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REACTION OF AMIDOXIMES WITH DIPHENYLCYCLOPROPENONE. SYNTHESIS OF 2-ARYL-5,6-DIPHENYLPYRIMIDIN-4-ONES

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The reaction of arylamidoximes with diphenylcyclopropenone in refluxing toluene gave 2-aryl-5,6-diphenylpyrimidin-4-ones in good yields.

The reaction of diphenylcyclopropenone (DPP) has attracted considerable synthetic interest recently.[1] In the previous paper we reported that the reaction of aromatic azines with DPP proceeded via 1:1 (2+3) cycloadducts to give 5-aryl-2,3-diphenyl-2-pyrrolin-4-ones.[2] As part of our synthetic study of heterocycles using DPP we examined the reaction of arylamidoximes with DPP and found that the reaction afforded 2-aryl-5,6-diphenylpyrimidin-4-ones in one step in good yields. Recently, Eicher et al. reported that the reaction of guanidines and amidines with DPP afforded 2-substituted 5,6-diphenyl-5,6-dihydropyrimidin-4-ones, which were then dehydrogenated by o-chloranil or elemental sulfur to 2-substituted 5,6-diphenylpyrimidin-4-ones.[3] We wish to report our more facile and general synthesis of the pyrimidin-4-ones.

The reaction was carried out in the following general procedure: a mixture of amidoxime (1) (1.0 mmol) and an equimolar amount of DPP in toluene (5 ml) was refluxed for 2 h. After cooling the precipitates were collected and recrystallized from DMF to give the product 4. The results are summarized in Table.

1-4	R
a	C_6H_5-
b	4-$MeOC_6H_4$-
c	4-MeC_6H_4-
d	4-BrC_6H_4-
e	3-$NO_2C_6H_4$-
f	4-ClC_6H_4-
g	2-Pyridyl-

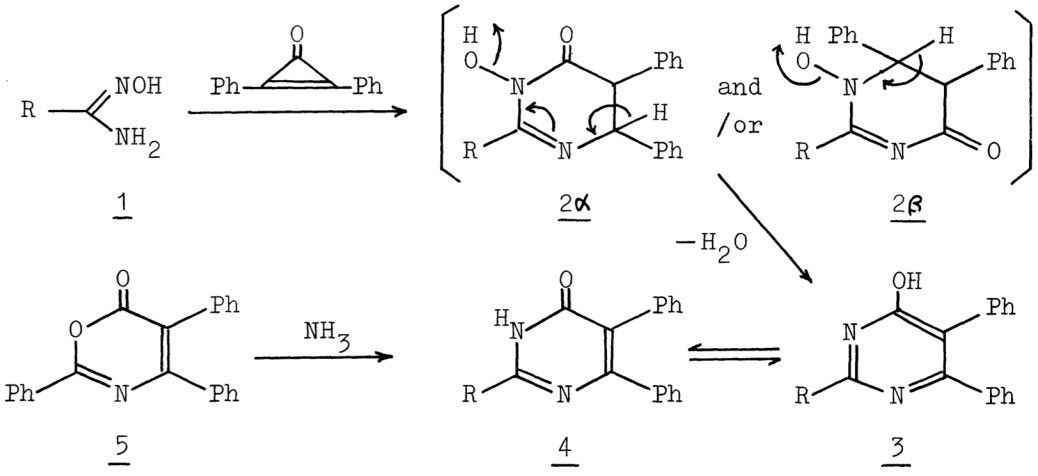

Table. 2-Aryl-5,6-diphenylpyrimidin-4-ones (4)[a)]

4	Yield %	Mp °C	IR (KBr) cm^{-1}	NMR (CF_3COOH) δ ppm	UV (MeOH) nm (log ε)
a	60	292-293[b)]	3000 2880 1630 1593	7.27-8.00 (m)	256 (4.35) 325 (4.07)
b	82	273-281	3140—2790 1645 1608	7.30-8.13 (m) 3.97 (s)	226 sh (4.33) 276 (4.35) 332 (4.27)
c	70	>300	3130—2760 1640 1590	7.28-8.07 (m) 2.55 (s)	262 (4.43) 328 (4.18)
d	63	>300	3140—2760 1640 1593	7.30-7.92 (m)	262 (4.45) 328 (4.17)
e	51	288-293	3080—2760 1633 1595	7.33-9.12 (m)	258 (4.54) 322 (4.05)
f	56	>300	3040—2760 1630 1593	7.30-8.15 (m)	261 (4.39) 327 (4.07)
g[c)]	58	258-259	3050 1650 1595	7.33-9.15 (m)	246 (4.27) 270 sh (4.25) 335 (4.10)

a) Satisfactory elemental analyses were obtained for all compounds. b) Lit.[5)] mp 290-294°C. c) 18 **h** of reflux for giving 4g.

The structure of the product obtained from 1a was assigned as 2,5,6-triphenylpyrimidin-4-one (4a) on the basis of the analytical and spectral data, especially agreement of the observed MS (M^+ 324) and UV data with those reported in the literatures.[4,5)] For further structural confirmation the ring transformation of 1,3-oxazin-6-one into pyrimidin-4-one[6)] was attempted. Thus, 2,4,5-triphenyl-1,3-oxazin-6-one[7)] (5) was treated with aqueous ammonia at room temperature to afford a product in a 79% yield, which was identical in all respects to 4a.

The reaction pathway may be visualized as follows: the initially formed 1:1 adduct 2α and/or its regioisomer 2β would be dehydrated and enolated to give 4-pyrimidinol (3), which tautomerizes to 4.

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