

## Cyanation of Adamantane and Diamantane with Acetonitrile and Tetrabromomethane in the Presence of $\text{Mo}(\text{CO})_6$

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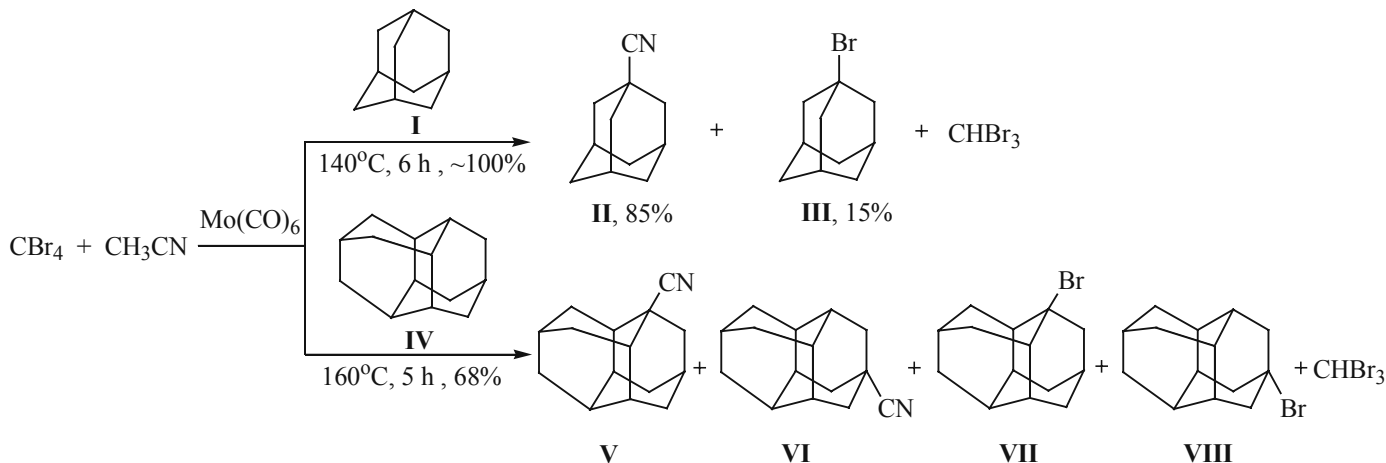
1-Adamantanecarbonitrile and its derivatives are initial raw material for preparation of a valuable drug Rimantadine, 1,2-dioxetane diagnosticums, and they are also used in the synthesis of polyurethanes underlying the production of stable to light polymer materials of high transparency, low optical density, high resistance against UV irradiation and enhanced hydrolytic stability [1].

1-Adamantanecarbonitriles substituted in the position 3 are commonly prepared from adamantane (I) derivatives already possessing functional groups like  $\text{COOH}$ ,  $\text{CONH}_2$ ,  $\text{OH}$ ,  $\text{Cl}$ ,  $\text{Br}$  [1–4].

2- and 3-Substituted nitriles of the adamantane series have been known since 1962 [5], the simplest 1-adamantanecarbonitrile (II) was obtained in 1974 from 1-ada-

mantanecarboxamide by its boiling with  $\text{SOCl}_2$  in benzene. In [7] a one-stage synthesis was reported of 1-adamantanecarbonitrile (II) and 1-diamantanecarbonitrile (V) from 1-chloro(1-bromo)adamantane (1-bromodiamantane) and trimethylsilyl cyanide catalyzed by Lewis acids ( $\text{SnCl}_4$ ,  $\text{AlBr}_3$ ). The yield of compounds II and V reached 59–90%. The reaction completed in 23–55 h in the presence of stoichiometric amounts of catalysts in anhydrous medium for the  $\text{Me}_3\text{SiCN}$  was easily hydrolyzed forming hydrocyanic acid.

We performed a direct cyanation of adamantane (I) with acetonitrile in the presence of molybdenum hexacarbonyl  $\text{Mo}(\text{CO})_6$  and tetrabromomethane  $\text{CBr}_4$ . The reaction proceeded at 140–160°C for 6 h and resulted in 85% yield of compound II at the total conversion of



adamantane (**I**). The side product, 1-bromoadamantane (**III**), was isolated in 15% yield. Under similar conditions we obtained from diamantane (**IV**) at 68% conversion a mixture of 1-diamantanecarbonitrile (**V**), 4-diamantanecarbonitrile (**VI**), 1- (**VII**) and 4- (**VIII**) bromodiamantanes in the ratio 1.5:1:0.3:0.2.<sup>o</sup>

The catalysts and reagents were used in the molar ratio  $[\text{Mo}(\text{CO})_6]:[\text{AdH or DAH}]:[\text{CBr}_4]:[\text{CH}_3\text{CN}]$  1:100:100:2000.

In the reaction mixture alongside compounds **II**, **III**, **V–VIII** we found by GLC and GC-MS methods also bromoform as the main reaction product thus indicating that  $\text{CBr}_4$  was involved not only into the bromination but also into the cyanation of adamantane and diamantane with acetonitrile. The reaction did not occur without  $\text{CBr}_4$ .

Considering the formation of 1-bromoadamantane (**III**) as the minor reaction product it was reasonable to suggest a two-stage mechanism of nitrile **II** formation via 1-bromoadamantane (**III**). However the reaction of 1-bromoadamantane (**III**) with  $\text{CH}_3\text{CN}$  in the presence of  $\text{Mo}(\text{CO})_6$ , but without  $\text{CBr}_4$ , provided nitrile **II** in no more than 15% yield. On adding  $\text{CBr}_4$  into the system the reaction turned to the formation of 1,3-dibromoadamantane (**IX**). The results of our experiments suggest that the governing part in the formation of 1-adamantanecarbonitrile (**II**) belongs evidently to the catalyst, in particular, to the nitrile complex of molybdenum that forms from  $\text{Mo}(\text{CO})_6$  and  $\text{CH}_3\text{CN}$ .

The structure of 1-bromo-, 1,3-dibromoadamantanes, 1- and 4-bromodiamantanes was proved by comparison with authentic samples and published data [1, 8, 9].

On replacement of  $\text{CBr}_4$  by  $\text{CHBr}_3$  the yield of nitrile **II** reduced to 30%.

The reaction was performed in a glass ampule of 20 ml capacity or in a pressure stainless-steel microreactor (17 ml). Results of parallel runs were materially identical. Into a microreactor (ampule) under an argon atmosphere was charged 0.1 mmol of  $\text{Mo}(\text{CO})_6$ , 10 mmol of adamantane (or 10 mmol of diamantane), 10 mmol of  $\text{CBr}_4$ , and 200 mmol of acetonitrile ( $\text{CH}_3\text{CN}$  was simultaneously a reagent and a solvent). The reactor was hermetically closed (the ampule was sealed) and heated at 140–160°C for 6 h with stirring. On completion of the reaction the microreactor (the ampule) was cooled to room temperature, opened, the excess acetonitrile was distilled off, the residue was dissolved in dichloromethane and subjected to column chromatography

on aluminum oxide of the II grade of activity, eluent the mixture dichloromethane–hexane, 1:1 v/v. The main fraction in reaction with adamantane after removing the solvent was colorless crystalline substance, mp 193–194°C, identical to authentic nitrile **II** (yield 85%). The second fraction (eluent dichloromethane) contained 1-bromoadamantane (**III**) (~15%), mp 119–120°C.

1- and 4-Diamantanecarbonitriles were isolated by column chromatography after a vacuum distillation, bp 90°C (10 mm Hg). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2200 ( $\text{C}^\circ\text{N}$ ).

**1-Adamantanecarbonitrile (II)**. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2250 ( $\text{C}^\circ\text{N}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.75 t (6H, 3 $\text{CH}_2$ ), 2.05 m (3H, 3CH), 1.60 t (6H, 3 $\text{CH}_2$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 29.51 ( $\text{C}^1$ ), 39.20 ( $\text{C}^2$ ,  $\text{C}^8$ ,  $\text{C}^9$ ), 26.43 ( $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^7$ ), 35.07 ( $\text{C}^4$ ,  $\text{C}^6$ ,  $\text{C}^{10}$ ), 124.33 ( $\text{C}^{\circ}\text{N}$ ). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %):  $[\text{M}]^+$  (0), 39 (12), 41 (12), 53 (5), 55 (5), 65 (5), 67 (10), 77 (10), 79 (21), 81 (7), 91 (7), 93 (17), 97 (7), 135 (100). Found, %: C 82.01; H 9.37; N 8.62.  $\text{C}_{11}\text{H}_{15}\text{N}$ . Calculated, %: C 81.93; H 9.38; N 8.69.

**1-Diamantanecarbonitrile (V)**.  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 25.35 ( $\text{C}^4$ ), 25.94 ( $\text{C}^9$ ), 33.53 ( $\text{C}^3$ ,  $\text{C}^{14}$ ), 36.44 ( $\text{C}^8$ ,  $\text{C}^{10}$ ), 36.72 ( $\text{C}^6$ ), 37.44 ( $\text{C}^7$ ,  $\text{C}^{11}$ ), 37.76 ( $\text{C}^1$ ), 38.66 ( $\text{C}^2$ ,  $\text{C}^{12}$ ), 38.80 ( $\text{C}^5$ ), 40.76 ( $\text{C}^{13}$ ), 124.86 ( $\text{C}^\circ\text{N}$ ). Found, %: C 84.08; H 8.82; N 7.1.  $\text{C}_{15}\text{H}_{19}\text{N}$ . Calculated, %: C 84.45; H 8.98; N 6.57.

**4-Diamantanecarbonitrile (VI)**.  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 25.35 ( $\text{C}^9$ ), 25.94 ( $\text{C}^2$ ,  $\text{C}^6$ ,  $\text{C}^{12}$ ), 29.82 ( $\text{C}^4$ ), 35.94 ( $\text{C}^1$ ,  $\text{C}^7$ ,  $\text{C}^{11}$ ), 37.17 ( $\text{C}^8$ ,  $\text{C}^{10}$ ,  $\text{C}^{13}$ ), 41.67 ( $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^{14}$ ), 124.54 ( $\text{C}^\circ\text{N}$ ). Found, %: C 84.21; H 8.85; N 6.94.  $\text{C}_{15}\text{H}_{19}\text{N}$ . Calculated, %: C 84.45; H 8.98; N 6.57.

The reaction products were analyzed by GLC on instruments Tsvet-102 and Chrom-5, flame-ionization detector, column 1200 mm  $\times$  3 mm, stationary phase silicon SE-30 (5%) on Chromaton N-AW-HMDS (1.125–0.160 mm), carrier gas helium, flow rate 50 ml/min, ramp from 50 to 220°C. IR spectra were recorded on a spectrophotometer UR-20 from pellets with KBr or mulls in mineral oil.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were registered on a spectrometer Jeol FXG at operating frequencies 90 and 22.5 MHz respectively, solvent  $\text{CDCl}_3$ , chemical shifts reported in  $\delta$ , ppm, from TMS. Mass spectra (electron impact, 70 eV) were taken on a GC-MS instrument Finnigan MAT-112 S. Elemental analyses were determined on an analyzer Karlo Erba, model 1106.

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