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The Interaction of 1,1,2-Tricarbamoyl-2-Cyanoethane with Alkyl Vinyl Ketones - A New Approach to [3.3.3]Propellanes

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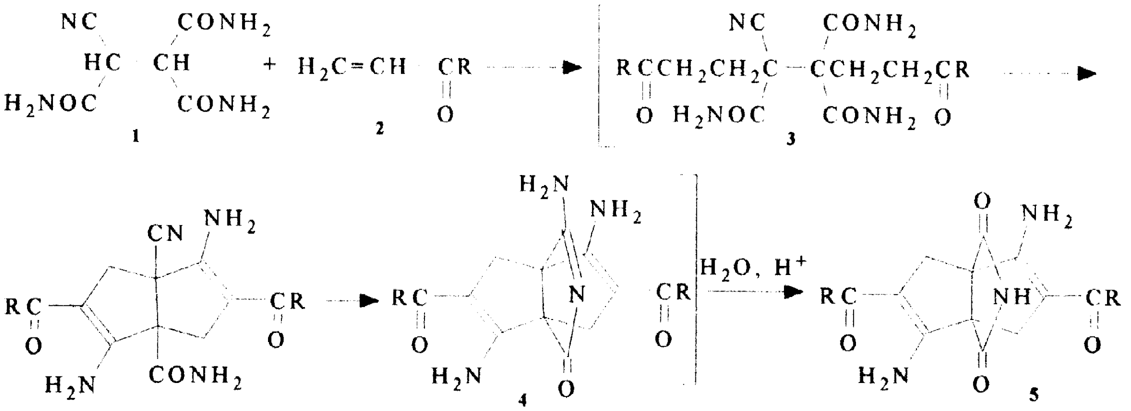
Abstract: Single-stage synthesis of 3,7-diacyl-2,6-diamino-9,11-dioxo-10-aza[3,3,3]propella-2,6-dienes from 1,1,2-tricarbamoyl-2-cyanoethane and alkyl vinyl ketones, is reported.

Significant research in the field of the synthesis of propellanes (about 100 papers) has been carried out by Ashkenazi and coworkers.[1,2] The synthesis of propellanes containing carbonyl groups is of great interest. The rearrangement of spiroketones [3] and Diels-Alder reaction [4] are used for their synthesis. In addition to this, there are reports on the interaction of cyclopentadione with β-oxodiesters leading to mixtures of propellanes [5] and on transformation of 4,5-bis(trimethylsilyl)cyclohepta-4-enone to [3,3,3]propellane-2,8-dione.[6] We have found that the interaction of amide **1** with ketones **2** in water yields propellanes **5**.[7]



2, **5**, R=CH$_3$ (**a**); R=C$_2$H$_5$ (**b**).

The structure of compound **5a** was established by an X-ray investigation,[8] figure1.

In order to synthesize amide **1** we used two reactions discovered by us previously. They proceed quickly, under mild conditions and in high yields. The first reaction is the reduction of tetracyanoethylene by dimethyl phosphite to 1,1,2,2-tetracyanoethane.[9] The second reaction is the hydrolysis of 1,1,2,2-tetracyanoethane to amide **1** by pyruvic acid.[10]

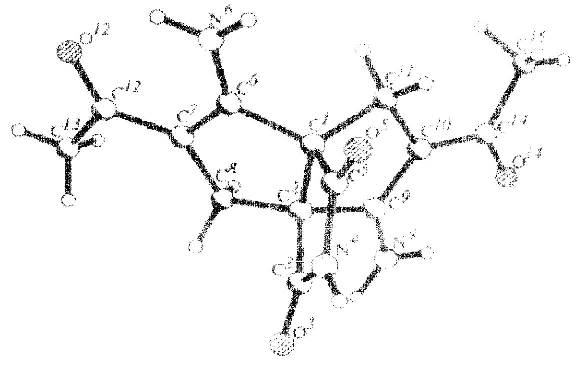


Figure 1. Molecular structure of 5a

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Initially the addition of 2 moles of alkyl vinyl ketones **2** to triamide **1** takes place as in the interaction of 1,1,2,2-tetracyanoethane with ketones **2a**.[11] Then, perhaps, the interaction of carboxamide groups and the elimination of two water molecules occur in intermediate **3**. The same cyclization takes place when triamide **1** interacts with crotonic aldehyde.[12] The last stage is the formation of 2-aminopyrroline cycle in intermediate **4**, which is hydrolyzed to propellanes **5**.

Thus, the novelty of our method for the production of propellanes is as follows: the complex, multi-stage chemical reaction that gives propellanes **5** was carried out by simple mixing reagents **1** and **2** under mild conditions; the new promising reagent, 1,1,2-tricarbamoyl-2-cyanoethane, was used for the first time to synthesize propellanes; the reaction is selective and it is not necessary to control the conditions of the reaction (pH, pressure, temperature); propellanes having unique combination of functional groups were obtained.

References and Notes

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7. 3,7-Diacyl-2,6-diamino-9,11-dioxo-10-aza[3,3,3]propell-2,6-dienes **5a,b**. 0.025 Mol of compound **1** were dissolved in 3 ml of 0.83 M aqueous sodium hydroxyde, 0.05 mol of vinyl ketone **2** were added dropwise. The reaction mixture was allowed to stay during 24 hours. Then the mixture was neutralized by acetic acid and heated to 80°C till the end of gas evolution. After cooling to room temperature the precipitate was filtered off and washed with 2-propanol. Compound; yield %; m.p. °C; IR (cm^{-1}): **5a**; 47; 332-335 (decomp.); 3400, 3345, 3280, 3165, 1760, 1720, 1625, 1600. **5b**; 41; 321-323 (decomp.); 3400, 3350, 3285, 3170, 1760, 1720, 1630, 1600.
8. Crystal data for **5a**: $C_{14}H_{15}N_3O_4$, M=289.29, orthorombic, space group Pbcn, at -120°C: a=20.415(4), b=8.545(2), c=15.115(3) Å, V=2636.8(9) $Å^3$, Z=8, d_c=1.458 g/cm^3. 3848 Independent reflections were measured with a Siemens P3/PC automated diffractometer $\lambda MoK\alpha$, graphite monochromator, $\theta/2\theta$-scan, $\theta<54°$. The structure was solved by direct method and refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms located objectively in the difference Fourier map were refined in isotropic approximation. The factor refinement converged at R_1=0.054 for 2689 reflections with $I>2\sigma(I)$ and wR_2=0.254 for all 3848 reflections. All the calculations were carried out using the SHELXTL PLUS program. Atomic coordinates, bond lengths and bond angles were deposited at the Cambridge Crystallographic Data Centre.
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