

Dehydrogenation of 2-Aryl-2-imidazolines with Selenium

R. E. Klem (1), H. F. Skinner (1), H. Walba and R. W. Isensee (2)

Department of Chemistry, San Diego State

A number of methods have been used for preparing 2-arylimidazoles. Some of these involve condensations, while others start with the corresponding dihydroimidazoles or 2-phenylimidazole. The ease of preparation of certain 2-substituted dihydroimidazoles by the method of Oxley and Short (3) made the dehydrogenation of these compounds an attractive possibility for the preparation of several 2-phenylsubstituted imidazoles. The dehydrogenation of imidazolines has been accomplished using nickel (4), iodine in liquid ammonia (5), chromium trioxide in acetic acid (6), and with various hydrogen acceptors, including selenium, described in a British patent (7). Preliminary work indicated that the use of selenium might be one of the better hydrogen removers. Details of a typical dehydrogenation with selenium (Table I) as well as a preparation of one of the imidazolines (Table II) are given. Data on the compounds, most of which have not been previously reported, are also given.

EXPERIMENTAL

Imidazolines.

Equimolar quantities of 3-chlorobenzonitrile (3.2 g.) and the 4-toluenesulfonate salt of ethylenediamine (5.5 g.) were refluxed for 4 hours at 210°. Ammonia was no longer being evolved. The cooled melt was dissolved in 40 ml. of hot water and on the addition of 30 ml. of 6*N* sodium hydroxide a white solid precipitated. The imidazoline was recrystallized from benzene.

2-(3-Chlorophenyl)-2-imidazoline (2.5 g.) was mixed with selenium powder (5.0 g.) and triphenylmethane (13.0 g.) in a 3-necked 100 ml. round bottom flask with a thermometer well containing a condenser, a stirrer and a nitrogen inlet tube. A dry trap followed by a lead nitrate solution trap were connected to the condenser. Dry nitrogen was slowly bubbled through the system during the nine hours at which the flask was heated at 310-320°. The cooled melt was treated with 50 ml. of hot benzene, 45 ml. of 1.2 *N* hydrochloric acid and 40 ml. of hot benzene. The hot combined mixture was filtered and separated. The acid phase was treated

TABLE I

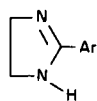
Synthesis of 2-Phenylsubstituted Imidazoles



Compound Ar Substituent	Reac. Time Hours	Reac. Temp. °C	Solvent	Mole Ratio Se/Cpd.	% Yield	Melting Point °C	Purif. Solv.	Molecular Formulae	Analyses			
									C Calcd.	C Found	H Calcd.	H Found
2-Phenyl-	5	275	Triphenyl- methane	4	56	148.2- 148.8	H ₂ O	C ₉ H ₈ N ₂				
2- <i>m</i> -Tolyl-	9	250	Triphenyl- methane	2.8	64	178.0- 179.3	alc.- H ₂ O	C ₁₀ H ₁₀ N ₂	75.92	75.66	6.37	6.41
2- <i>m</i> -Fluoro- phenyl-	24	270	<i>m</i> -diphenyl- benzene	3.1	73	171.6- 173.2	benz.	C ₉ H ₇ FN ₂	66.66	66.91	4.35	4.20
2- <i>m</i> -Trifluoro- methylphenyl-	24	275	<i>m</i> -diphenyl- benzene	4.0	74	157.5- 158.4	H ₂ O	C ₁₀ H ₇ F ₃ N ₂	56.61	56.87	3.33	3.39
2- <i>m</i> -Chloro- phenyl-	9	300	Triphenyl- methane	4.5	40	134.5- 135.5	H ₂ O	C ₉ H ₇ ClN ₂	60.52	60.61	3.95	3.85

TABLE II

Synthesis of 2-Phenylsubstituted-2-Imidazolines



Compound Ar Substituent	Reac. Time Hours	Reac. Temp. °C	% Yield	Melting Point °C	Purif. Solv.	Molecular Formulae	Analyses			
							C Calcd.	C Found	H Calcd.	H Found
2- <i>m</i> -Tolyl-	3.5	195	72	101.1- 101.9	Benz.	C ₁₀ H ₁₂ N ₂	74.96	75.24	7.55	7.39
2- <i>m</i> -Fluoro- phenyl	6.5	205	92	83.7- 85.4	Benz.	C ₉ H ₉ FN ₂	65.84	65.78	5.52	5.81
2- <i>m</i> -Trifluoro- methylphenyl-	6.5	205	92	130.0- 131.1	Benz.	C ₁₀ H ₉ F ₃ N ₂	56.07	56.37	4.24	4.42
2- <i>m</i> -Chloro- phenyl-	3.0	200	91	136.2- 137.7	Benz.	C ₉ H ₉ ClN ₂	59.84	59.46	5.02	4.94

with concentrated ammonia to pH 9.0 to yield the imidazole which was recrystallized from benzene or water.

REFERENCES

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San Diego, California 92115