UDC 547.594.4:547.551

SYNTHESIS OF N-ARYL ENAMINO KETONES

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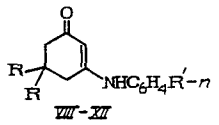
Translated from Khimiko-Farmatsevticheskii Zhurnal, Vol. 29, No. 2, p. 58, February, 1995.

Original article submitted May 16, 1994.

Dihydroresorcinol and dimedone are condensed with aromatic amines at room temperature under the action of $ClSiMe_3$-DMFA system to give 3-anilino-2-cyclohexene derivatives in 70 – 90% yield.

N-aryl enamino ketones (AE) exhibit anti-inflammatory activity [1] and are used in the synthesis of analgesics [2]. AE are obtained by the heating of β-diketones with aromatic amines for many hours, usually in boiling benzene and in the presence of acid catalysts [1, 3, 4].

We have demonstrated for the first time that this reaction can also be carried out at room temperature if the ClSiMe – DMF system is used as a condensing agent. For example, under these conditions, dihydroresorcinol (I) and dimedone (II) react with *p*-chloroaniline (III), aniline (IV), *p*-toluidine (V), and methyl- and ethyl-*p*-aminobenzoates (VI) and (VII) to give the corresponding enamines (XIII – XII) in 70 – 90% yields (see Table 1).



VIII – XII

R = H (VIII), Me (IX – XII), R′ = Cl (VIII), H (IX), Me (X), COOMe (XI), COOEt (XII).

TABLE 1. Enamino Ketones VIII – XII

Starting compound		Enamino ketones VIII – XII	Yield, %	M. p., °C	Empirical formula
diketone	aromatic amines				
I	III	VIII [1]	72	188 – 189	$C_{12}H_{12}ClNO$
II	IV	IX [5]	73	181 – 183	$C_{14}H_{17}NO$
II	V	X [4]	70	201 – 203	$C_{15}H_{19}NO$
II	VI	XI	88	167 – 170	$C_{16}H_{19}NO_3$
II	VII	XII	90	162 – 163	$C_{17}H_{21}NO_3$

Note. Enamino ketones VIII and X were recrystallized from ethylacetate, IX a benzene – hexane mixture (1 : 1), XI and XII – from a water – ethanol mixture (2 : 1).

The low-temperature formation of enamines is attained as a result of stirring the diketone with amines in a ClSiMe – DMF medium. The reaction products are isolated by a simple treatment of the reaction mixtures with an aqueous solution of K_2CO_3.

Owing to the high yields and the simple isolation procedure, the proposed technique for the synthesis of AE is competitive with those reported earlier in [1, 3, 4].

EXPERIMENTAL PART

The PMR spectra were recorded on a JEDL FX-900Q instrument (Japan) in $CDCl_3$. The purity of the synthesized compounds and the course of the reaction were monitored by TLC on Silufol UV-254 (benzene – ethylacetate, 1 : 1, detection with I_2 vapors and in UV light). The elemental analysis data for enamines XI and XII are consistent with the calculated values.

A general procedure for the preparation of N-aryl enamino ketones (VIII – XII). A mixture of diketone I or II (3.1 mmole), aromatic amine III – VII (3 mmole), $ClSiMe_3$ (4 ml) and DMF (3 ml) was stirred at about 20°C for 10 – 12 h and treated with an excess of an aqueous solution of K_2CO_3; the precipitate formed was filtered, washed with water, and air dried. Enamino ketones VIII – XII were obtained (see Table 1). PMR spectra (δ, ppm): XI: 1.17 s (6H, $2CH_3$); 2.50 s (2H, CH_2); 2.70 s (2H, CH_2); 4.0 s (3H, CH_3); 6.02 br. s (1H, CH); 7.40 and 8.15 m (5H, arom. protons, NH); XII: 1.10 s (6H, $2CH_3$); 1.40 s (3H, CH_3, J = 7 Hz); 2.38 s (2H, $2CH_2$); 2.60 s (2H, CH_2); 4.38 s (2H, CH_2, J = 7 Hz); 6.08 br. s (1H, CH); 7.35 and 8.00 m (5H, arom. protons, NH). The melting

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points and PMR spectra of enamines VIII – XII are consistent with those reported in [1, 3 – 6].

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