Synthesis of 5-(Arylmethylene)-2-piperidino(or morpholino)-2,4-diphenyl-3-thiazolines

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Several methods have been adopted for the synthesis of 3-thiazolines: action of elemental sulfur and gaseous ammonia on several types of ketones having at least one H atom α to the carbonyl group[1,2], ammonia on a mixture of α-mercapto-oxo compounds and ketones[1], hydrogen sulfide and ammonia on a mixture of α,α'-dioxodisulfides and oxo components[1], sulfur on alkylidenevinylamines[1], and thiourea on α-haloaldehydes[3]. Some 2-methyl-2,4-diaryl-3-thiazolines were also reported to be ring contraction products of 3,5-diaryl-2H-1,4-thiazines after treatment with hydrogen gas in the presence of palladized carbon or platinum oxide[4].

Now we report a new and easy conversion of 2-thiazolin-4-ones into 3-thiazolines through the action of Grignard reagents. Thus, an excess of phenylmagnesium bromide attacks the 5-(arylmethylene)-2-piperidino(or morpholino)-2-thiazolin-4-ones (**1a-c**) to give the corresponding 5-(arylmethylene)-2-piperidino(or morpholino)-2,4-diphenyl-3-thiazolines (**2a-c**), respectively. The structures of **2a-c** are based on microanalyses (which

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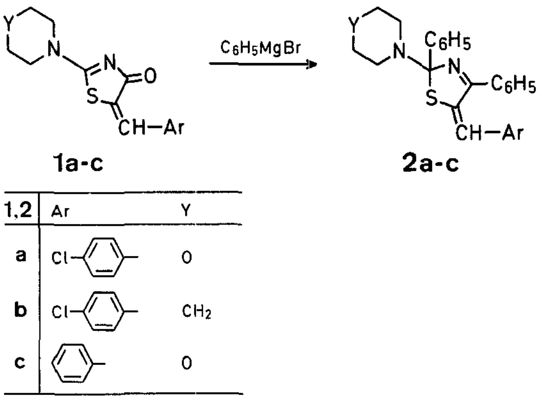
Table. 5-(Arylmethylene)-2-piperidino(or morpholino)-2,4-diphenyl-3-thiazolines (**2a-c**)

Product	Yield [%]	m.p. [°C]	Molecular formula[a]		I.R. (KBr) [cm^{-1}] ν_{CH}	$\nu_{C=N}$	U.V. (CH$_3$OH) λ_{max} [nm] (ε)
2a[b]	45	233-235°	$C_{26}H_{23}ClN_2OS$	(446.5)	3100-2700	1600	222 (15530); 274-294 (10200)
2b	48	207-209°	$C_{27}H_{25}ClN_2S$	(444.5)	3100-2800	1600	222 (12485); 281 (12350)
2c	50	213-215°	$C_{26}H_{24}N_2OS$	(412.6)	3080-2800	1600	222 (11290); 278 (11850)

[a] Satisfactory microanalyses obtained: C ±0.15, H ±0.07, N ±0.20.

[b] ^{1}H-N.M.R. (CD$_3$COOD): δ = 3.0-3.2 (m, 4H); 3.4-3.6 (m, 4H); 6.8-7.0 ppm (m, 15H).

infers the incorporation of two mol of the Grignard reagent and the elimination of one mol of water), the I.R. spectra which exhibit the stretching absorptions of the CH and C=N groups and absence of the NH and C=O absorptions, and the ^{1}H-N.M.R. spectra.



The 5-(arylmethylene)-2-piperidino(or morpholino)-2-thiazolin-4-ones (**1a-c**) used were synthesized earlier in our laboratories[5,6].

5-(Arylmethylene)-2-piperidino(or morpholino)-2,4-diphenyl-3-thiazolines (2a-c):

A solution of **1** (≈1.5 g, 0.005 mol) in anhydrous benzene (100 ml) is slowly added to a stirred solution of phenylmagnesium bromide [from magnesium turnings (0.48 g) and bromobenzene (3.2 g, 0.02 mol)] in anhydrous ether (50 ml), and the mixture stirred for 3 h at room temperature. After being stirred for 6 h in a water bath (90-100 °C), the mixture is allowed to stand overnight and decomposed by addition of saturated ammonium chloride solution (50 ml). The mixture is extracted with ether (100 ml); the benzene-ether extract is washed several times with small portions of water, dried with anhydrous sodium sulfate and evaporated. The residual semi-solid is triturated several times with light petroleum (b.p. 40-60 °C) and the crude product thus obtained is recrystallized from benzene/ethanol to give the pure **2**.

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[1] F. Asinger, H. Offermanns, *Angew. Chem.* **79**, 953 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 907 (1967); and references cited therein.

[2] F. Asinger, W. Schäfer, H. Diem, *Monatsh. Chem.* **97**, 1510 (1966).

[3] I. Carreau, *Bull. Soc. Chim. Fr.* **1956**, 1163.

[4] S. Donato, S. Ciro, N. Rodolfo, *Gazz. Chim. Ital.* **98**, 488 (1968).

[5] A. R. A. Raouf, M. T. Omar, S. M. A. Omran, K. E. El-Bayoumy, *Acta Chim. (Budapest)* **83**, 359 (1974).

[6] M. T. Omar, F. A. Sherif, *J. Prakt. Chem.* in press (1980).