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SHORT COMMUNICATIONS

Formation of 2,2-Dinitropiperidin-4-ones in the Addition of Tetranitromethane to Bicyclobutylidene and Methylenecyclopropanes

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We previously studied reactions of tetranitromethane (TNM) with olefins containing small rings and found that the main reaction pathway is formation of 3,3-dinitroisoxazolidines [1, 2]. Unlike other strained olefins, methylenecyclopropanes did not give rise to adducts with TNM because of fast polymerization processes [1]. On the other hand, methylenecyclopropanes are known to react with various nitrones, following the 1,3-dipolar cycloaddition pattern and yielding spirocyclopropylisoxazolidines [3].

Taking into account the above stated, the goal of the present study was to examine the behavior of methylenecyclopropane and its derivatives in the reaction with tetranitromethane. The reactions were carried out in the presence of bicyclobutylidene which (as we showed previously) readily gives rise to *aci*-nitro ester by the action of TNM [4].

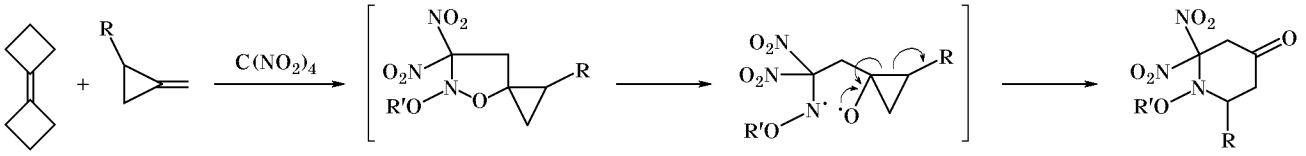
We have found that the reaction of TNM with equimolar amounts of bicyclobutylidene and methylenecyclopropane, instead of the expected isoxazolidine **A**, yields isomeric 1-substituted 2,2-dinitropiperidin-4-one **I** (Scheme 1). Its formation may be explained by spontaneous rearrangement of the initially formed 5-spiro isoxazolidine **A** via homolytic cleavage of the N–O bond and subsequent opening of the three-membered ring and closure of six-membered ring.

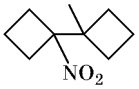
An analogous rearrangement was reported in [4] for 3-substituted isoxazolidine-5-spirocyclopropanes; however, it required elevated temperature (80–400°C). In our case, the rearrangement **A** → **I** occurs spontaneously under surprisingly mild conditions (at room temperature), presumably due to specific structure of primary adduct **A**. Likewise, the reaction of TNM with bicyclobutylidene and methyl 2-methylenecyclopropanecarboxylate gave dinitropiperidinone **II** as the sole product.

Of particular interest was to examine the behavior of methylenespiropentane in the same reaction. According to the data of [5], thermal rearrangement of dihydroisoxazole-5-spirocyclopentanes gives only one of the two possible dihydropyridinones. In the reaction under study, the small ring in isoxazolidine **B** was cleaved in two possible modes, affording two isomeric piperidinones **IIIa** and **IIIb** (Scheme 2).

Pure compounds **IIIa** and **IIIb** were isolated by column chromatography in 23% yield (ratio 1 : 1). The structure of both isomers was confirmed by their ^{1}H and ^{13}C NMR spectra.

Scheme 1.



I, R = H; **II**, R = COOMe; R′ =  .

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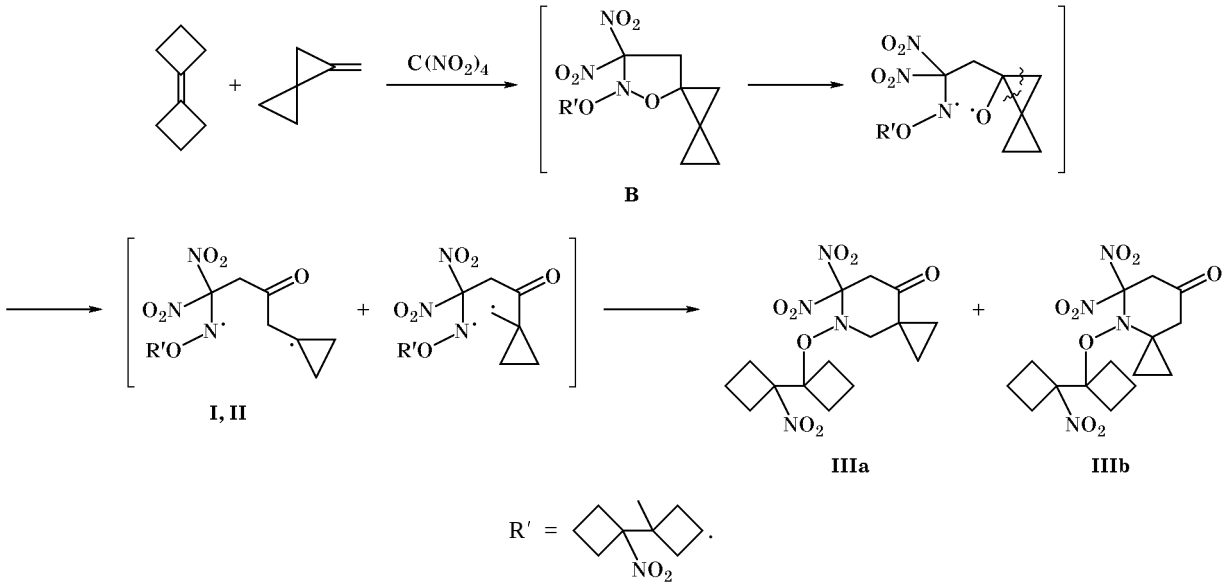
Scheme 2.



Thus we have shown that methylenecyclopropanes add to tetranitromethane in the presence of bicyclobutylidene with formation of 2,2-dinitropiperidin-4-ones. This reaction extends the synthetic potential of of the reaction of TNM with olefins.

2,2-Dinitro-1-(1′-nitrobicyclobutan-1-yloxy)-piperidin-4-one (I). Yield 0.10 g (11%), R_f 0.15. 1H NMR spectrum, δ, ppm (*J*, Hz): 1.65–2.14 m (5H, cyclobutyl), 2.37–2.87 m (7H, cyclobutyl), 3.20 t (2H, CH_2CO, ^3J = 5.9), 4.06 s [2H, $CH_2C(NO_2)_2$], 4.65 t (2H, CH_2NO, ^3J = 5.9). ^{13}C NMR spectrum, δ_C, ppm: 13.50 (CH_2, cyclobutyl), 14.04 (CH_2, cyclobutyl), 27.65 (CH_2, cyclobutyl), 28.78 (CH_2, cyclobutyl), 29.04 (CH_2, cyclobutyl), 30.66 (CH_2, cyclobutyl), 38.11 (**C**H_2CO), 38.93 [**C**$H_2C(NO_2)_2$], 68.38 (CH_2NO), 90.57 (C, cyclobutyl), 91.71 (C, cyclobutyl), 128.87 [$C(NO_2)_2$], 196.62 (CO). Mass spectrum (EI, 70 eV), *m*/*z* (I_{rel}, %): 284 (3) [M–NO_2–C_2H_4]$^+$, 237 (2), 218 (2), 170 (7), 156 (44), 146 (3), 124 (61), 107 (54), 96 (65), 79 (55), 67 (55), 55 (100).

Methyl 6,6-dinitro-1-[1′-nitrobicyclobutan-1-yloxy]-4-oxopiperidine-2-carboxylate (II). Yield 0.10 g (10%), R_f 0.15. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.58–2.90 m (12H, cyclobutyl), 3.27 d.d (1H, C**H**$_2$CH, ^2J = 15.0, ^3J = 4.7), 3.62 d.d (1H, C**H**$_2$CH, ^2J = 15.0, ^3J = 8.2), 3.81 s (3H, CH_3), 4.05 s [2H, $CH_2C(NO_2)_2$], 5.56 d.d (1H, CHNO, ^3J = 4.7, ^3J = 8.2). ^{13}C NMR spectrum, δ_C, ppm: 13.68 (CH_2, cyclobutyl), 14.07 (CH_2, cyclobutyl), 27.73 (CH_2, cyclobutyl), 28.95 (CH_2, cyclobutyl), 29.20 (CH_2, cyclobutyl), 30.76 (CH_2, cyclobutyl), 38.83 (**C**H_2CO), 41.79 [**C**$H_2C(NO_2)_2$], 54.02 (CH_3), 82.05 (CHNO), 90.87 (C, cyclobutyl), 91.76 (C, cyclobutyl), 132.70 [$C(NO_2)_2$], 164.15 (**C**$OOCH_3$), 195.59 (CO).

6,6-Dinitro-5-(1′-nitrobicyclobutan-1-yloxy)-5-azaspiro[2.5]octan-8-one (IIIa) and 5,5-dinitro-4-(1′-nitrobicyclobutan-1-yloxy)-4-azaspiro[2.5]octan-7-one (IIIb) (2 : 1 isomer mixture). Yield 0.19 g (23%), R_f 0.34 (**IIIa**), 0.10 (**IIIb**). ^1H NMR spectrum, δ, ppm: **IIIa** 1.30 m (2H, cyclopropyl), 1.68 m (2H, cyclopropyl), 1.70–2.15 m (3H, cyclobutyl), 2.45–2.90 m (9H, cyclobutyl), 3.81 s [2H, $CH_2C(NO_2)_2$], 4.56 s (2H, CH_2NO); **IIIb**: 1.03 m (2H, cyclopropyl), 1.48 m (2H, cyclopropyl), 1.60–2.90 m (12H, cyclobutyl), 3.71 s (2H, CH_2CO), 4.02 s [2H, $CH_2C(NO_2)_2$]. ^{13}C NMR spectrum, δ_C, ppm ($^1J_{CH}$, Hz): **IIIa**: 13.97 (CH_2, cyclobutyl, J = 137), 14.38 (CH_2, cyclobutyl, J = 138), 15.76 ($2CH_2$, cyclopropyl), 24.37 (C_{spiro}), 27.83 ($2CH_2$, cyclobutyl, J = 137), 29.32 ($2CH_2$, cyclobutyl, J = 139), 30.64 (**C**H_2CO, J = 132), 77.50 (CH_2NO, J = 147), 90.74 (C, cyclobutyl), 91.93 (C, cyclobutyl), 198.19 (CO); **IIIb**: 14.00 (CH_2, cyclobutyl), 14.01 (CH_2, cyclobutyl), 15.49 ($2CH_2$, cyclopropyl), 27.63 ($2CH_2$, cyclobutyl), 28.75 (**C**H_2CO), 29.03 ($2CH_2$, cyclobutyl), 30.62 [**C**$H_2C(NO_2)_2$], 69.37 (C_{spiro}), 90.24 (C, cyclobutyl), 92.64 (C, cyclobutyl), 202.08 (CO); No $C(NO_2)_2$ signal was observed in the ^{13}C NMR spectra of **IIIa** and **IIIb**. Mass spectrum (CI), *m*/*z* (I_{rel}, %): 354 (5) [M–NO]$^+$, 338 (6) [M–NO_2]$^+$, 291 (20) [M–2NO_2–H]$^+$, 170 (39), 139 (20), 125 (43), 124 (58), 107 (100).

The ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz,

respectively) from solutions in $CDCl_3$. The mass spectra were obtained on Varian MAT-311A and MKh-1321A instruments (70 eV for EI).

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