The Cyanoethylation of Diarylureas

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The bis-cyanoethylation of symmetrical diarylureas in pyridine solution has been performed. The corresponding bis(β-carbamoyl) 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*). Monocyanoethylated 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 hydrolized 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.

Table I. Bis-Cyanoethylation of Symmetrical Diarylureas

		Yield,	Recrystg.	Nitrogen Analysis	
R	M.P., ° C.	%	Solvent	Calcd.	Found
1,3-Bis(β-cyanoethyl)-1,3-diarylureas $OC(NRC_2H_4CN)_2$					
C_6H_5	78.5–80	34	25% Aq. acetic acid	17.60	17.42
o-C_7H_7	102–104	38	EtOH	16.17	16.37
p-C_7H_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 $OC(NRC_2H_4CONH_2)_2$					
C_6H_5	161–163	25	Methylethyl ketone	15.81	15.53
o-C_7H_7	220	61	Water	14.65	14.65
p-C_7H_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] $OC(NRC_2H_4CO_2H)_2$					
o-C_7H_7	176	48	Xylene	7.29	7.09
p-C_7H_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

[a] The corresponding diphenyl compound could not be isolated.

LITERATURE CITED

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RECEIVED for review October 2, 1964. Accepted April 19, 1965.

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.