

New Reaction of Diazomethane

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Abstract

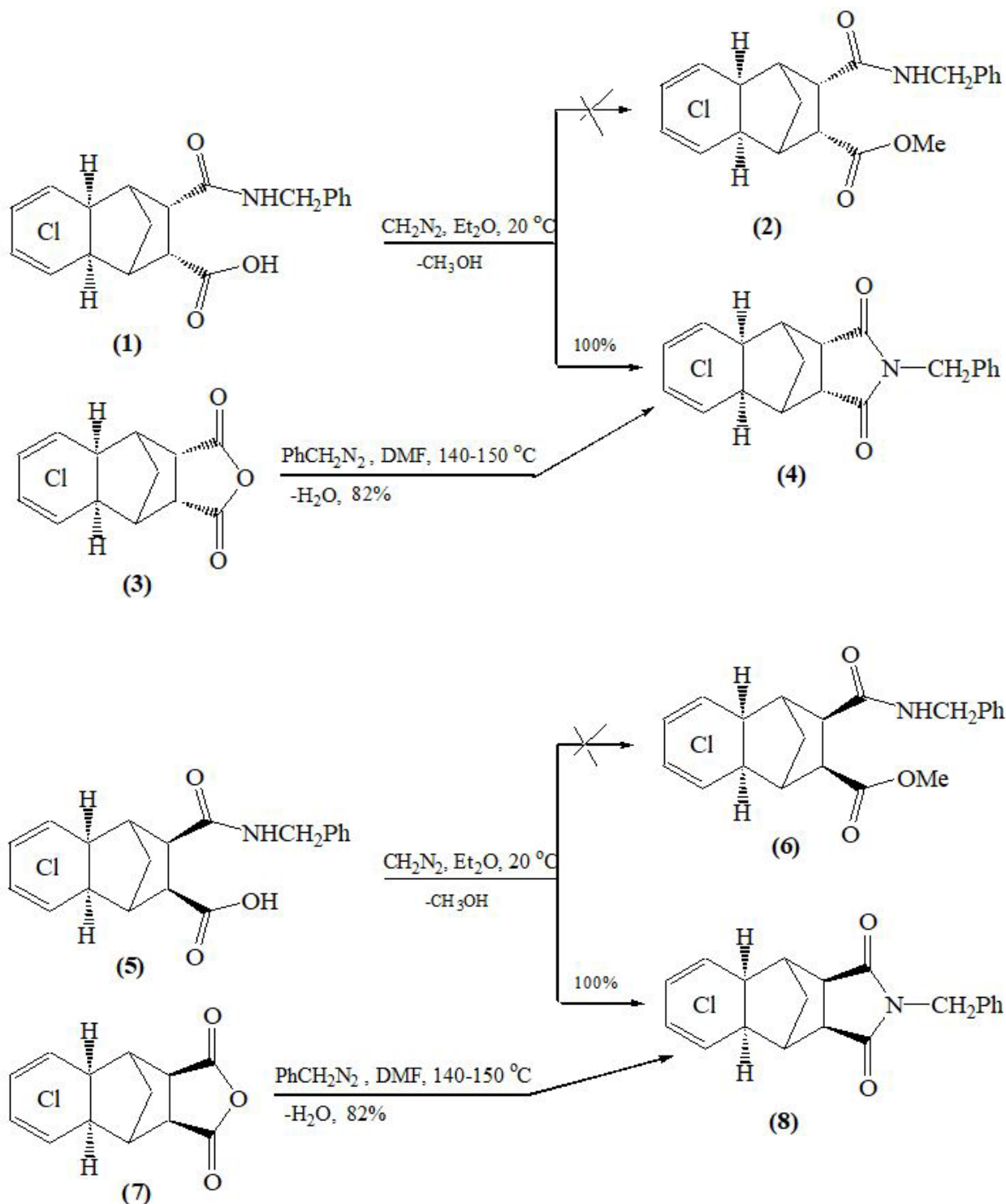
A new reaction of diazomethane with cyclic amide acids was discovered, and a reaction mechanism was proposed.

Keywords: diazomethane, amide acids, methyldiazonium.

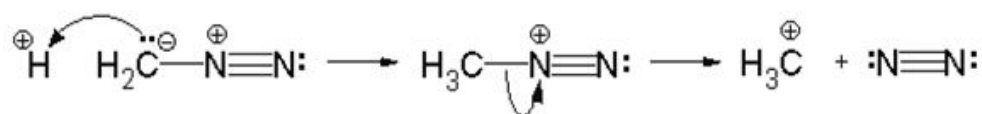
Introduction

Recently, [1, 2] we found that the interaction of diazomethane with cyclic cis-amide acids (1, 5) removing water from the latter with quantitative yields, leads to cyclic endo- and exo-imides (4, 8). It should be noted that the water-taking ability of diazomethane is still unknown.

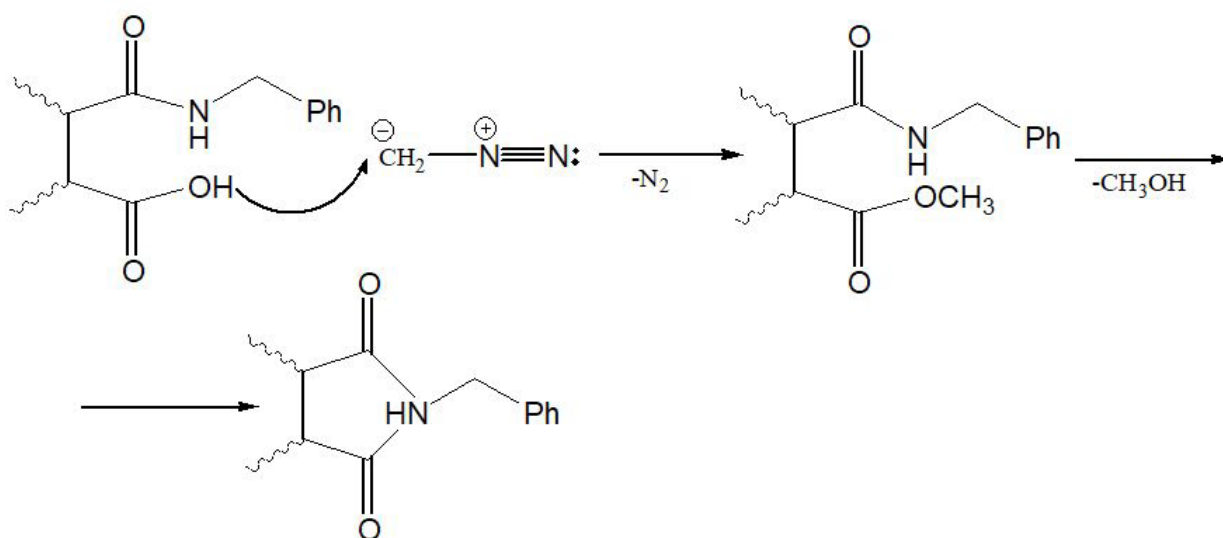
The structures of compounds (4) and (8) were confirmed by NMR ^1H , ^{13}C spectroscopy and counter synthesis (scheme). Note that the known methods for producing imides from amide acids require more stringent conditions, in particular, their prolonged heating in high-boiling solvents (usually in DMF, Ac_2O) in the presence of water-removing agents [4].



Instead of methylation of the carboxyl group, the process of water separation and the formation of an imide ring can be explained by the steric action of the reaction centers. No trace of compounds (2) and (6) was found in this reaction. It is known [3] that during protonation from diazomethane a methyldiazonium cation is formed:



Analysis of the reaction mass showed the existence of CH_3OH in its composition. Therefore, the separation of methanol and stereoisomeric imides (4, 8) as a result of the interaction of diazomethane with amide acids (1, 5) allowed us to suggest a mechanism according to the following scheme:



Experimental Section

The IR spectra were taken with a Specord M-80 spectrophotometer in a liquid film and in a suspension in Vaseline oil, the absorption frequencies are given in cm^{-1} . The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrophotometer operating at 300 and 75 MHz, respectively, the internal standard was TMS, and the solvent was DMF-d_7 . The chemical shifts of ^1H and ^{13}C NMR signals are shown in the scale δ , in parts per million (ppm). rel- (1S, 2R, 3S, 4R) -2,3- (N-benzylimide) -5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-1,4-methanonaphthalene-2, 3-dicarboxylic acid (4)

To a suspension of 0.02 g-mol (~ 0.9 g) of amide acid (1) in ether, an ether solution of diazomethane was added until a yellow color of the solution formed. After evaporation of the ether (at 20°C), the precipitated white crystals were filtered off, washed with hexane, and characterized. Yield – 100%. Mp. $207\text{--}209^\circ\text{C}$. IR spectrum (cm^{-1}): 1720, 1780 (C = O), 1616 (C = C). ^{13}C NMR spectrum (DMF-d_7 , δ , ppm): 177.38 s (C = O), 137.40 s (C^1 benzyl), 131.68 s (C6 and C7), 129.23 d (benzyl CH), 128.83 d (CH benzyl), 124.00 s (C5 and C8), 48.76 d (2CH), 48.21 d (2CH), 47.99 d (2CH), 42.62 t (CH_2 benzyl), 38.49 t (C9). ^1H NMR spectrum (DMF-d_7 , δ , ppm): 1.85 d (1H, C9H, J 11 Hz), 2.00 d (1H, C9H, J 11 Hz), 2.75 m (1H), 2.95 m (1H), 3.10 m (2H), 3.51 m (2H), 4.65 s (2H, CH_2 benzyl), 7.32 m (5H, C_6H_5). Found%: C 54.32; H 3.15; Cl 32.15; N 3.05. $\text{C}_{20}\text{H}_{15}\text{Cl}_4\text{NO}_2$. Calculated%: C 54.42; H 3.05; Cl 32.20; N 3.18.

Similarly, was obtained rel- (1R, 2S, 3R, 4S) -2,3- (N-benzylimide) -5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-1,4-methanonaphthalene 2,3-dicarboxylic acid (**8**). Yield – 100%. Mp. 215-216 °C. IR spectrum (cm⁻¹): 1725, 1780 (C = O), 1615 (C = C). ¹³C NMR spectrum (DMF-d₇, δ, ppm): 177.35 s (C = O), 137.52 s (C1 benzyl), 131.60 s (C6 and C7), 129.04 d (benzyl CH), 128.75 d (CH benzyl), 124.20 s (C5 and C8), 48.65 d (2CH), 48.25 d (2CH), 47.84 d (2CH), 42.70 t (CH₂ benzyl), 38.53 t (C9). ¹H NMR spectrum (DMF-d₇, δ, ppm): 1.81 d (1H, C9H, J 11 Hz), 2.10 d (1H, C9H, J 11 Hz), 2.70 m (1H), 2.83 m (1H), 3.00 m (2H), 3.58 m (2H), 4.60 s (2H, CH₂ benzyl), 7.29 m (5H, C₆H₅). Found%: C 54.54; H 2.97; Cl 32.33; N 3.20. C₂₀H₁₅Cl₄NO₂. Calculated%: C 54.42; H 3.05; Cl 32.20; N 3.18.

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