Reaction of diazoalkanes with unsaturated compounds
13.* A new method of preparation and [1+2]- and [3+2]-cycloaddition reactions of diazopropyne

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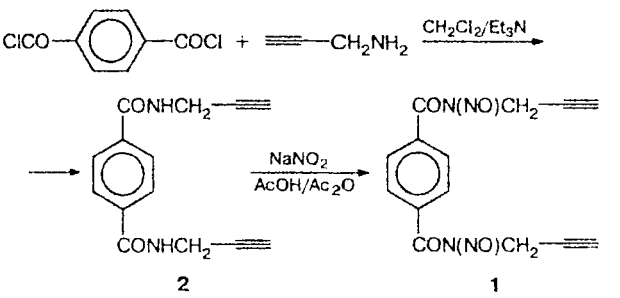
A THF solution of diazopropyne was obtained in 60% yield by the reaction of a 30% aqueous solution of methylamine with *N,N'*-dinitroso-*N,N'*-dipropargylterephthalodiamide. The reactions of diazopropyne with methyl acrylate and methyl methacrylate giving various ethynylpyrazolines as well as its CuCl-catalyzed decomposition in the presence of norbornene or norbornadiene yielding ethynylcyclopropanes were studied. The main products of catalytic deazotization of diazopropyne in the absence of unsaturated compounds are isomeric *E*- and *Z*-hex-3-ene-1,5-diynes resulting from propargylene dimerization.

Key words: diazopropyne, 3- or 5-ethynylpirazolines, ethynylcyclopropanes, 1,3-dipolar cycloaddition, catalytic ethynylcyclopropanation, NMR spectra.

Diazopropyne (DAP), which has been used[2–5] as the source of propargylene in order to study its physicochemical characteristics, can also be regarded as a convenient reagent for the synthesis of ethynyl-substituted cyclopropanes and nitrogen-containing heterocycles. Although the first examples of preparation of DAP date back to the early 1960s, its use in organic synthesis still remains quite limiting.[2,6–9] Known methods for the synthesis of DAP, by analogy with the synthesis of diazoalkanes, are based on decomposition of *N*-nitroso-*N*-propargylurea[2–5,8] or *N*-nitroso-*N*-propargylacetamide[6,7,9] under the action of strong bases. Most publications do not present the yields of DAP (they are likely to be relatively low) and only in one study[9] is it noted that when nitrosopropargylacetamide is used, the yields vary from 20% to 38%. Treatment of *N*-nitroso-*N*-propargylamides with weak bases gives mostly the products of deazotization of the corresponding diazonium ion.[10] In the present study, we propose a fairly efficient method for the preparation of DAP and study typical reactions of its cycloaddition to unsaturated compounds, which can occur both with elimination and with retention of the nitrogen atoms.

N,N'-Dimethyl-*N,N'*-dinitrosoterephthalodiamide is known[11] to be a convenient starting compound for generation of diazomethane in a high yield. Keeping to this analogy, we synthesized *N,N'*-dinitroso-*N,N'*-dipropargylterephthalodiamide (**1**) and studied its decomposition in the presence of bases in order to prepare DAP. Compound **1** was synthesized by the reaction of terephthaloyl dichloride with propargylamine in the presence of Et_3N and subsequent nitrosation of the resulting dipropargyldiamide **2** by a $NaNO_2$—MeCOOH—$(MeCO)_2O$ mixture, according to the previously reported procedure.[12]



2 **1**

As should be expected, nitroso amide **1** is decomposed fairly readily by bases to give DAP; however, the yield of DAP largely depends on the reaction conditions and the nature of the base used. Thus decomposition of **1** on treatment with 2.5 equiv. of MeONa in ether at −15 °C and subsequent distillation of the resulting DAP together with the solvent at 40—50 Torr into a trap cooled to −60 °C yields an orange-yellow solution in which the content of DAP does not exceed 25% of the theoretically possible amount (determined from the integral intensity of the non-overlapped signal of DAP at ~4.2 ppm (see Ref. 5) using *o*-dichlorobenzene protons as the internal standard). The reaction mixture itself is colored intensely red. When compound **1** is decomposed by a 30% solution of KOH under similar conditions, the yield of DAP increases to 40%; in this case, the residue is colored much less intensely. However, the best results

* For Part 12, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2278—2282, November, 1998.

1066-5285/98/4711-2208$20.00

were achieved upon the reaction of nitroso amide **1** dissolved in THF with 2 equiv. of a 30% solution of $MeNH_2$ at −20 °C. In this case, the yield of DAP in the material condensed in the trap proves to be fairly constant and amounts to 57—60%.

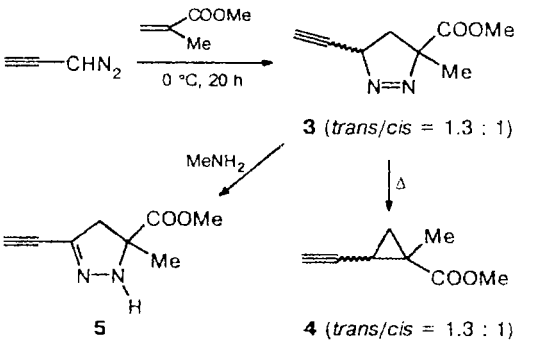
DAP

To prepare a solution of DAP exhibiting no NMR signals due to protic solvents, we used dimethyl ether of diethyleneglycol from which the DAP being formed was recondensed into a trap with $CDCl_3$. The ^1H NMR spectrum of the resulting sample is fully consistent with the previously published data[5] and contains two doublets in the expected region (δ 4.22 and 3.56). Therefore, it appears quite unexpected that in the reported[13,14] ^1H NMR spectrum of an unsaturated diazo compound, *viz.*, 3-diazoprop-1-ene, the signal for the methylene protons of the vinyl group occurs in an unusually high field (δ 1.07); this was explained by conjugation of the double bond with the diazo group:

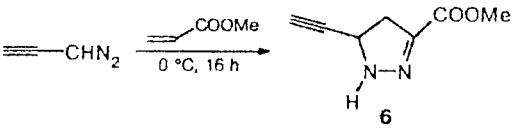
In order to verify these data, we prepared a solution of diazopropene in $CDCl_3$ and showed that its ^1H NMR spectrum actually differs in the positions of signals, which occur at δ 5.9 (1 H) and 4.5—4.7 (3 H) (see Experimental). Apparently, in Ref. 13, the signals of the protons of diethyl ether used as the solvent were mistakenly assigned to diazopropene. Thus, both diazopropene and DAP can be legitimately regarded as typical aliphatic diazo compounds without substantial displacement of the electron density of the multiple bonds.

Then we studied some reactions of cycloaddition of DAP to electron-deficient and strained unsaturated compounds. At 5—10 °C, DAP slowly reacts with methyl methacrylate to give the corresponding 5-ethynyl-1-pyrazoline **3**, which is partially deazotized to yield ethynylcyclopropane **4** even during this reaction. According to the ^1H NMR spectrum, the reaction mixture contains ~85% isomeric pyrazolines **3** in a ratio of ~1.3 : 1 and ~15% isomeric ethynylcyclopropanes **4** in approximately the same ratio. Heating this mixture at 60 °C for 10—15 min affords compound **4** in a virtually quantitative yield. It is noteworthy that the reaction of DAP with methyl methacrylate in the presence of $MeNH_2$ gives 3-ethynyl-2-pyrazoline **5**, stable in organic solvents, as the major product (according to the ^1H NMR data); this product results from isomerization of the initially formed pyrazoline **3** under the action of a base. In the presence of neutral alumina, compound **3** also partially isomerizes to pyrazoline **5**.

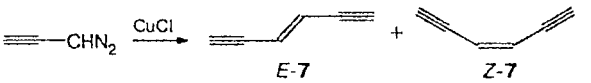
1,3-Dipolar cycloaddition of DAP to methyl acrylate, which contains an active H atom near the electron-



withdrawing substituent, results, as expected, in the selective formation of previously unknown 5-ethynyl-3-methoxycarbonyl-2-pyrazoline (**6**), which was isolated in the crystalline state in ~90% yield.

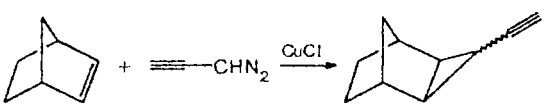


Solutions of DAP in ether or THF containing no amines readily decompose with nitrogen evolution on treatment with CuCl, giving rise to *E*- and *Z*-hex-3-ene-1,5-diynes (**7**), which formally result from dimerization of ethynylcarbene. These products were identified based on the ^1H NMR spectrum, which exhibited two singlets (2.2 : 1) for the olefinic and two singlets (2.2 : 1) for the acetylenic protons; the chemical shifts are fully consistent with the previously reported values.[15]



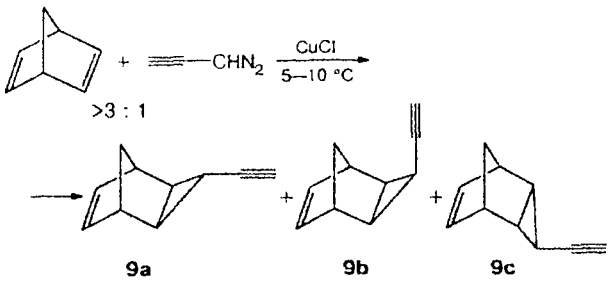
2.2 : 1

The catalytic decomposition of DAP in excess norbornene in the presence of CuCl at 5—10 °C results in trapping of ethynylcarbene and gives isomeric 3-ethynyl-*exo*-tricyclo[3.2.1.$0^{2,4}$]octanes (**8**) in an overall yield of 65—70%. The *syn*-isomer predominates in this mixture. The addition of MeONa to a solution of *anti*- and *syn*-**8** in $CDCl_3$ leads to H—D exchange of the acetylenic protons in both isomers, which is manifested as a sharp decrease in the intensity of their ^1H NMR signals, the change in the multiplicity of the signal for the proton at C(3), and the appearance of a signal for $CHCl_3$. The isomeric composition of the reaction mixture virtually does not change.



8 (*anti* : *syn* = 1 : 1.4)

The reaction of DAP with a threefold molar excess of norbornadiene in the presence of CuCl involves mostly one double bond in the initial diene and affords a mixture of isomeric 3-ethynyltricyclo[3.2.1.$0^{2,4}$]oct-6-enes (**9**) in a yield of up to 70%. However, in this case, as for example in the catalytic reaction of norbornadiene with diazomethane[1] or diazopropene[16] in the presence of copper salts, *endo*-isomer **9c** is formed together with *exo*-isomers **9a,b** (the ratio **a** : **b** : **c** ≈ 1 : 1.4 : 0.2). The structures of the resulting compounds can be derived from the character of the ^1H and ^{13}C NMR signals and also from the {^1H—^{13}C} correlation data. The isomers were assigned based on the facts that the spin-spin coupling constants of the cis protons in the cyclopropane ring are greater than those of the trans protons and that the signals of the olefinic protons in *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-enes (δ 6.3—6.5) are shifted downfield with respect to the signals for the corresponding *endo*-isomers (δ 5.77).



Attempts at using palladium compounds ($Pd(OAc)_2$, $(PhCN)_2PdCl_2$, $Pd(acac)_2$) as catalysts instead of CuCl failed because these compounds virtually do not decompose DAP at 20—25 °C.

Thus, according to our results and published data,[6—9] DAP is a fairly stable compound, which behaves as a typical aliphatic diazo compound in 1,3-dipolar cycloaddition and catalytic deazotization. Decomposition of DAP catalyzed by CuCl does not give any isomeric compounds containing a >C=C=CH_2 fragment.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz) and Bruker AM-300 (300 MHz) spectrometers for solutions in $CDCl_3$ containing 0.05% tetramethylsilane as the internal standard. GC/MS analysis was carried out on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, a 30 m-long RSL-200 capillary column).

Terephthalic acid *N,N'*-dipropargyldiamide (2). A solution of propargylamine (3.85 g, 70 mmol) in 10 mL of CH_2Cl_2 was added with vigorous stirring to a suspension of terephthaloyl dichloride (7.08 g, 35 mmol) in 90 mL of CH_2Cl_2 cooled to 0 °C; then Et_3N (7.06 g, 70 mmol) was added at the same temperature, and the mixture was stirred for 1 h. The resulting precipitate was filtered off, washed with EtOH and CH_2Cl_2, and dried in air to give 7.73 g (92%) of **2** as a colorless finely crystalline compound with m.p. >280 °C (dec.). Partial mass spectrum, *m/z* (I_{rel} (%)): 240 (55) $[M]^+$, 186 (100), 158 (28), 130 (27), 104 (50), 103 (57).

Terephthalic acid *N,N'*-dinitroso-*N,N'*-dipropargyldiamide (1). Sodium nitrite (8.6 g, 125 mmol) was added at 0 °C with vigorous stirring over a period of 5 h to a mixture of diamide **2** (7.7 g, 32 mmol), AcOH (16 mL), and Ac_2O (81 mL), and the mixture was kept for 16 h at 0°C; then an additional $NaNO_2$ (8.6 g, 125 mmol) was added over a period of 5 h, and the mixture was stirred for 24 h at 0 °C. Then the reaction mixture was poured on ice and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with a 5% solution of $NaHCO_3$ (100 mL) and water (100 mL), dried with anhydrous Na_2SO_4, and concentrated to dryness to give 6.62 g (70%) of dinitroso amide **1** as a yellow finely crystalline powder, m.p. 120—122 °C (dec.). ^1H NMR, δ: 7.89 (s, 4 H, C_6H_4), 4.63 (d, 4 H, 2 CH_2, ^4J = 2.5 Hz), 2.14 (t, 2 H, 2 ≡CH, ^4J = 2.5 Hz). Partial mass spectrum, *m/z* (I_{rel} (%)): 215 (100) $[M-N(NO)CH_2C{\equiv}CH)]^+$, 157 (50), 104 (95), 76 (50).

Synthesis of diazopropyne (DAP). ***A.*** A 30% aqueous solution (0.83 g) of $MeNH_2$ (8 mmol) was added over a period of 10 min at −20 °C to a solution of **1** (1.20 g, 4 mmol) in 4 mL of THF, and the reaction mixture was stirred for 20 min at 0 °C and dried with Na_2SO_4. The resulting DAP together with THF was recondensed at 30 Torr into a trap cooled to −60 °C. The yield of DAP found by ^1H NMR spectroscopy (based on the integral intensities of the non-overlapped signals of DAP at ~4.2 ppm and the protons of *o*-dichlorobenzene taken as the internal standard) amounted to 57—60%; the molar concentration was ~1.2 mol L^{-1}.

B. A 30% aqueous solution (0.56 g) of KOH was added at −5 °C to a solution of nitroso amide **1** (0.30 g, 1 mmol) in 1.5 mL of THF, and the mixture was stirred for 30 min. Then the reaction mixture, together with the precipitate formed, was dried with Na_2SO_4, and DAP and the solvent were distilled at 30 Torr into a trap cooled to −60 °C. Yield ~40%.

***E*- and *Z*-Hex-3-ene-1,5-diynes (7).** A solution of DAP in $CDCl_3$ (0.4 mL) was added at −5 °C with stirring to a suspension of CuCl (~2 mg) in 0.3 mL of $CDCl_3$; evolution of N_2 was observed. The ^1H NMR spectrum of the reaction mixture contained four singlets having, by pairs, equal intensities (δ 6.04 and 3.20, 5.91 and 3.41, ratio 2.2:1) and corresponding to *E*- and *Z*-**7** (see Ref. 15).

Reaction of DAP with methyl methacrylate. A solution of DAP (1.6 mL, ~2 mmol) in THF was added at 0 °C to a solution of methyl methacrylate (0.30 g, 3.0 mmol) in 1.0 mL of ether. The reaction mixture was kept at 0 °C until it became colorless (~20 h), then it was concentrated *in vacuo* at the same temperature to give 0.32 g of a residue as a yellowish liquid containing ~85% isomeric pyrazolines **3** and ~15% ethynylcyclopropanes **4** (the isomer ratio in both products is ~1.3 : 1). Half the resulting reaction mixture was kept in CCl_4 for 15 min at 60 °C; this was accompanied by nitrogen evolution. Removal of the solvents and vacuum microdistillation (9 Torr, bath temperature ~70 °C) gave 0.13 g (93%) of methyl 1-methyl-2-ethynylcyclopropanecarboxylate (**4**) as a mixture of *trans*- and *cis*-isomers in a ratio of ~1.3 : 1. Found (%): C, 69.32; H, 7.19. $C_8H_{10}O_2$. Calculated (%): C, 69.55; H, 7.30.

***trans*-5-Ethynyl-3-methoxycarbonyl-3-methyl-1-pyrazoline (*trans*-3).** ^1H NMR, δ: 5.25 (ddd, 1 H, H-5, $J_{4a,5}$ = 9.1 Hz, $J_{4b,5}$ = 7.3 Hz, ^4J = 2.5 Hz); 3.76 (s, 3 H, OMe); 2.67 (d, 1 H, ≡CH, ^4J = 2.5 Hz); 2.53 (dd, 1 H, H-4a, $J_{4a,5}$ = 9.1 Hz, ^2J = 13.0 Hz); 1.75 (s, 3 H, Me); 1.53 (dd, 1 H, H-4b, $J_{4b,5}$ = 7.3 Hz, ^2J = 13.0 Hz). ^{13}C NMR, δ: 170.1 (COO),

97.2 (C-3), 80.0 (C-5), 79.2 (≡C), 76.1 (≡CH), 53.1 (OMe), 36.1 (C-4), 22.5 (Me).

Compound ***cis*-3**. ^{1}H NMR, δ: 5.12 (dt, 1 H, H-5, $J_{4a,5}$ = $J_{4b,5}$ = 8.6 Hz, ^4J = 2.5 Hz); 3.82 (s, 3 H, OMe); 2.66 (d, 1 H, ≡CH, ^4J = 2.5 Hz); 2.11 (dd, 1 H, H-4a, $J_{4a,5}$ = 8.6 Hz, ^2J = 13.0 Hz); 1.99 (dd, 1 H, H-4b, $J_{4b,5}$ = 8.6 Hz, ^2J = 13.0 Hz); 1.52 (s, 3 H, Me). ^{13}C NMR, δ: 174.5 (COO), 96.2 (C-3), 78.6 (C-5), 78.6 (≡C), 76.0 (≡CH), 52.0 (OMe), 35.3 (C-4), 21.0 (Me).

Methyl 2-ethynyl-1-methylcyclopropanecarboxylate (*trans*-4). ^{1}H NMR, δ: 3.60 (s, 3 H, OMe); 1.92 (ddd, 1 H, H-2, J_{cis} = 8.8 Hz, J_{trans} = 6.3 Hz, ^4J = 2.1 Hz); 1.80 (d, 1 H, ≡CH, ^4J = 2.1 Hz); 1.50 (dd, 1 H, H-3a, J_{cis} = 8.8 Hz, ^2J = 4.0 Hz); 1.37 (s, 3 H, Me); 0.77 (dd, 1 H, H-3b, J_{trans} = 6.3 Hz, ^2J = 4.0 Hz). ^{13}C NMR, δ: 173.8 (COO), 82.2 (≡C), 68.3 (≡CH), 52.2 (OMe), 24.6 (C-1), 23.8 (C-3), 16.3 (C-2), 15.0 (Me).

Compound ***cis*-4**. ^{1}H NMR, δ: 3.65 (s, 3 H, OMe); 1.79 (d, 1 H, ≡CH, ^4J = 2.1 Hz); 1.61 (dd, 1 H, H-3a, J_{trans} = 6.5 Hz, ^2J = 4.0 Hz); 1.44 (ddd, 1 H, H-2, J_{cis} = 8.6 Hz, J_{trans} = 6.5 Hz, ^4J = 2.1 Hz); 1.28 (s, 3 H, Me); 0.93 (dd, 1 H, H-3b, J_{cis} = 8.6 Hz, ^2J = 4.0 Hz). ^{13}C NMR, δ: 171.5 (COO), 81.7 (≡C), 68.1 (≡CH), 51.9 (OMe), 27.5 (C-1), 22.0 (C-3), 17.1 (C-2), 20.3 (Me).

3-Ethynyl-5-methoxycarbonyl-5-methyl-2-pyrazoline (5). A drop of a 20% solution of $MeNH_2$ was added at 10 °C to the remaining reaction mixture prepared in the previous experiment, which contained ~85% isomeric pyrazolines **3** and ~15% ethynylcyclopropanes **4**, and the mixture was stirred for 30 min. Then it was dried with Na_2SO_4, and the solvent was evaporated *in vacuo*. According to the ^{1}H NMR spectra (obtained upon subtracting the signals of the initial ethynylcyclopropanes **4** present as impurities), both isomeric pyrazolines **3** have quantitatively isomerized to 2-pyrazoline **5**. ^{1}H NMR, δ: 6.38 (br.s, 1 H, NH); 3.75 (s, 3 H, OMe); 3.35 and 2.70 (both d, 1+1 H, CH_2, ^2J = 16.8 Hz); 3.20 (s, 1 H, ≡CH); 1.55 (s, 3 H, Me). ^{13}C NMR, δ: 174.7 (COO), 134.9 (C-3), 81.7 (≡CH), 76.7 (≡C), 68.7 (C-5), 53.0 (OMe), 45.4 (C-4), 23.9 (Me). Partial mass spectrum, *m/z* (I_{rel} (%)): 166 (15) $[M]^+$, 107 (100), 84 (39), 66 (21). On attempted purification of pyrazoline **5** by TLC (SiO_2 or Al_2O_3), the spectrum of the fraction being isolated somewhat changed. Simultaneously with the decrease in the intensity of the signals of the initial ethynylcyclopropanes **4**, signals for other impurities appeared, indicating that pyrazoline **5** underwent subsequent transformations during chromatography.

5-Ethynyl-3-methoxycarbonyl-2-pyrazoline (6). A solution of DAP (1.7 mL, ~2 mmol) in THF was added at 0 °C to a solution of methyl acrylate (0.26 g, 3 mmol) in 2 mL of ether, and the resulting solution was kept at 0 °C until it became colorless (~16 h). Evaporation of the solvents and excess olefin *in vacuo* gave 0.26 g (87%) of pyrazoline **3** as a slightly yellowish crystals with m.p. 64–65 °C (from a 1 : 2 benzene–hexane mixture). ^{1}H NMR, δ: 6.30 (br.s, 1 H, NH); 4.60 (m, 1 H, H-5); 3.84 (s, 3 H, OMe); 3.16 (dd, 1 H, H-4a, $J_{4a,5}$ = 10.4 Hz, ^2J = 16.5 Hz); 3.12 (dd, 1 H, H-4b, $J_{4b,5}$ = 6.8 Hz, ^2J = 16.5 Hz); 2.41 (d, 1 H, ≡CH, ^4J = 2.3 Hz). ^{13}C NMR, δ: 162.4 (COO), 142.4 (C-3), 82.1 (≡C), 72.8 (≡CH), 52.3 (OMe), 51.2 (C-5), 38.1 (C-4). Found (%): C, 55.07; H, 5.21; N, 18.56. $C_7H_8N_2O_2$. Calculated (%): C, 55.26; H, 5.30; N, 18.41.

3-Ethynyl-*exo*-tricyclo[3.2.1.0^{2,4}]octane (8). Copper(I) chloride (0.006 g, 0.06 mmol) was added at 5 °C to a solution of norbornene (0.28 g, 3 mmol) in 1 mL of CH_2Cl_2; then the THF solution of DAP (1 mL, ~1.2 mmol) prepared by method ***B*** was added dropwise with stirring over a period of 10 min. When gas evolution ceased, the mixture was stirred for an additional 10 min, the greater part of the solvents was removed *in vacuo*, the residue was diluted with 5 mL of hexane, and the mixture was filtered through a thin layer of silica gel. Vacuum microdistillation gave 0.105 g (66%) of a colorless liquid (bath temperature ~75 °C, 25 Torr), which was a mixture of *anti*- and *syn*-**8** in 1 : 1.4 ratio. Partial mass spectrum, *m/z* (I_{rel} (%)): 131 (20) $[M-H]^+$, 117 (76), 104 (30), 103 (26), 91 (66), 80 (83), 78 (100).

Compound ***anti*-8**. ^{1}H NMR, δ: 2.33 (m, 2 H, H-1, H-5); 1.72 (d, 1 H, ≡CH, ^4J = 2.0 Hz); 1.43 (m, 2 H, *exo*-H-6 and H-7); 1.24 (m, 2 H, *endo*-H-6 and H-7); 1.17 (br.q, 1 H, H-3, $J \approx 2.2$ Hz); 1.11 (br.d, 2 H, H-2, H-4, $J_{2,3}$ = 2.3 Hz); 0.83 (d.quint, 1 H, H-8a, ^2J = 10.4 Hz, J = 2.0 Hz); 0.63 (d.quint, 1 H, H-8b, ^2J = 10.4 Hz, J = 1.3 Hz). ^{13}C NMR, δ: 86.5 (≡C), 64.1 (≡CH), 35.7 (C-1, C-5), 28.9 (C-6, C-7), 27.6 (C-8), 25.6 (C-2, C-4), 2.3 (C-3).

Compound ***syn*-8**. ^{1}H NMR, δ: 2.47 (m, 2 H, H-1, H-5); 2.21 (d.quint, 1 H, H-8a, ^2J = 10.2 Hz, J = 2.0 Hz); 2.06 (d, 1 H, ≡CH, ^4J = 2.2 Hz); 1.48 (m, 2 H, *exo*-H-6 and H-7); 1.26 (m, 2 H, *endo*-H-6 and H-7); 1.05 (m, 3 H, H-2, H-3, H-4); 0.68 (d.quint, 1 H, H-8b, ^2J = 10.2 Hz, J = 1.3 Hz). ^{13}C NMR, δ: 84.5 (≡C), 70.3 (≡CH), 35.9 (C-1, C-5), 29.5 (C-6, C-7), 29.3 (C-8), 23.2 (C-2, C-4), 5.4 (C-3).

3-Ethynyltricyclo[3.2.1.0^{2,4}]oct-6-ene (9). A similar procedure starting from norbornadiene (0.37 g, 4 mmol) and ~1.2 mmol of the THF solution of DAP in the presence of CuCl followed by evaporation of the solvents and vacuum microdistillation gave 0.10 g (64%) of a colorless liquid (bath temperature ~70 °C, 20 Torr) consisting of a mixture of *exo,anti*-, *exo,syn*-, and *endo,anti*-isomers in ~1 : 1.4 : 0.2 ratio. Partial mass spectrum, *m/z* (I_{rel} (%)): 129 (87) $[M-H]^+$, 128 (81), 126 (46), 115 (100).

exo,anti-Isomer (**9a**). ^{1}H NMR, δ: 6.32 (t, 2 H, H-6, H-7, J = 1.8 Hz); 2.90 (m, 2 H, H-1, H-5); 2.24 (q, 1 H, H-3, $J_{2,3}$ = $J_{3,4}$ = ^4J = 2.1 Hz); 2.02 (d, 1 H, ≡CH, ^4J = 2.1 Hz); 1.41 (dq, 2 H, H-2, H-4, $J_{2,3}$ = $J_{3,4}$ = 2.5 Hz, J = 0.9 Hz); 1.06 and 0.95 (both m, 2 H, 2 H-8, ^2J = 9.5 Hz). ^{13}C NMR, δ: 140.5 (C-6, C-7), 85.2 (≡C), 65.4 (≡CH), 40.3 (C-1, C-5), 38.3 (C-8), 31.7 (C-2, C-4), 18.9 (C-3).

exo,syn-Isomer (**9b**). ^{1}H NMR, δ: 6.50 (t, 2 H, H-6, H-7, J_2 = 1.9 Hz); 3.02 (m, 2 H, H-1, H-5); 2.48 (br.dt, 1 H, *syn*-H-8, ^2J = 9.3 Hz, J = 1.8 Hz); 2.40 (d, 1 H, ≡CH, ^4J = 2.4 Hz); 2.10 (dt, 1 H, H-3, $J_{2,3}$ = $J_{3,4}$ = 6.9 Hz, ^4J = 2.4 Hz); 1.34 (dq, 2 H, H-2, H-4, $J_{2,3}$ = $J_{3,4}$ = 7.0 Hz, J = 0.9 Hz); 1.04 (br.dt, 1 H, *anti*-H-8, ^2J = 9.3 Hz, J = 1.8 Hz). ^{13}C NMR, δ: 142.8 (C-6, C-7), 83.9 (≡C), 74.0 (≡CH), 42.2 (C-1, C-5), 41.7 (C-8), 30.0 (C-2, C-4), 24.8 (C-3).

endo,anti-Isomer (**9c**). ^{1}H NMR, δ: 5.77 (t, 2 H, H-6, H-7, J = 2.0 Hz); 2.92 (m, 2 H, H-1, H-5); 1.95 (d, 1 H, ≡CH, ^4J = 2.2 Hz); 1.79 (m, 3 H, H-2, H-4 and H-8a); 1.66 (br.dt, 1 H, H-8b, ^2J = 6.9 Hz, J = 1.2 Hz); 1.10 (q, 1 H, H-3, $J_{2,3}$ = $J_{3,4}$ = ^4J = 2.2 Hz). ^{13}C NMR, δ: 131.4 (C-6, C-7), 85.9 (≡C), 64.6 (≡CH), 63.4 (C-8), 42.7 (C-1, C-5), 22.8 (C-2, C-4), 17.4 (C-3).

3-Diazoprop-1-ene was prepared by a previously described procedure[17] from *N*-allyl-*N*-nitrosourea using diethyleneglycol dimethyl ether as the solvent and distillation of products at 40 Torr into a trap with $CDCl_3$ cooled to −60 °C. ^{1}H NMR, δ: 5.90 (ddd, 1 H, H-2, J_{trans} = 17.0 Hz, J_{cis} = 10.7 Hz, $J_{2,3}$ = 8.0 Hz); 4.74 (d, 1 H, H-1, J_{trans} = 17.0 Hz); 4.63 (d, 1 H, H-1, J_{cis} = 10.7 Hz); 4.52 (d, 1 H, H-3, $J_{2,3}$ = 8.0 Hz).

This work was financially supported by the Russian Foundation for Basic Research (Projects No. 96-03-33035 and 96-15-97323).

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Received April 20, 1998