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The first synthesis of nitro-substituted cyclopropanes and spiropentanes via oxidation of the corresponding amino derivatives

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ABSTRACT

A novel approach to nitro-substituted cyclopropanes and spiropentanes via oxidation of the corresponding amines with dimethyldioxirane is reported. The method is used successfully for the preparation of a series of nitrocyclopropanes as well as for the first synthesis of 1,4-dinitrospiro[2.2]pentane.

Taking aniline production as an example, the general logic of organic synthesis is to consider nitro-compounds as precursors of amino derivatives. However, in some particular cases, it is necessary to use the reverse process for the synthesis of, for example, nitrocyclopropanes. Nitro- and polynitro-cyclopropanes are of considerable interest as potential high energy materials where the strained cyclopropane-containing skeleton is in favorable conjunction with explosophore nitro functionalities.[1] The synthesis of nitro-substituted cyclopropanes is a complicated procedure in comparison with the preparation of their open-chain analogs.[1,2] Methods for the direct introduction of nitro group(s) into three-membered rings are impractical due to considerable decomposition and poor yields of the desired products.[3] A few approaches to nitrocyclopropanes consist of the formation of a small ring from precursors that already contain nitro groups. Among these methods are the 1,3-elimination of γ-X-substituted nitropropanes,[4] deazotization of nitropyrazolines,[5] [1+2] cycloaddition of nitrocarbenes to alkenes,[6] reaction of α,β-unsaturated nitro-compounds with sulfur ylides and related processes,[7] etc. Recently, we proposed novel approaches to nitro derivatives of triangulanes[8] via [1+2] cycloaddition of ethyl nitrodiazoacetate to methylenecyclopropanes[9] and to 1,1-dinitrocyclopropanes through [3+2] cycloaddition of diazo-compounds to dinitroethenes.[10] However, all these methods have disadvantages such as the formation of complex mixtures of products, low yields and difficult to access starting materials. Therefore, the transformation of an N-containing functional group(s) in a small ring into a nitro group, for example, oxidation of the amino group, seems to be an improved alternative to the methods proposed earlier. Herein, we report a novel synthetic approach to nitro-substituted cyclopropanes and spiropentanes via oxidation of aminocyclopropane derivatives.

It is well known that the oxidation of substituted aminocyclopropanes under different oxidation conditions leads to ring-opened products.[11] In this connection, the main goal of our investigation involved the search for appropriate conditions for the chemoselective oxidation of an amino group wherein a cyclopropane or spirocyclic system would be not affected.

For our investigation we used commercially available aminocyclopropane **1a** and various other aminocyclopropanes and spiropentanes **1b–g** which were prepared via a known and efficient synthetic sequence[12] as shown in Scheme 1.[13] The transformations of **3b–g** into **6b–g** were carried out without isolation of the intermediate azides **4b–g** and the products of Curtius rearrangement **5b–g**. The hydrochlorides **6b–g** were purified by recrystallization before conversion into the corresponding amines **1b–g**.

According to the literature, the most efficient oxidants for the transformation of primary amino groups at secondary alkyl carbons into a nitro functionality are *m*-chloroperbenzoic acid (MCPBA),[14] ozone,[15] and dimethyldioxirane (DMDO).[16] We carried out a brief survey of these oxidizing agents employing aminocyclopropanes **1b,e** as model substrates for optimization of the oxidation conditions (Table 1). Unfortunately, the simplest aminocyclopropane **1a** was found to be an unsuitable model due to its high volatility.

We found that the oxidation of amines **1b,e** with MCPBA afforded 4,5-dihydroisoxazoles **7b,e** as the only products (Table 1, entries 1 and 2). The formation of **7b,e** proceeded presumably via oxidation of **1b,e** into unstable nitrosocyclopropanes **A** followed

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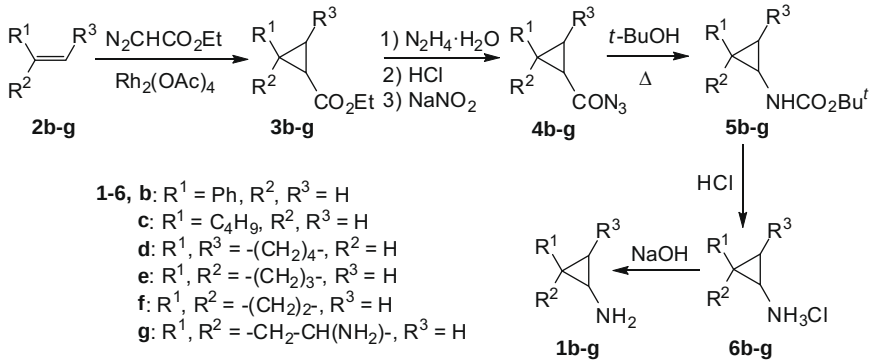
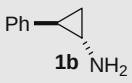
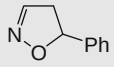
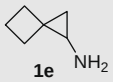
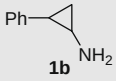
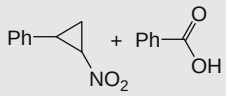
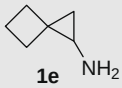
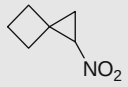
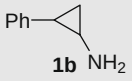
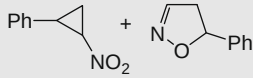
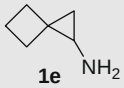


Scheme 1. Synthesis of starting aminocyclopropanes **1b–g**.

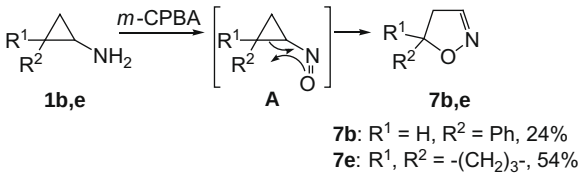
Table 1
Screening of oxidants with aminocyclopropanes **1b**,**e**

Entry	Amine	[O]	Product
1	 **1b**	MCPBA[a]	 **7b**, 24%
2	 **1e**	MCPBA[a]	 **7e**, 54%
3	 **1b**	O_3[b]	 **8b**, 2% 27%
4	 **1e**	O_3[b]	 **8e**, 3%
5	 **1b**	DMDO[c]	 **8b**, 7% **7b**, 42%
6	 **1e**	DMDO[c]	 **8e**, 60%

[a] Reaction conditions: tenfold molar excess of MCPBA, 1,2-dichloroethane, reflux, 4 h.
[b] Reaction conditions: 6 wt % O_3/O_2–SiO_2, 1.8 mL/s, −78 °C, 50 min.
[c] Reaction conditions: 0.08 M DMDO in acetone, sevenfold molar excess of DMDO, rt, 1 h, dark.

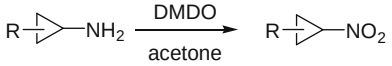
by ring cleavage and subsequent formation of the five-membered heterocycle **7** (Scheme 2). Circumstantial evidence for intermediate **A** was obtained by the immediate appearance of a blue color when **1b,e** were treated with MCPBA. To the best of our knowledge, such rearrangement of nitrosocyclopropanes into isoxazolines has not been reported previously. At the same time, it seems to be analogous to the well-known 1,3-sigmatropic vinylcyclopropane–cyclopentene rearrangement and related processes.[17]

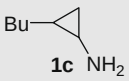
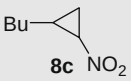
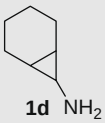
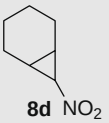
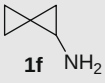
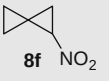
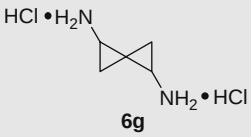
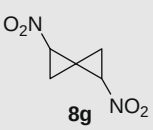
Unfortunately, ozone was also found to be unsuitable as an oxidant for aminocyclopropanes **1b,e** affording the desired nitrocyclopropanes **8b,e** in very poor yields (Table 1, entries 3 and 4). However, DMDO proved to be a suitable oxidizing agent. In spite of the low conversion of **1b** into target nitrocyclopropane **8b** (Table 1, entry 5), DMDO was efficient for the oxidation of **1e** into the corresponding nitrocyclopropane **8e** in a good yield (Table 1, entry 6). We therefore utilized a 0.08 M solution of DMDO[18] in acetone as the oxidant for the conversion of a series of aminocyclopropanes **1a,c,d,f** and hydrochloride **6g** into the corresponding nitrocyclopropanes **8a,c,d,f,g** (Table 2).



Scheme 2. Oxidation of aminocyclopropanes **1b,e** into isoxazolines **7b,e**.

Table 2
Oxidation of amines **1a**,**c**,**d**,**f** and hydrochloride **6g** with DMDO



Entry	Amine	Product	Yield (%)
1	 **1a**	 **8a**	40[a]
2	 **1c**	 **8c**	61[a]
3	 **1d**	 **8d**	76[a]
4	 **1f**	 **8f**	56[a]
5	 **6g**	 **8g**	56[b]

[a] Reaction conditions: 0.08 M DMDO in acetone, sevenfold molar excess of DMDO, rt, 1 h, dark.
[b] Reaction conditions: 0.08 M DMDO in acetone–water (9:1), tenfold molar excess of DMDO per amino group, rt, 24 h, dark.

Thus, we found that the oxidation of monoamines **1a,c,d,f** with DMDO proceeded chemoselectively resulting in the corresponding nitrocyclopropanes **8a,c,d,f** in good yields (Table 2, entries 1–4).[19] It should be noted that the use of MCPBA in the case of amines **1c,d** was also successful and led to the corresponding nitrocyclopropanes **8c,d** as single products in 50% and 54% yields, respectively.

Finally, an important application of the reported oxidation procedure was the successful synthesis of 1,4-dinitrospiro[2.2]pentane (**8g**) (Table 2, entry 5).[20] Dinitrospiropentane **8g** is a novel representative of polynitrotriangulanes in which each ring is substituted with a nitro group. Earlier, a 1,2-dinitrospiro[2.2]pentane bearing both nitro functionalities on the same cyclopropane ring was synthesized via oxidative cyclization in moderate yield.[4g] For the synthesis of dinitrospiropentane **8g** we simplified the oxidation procedure by utilization of the double hydrochloride salt **6g** instead of the free diamine **1g** which was less stable and less convenient to work with. The oxidation of **6g** into the corresponding dinitrospiropentane **8g** was realized under the standard conditions using a tenfold molar excess of DMDO per amino group.

In conclusion, DMDO was found to be an efficient oxidizing agent for the conversion of amino-substituted cyclopropanes and spiropentanes into the corresponding nitrocyclopropane derivatives. The reported method is chemoselective and proceeds under mild conditions and in moderate to good yields to afford a variety of strained nitro-substituted compounds bearing a cyclopropane ring and spiroannulated moieties which are difficult to access via other synthetic approaches.

Caution: Although we have not met any problems in handling these compounds, full safety precautions should be taken due to their potentially explosive nature.

Acknowledgments

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13. Gen*eral procedure for the synthesis of azides* **4b–g**: hydrazine hydrate (4 mL) was added to a solution of ethyl carboxylate **3** (0.01 mol) in CH_3OH (30 mL) and the resulting mixture was maintained at room temperature for 3 d. The solvent was evaporated and the resulting white crystalline residue was dissolved in water (15 mL) and concentrated HCl (3.0 mL) was added dropwise with stirring over 30 min under cooling with an ice-salt-bath. The mixture was diluted with Et_2O (15 mL) and a solution of $NaNO_2$ (1.4 g) in water (5 mL) was added dropwise over 30 min at 5 °C. The organic layer was separated and the aqueous phase was extracted with Et_2O (2 × 10 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution (3 × 5 mL), water (5 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was used without purification.
1,4-Diazidospiro[2.2]pentane (**4g**): mixture of four isomers **A**:**B**:**C**:**D** = 50:20:20:10; R_f 0.49 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) of the mixture of four isomers: δ 1.50–1.69 (m, 12H, CH_2), 1.71–1.76 (m, 2H, CH_2, **B**), 1.85–1.91 (m, 2H, CH_2, **A**), 2.05–2.15 (m, 4H, CH, **C+D**), 2.17–2.20 (m, 2H, CH, **B**), 2.23–2.29 (m, 2H, CH, **A**); ^{13}C NMR (100 MHz, $CDCl_3$): isomer **A**: δ 10.5 ($2CH_2$), 18.3 (2CH), 26.5 (C), 176.6 (2C); isomer **B**: δ 13.1 ($2CH_2$), 19.6 (2CH), 26.2 (C), 176.4 (2C); isomer **C**: δ 13.4 ($2CH_2$), 19.7 (2CH), 26.6 (C), 176.6 (2C); isomer **D**: δ 13.9 ($2CH_2$), 20.9 (2CH), 26.6 (C), 176.6 (2C).
General procedure for the synthesis of amine hydrochlorides **6b–g**:
Method A. A solution of azide **4b,e–g** (10 mmol) in *tert*-butanol (40 mL) was refluxed until completion of nitrogen evolution (about 12 h). The solvent was evaporated and the residue was treated with a saturated 1,4-dioxane solution of HCl (20 mL). The resulting mixture was stirred for 2 h at room temperature and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from chloroform or methanol.
Method B. A solution of azide **4c,d** (10 mmol) in toluene (12 mL) was refluxed until completion of nitrogen evolution (about 6 h). The reaction mixture was allowed to cool to room temperature and then treated dropwise with concentrated HCl (20 mL). The resulting mixture was refluxed for 2 h and concentrated under reduced pressure. The crude product was purified by recrystallization from chloroform or methanol.
Spiro[2.2]pentane-1,4-diamine dihydrochloride (**6g**): mixture of four isomers **A**:**B**:**C**:**D** = 35:30:25:10; ^{1}H NMR (400 MHz, D_2O) of the mixture of four isomers: δ 1.36–1.47 (m, 10H, CH_2), 1.54–1.61 (m, 6H, CH_2), 3.11 (dd, ^3J = 3.8, 7.0 Hz, 2H, CH, **D**), 3.16 (dd, ^3J = 3.9, 7.0 Hz, 2H, CH, **B**), 3.22 (dd, ^3J = 3.9, 7.5 Hz, 2H, CH, **C**), 3.30 (dd, ^3J = 5.3, 6.5 Hz, 2H, CH, **A**); ^{13}C NMR (100 MHz, $CDCl_3$): isomer **A**: δ 10.7 (^1J = 169 Hz, $2CH_2$), 15.5 (C), 28.8 (^1J = 190 Hz, 2CH); isomer **B**: δ 8.72 (^1J = 167 Hz, $2CH_2$), 15.8 (C), 27.9 (^1J = 190 Hz, 2CH); isomer **C**: δ 9.0 (^1J = 168 Hz, $2CH_2$), 16.1 (C), 26.9 (^1J = 188 Hz, 2CH), isomer **D**: δ 11.0 (^1J = 167 Hz, $2CH_2$), 16.1 (C), 28.5 (^1J = 190 Hz, 2CH).
General procedure for the isolation of free amines **1b–f**. Hydrochloride **6** (1 mmol) was treated with a 25 M aqueous solution of NaOH (0.05 mL). The resulting solution was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over 4 Å molecular sieves and the solvent was removed under reduced pressure. The crude amine was employed immediately in the oxidation reaction.
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19. Gen*eral procedure for the oxidation of amines* **1b–f** *with DMDO*. Free amine **1** (0.5 mmol) in acetone (1 mL) was added to a 0.08 M solution of DMDO in acetone (45 mL). The resulting mixture was maintained at room temperature for 1 h in the dark. The solvent was removed on a rotary evaporator under normal pressure. The crude product was purified by column chromatography (eluent: chloroform). The resulting nitrocyclopropanes **8a**,**c**,**d**,**f** are stable on storage at 5 °C over a long time.
20. Oxi*dation of amine hydrochloride* ***6g*** *with DMDO*. A solution of amine hydrochloride **6g** (0.5 mmol) in distilled water (3 mL) was added to a 0.08 M solution of DMDO in acetone (125 mL). The resulting mixture was maintained at room temperature for 1 h in the dark. Acetone was removed on a rotary evaporator under normal pressure. The resulting aqueous solution was extracted with chloroform (3 × 5 mL). The combined organic layer was dried over 4 Å molecular sieves and the solvent was removed under reduced

pressure. The crude product was purified by column chromatography (eluent: chloroform). The resulting nitrocyclopropane **8g** is stable on storage at 5 °C over a long time.

1,4-Dinitrospiro[2.2]pentane (**8g**): mixture of four isomers **A**:**B**:**C**:**D** = 34:30:26:10; R_f 0.54 ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): isomer **A**: δ 1.89 (dd, ^2J = 6.5, ^3J = 6.2 Hz, 2H, CH_2), 2.34 (dd, ^2J = 6.5, ^3J = 3.4 Hz, 2H, CH_2), 4.88 (dd, ^3J = 3.4, 6.2 Hz, 2H, CH); isomer **B**: δ 1.91 (dd, ^2J = 6.8, ^3J = 7.0 Hz, 2H, CH_2), 2.52 (dd, ^2J = 6.8, ^3J = 3.6 Hz, 2H, CH_2), 4.77 (dd, ^3J = 3.6, 7.0 Hz, 2H, CH); isomer **C**: δ 2.03 (dd, ^2J = 6.8, ^3J = 6.7 Hz, 2H, CH_2), 2.29 (dd, ^2J = 6.8, ^3J = 3.7 Hz, 2H, CH_2), 4.69 (dd, ^3J = 3.7, 6.7 Hz, 2H, CH); isomer **D**: δ 2.13 (dd, ^2J = 6.9, ^3J = 6.9 Hz, 2H, CH_2), 2.36 (dd, ^2J = 6.9, ^3J = 3.9 Hz, 2H, CH_2), 4.69 (dd, ^3J = 3.9, 6.9 Hz, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): isomer **A**: δ 17.1 (^1J = 170 Hz, $2CH_2$), 28.4 (C), 58.5 (^1J = 192 Hz, 2CH); isomer **B**: δ 16.3 (^1J = 173 Hz, $2CH_2$), 30.9 (C), 59.5 (^1J = 197 Hz, 2CH); isomer **C**: δ 16.8 (^1J = 171 Hz, $2CH_2$), 27.5 (C), 59.9 (^1J = 195 Hz, 2CH), isomer **D**: δ 18.0 (^1J = 171 Hz, $2CH_2$), 26.7 (C), 58.5 (^1J = 197 Hz, 2CH). MS (EI, 70 eV) *m*/*z*: 66 ([M−2NO_2]$^+$, 5), 65 (18), 55 (37), 53 (20), 41 (23), 39 (100), 30 (38), 27 (32). MS (ESI) calcd for $C_5H_6N_2O_4$ (M+H)$^+$: 159.12, found: 159.10.