Synthesis of nitrosubstituted triangulanes

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The [1+2] cycloaddition of ethyl nitrodiazoacetate to various methylenecyclopropanes afforded 1-ethoxycarbonyl-1-nitropolyspirocyclopropanes. These compounds were used in the synthesis of first representatives of nitrosubstituted triangulanes. Nitrospiropentane was prepared also by dehydrohalogenation of 1-bromomethyl-1-(nitromethyl)cyclopropane.

Key words: nitrocyclopropanes, ethyl nitrodiazoacetate, 1-ethoxycarbonyl-1-nitropolyspirocyclopropanes, nitrosubstituted triangulanes.

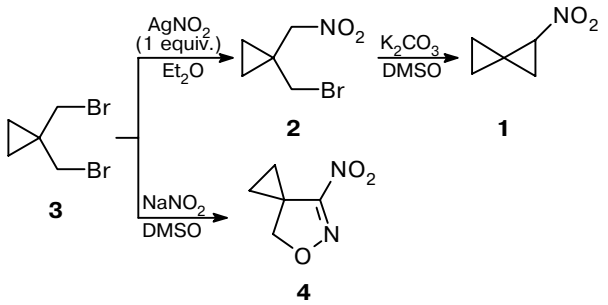
As part of our continuing studies devoted to triangulanes,[1,2] we carried out research on the synthesis of their functional derivatives among which nitrosubstituted triangulanes are of considerable interest as novel high-energy compounds. However, the synthesis of these nitro compounds is an experimentally complicated problem. Presently, nitro and polynitro derivatives of cyclopropanes and polyspirocyclopropanes are difficultly accessible. Only a few examples of compounds of this series are known: nitrocyclopropanes,[3—8] 1,2-dinitrocyclopropanes,[9] 1,2-dinitrospiropentane,[10] and their functional derivatives.[9—13]

In the present study, we examined synthetic approaches to the preparation of nitro derivatives of the simplest triangulanes.

One conventional procedure for the synthesis of substituted cyclopropanes involves 1,3-dehydrohalogenation of the corresponding halonitropropanes. In particular, this procedure has been used for the preparation of nitrocyclopropane starting from 1-iodo-3-nitropropane.[7]

Yet another representative of nitrocyclopropanes, *viz.*, nitrospiro[2.2]pentane (**1**), has been previously unavailable. We examined the possibility of the synthesis of **1** based on 1,3-dehydrohalogenation of 1-bromomethyl-1-(nitromethyl)cyclopropane (**2**) (Scheme 1).

Scheme 1



The starting nitrobromide **2** was synthesized in 22% yield by the reaction of 1,1-bis(bromomethyl)cyclopropane (**3**) with 1 equiv. of $AgNO_2$ in ether. On the contrary, the reaction of dibromide **3** with $NaNO_2$ in DMSO afforded the only product, *viz.*, nitrospirocyclopropylisoxazoline **4**, regardless of the ratio of the starting reagents. Cyclization of nitrobromide **2** under the action of K_2CO_3 in DMSO gave rise to nitrospiropentane **1** in 50% yield. The structure of the latter was confirmed by the data from ^1H and ^{13}C NMR spectroscopy and mass spectrometry. In the ^1H NMR spectrum of compound **1** (see the Experimental section), the proton of the $CHNO_2$ group gives a low-field signal at δ 4.52 as a doublet of doublets (^3J = 2.8 and 6.5 Hz) due to spin-spin coupling with the protons of the methylene group of the substituted three-membered ring. Due to the effect of the electronegative substituent, these protons are also noticeably deshielded (δ 1.66 and 2.15) and have the geminal constant (^2J = 5.4 Hz) typical of cyclopropane compounds. The protons of the unsubstituted ring give high-field signals with a developed multiplet structure at δ 0.95—1.24. The ^{13}C NMR spectrum has a signal for the C atom bound to the nitro group at δ 60.6 with the large spin-spin coupling constant $^1J_{C,H}$ = 191 Hz. The signals for the nonsubstituted C atoms are observed in the high-field region typical of spiropentanes, the methylene groups possessing the characteristic constants ($^1J_{C,H}$ = 164—167 Hz).

Apparently, the use of 1,3-dehydrohalogenation of halonitropropanes in the synthesis of nitropolyspirocyclopropanes with more complex structures is a preparatively complicated problem. The procedure for their preparation based on the [1+2] cycloaddition of nitrosubstituted carbenes to methylenecyclopropanes seems to be more efficient.

Actually, the cycloaddition of nitrocarbene to olefins of the polyspirocyclopropane series afforded directly the target polycyclic nitro compounds. However, the generation of nitrocarbene is a rather intricate and dangerously explosive procedure.[14] More stable ethyl nitrodiazo-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2008—2012, November, 2001.

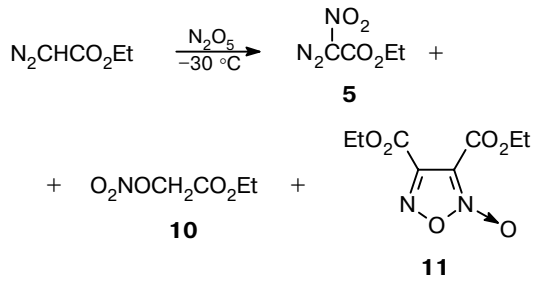
1066-5285/01/5011-2101 $25.00

acetate (**5**) has been synthesized earlier and its reactions with sterically nonhindered olefins in the presence of $Rh_2(OAc)_4$ have been described.[14—17]

We studied an analogous reaction of ester **5** with olefins of the methylenecyclopropane series, *viz.*, with methylenecyclopropane (**6**), methylenespiro[2.2]pentane (**7**), bicyclopropylidene (**8**), and methyl 2-methylenecyclopropanecarboxylate (**9**).

Ethyl nitrodiazoacetate (**5**) was prepared by nitration of ethyl diazoacetate with N_2O_5 in CCl_4.[14] Previously,[14] it has been noted that this reaction gave rise to nitroacetate **10** as a by-product. However, we found that nitration afforded yet another by-product, *viz.*, 3,4-diethoxycarbonylfuroxan (**11**) (Scheme 2).

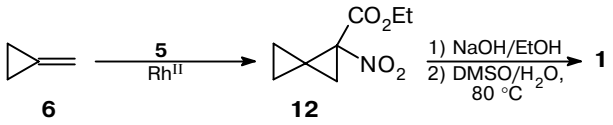
Scheme 2



The resulting three-component mixture (**5** : **10** : **11** = 2 : 2 : 1) was separated by preparative column flash chromatography.

The reaction of compound **5** with methylenecyclopropane (**6**) in the presence of catalytic amounts of $Rh_2(OAc)_4$ afforded ethyl 1-nitrospiro[2.2]pentane-1-carboxylate (**12**) in 85% yield (Scheme 3).

Scheme 3

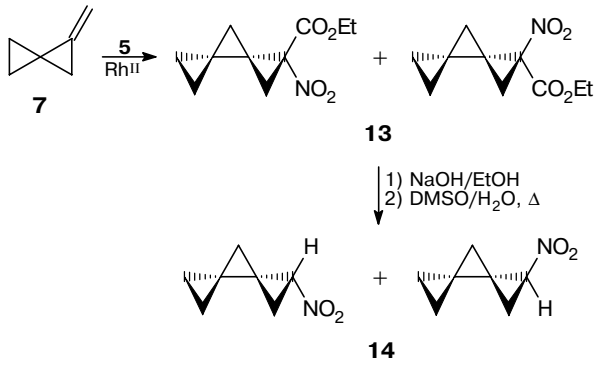


The ^1H NMR spectrum of spiropentane **12** has signals of the CH_2 group of the substituted cyclopropane fragment as an AB system at δ 2.13 and 2.38 (^2J = 5.7 Hz). The ^{13}C NMR spectrum shows a characteristic signal at δ 70.3 corresponding to the quaternary C atom, which is bound simultaneously to the nitro and ethoxycarbonyl groups.

Hydrolysis followed by decarboxylation of nitro derivative **12** upon heating in wet DMSO afforded nitrospiropentane **1** in 20% yield. The ^1H and ^{13}C NMR spectral data for **1** are in complete agreement with the above-mentioned data for this compound prepared by 1,3-dehydrohalogenation of bromonitropropane **2**.

Cyclopropanation of methylenespiropentane **7** with ethyl nitrodiazoacetate (**5**) also proceeded in high yield (>80%) to give isomeric 1-ethoxycarbonyl-1-nitrodispiro[2.0.2.1]heptanes (**13**) (Scheme 4).

Scheme 4

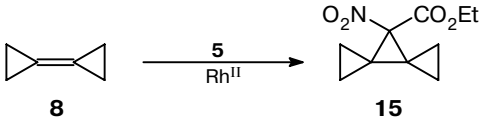


The ^1H and ^{13}C NMR spectra of nitrospirane **13** have two sets of signals corresponding to two isomers in a ratio of 3 : 1 (see the Experimental section). The ^1H NMR spectrum of the stereoisomers of **13** shows well-resolved signals of three cyclopropane fragments at high field. Thus the multiplets of the AB systems at δ 2.0—2.4 and 1.5—1.6 correspond to the CH_2 groups of the substituted and central rings, respectively, and the ABCD systems of the methylene protons of the third ring are observed at δ 0.8—1.0. The presence of three spiro-fused rings in compound **13** was confirmed by the ^{13}C NMR spectra. This fact is supported by strong shielding of the carbon atoms and the rather large spin-spin coupling constant ($^1J_{C,H}$ = 163—168 Hz). The shielding of the signals for the quaternary C atoms bound to the nitro and ethoxycarbonyl groups is identical with that observed for compound **12** (δ 70.0 and 70.1). The composition of dispiroheptane **13** was also confirmed by the data from elemental analysis.

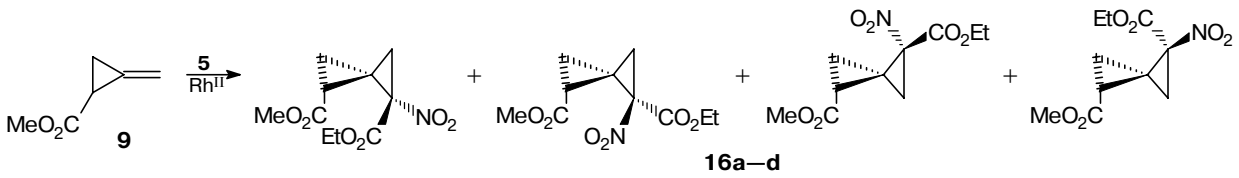
Saponification followed by decarboxylation of nitro ester **13** afforded 1-nitrodispiro[2.0.2.1]heptane (**14**) as a mixture of two stereoisomers in a ratio of 7 : 5 in 56% yield (see Scheme 4). The structures of these stereoisomers were confirmed by the data from ^1H and ^{13}C spectroscopy and mass spectrometry.

Bicyclopropylidene (**8**) belongs to tetrasubstituted olefins whose reactions with ethyl nitrodiazoacetate (**5**), according to the data published in the literature,[16] did not give rise to three-membered rings. However, we succeeded in preparing ethyl 7-nitrodispiro[2.0.2.1]heptane-7-carboxylate (**15**) in 13% yield by the reaction of olefin **8** with ester **5** (Scheme 5).

Scheme 5



Scheme 6



Nitro ester **15** was isolated in the individual state by column chromatography and was completely characterized by the data from ^{1}H and ^{13}C spectroscopy and mass spectrometry.

The symmetry of molecule **15** is responsible for the isochronism of the atoms of the corresponding groups in two external three-membered rings observed in the NMR spectra (see the Experimental section). The quaternary C atom of the central ring has a typical chemical shift (δ 73.2).

The reactions of ethyl nitrodiazoacetate (**5**) with substituted methylenecyclopropanes are of particular interest because they can be considered as an approach to the synthesis of functionally substituted nitropolyspirocyclopropanes. Thus, the reaction of compound **5** with ester **9** gave rise to 1-ethyl 4-methyl 1-nitrospiro[2.2]pentane-1,4-dicarboxylate as a mixture of four diastereomers **16a—d** in 36% yield (Scheme 6).

Most likely, the low yield of adduct **16** is associated with a somewhat lower activity of the double bond of methylenecyclopropane **9** in the [1+2] cycloaddition due to the presence of the electron-withdrawing ester group in the adjacent small ring. It should be noted that derivative **16** is a precursor of 1-aminospiro[2.2]pentane-1,4-dicarboxylic acid, which should, apparently, exhibit high biological activity.[18]

Nitro diester **16** can exist as four diastereomers (**a—d**) due to the presence of two asymmetric centers and the possible manifestation of the geometric isomerism. Unfortunately, we failed to make the assignment in the series of diastereomers of diester **16** based on the NMR spectral data; however, the ratio of the isomers (**a** : **b** : **c** : **d** ≈ 50 : 45 : 5 : 1) indicates that the addition of ethyl nitrodiazoacetate (**5**) to substituted olefins proceeded with high diastereoselectivity.[15] Chromatographic separation of the reaction mixture afforded two fractions. One of these fractions contained a mixture of two major diastereomers (**16a** and **16b**), whereas another fraction contained a mixture of two minor (**16c** and **16d**) diastereomers. The NMR spectra of all diastereomers have signals similar in multiplicity and chemical shifts. The ^{13}C NMR spectra of all diastereomers **16a—d** have a characteristic signal for the quaternary ethoxycarbonylnitro-substituted C atom at δ 69—73.

Hence, the [1+2] cycloaddition of ethyl nitrodiazoacetate to methylenecyclopropanes in the presence of $Rh_2(OAc)_4$ can be used as a general procedure for the preparation of nitro derivatives of triangulanes.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR-400 (400 and 100 MHz, respectively) and Bruker DPX-300 (300 and 75 MHz, respectively) instruments. The mass spectra were obtained on Varian MAT-311A and MX-1321A spectrometers (the energy of ionizing electrons was 70 eV). The course of the reactions and the purities of the compounds were monitored by TLC on Silufol UV-254 plates. Preparative column chromatography was carried out using SiO_2 (Merck, 40/60). The GLC analysis was performed on a Chrom-5 chromatograph equipped with a flame ionization detector and a 3000×5-mm column (10% SE-30 on Inerton AW) at 130—180 °C. The products were separated by preparative GLC on a PAVKh-08 instrument equipped with a katharometer as a detector and a 3000×5-mm column (10% SE-30 on Inerton AW) using He as the carrier gas (the flow rate was 80—120 mL min^{-1}).

Silver nitrite and N_2O_4 were prepared according to a procedure reported previously.[19] The reagent $Rh_2(OAc)_4$ was purchased from Merck. The starting compounds, *viz.*, 1,1-di(bromomethyl)cyclopropane (**3**),[20] ethyl diazoacetate,[21] methylenespiro[2.2]pentane (**7**),[22] bicyclopropylidene (**8**),[23] and methyl 4-methylenespiro[2.2]pentane-1-carboxylate (**9**),[24] were synthesized according to known procedures.

Compounds **1**, **2**, and **14—16** were not studied by elemental analysis because of their low stability.

1-Bromomethyl-1-(nitromethyl)cyclopropane (2). Dibromide **3** (3.00 g, 13.2 mmol) was added to a stirred suspension of $AgNO_2$ (2.63 g, 16.5 mmol) in anhydrous ether (7 mL) at 0 °C for 1 h. The reaction mixture was stirred at 0 °C for 24 h and then at ~20 °C for 2 h. The precipitate that formed was filtered off and washed with ether. The combined ethereal fractions were dried with $MgSO_4$. The solvent was distilled off and the residue was purified by column chromatography (a 3 : 1 light petroleum ether—benzene mixture as the eluent). Product **2** was isolated in a yield of 0.5 g (22%), R_f 0.4. ^{1}H NMR ($CDCl_3$), δ: 0.82 (m, 2 H); 1.00 (m, 2 H); 3.42 (s, 2 H, CH_2Br); 4.38 (s, 2 H, CH_2NO_2). ^{13}C NMR ($CDCl_3$), δ: 15.38 (2 CH_2); 22.38 (C); 40.05 (CH_2Br); 80.00 (CH_2NO_2). MS, m/z (I_{rel} (%)): 193, 195 $[M]^+$ (2), 147, 149 $[M - NO_2]^+$ (20), 119, 121 (5), 107, 109 (5), 93, 95 (5), 67 $[M - NO_2 - Br]^+$ (100).

1-Nitrospiro[2.2]pentane (1). 1-Bromomethyl-1-(nitromethyl)cyclopropane (**2**) (0.35 g, 1.8 mmol) was added with stirring to a suspension of K_2CO_3 (0.50 g, 3.6 mmol) in DMSO (5 mL). The reaction mixture was stirred at ~20 °C for 3—4 h, poured into ice water (5 mL), and extracted with ether (4×5 mL). The ethereal extract was washed with water (2×5 mL) and dried with $MgSO_4$. The solvent was distilled off under reduced pressure and the residue was purified by preparative GLC. Nitrospiropentane **1** was obtained in a yield of 0.10 g (49%). ^{1}H NMR ($CDCl_3$), δ: 0.95—1.06 (m, 2 H); 1.12—1.24 (m, 2 H); 1.66 (dd, 1 H, H(2a), $^3J_{1,2a}$ = 6.5 Hz, $^2J_{2a,b}$ = 5.4 Hz); 2.15 (dd, 1 H, H(2b), $^2J_{2a,b}$ = 5.4 Hz, $^3J_{1,2b}$ =

2.8 Hz); 4.52 (dd, 1 H, H(1), $^3J_{1,2b}$ = 2.8 Hz, $^3J_{1,2a}$ = 6.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 5.93 (CH_2, $^1J_{C,H}$ = 164 Hz); 8.4 (CH_2, $^1J_{C,H}$ = 165 Hz); 17.9 (C(2), $^1J_{C,H}$ = 167 Hz); 21.3 (C_{spiro}); 60.6 (C(1), $^1J_{C,H}$ = 191 Hz). MS, *m/z* (I_{rel} (%)): 114 $[M + 1]^+$ (2), 67 $[M - NO_2]^+$ (22), 65 $[C_5H_5]^+$ (37), 55 (28), 53 (40), 46 $[NO_2]^+$ (14), 42 (68), 39 $[C_3H_3]^+$ (100).

3-Nitrospiro[4,5-dihydroisoxazole-4,1′-cyclopropane] (4). Sodium nitrite (3.37 g, 48.8 mmol) was added in one portion to a solution of 1,1-bis(bromomethyl)cyclopropane (**3**) (5.30 g, 23.2 mmol) in DMF (20 mL) at 0—5 °C. The reaction mixture was slowly heated to ~20 °C and stirred at this temperature for 15 h. Then DMF was distilled off under reduced pressure (18 Torr) and the residue was diluted with water (10 mL) and extracted with benzene (3×10 mL). The extract was dried with $MgSO_4$, the solvent was distilled off, and the residue was purified by column chromatography (SiO_2, a 3 : 1 light petroleum ether—AcOEt mixture as the eluent). Compound **4** was obtained in 43% yield, m.p. 37—38 °C (from light petroleum ether), R_f 0.6. Found (%): C, 42.19; H, 3.94; N, 19.67. $C_5H_6N_2O_3$. Calculated (%): C, 42.25; H, 4.23; N, 19.72. ^{1}H NMR, ($CDCl_3$), δ: 1.09 (m, 2 H); 1.70 (m, 2 H); 4.77 (s, 2 H, CH_2O). ^{13}C NMR ($CDCl_3$), δ: 13.64 (CH_2); 24.62 (C); 81.96 (CH_2O); 165.7 (CNO_2).

Synthesis of ethyl nitrodiazoacetate (5).[15] Tetrachloromethane (25 mL), which was pre-cooled to −25 °C, was added to solid N_2O_5,[25] which was prepared from N_2O_4 (4 g), with cooling to −40 °C. The resulting transparent solution was transferred into a cooled dropping funnel at −25 °C under a stream of argon and added to a solution of ethyl diazoacetate (4 g, 35 mmol) in CCl_4 (25 mL) at the temperature from −25 to −30 °C. The completion of the reaction was judged from cessation of N_2 evolution. The solvent was distilled off under reduced pressure (the temperature was no higher than 35 °C) and ethyl nitrodiazoacetate (**5**) was isolated by column flash chromatography (ether—light petroleum ether as the eluent, 0—30%). Ester **5** was obtained in a yield of 0.81 g (28%), R_f 0.25 (light petroleum ether—AcOEt, 4 : 1). ^{13}C NMR ($CDCl_3$), δ: 13.74 (Me); 62.63 (CH_2O); 101.4 (C—N_2); 154.36 (CO).

Addition of ethyl nitrodiazoacetate (5) to olefins (general procedure). Ethyl nitrodiazoacetate **5** (0.30 g, 1.89 mmol) was slowly added to a stirred mixture of alkene (5—10 equiv.) and $Rh_2(OAc)_4$ (3 mol.%) at 0—5 °C. Then the reaction mixture was stirred at ~20 °C for 1 h. An excess of alkene was removed under reduced pressure and the product (a colorless oil) was isolated by column flash chromatography (ether—light petroleum ether as the eluent, 0—30%).

Saponification of 1-nitrocyclopropanecarboxylates and decarboxylation of sodium 1-nitrocyclopropanecarboxylates (general procedure). A 1 *M* solution of NaOH in EtOH (1.3 mL) was added with stirring to a solution of ethyl 1-nitrocyclopropanecarboxylate (1.28 mmol) in anhydrous EtOH (1.5 mL). After 30 min, the solvent was distilled off under reduced pressure. The residue was dissolved in a 10 : 1 DMSO—water mixture (3.3 mL) and heated at 80 °C for 0.5 h. The solution was cooled, diluted with an equal volume of water, and extracted with ether (4×15 mL). The organic layer was washed with water (4×10 mL) and dried with $MgSO_4$. The solvent was distilled off under reduced pressure and the residue was purified by column flash chromatography (ether—light petroleum ether as the eluent, 0—10%).

Ethyl 1-nitrospiro[2.2]pentane-1-carboxylate (12). The yield was 83%, R_f 0.45 (light petroleum ether—AcOEt, 4 : 1). Found (%): C, 51.71; H, 6.12. $C_8H_{11}NO_4$. Calculated (%): C, 51.89; H, 5.95. ^{1}H NMR ($CDCl_3$), δ: 1.12—1.26 (m, 4 H, CH_2CH_2); 1.30 (t, 3 H, Me, ^3J = 7.1 Hz); 2.13, 2.38 (AB system, 2 H, C(2)H_2, ^2J = 5.7 Hz); 4.28 (q, 2 H, OCH_2, ^3J = 7.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 7.13 (CH_2); 7.92 (CH_2); 14.09 (Me); 22.45 (CH_2); 25.72 (C_{spiro}); 62.70 (CH_2O); 70.33 (C); 164.93 (CO). MS, *m/z* (I_{rel} (%)): 168 $[M - OH]^+$ (8)*, 156 $[M - C_2H_5]^+$ (2), 140 $[M - OC_2H_5]^+$ (16), 129 (3), 111 (68), 65 $[C_5H_5]^+$ (75), 53 (30), 39 $[C_3H_3]^+$ (62), 29 $[C_2H_5]^+$ (100).

Ethyl 1-nitrodispiro[2.0.2.1]heptane-1-carboxylate (13). The yield was 81%. R_f 0.50 (light petroleum ether—AcOEt as the eluent, 4 : 1), the ratio of the isomers was 3 : 1. Found (%): C, 57.08; H, 6.30. $C_{10}H_{13}NO_4$. Calculated (%): C, 56.87; H 6.16. MS, *m/z* (I_{rel} (%)): 194 $[M - OH]^+$ (2), 183 $[M - C_2H_4]^+$ (3), 182 $[M - C_2H_5]^+$ (2), 166 $[M - OC_2H_5]^+$ (3), 155 (4), 91 $[C_7H_7]^+$ (86), 92 (18), 77 (34), 65 $[C_5H_5]^+$ (41), 53 (31), 39 $[C_3H_3]^+$ (47), 29 $[C_2H_5]^+$ (100). Major isomer. ^{1}H NMR ($CDCl_3$), δ: 0.82—0.86 (m, 2 H); 0.91—0.97 (m, 2 H); 1.30 (t, 3 H, Me, ^3J = 7.1 Hz); 1.47 and 1.58 (AB system, 2 H, CH_2, ^2J = 5.0 Hz); 2.15 and 2.26 (AB system, 2 H, CH_2, ^2J = 6.0 Hz); 4.29 (q, 2 H, CH_2O, ^3J = 7.1 Hz); ^{13}C NMR ($CDCl_3$), δ: 3.2 (CH_2, $^1J_{C,H}$ = 164 Hz); 5.5 (CH_2, $^1J_{C,H}$ = 163 Hz); 12.8 (CH_2, $^1J_{C,H}$ = 163 Hz); 14.0 (Me, $^1J_{C,H}$ = 125 Hz); 15.6 (C_{spiro}); 22.1 (CH_2, $^1J_{C,H}$ = 168 Hz); 29.6 (C_{spiro}); 62.6 (CH_2O, $^1J_{C,H}$ = 149 Hz); 70.0 (C); 164.3 (CO). Minor isomer. ^{1}H NMR ($CDCl_3$), δ: 0.84—0.98 (m, 4 H); 1.25 (t, 3 H, Me, ^3J = 7.1 Hz); 1.54 and 1.55 (AB system, 2 H, CH_2, ^2J = 5.1 Hz); 2.02 and 2.40 (AB system, 2 H, CH_2, ^2J = 5.9 Hz); 4.20 (q, 2 H, CH_2O, ^3J = 7.1 Hz); ^{13}C NMR ($CDCl_3$), δ: 5.0 (CH_2, $^1J_{C,H}$ = 164 Hz); 5.6 (CH_2, $^1J_{C,H}$ = 163 Hz); 12.6 (CH_2, $^1J_{C,H}$ = 163 Hz); 13.9 (Me, $^1J_{C,H}$ = 125 Hz); 16.5 (C_{spiro}); 21.9 (CH_2, $^1J_{C,H}$ = 168 Hz); 30.4 (C_{spiro}); 62.5 (CH_2O, $^1J_{C,H}$ = 149 Hz); 70.1 (C); 164.8 (CO).

1-Nitrodispiro[2.0.2.1]heptane (14). The yield was 56%, R_f 0.30 (light petroleum ether—AcOEt as the eluent, 4 : 1), the ratio of the isomers was 7 : 5. MS, *m/z* (I_{rel} (%)): 139 $[M]^+$ (2), 93 $[M - NO_2]^+$ (11), 91 $[C_7H_7]^+$ (100), 77 (90), 65 $[C_5H_5]^+$ (43), 53 (83), 39 $[C_3H_3]^+$ (77). Major isomer. ^{1}H NMR ($CDCl_3$), δ: 0.84—1.04 (m, 4 H); 1.39 and 1.61 (AB system, 2 H, C(3)H_2, ^2J = 4.9 Hz); 1.54 (dd, 1 H, H(2a), $^2J_{2a,b}$ = 5.6 Hz, $^3J_{1,2a}$ = 6.5 Hz); 2.19 (dd, 1 H, $^3J_{1,2b}$ = 3.0 Hz, $^2J_{2a,b}$ = 5.6 Hz); 4.31 (dd, 1 H, H(1), $^3J_{1,2a}$ = 6.5 Hz, $^3J_{1,2b}$ = 3.0 Hz); ^{13}C NMR ($CDCl_3$), δ: 5.8 (CH_2, $^1J_{C,H}$ = 163 Hz); 6.0 (CH_2, $^1J_{C,H}$ = 162 Hz); 12.8 (CH_2, $^1J_{C,H}$ = 164 Hz); 16.9 (C_{spiro}); 17.53 (CH_2, $^1J_{C,H}$ = 166 Hz); 27.2 (C_{spiro}); 59.7 ($CHNO_2$, $^1J_{C,H}$ = 193 Hz). Minor isomer. ^{1}H NMR ($CDCl_3$), δ: 0.70—0.80 (m, 4 H); 1.32 and 1.44 (AB system, 2 H, C(3)H_2, ^2J = 4.4 Hz); 1.65 (dd, 1 H, $^2J_{2a,b}$ = 5.5 Hz, $^3J_{1,2a}$ = 6.4 Hz); 1.95 (dd, 1 H, $^3J_{1,2b}$ = 3.0 Hz, $^2J_{2a,b}$ = 5.5 Hz); 4.59 (dd, 1 H, H(1), $^3J_{1,2a}$ = 6.4 Hz, $^3J_{1,2b}$ = 3.0 Hz); ^{13}C NMR ($CDCl_3$), δ: 2.8 (CH_2, $^1J_{C,H}$ = 164 Hz); 5.4 (CH_2, $^1J_{C,H}$ = 163 Hz); 12.9 (CH_2, $^1J_{C,H}$ = 164 Hz); 14.7 (C_{spiro}); 17.0 (CH_2, $^1J_{C,H}$ = 166 Hz); 24.7 (C_{spiro}); 60.9 ($CHNO_2$, $^1J_{C,H}$ = 195 Hz).

Ethyl 7-nitrodispiro[2.0.2.1]heptane-7-carboxylate (15). The yield was 13%, R_f 0.50 (light petroleum ether—AcOEt as the eluent, 4 : 1). ^{1}H NMR ($CDCl_3$), δ: 1.04 (m, 2 H); 1.10 (m, 2 H); 1.29 (t, 3 H, Me, ^3J = 7.1 Hz); 1.34 (m, 2 H, CH_2); 1.40 (m, 2 H, CH_2); 4.29 (q, 2 H, CH_2O, ^3J = 7.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 6.7 (2 CH_2); 7.0 (2 CH_2); 13.7 (Me); 28.5 (2 C_{spiro}); 62.0 (CH_2O); 73.20 (C); 164.32 (CO). MS, *m/z* (I_{rel} (%)): 211 $[M]^+$ (1), 183 (1), 182 $[M - C_2H_5]^+$ (4), 166 $[M - OC_2H_5]^+$ (9), 153 (29), 137 (52), 121 (24), 119 (28),

* The $[M - OH]^+$ fragments were observed in nitro compounds bearing protons at the adjacent carbon atom.[26]

108 (42), 106 (58), 93 (72), 92 (70), 91 $[C_7H_7]^+$ (89), 77 (77), 65 $[C_5H_5]^+$ (80), 53 (69), 39 $[C_3H_3]^+$ (67).

1-Ethyl 4-methyl 1-nitrospiro[2.2]pentane-1,4-dicarboxylate (16). The yield was 36%, R_f 0.50 (light petroleum ether—AcOEt as the eluent, 4 : 1), the ratio of the isomers **a** : **b** : **c** : **d** ≈ 50 : 45 : 5 : 1. MS, *m/z* (I_{rel} (%)): 212 $[M - OCH_3]^+$ (6), 198 $[M - OC_2H_5]^+$ (7), 197 $[M - NO_2]^+$ (8), 169 (45), 167 $[M - OC_2H_5 - OCH_3]^+$ (63), 156 (30), 137 (42), 123 (37), 65 $[C_5H_5]^+$ (42), 53 (71), 39 $[C_3H_3]^+$ (80). Isomer **16a**. ^{1}H NMR ($CDCl_3$), δ: 1.22 (t, 3 H, Me, ^3J = 7.1 Hz); 1.67 (dd, 1 H, C$\underline{H}_2$CH, ^2J = 5.2 Hz, ^3J = 8.0 Hz); 1.76 (dd, 1 H, C$\underline{H}_2$CH, ^2J = 5.2 Hz, ^3J = 5.6 Hz); 2.10 and 2.43 (AB system, 2 H, C(2)H_2, ^2J = 6.7 Hz); 2.30 (dd, 1 H, C(4)H, ^3J = 5.6 Hz, ^3J = 8.0 Hz); 3.64 (s, 3 H, OMe); 4.23 (q, 2 H, CH_2O, ^3J = 7.1 Hz); ^{13}C NMR ($CDCl_3$), δ: 13.4 (Me, $^1J_{C,H}$ = 127 Hz); 14.2 (C(3)H_2, $^1J_{C,H}$ = 168 Hz); 21.0 (CH, $^1J_{C,H}$ = 172 Hz); 21.2 (C(2)H_2, $^1J_{C,H}$ = 170 Hz); 31.0 (C_{spiro}); 52.0 (OMe, $^1J_{C,H}$ = 147 Hz); 63.0 (OCH_2, $^1J_{C,H}$ = 149 Hz); 69.6 (C(NO_2)); 163.9 ($\underline{C}O_2$Et); 171.0 ($\underline{C}O_2$Me). Isomer **16b**. ^{1}H NMR ($CDCl_3$), δ: 1.23 (t, 3 H, Me, ^3J = 7.1 Hz); 1.65—1.70 (m, 2 H, C$\underline{H}_2$CH); 2.21 and 2.33 (AB system, 2 H, C(2)H_2, ^2J = 6.7 Hz); 2.33 (m, 1 H, C(4)H); 3.63 (s, 3 H, OMe); 4.22 (q, 2 H, CH_2O, ^3J = 7.1 Hz); ^{13}C NMR ($CDCl_3$), δ: 13.8 (Me, $^1J_{C,H}$ = 127 Hz); 14.9 (C(3)H_2, $^1J_{C,H}$ = 167 Hz); 20.2 (CH, $^1J_{C,H}$ = 171 Hz); 21.3 (C(2)H_2, $^1J_{C,H}$ = 170 Hz); 30.9 (C_{spiro}); 52.1 (OMe, $^1J_{C,H}$ = 147 Hz); 62.9 (OCH_2, $^1J_{C,H}$ = 149 Hz); 69.4 (C(NO_2)); 163.6 ($\underline{C}O_2$Et); 171.2 ($\underline{C}O_2$Me). Isomer **16c**. ^{1}H NMR ($CDCl_3$), δ: 1.33 (t, 3 H, Me, ^3J = 7.1 Hz); 1.58 (dd, 1 H, C$\underline{H}_2$CH, ^2J = 5.2 Hz, ^3J = 8.2 Hz); 1.84 (dd, 1 H, C$\underline{H}_2$CH, ^2J = 5.2 Hz, ^3J = 5.4 Hz); 2.23 and 2.37 (AB system, 2 H, C(2)H_2, ^2J = 6.2 Hz); 2.51 (dd, 1 H, C(4)H, ^3J = 5.4 Hz, ^3J = 8.2 Hz); 3.64 (s, 3 H, OMe); 4.35 (q, 2 H, CH_2O, ^3J = 7.1 Hz); ^{13}C NMR ($CDCl_3$), δ: 14.0 (Me); 14.3 (C(3)H_2); 21.7 (CH); 22.3 (C(2)H_2); 30.5 (C_{spiro}); 51.9 (OMe); 62.8 (OCH_2); 72.3 (C(NO_2)); 163.3 ($\underline{C}O_2$Et); 170.5 ($\underline{C}O_2$Me). Isomer **16d**. ^{1}H NMR ($CDCl_3$), δ: 1.34 (t, 3 H, Me, ^3J = 7.1 Hz); 1.74 (dd, 1 H, C$\underline{H}_2$CH, ^2J = 5.2 Hz, ^3J = 8.1 Hz); 1.87 (dd, 1 H, C$\underline{H}_2$CH, ^2J = 5.2 Hz, ^3J = 5.5 Hz); 2.22 and 2.39 (AB system, 2 H, C(2)H_2, ^2J = 6.3 Hz); 2.34 (dd, 1 H, C(4)H, ^3J = 5.5 Hz, ^3J = 8.1 Hz); 3.66 (s, 3 H, OMe); 4.31 (q, 2 H, CH_2O, ^3J = 7.1 Hz); ^{13}C NMR spectrum ($CDCl_3$), δ: 13.9 (Me); 14.2 (C(3)H_2); 21.6 (CH); 21.9 (C(2)H_2); 30.6 (C_{spiro}); 51.9 (OMe); 62.3 (OCH_2); 67.9 (C(NO_2)); 164.3 ($\underline{C}O_2$Et); 171.1 ($\underline{C}O_2$Me).

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Received July 5, 2001;
in revised form September 19, 2001