

The Cyanoethylation of Diarylureas

MOSHE AVRAMOFF

Department of Organic Chemistry, Weizmann Institute of Science, Rehovoth, Israel

The bis-cyanoethylation of symmetrical diarylureas in pyridine solution has been performed. The corresponding bis(β -carbamoylethyl) and bis(β -carboxyethyl) compounds were obtained by hydrolysis.

THE CYANOETHYLATION of urea and its derivatives has been mentioned in a review of the chemistry of acrylonitrile (1). However, no description of this reaction could be found in the literature. The reaction of amides with acrylonitrile has been reviewed and was found to proceed particularly well with the aromatic compounds (2, 3). Monocycanoethylated ureas were obtained by the reaction of an arylisocyanate with β -aminopropionitrile or its *N*-substituted derivatives (4, 5). Symmetrical diarylureas react vigorously with an excess of acrylonitrile in the presence of Triton B (benzyltrimethylammonium hydroxide). The reaction is moderated by the use of pyridine as a diluent and the dicyanoethylated derivatives, 1,3-bis(β -cyanoethyl)-1,3-diarylureas, are obtained (Table I). The reaction could not be performed in the presence of a solvent (*tert*-butanol) or any other diluent—e.g., dioxane. The nitriles are hydrolyzed in concentrated hydrochloric acid at room temperature to the corresponding diamides (Table I) or in a mixture of diluted sulfuric and acetic acids at reflux temperature to the corresponding diacids (Table I).

Melting points were determined in open capillaries using an electrically heated aluminum block, and they are corrected.

LITERATURE CITED

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Table I. Bis-Cyanoethylation of Symmetrical Diarylureas

R	M.P., °C.	Yield, %	Recrystg. Solvent	Nitrogen Analysis	
				Calcd.	Found
1,3-Bis(β -cyanoethyl)-1,3-diarylureas OC(NRC ₂ H ₄ CN) ₂					
C ₆ H ₅	78.5-80	34	25% Aq. acetic acid	17.60	17.42
<i>o</i> -C ₇ H ₇	102-104	38	EtOH	16.17	16.37
<i>p</i> -C ₇ H ₇	131-132	61	EtOH	16.17	15.90
α -C ₁₀ H ₇	141-142	68	MeOH	13.38	13.43
β -C ₁₀ H ₇	98.5-99.5	58	MeOH	13.38	13.34
1,3-Bis(β -carbamoylethyl)-1,3-diarylureas OC(NRC ₂ H ₄ CONH ₂) ₂					
C ₆ H ₅	161-163	25	Methylethyl ketone	15.81	15.53
<i>o</i> -C ₇ H ₇	220	61	Water	14.65	14.65
<i>p</i> -C ₇ H ₇	165-167	32	Acetone	14.65	14.79
α -C ₁₀ H ₇	258	68	EtOH	12.33	12.11
β -C ₁₀ H ₇	144-146	83	40% Aq. ethanol	12.33	12.05
1,3-Bis(β -carboxyethyl)-1,3-diarylureas ^a OC(NRC ₂ H ₄ CO ₂ H) ₂					
<i>o</i> -C ₇ H ₇	176	48	Xylene	7.29	7.09
<i>p</i> -C ₇ H ₇	130-131	63	Benzene	7.29	7.30
α -C ₁₀ H ₇	210-212	73	Methylethyl ketone	6.14	6.05
β -C ₁₀ H ₇	164-166	64	40% Aq. acetone	5.30	6.30

^aThe corresponding diphenyl compound could not be isolated.

CORRECTION

In the article "Liquid-Liquid Equilibria for the System Ethylene Glycol-Toluene-Acetone," [*J. CHEM. ENG. DATA* **10**, 111 (1965)], there is an error. The triangular diagram presented as Figure 3 is actually data at 0° C. and should be presented as Figure 2. The triangular diagram presented as Figure 2 is actually data at 24° C. and should be presented as Figure 3.