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REACTION OF AZINES WITH DIPHENYLCYCLOPROPENONE. SYNTHESIS OF 5-ARYL-2, 3-DIPHENYL-Δ^2-PYRROLIN-4-ONES

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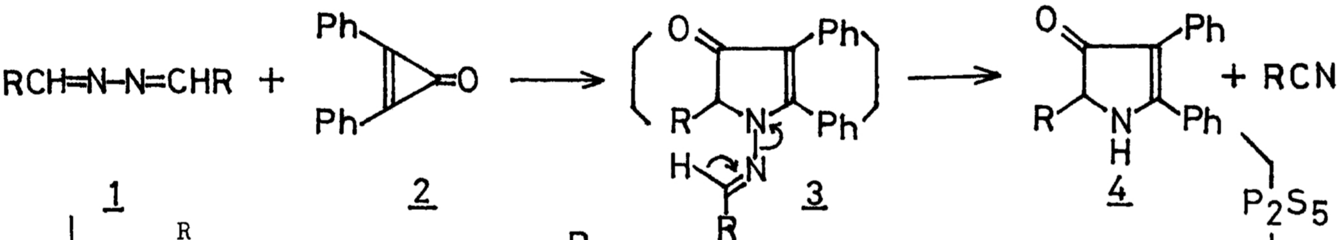
The reactions of aromatic aldehyde azines with diphenylcyclopropenone in refluxing toluene afforded 5-aryl-2, 3-diphenyl-Δ^2-pyrrolin-4-ones in moderate yields.

The cycloaddition reactions of azines with various dipolarophiles give generally criss-cross 1:2 adducts and were reviewed recently.[1)] Eicher et al. have reported [2+3] cycloaddition reactions of aldimines,[2)] ketimines,[3)] guanidines,[4)] and benzamidines[4)] with diphenylcyclopropenone to give 2, 3-diphenyl-Δ^2-pyrrolin-4-ones as reaction intermediates or products. During our course of study of cycloaddition reactions of heterodienes,[5)] these publications prompted us to investigate the reaction of azines with diphenylcyclopropenone and we wish to report our results.

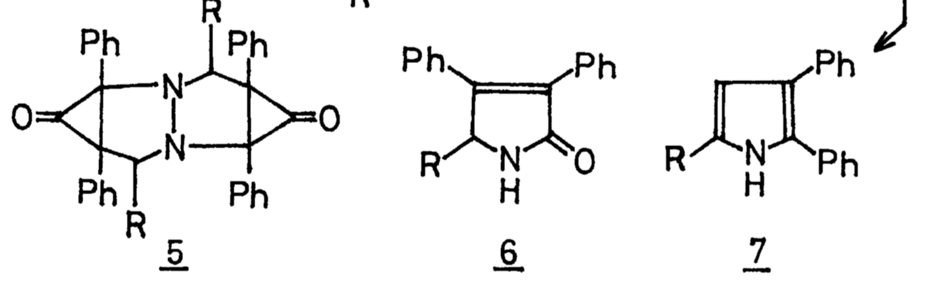
The reaction was carried out in the following general procedure; a mixture of azine 1 (1.0 mmol) and diphenylcyclopropenone 2 (1.2 mmol) in toluene (10 ml) was refluxed for 18-48 h. After cooling the precipitates were filtered and recrystallized. The results are summarized in Table.

The product from 1a and 2 showed the following spectral data: MS m/e (%); 341 (M^+, 42), 339 (M^+-H_2, 28), 326 (M^+-NH, 28), 298 (326-CO, 5.1), 178 (PhC≡CPh, 100). IR (KBr); 3200 (NH), 1640 (CO) cm^{-1}. These data suggest that the product is not such expected compounds as criss-cross 1:2 adduct 5a or [2+3] 1:1 adduct 3a, but addition-elimination product 4a or 6a.



1 2 3 4

	R
a	4-MeO-C_6H_4-
b	4-Me_2N-C_6H_4-
c	4-Me-C_6H_4-
d	4-Me_2CH-C_6H_4-
e	C_6H_5-



5 6 7

In order to distinguish between 4a and 6a, conversion of the product into the known pyrrole derivative was attempted. Thus, treatment of the product with phosphorus pentasulfide in refluxing benzene for 3 h gave 2, 3-diphenyl-5-(4-methoxyphenyl)pyrrole 7a, mp 180-182°C, in 70% yield, which was identical with an authentic specimen$^{6)}$ prepared from 1, 2-diphenyl-4-(4-methoxyphenyl)butane-1, 4-dione and formamide. These results have revealed the structure of the product to be 2, 3-diphenyl-5-(4-methoxyphenyl)-Δ^2-pyrrolin-4-one 4a.

As shown in the scheme the reaction is considered to proceed via [2+3] cycloadduct 3 followed by elimination of RCN. A similar example of the initial cycloaddition to C=N bond of azine followed by elimination of RCN has been reported in the case of the reaction of azines with diphenylketene.$^{7)}$

Table. 5-Aryl-2, 3-diphenyl-Δ^2-pyrrolin-4-ones 4$^{a)}$

4	Reaction time (h)	Yield (%)	Mp (°C) (Solvent)	IR (KBr) cm^{-1}		UV (MeOH) nm (log e)	
a	18	55	283-285 (C_6H_6)	3200	1640	243 (4.35) 250 sh (4.34)	383 (3.88)
b	18	87	244-247 (C_6H_6)	3200	1633	261 (4.35)	400 (4.09)
c	48	49	269-271 (C_6H_6)	3230	1640	254 (4.33)	383 (3.84)
d	48	42	274-275 (THF-MeOH)	3240	1640	255 (4.32)	378 (3.81)
e	24	35	279-284$^{b)}$ (DMF)	3230	1640	254 (4.31)	385 (3.84)

a) Satisfactory elemental analysis was obtained for all compounds.
b) Sublimation

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