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SHORT COMMUNICATIONS

Synthesis of 1-Amino-3-oxo-2-azabicyclo[3.2.1]octane-4,5,5-tricarbonitriles

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We previously reported on the procedure for preparation of 5-oxocyclohexane-1,1,2,2-tetracarbonitriles **I** by reaction of tetracyanoethylene with appropriate α,β-unsturated ketones [1, 2]. We have found that compounds **IIa**–**IIf** are formed in high yields by the action of ammonia on cyclohexanones **Ia**–**If** in 30–40 s. Ammonia as nucleophile adds at the electrophilic carbonyl carbon atom of compound **I**, and the adduct undergoes cyclization to oxabicyclic derivative whose subsequent recyclization yields 1-amino-3-oxo-2-azabicyclo[3.2.1]octane-4,5,5-tricarbonitrile **IIa**–**IIf**.

The structure of products **II** was confirmed by the IR, ^{1}H NMR, and mass spectra. The structure of **IIa** was proved by X-ray analysis.

Table 1. Yields, melting points, and IR and mass spectra of compounds **IIa**–**IIf**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}	M^+
IIa	95	238–239 (decomp.)	3415, 3300, 3210, 2265, 1710, 1645	305
IIb	95	223–224 (decomp.)	3435, 3335, 3225, 2270, 1710, 1645	333
IIc	97	238–239 (decomp.)	3410, 3310, 3235, 2270, 1710, 1640	335
IId	97	241–242 (decomp.)	3410, 3350, 3220, 2275, 1710, 1645	335
IIe	94	198–199 (decomp.)	3415, 3350, 3215, 2265, 1720, 1640	349
IIf	93	226–227 (decomp.)	3410, 3350, 3220, 2275, 1710, 1645	363

Table 2. ^{1}H NMR spectra of azabicyclooctanes **IIa**–**IIf**

Comp. no.	Chemical shifts δ, ppm
IIa	8.9 s (1H, NHCO), 7.57 t (2H, *m*-H), 7.47 m (3H, *o*-H, *p*-H), 3.53 d.d (1H, PhCH), 2.61 q (1H, MeCH), 2.57 s (2H, NH$_2$), 2.47 t (1H, CHC**H**$_2$), 2.08 d.d (1H, CHC**H**$_2$), 1.27 d (3H, CH$_3$)
IIb	9.26 s (1H, NHCO), 7.54 t (2H, *m*-H), 7.48 m (3H, *o*-H, *p*-H), 3.10 d (1H, PhCH), 2.88 d (1H, CH$_2$), 2.56 d (1H, CH$_2$), 2.50 s (2H, NH$_2$), 2.33 m (1H, CHPr), 1.45–0.9 m (4H, C**H**$_2$C**H**$_2$CH$_3$), 0.63 t (3H, CH$_3$)
IIc	8.78 s (1H, NHCO), 7.47 d (2H, *o*-H), 7.0 d (2H, *m*-H), 3.81 s (3H, CH$_3$O), 3.48 d.d (1H, ArCH), 2.6 q (1H, MeCH), 2.55 s (2H, NH$_2$), 2.39 t (1H, CHC**H**$_2$), 2.03 d.d (1H, CHC**H**$_2$), 1.25 d (3H, CH$_3$)
IId	9.22 s (1H, NHCO), 7.42 d (2H, *o*-H), 7.0 d (2H, *m*-H), 3.83 s (3H, CH$_3$O), 2.92 d (1H, ArCH), 2.87 d (1H, CH$_2$), 2.53 s (1H, CH$_2$), 2.50 s (2H, NH$_2$), 2.42 m (1H, MeCH), 0.73 d (3H, CH$_3$)
IIe	9.12 s (1H, NHCO), 7.42 d (2H, *o*-H), 7.0 d (2H, *m*-H), 3.82 s (3H, CH$_3$O), 2.95 d (1H, ArCH), 2.68 q 1H, C**H**CH$_3$), 2.44 m [1H, C**H**(CH$_3$)CHAr], 2.30 s (2H, NH$_2$), 1.31 d (3H, CHC**H**$_3$), 0.77 d [3H, CH(C**H**$_3$)CHAr]
IIf	9.3 s (1H, NHCO), 7.5 d (2H, *o*-H), 7.04 d (2H, *m*-H), 3.8 s (3H, CH$_3$O), 3.1 d (1H, ArCH), 2.89 d (1H, CH$_2$), 2.58 d (1H, CH$_2$), 2.60 s (2H, NH$_2$), 2.34 m (1H, CHPr), 1.45–0.9 m (4H, C**H**$_2$C**H**$_2$CH$_3$), 0.61 t (3H, CH$_3$)

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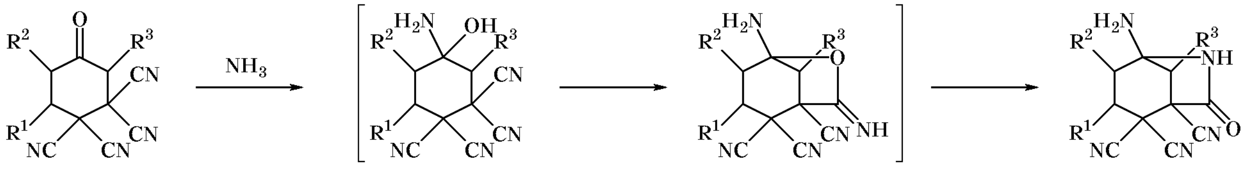

Ia–If **IIa–IIf**

II, R^1 = C_6H_5 (**a**, **b**), 4-$CH_3OC_6H_4$ (**c–f**); R^2 = H (**a**, **c**), C_3H_7 (**b**, **f**), CH_3 (**d**, **e**); R^3 = CH_3 (**a**, **c**, **e**), H (**b**, **d**, **f**).

6-R^1-7-R^2-8-R^3-1-Amino-3-oxo-2-azabicyclo-[3.2.1]octane-4,5,5-tricarbonitriles IIa–IIf (*general procedure*). Concentrated ammonia, 5 ml, was added under continuous stirring to 0.2 g of ketone **Ia**–**If**, and the mixture was stirred for 1–2 min (the precipitate did not dissolve). The precipitate was filtered off, washed with water, isopropyl alcohol, and diethyl ether, and dried in air.

The progress of reactions and the purity of products was monitored by TLC on Silufol UV-254 plates. The IR spectra were recorded on a UR-20 instrument in mineral oil (Table 1). The ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 MHz using DMSO-d_6 as solvent (Table 2). The molecular weights were determined from the mass spectra which were obtained on a Finnigan MAT instrument (70 eV). The X-ray diffraction data (unit cell parameters and reflection intensities) for compound **IIa** were acquired using a Siemens P3/PC four-circle diffractometer (λMoK_α irradiation, graphite monochromator, $\theta/2\theta$ scanning).

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