

PENTAAZABICYCLONONANES

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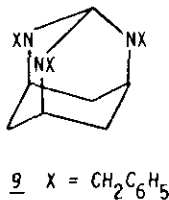
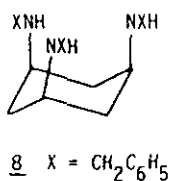
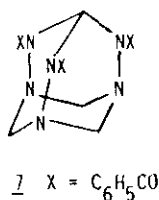
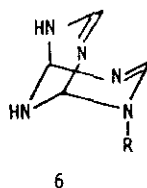
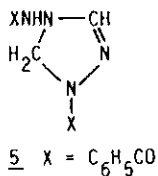
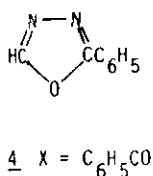
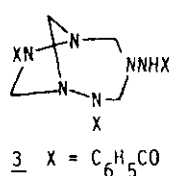
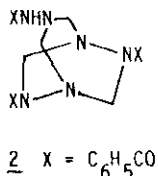
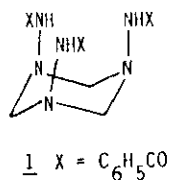
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Abstract - The synthesis of 3-benzamido-6,8-dibenzoyl-1,3,5,6,8-pentaazabicyclo[3.2.2]-nonane 2 and 2,7-dibenzoyl-4-benzamido-1,2,4,6,7-pentaazabicyclo[4.2.1]nonane 3 provides the first examples of pentaazabicyclononanes.

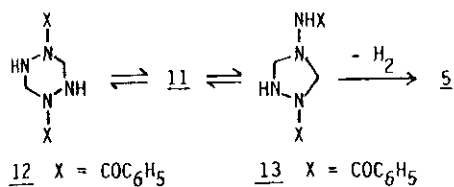
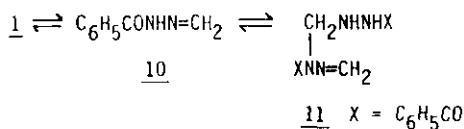
Treatment of 1,3,5-tribenzamidohexahydro-1,3,5-triazine 1 as the monohydrate^{1,2} with ethyl orthoformate and a few drops of concentrated sulfuric acid in toluene at 110°C for 0.5 h gave 3-benzamido-6,8-dibenzoyl-1,3,5,6,8-pentaazabicyclo[3.2.2]nonane 2. When sulfuric acid was not present in the mixture a different isomerization of the heterocycle 1 gave 2,7-dibenzoyl-4-benzamido-1,2,4,6,7-pentaazabicyclo[4.2.1]nonane 3, 2-phenyl-1,3,4-oxadiazole 4,³ and 1-benzoyl-4-benzamido- Δ^2 -1,2,4-triazoline 5. Structures 1-3 and 5, were determined by x-ray crystallographic analyses.² Compounds 2 and 3 introduced 1,3,5,6,8-pentaazabicyclo[3.2.2]nonane and 1,2,4,6,7-pentaazabicyclo[4.2.1]nonane as parent molecules of new ring systems. Except for compounds 2, 3, and examples claimed in a patent to be 2,4,6,8,9-pentaazabicyclo[3.3.1]nonadienes 6⁴ pentaazabicyclononanes remain unknown.

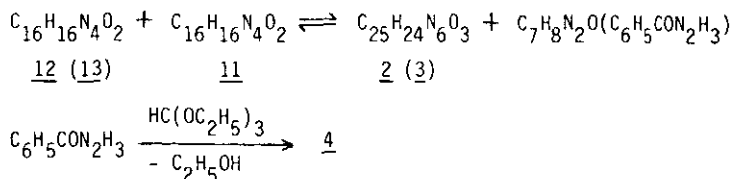
An anticipated interaction between the hexahydrotriazine 1 and ethyl orthoformate to give 2,8,9-tribenzoyl-2,3,5,7,8,9-hexaazatricyclo[3.3.1.1^{3,7}]decane 7 was patterned after a similar conversion of *cis-cis*-1,3,5-tris-benzylaminocyclohexane 8 to 2,4,10-tribenzyl-2,4,10-triazaadamantane 9.⁵ Formation of the hexaazatricyclodecane 7 was not detected.

When ethyl orthoformate was not included in the reaction mixture, the hexahydrotriazine 1 in toluene containing a catalytic amount of concentrated sulfuric acid, was recovered and gave the pentaazabicyclo[3.2.2]nonane 2 in a trace amount. Longer heating gave intractable mixtures. Similar treatment in the absence of both ethyl orthoformate and concentrated sulfuric acid had negligible effect on the hexahydrotriazine; again prolonged heating brought about degradation and the formation of many products.



A rationale for the formation of products 2 - 5 depended on the presence of the hydrazone 10 derived from the hexahydrotriazine 1 by depolymerization.^{6,7} The hydrazone 10 afforded 1,4-dibenzoyl-hexahydro-*s*-tetrazine 12 and 1-benzoyl-4-benzamidotetrahydro-1,2,4-triazole 13 by ring-closures from the dimer 11.⁸ A reaction between the reduced tetrazine 12 and the dimer 11 then afforded the pentaazabicyclo[3.2.2]nonane 2 with the formal ejection of benzhydrazide. From the isomeric dimer 13 a reaction with the dimer 11 afforded the pentaazabicyclo[4.2.1]nonane 3. A critical role for ethyl orthoformate, beyond the known reaction with benzhydrazide to form the oxadiazole 4³ which thereby favorably shifted the equilibrium 1 ⇌ 2 (3), has not been ascertained. Dehydrogenation of the triazolidine 13 to the triazoline 5 was assumed.





EXPERIMENTAL

Instruments included Pye-Unicam SP-200 IR, Varian A-60 and T-60 NMR Spectrometers. Elemental analyses were provided by Micro-Tech Laboratories, Inc., Skokie, Illinois.

3-Benzamido-6,8-dibenzoyl-1,3,5,6,8-pentaazabicyclo[3.2.2]nonane 2. To a suspension of the monohydrate of 1,3,5-trisbenzamido-hydroxytriazine 1^{1,9} (0.9 g, 0.002 mol) in toluene (25 ml) triethylorthoformate (0.30 g, 0.002 mol) and a drop of concentrated sulfuric acid were added. The mixture was heated at 110°C for 30 min. Toluene was removed and the residue was separated chromatographically (silica gel, chloroform) to give a colorless solid (0.31 g, 34%), mp 238-240°C (decomp.) after recrystallization from toluene; ir (KBr): 3200-3500 (broad, NH) 1620-1660 cm⁻¹ (C=O); nmr (CDCl₃): δ 4.5 (broad s, 4H, N-CH₂-N) 5.0 (broad s, 4H, N-CH₂-N), 7.2-7.8 (m, 15H, aromatic) and 8.8 (broad s, 1H, NH); anal. calcd. for C₂₅H₂₄N₆O₃: C, 65.79; H, 5.26; N, 18.42; found: C, 65.70; H, 5.29; N, 18.26.

2,7 Dibenzo-4-benzamido-1,2,4,6,7-pentaazabicyclo[4.2.1]nonane 3. A suspension of 1,3,5-trisbenzamido-hydroxytriazine 1^{1,9} (0.9 g, 0.002 mol) in toluene (25 ml) was mixed with triethylorthoformate (0.30 g, 0.002 mol) and heated at 110°C for 30 min. Toluene was removed and the residue was separated chromatographically (silica gel, chloroform) to give 2-phenyl-1,3,4-oxadiazole 4 as a colorless liquid (0.075 g, 8%); ir (neat): 3110, 1605, 1550, 1480, 1100, 1060, 700, and 680 cm⁻¹; nmr (CDCl₃): δ 8.50 (s, 1H, H-5), 7.33-7.76 (m, 3H, phenyl), 7.83-8.26 (m, 2H, phenyl).¹⁰ Further elution gave the bicyclononane 3 (0.26 g, 28%) as a colorless solid, mp 217-219°C after recrystallization from toluene; ir (KBr): 3250 (NH) and 1650 cm⁻¹ (C=O); nmr (CDCl₃): δ 3.6-5.5 (m, 8H, CH₂), 7.3-7.8 (m, 15H, aromatic) 9.2 (s, 1H, NH); anal. calcd. for C₂₅H₂₄N₆O₃: C, 65.79; H, 5.26; N, 18.42; found: C, 65.74; H, 5.50; N, 18.43. The recrystallization of product 3 for x-ray crystallographic analysis also gave a few crystals of the triazolone 5, a structure confirmed by x-ray crystallographic analysis but not characterized further.

ACKNOWLEDGMENT

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REFERENCES

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2. We are indebted to R. Gilardi, C. George, and J. L. Flippen-Anderson of the Naval Research

Laboratory, Washington, D. C., for the x-ray analyses of compounds 1 (the three benzamido groups are all on the same side of the hexahydrotriazine ring), 2, 3, and 5. The data will be published elsewhere.

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9. The monohydrate $C_{24}H_{24}N_6O_3 \cdot H_2O$, mp 160-163°C (dec) gave satisfactory elemental analysis;¹ we obtained values for an anhydrous analytic sample, mp 160-163°C (dec): calcd for $C_{24}H_{24}N_6O_3$: C, 64.85; H, 5.44; N, 18.91; found: C, 64.43; H, 5.51; N, 19.00.
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