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NOVEL REACTION OF AMIDOCUBANES WITH THIONYL CHLORIDE; SECOCUBANES

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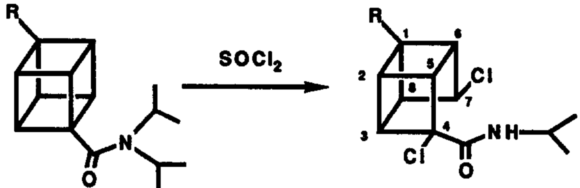
Summary: Reaction of (diisopropylamino)carbonylcubanes with thionyl chloride gave substituted secocubanes.

There is considerable current interest in the synthesis and chemistry of polynitrocage compounds, mainly due to their high density and strain energy.[1] In this connection we have been involved in the synthesis of polynitrosecocubanes as potential energetic materials.

In recent studies on the synthesis of substituted cubanes the diisopropylamido group was used for the ortho-directed functionalization of the cubane skeleton.[2] We now report diisopropylamido directed cleavage of the cubane skeleton to give secocubanes. Thus, when the amidocubanes **1a-c** were heated with thionyl chloride, secocubanes **2a-c** were obtained in 86-92 % yields.[3] The mass spectra of **2a-c** showed incorporation of two chlorine atoms with the concomitant loss of a C_3H_6 fragment from the starting materials. Single crystal X-ray determination confirmed the structure of **2a** in which the two chlorine atoms occupy exo positions relative to the secocubane skeleton.[4] The distance between the seco-carbon atoms C_4 and C_7 is 2.740 Å.



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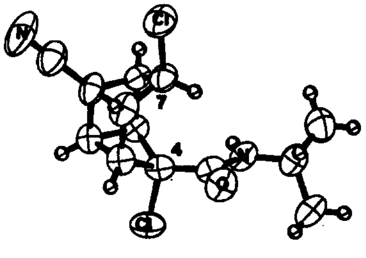
a: R = CN
b: R = CON(iPr)₂
c: R = COOMe

2



ORTEP drawing of **2a**

It is interesting to note that while cubane carboxylic acid reacts with HBr/acetic acid to give secocubanes,[5] diisopropylamido cubanes are very resistant to this reaction condition and either hot concentrated nitric or hydrochloric acids. Thus, this unexpected interaction of thionyl chloride with the amido group resulting in a ring opening process is a novel reaction with substantial synthetic potential. This cleavage is highly regioselective and stereospecific in that it occurs only at the C-C bond adjacent to the amido group with the formation of the exo 4,7-dichlorosecocubane. Other functional groups such as cyano and carbomethoxy are unaffected.

With the ready availability of functionalized amidocubanes, this method provides a new approach to substituted secocubanes. We are investigating the application of this methodology to other cage molecules, along with the mechanism of the reaction.

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3. In a typical experiment one gram of **1a** was treated with 5.0 ml of $SOCl_2$ under reflux for 48 hours. The reaction mixture was poured into ice water and extracted with methylene chloride. The product was obtained by chromatography (Silica gel/ CH_2Cl_2). **2a** (86%) mp. 180-182°C mass spectrum (CI) 289(10), 287(60), 285(90), 251(30), 241(10); ^1H NMR (CDCl$_3$) 1.21 (d, 6H,), 3.74 (m, 4H), 3.92 (m, 1H), 4.10 (septet, 1H), 4.72 (s, 1H), 6.40 (m, 1H). **2b** (87%, mp. 185-186°C); **2c** (92%, mp. 205-206°C).
4. Crystals from acetone/CH_2Cl_2. Enraf-Nonius CAD-4 diffractometer, Cu radiation. Monoclinic space group, Cc, a = 10.879 (2), b = 15.795 (5), c = 17.825 (6) Å, β = 107.69 (2), Z = 8.1953 I > 3σ (I). Final R = 0.045, wtd R = 0.062.
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