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THE REACTION OF POTASSIUM CYANAMIDE WITH NORMAL ALKYL BROMIDES

Yu. N. Polivin, V. V. Yurechko, T. P. Vishnyakova, and E. A. Ageev UDC 542.91:547.491.6'132:547.223

A study was carried out on the reaction of potassium cyanamide with normal alkyl bromides in 2-propanol, methanol, and dimethyl formamide in order to obtain dialkylcyanamides. A virtually quantitative yield of dialkylcyanamides is achieved in dimethyl formamide.

Dialkylcyanamides (DACA) have found use as wetting agents for fabrics, water-repellant materials [1], and additives to solid [2] and liquid diesel fuels [3].

Methods have been reported for the preparation of DACA from alkali and alkaline-earth metal cyanamides in protic media [4-5]. The yields of the desired product under these conditions did not exceed 50%.

In order to develop a preparative synthesis for DACA, we studied the reaction of potassium cyanamide (I) with normal 1-bromoalkanes (IIa)-(IId) in various solvents:

$$K_2 N - C \equiv N + RCH_2 Br \rightarrow (RCH_2)_2 N - C \equiv N$$
(I)
(IIa-d)
(IIIa-d)

 $R = C_7 H_{15}(a), C_{11} H_{23}(b), C_{14} H_{29}(c), C_{15} H_{31}(d).$

This reaction does not proceed when the reagents are heated in dimethoxyethane, which is an aprotic solvent, at reflux, probably as a consequence of the poor solubility of salt (I).

We have found that the use of dimethylformamide as the solvent leads to a virtually quantitative yield of dialkylcyanamides (IIIa)-(IIId).

The addition of 2-propanol into the reaction mixture in dimethoxyethane leads to the appearance of significant amounts of *n*-alkyl isopropyl ether (IVa)-(IVd) as side-products in addition to (IIIa)-(IIId) as indicated by thin-layer chromatography.

Carrying out the reaction of potassium cyanamide with alkyl bromides (IIa)-(IId) in 2-propanol leads to the predominant formation of (IVa)-(IVd) (see Table 1).

Potassium cyanamide apparently acts as a nucleophile and base in this reaction.

$$2K_{2}N-CN + 4i-C_{3}H_{7}OH \rightarrow 4KOCH(CH_{3})_{2} + (NH_{2}CN)_{2}$$

KOCH(CH_{3})_{2} + RCH_{2}Br \rightarrow RCH_{2}^{\alpha}-O-CH^{\beta}(CH_{3}^{\nu})_{2}
(IIa-d) (IVa-d)

Heating salt (I) at reflux under comparable conditions in 2-propanol, decantation of the precipitation, and the addition of alkyl bromides (IIa)-(IId) to the mother liquor also leads to the formation of ethers (IVa)-(IVd).

Cyanamide dimer formed as a result of the alcoholysis of salt (I) was isolated from the reaction mixture, which supports the reaction scheme presented above.

Thus, DACA may be synthesized in high yield from alkyl bromides and potassium cyanamide in aprotic solvents, in which potassium cyanamide has satisfactory solubility. The reduction in the yield of DACA in protic solvents is related to the hydrolysis of (I), which proceeds by analogy to the hydrolysis of potassium cyanamide [6].

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Yield Found/Calcu-Hg) vG=N (vC-0-C), cm⁻¹ ^п 3, 3Н 6Н) Compound mdd lated, % δCa 2-pro-panol DMF 6 cH f d ô **(ð**C^β), ðСН, ppm <u>ه</u> ف С н N -<u>-</u>9E (IIIa) 1,4500 195 22 2220 91 0,98 76,48 12.73 10,79 (23)(5) 76.62 12,86 10,51 (IIIb) 1,4573 212 93 39 2220 0.90 ----79.63 13,30 7,07 (22) (1)79.29 13,31 7,40 28 * (IIIc) 94 31 22200,9280,22 13.73 6,05 ----80,44 13,47 6,08 (IIId) 90 42 2220 41 * 0,86 _ 80.36 13.48 6,16 80,74 13,55 5,71 1.4145 67 (IVa) 70 _ (1130)(1,15)3,54 77.35 14.19 68,30 (23,5)(5)76,74 13,95 (71, 28)(IVb) 1,4270 120 52(1130)(1,13) 3,50 79.08 68,23 -14,24 (23)(1) 78,95 14,04 (71,22) (IVc) 1.4350 144 54(1130)(1.15)79.74 _ 3.55 14.11 68.30 (23)(1) 80,01 14,15 (71, 29)(IVd) 1,4390 150 ----50(1125)11,12 3,50 80,44 14.00 68,25 (18,5) (2)80,28 | 14,08 (71,23)

TABLE 1. Yields and Indices of (IIIa)-(IIId) and (IVa)-(IVd)

EXPERIMENTAL

Potassium cyanamide was obtained according to Shushunov and Pavlov [7].

Synthesis of Dialkylcyanamides (IIIa)-(IIId) in DMF. A sample of 0.01 mole finely ground potassium cyanamide was added to a solution of 0.02 mole 1-bromoalkane. After heating at reflux for 1 h with strong stirring, the reaction mixture was cooled and 100 ml benzene was added. The organic layer was washed with water. The solvent was distilled off and the precipitate was subjected to chromatography on alumina with benzene as the eluent.

Synthesis of Potassium Cyanamide with 1-Bromoalkanes in 2-Propanol. A sample of 0.02 mole 1-bromoalkane was added to a suspension of 0.01 mole potassium cyanamide in 50 ml 2-propanol. After heating at reflux for 2 h with strong stirring, the reaction mixture was cooled and the potassium cyanamide precipitate was filtered off. The filtrate was evaporated. The residue was purified on an alumina column. Ethers (IVa)-(IVd) were eluted with petroleum ether and dialkylcyanamides (IIIa)-(IIId) were eluted with benzene. Cyanamide dimer was eluted with ethanol.

The yields and physicochemical indices of the compounds obtained are given in Table 1.

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