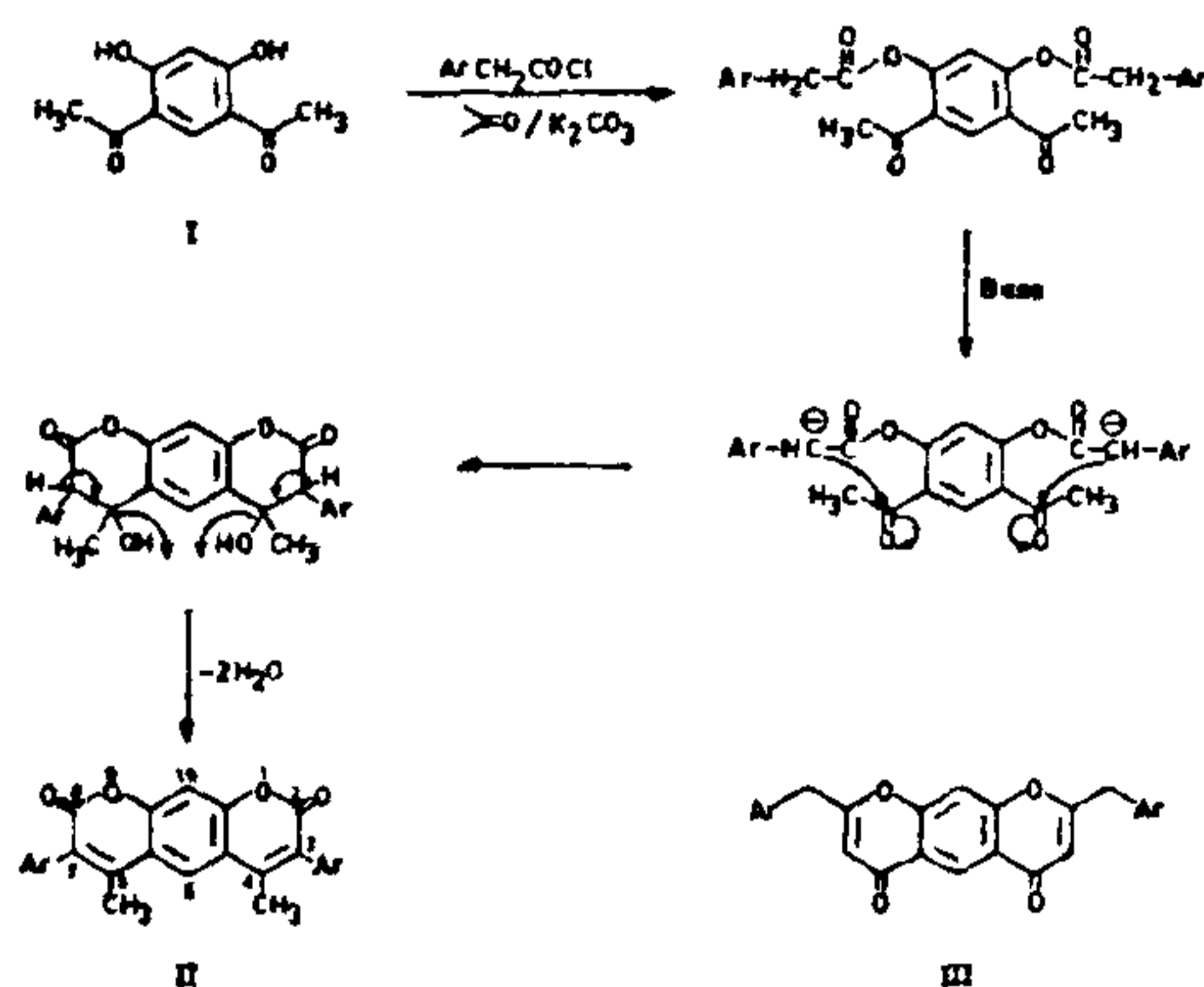
In the present investigation, an alternative and more facile approach involving modified Baker-Venkatraman transformation²⁻⁴ has been explored. Thus 2,4-dihydroxy-5-acetylacetophenone⁵ (0.01 mol) and phenylacetylchloride (0.02 mol) were dissolved in dry acetone and refluxed with anhydrous potassium carbonate for 6 hr. The acetone solution was filtered and the potassium carbonate was washed with acetone. The combined acetone solution on evaporation yielded a brown semisolid which was treated with ice-cold water. The solid that separated was crystallized from acetone as colourless needles in good yields (81%), m.p. 278°, C₂₆H₁₈O₄, M⁺ 394.

The IR spectrum of the product showed absorption at 1710 cm⁻¹ which is characteristic of carbonyl group of coumarins. The UV absorption data $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ) 275 (4.36), 343 (4.28) are in good agreement with those of 3-phenylcoumarins⁶. The ¹H NMR spectrum of IIa exhibited a singlet at δ 2.39 (6 H) due to protons of allylic methyl groups situated at C-4 and C-6 carbons. The spectrum also revealed two sharp singlets at δ 7.43 (1 H) and 7.91 (1 H) assignable to the H-10 and H-5 respectively. The aromatic region of the spectrum showed a multiplet at δ 7.30 (10 H) for C-3 and C-7 phenyl ring protons. The mass spectrum of IIa showed molecular ion peak at 394 (100%). The prominent fragmentation ions at m/z 366 (22%) [M-CO], 338 (25%) [M-2CO] were

highly diagnostic⁷. On the basis of the above analytical and spectral data IIa has been identified as 4,6-dimethyl-3,7-diphenyl-2,8-dioxo-2H,8H-benzo [1,2-b:5,4-b'] dipyran (IIa). Though there is a possibility of the formation of isomeric compound 2,8-dibenzyl-4,6-dioxo-4H,6H-benzo [1,2-b:5,4-b'] dipyran (IIIa), such product is not found even in traces. Following the above method several substituted 2,8-dioxo-2H,8H-benzo [1,2-b:5,4-b'] dipyrans (IIb-i) were synthesized. The analytical and spectral data of all the compounds synthesized are given in table 1.

This method is an one-step reaction, the conditions are mild, there was no significant substituent effect on the reaction, the yields are good to excellent and byproducts were not detected.

All the compounds synthesized have been tested for their fish-toxicity following the "survival time method" of Powers⁸ and Gersdorff⁹ as well as the "turning time method" of Krishnaswami and Seshadri¹⁰ taking rotenone as standard. The fish species, *Cyprinus carpio communis* and *Oreochromis mossambicus* were employed as test animals for evaluating turning time and survival time respectively. The antifeedant activity of the above compounds was assessed by the "non-choice test



Ar :- a = phenyl
b = p-methoxyphenyl
c = p-chlorophenyl
d = p-bromophenyl
e = p-hydroxyphenyl

f = p-acetoxyphenyl
g = p-nitrophenyl
h = p-methoxyphenyl
i = p-chlorophenyl

Table 1

Comp. No.	M. P. °C	M ⁺	IR $\nu_{\text{max}}^{\text{KBr}}$ >C=O	UV $\lambda_{\text{nm}}^{\text{max}}(\log \epsilon)$	Yield %	Turning time min-sec	Survival time min-sec	% Anti-feedant activity
IIa	278 (Lit. ¹ 276-7)	394	1710	275(4.36) 345(4.28)	81	35-12	**	61.75
IIb	264 (lit. ¹ 263-4)	454	1705	273(4.40) 345(4.28)	80	04-11	53-29	89.84
IIc	285	—	1700	270(4.37) 343(4.25)	76	03-07	42-33	97.46
IId	291	—	1710	260(4.39) 340(4.28)	80	01-59	14-39	98.57
IIe	310	—	1700	265(4.38) 345(4.27)	73	07-09	63-49	79.36
IIIf	270	—	1710	260(4.40) 346(4.33)	75	05-20	19-43	83.01
IIg	>320 (lit. ¹ >330)	—	1710	263(4.32) 345(4.30)	71	14-40	129-36	76.98
IIh	257	—	1710	268(4.37) 342(4.25)	79	08-01	53-17	83.49
IIi	295	—	1705	264(4.33) 350(4.28)	74	06-40	57-30	73.96

**Not toxic within 4 hr. All the compounds gave satisfactory percentages for carbon and hydrogen.

method¹¹ using 6 hr prestarved fourth instar larvae of *Spodoptera litura*. The results are shown in table 1. The present study revealed that 4,6-dimethyl-3,7-di(*p*-bromophenyl) 2,8-dioxo-2H,8H-benzo-[1,2-*b*:5,4-*b'*] dipyrans (IId) exhibited the highest fish-toxicity and antifeedant activity.

The general procedure for the synthesis of 4,6-dimethyl-3,7-diaryl-2,8-dioxo-2H,8H-benzo [1,2-*b*:5,4-*b'*] dipyrans is as follows.

A solution of the 2,4-dihydroxy-5-acetylacetophenone (0.01 mol) and phenyl acetyl chlorides (0.02 mol) in acetone (200 ml) was refluxed with anhydrous potassium carbonate (5 g) for 6-8 hr on a water bath. The acetone solution was filtered, potassium carbonate washed with acetone. The combined acetone solution was evaporated and cold water was added to the residue. The separated product was filtered and washed successively with 2% aqueous sodium bicarbonate and water. The crude products were crystallized from acetone/methanol.

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