products and were purified by recrystallization or fractional distillation. Melting points correspond to within 1° of literature values,[13] and, where applicable, analysis of the group displaced by excess base in 80% DMSO–methanol at 100° was quantitative.

1,2,4-Trinitrobenzene was donated by Dr. D. E. Giles.

2-Fluoronitrobenzene, bp 90–95° (9 mm) [lit.[13] bp 86–87° (11 mm)], was prepared by halide exchange of 2-chloronitrobenzene with potassium fluoride in DMSO.[14] A Beilstein flame test confirmed the absence of chlorine in the product.

3,4-Dinitrotoluene, mp 61° (ethanol) (lit.[13] mp 61°), was prepared by stepwise oxidation of 4-amino-3-nitrotoluene using Caro's acid and hot fuming nitric acid. 4-Amino-3-nitrotoluene was obtained by nitration of *p*-methylacetanilide followed by hydrolysis.

4-Hydroxy-3-nitrotoluene, mp 30–33° (ethanol–water) (lit.[13] mp 36.5°), was prepared by the hydroxydechlorination of 4-chloro-3-nitrotoluene at 100° in 70% DMSO–water.

[2,4,6-$^2H_3$]-Iodobenzene. [N,N,N,2,4,6-$^2H_6$]-aniline hydrochloride was prepared by heating aniline hydrochloride with deuterium oxide for 24 hr at 100°, removing the water, and repeating the procedure twice.[15] The NMR spectrum consisted of one peak (τ 2.60) (2 H, referred to internal standard of methylene chloride). Diazotization and decomposition of the diazonium salt with potassium iodide gave [2,4,6-$^2H_3$]-iodobenzene. The NMR spectrum consisted of one peak (τ 3.00) (2 H).

[4,6-$^2H_2$]-2-Nitro- and [2,6-$^2H_2$]-4-nitroiodobenzene[16] were prepared as a mixture from the nitration of [2,4,6-$^2H_3$]-iodobenzene with a solution of potassium nitrate (10 g) in [$^2H_2$]-sulfuric acid at 25° for 24 hr. Fractional crystallization (pentane) of the product gave [2,6-$^2H_2$]-4-nitroiodobenzene, mp 171–172° (lit.[13] $^1H_4$ mp 172°). The NMR spectrum consisted of one peak (τ 2.04) (2 H). Steam distillation of the product mixture gave [4,6-$^2H_2$]-2-nitroiodobenzene, mp 53–54° (lit.[13] $^1H_4$ mp 54°). The NMR spectrum consisted of two broad doublets [τ 2.64, 3.10 (2 H) with J_{meta} = 5 Hz].

Analytical grade sodium nitrite was dried by heating to 120° for 2 hr and stored in a desiccator. Spectrophotometric analysis[17] showed this material to be 99.5% sodium nitrite.

Nitrous anhydride was prepared by the oxidation of arsenious oxide with dilute nitric acid[18] (sp gr 1.3). Condensation of the equimolar gaseous mixture of nitric oxide and nitrogen dioxide in a Dry Ice–acetone trap gave liquid nitrous anhydride (N_2O_3).

General Reaction Conditions. Sodium nitrite (3.5 g, 0.05 mol) was added to a stirred solution of the aromatic compound (0.02 mol) in DMSO (50 ml). The mixture was allowed to react, diluted with water (200 ml), and extracted with ether to get neutral products. The aqueous layer was acidified (1 *M* HCl) and extracted with ether. The ether extract was dried (Na_2SO_4) and evaporated to dryness to get acidic products.

For reactions yielding 2-nitrophenol and 4-nitrophenol, excess 2-chloroaniline was added to prevent further nitrosation of the phenol. Spectroscopic measurements of rate data were carried out directly in a 1-cm cell using a Gilford Model 240 spectrophotometer. Measurement was at the absorption maximum of the phenoxide ion. At least a 20-fold excess of NO_2^- was used with aromatic substrates at 10^{-4}–10^{-5} *M* to give pseudo-first-order rate constants.

GC Analysis. *o*-and *p*-nitrofluoro-, nitrochloro-, and dinitrobenzene were separated on a 6 ft × 0.25 in. packed column coated with APL in the temperature range 140–180°. 4-Nitroiodobenzene and *p*-dinitrobenzene were separated on a 6 ft × 0.25 in. packed column coated with Carbowax 20M at a temperature of 190°. Peak areas were measured by planimetry. The extent of reaction was determined from the reaction time and decrease in the area of the substrate peak.

Registry No.—3,4-Dinitrotoluene, 610-39-9; 4-amino-3-nitrotoluene, 89-62-3; 4-hydroxy-3-nitrotoluene, 119-33-5; 4-chloro-3-nitrotoluene, 89-60-1; [2,4,6-$^2H_3$]-iodobenzene, 13122-40-2; [N,N,N,2,4,6-$^2H_6$]-aniline hydrochloride, 55223-35-3; [4,6-$^2H_2$]-2-nitroiodobenzene, 55223-36-4; [2,6-$^2H_2$]-4-nitroiodobenzene, 55223-37-5.

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Reaction of 2-Carboalkoxymethylenecyclopropanes with Phenyl Azide[1a]

Jack K. Crandall,* Woodrow W. Conover,[1b] and Joyce B. Komin

Contribution No. 2616 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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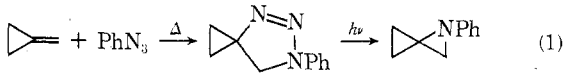
The reaction of phenyl azide with several 2-carboalkoxymethylenecyclopropanes has been examined. 2,3-Dicarbomethoxymethylenecyclopropane (**1a**) gives 1-phenyl-4-(1,2-dicarbomethoxyethyl)-1,2,3-triazole (**2a**). Similarly, esters **1b** and **1c** yield triazoles **2b** and **2c**, respectively. The ^{13}C spectra of triazoles **2a–c** are given. The formation of these triazoles is rationalized in terms of a rearrangement of an intermediate triazoline adduct.

We have recently reported on the synthesis of the novel 1-azaspiropentane structure.[2,3] This highly strained heterocyclic system was formed by photochemical expulsion of molecular nitrogen from the appropriate triazoline precursor, which was itself obtained from the thermal cycloaddition of phenyl azide to the corresponding methylenecyclopropane (see eq 1). In the present paper we relate our unsuccessful attempts to apply this synthetic scheme to methylenecyclopropanes bearing alkoxycarbonyl substituents on the cyclopropyl ring. In this instance, 1,2,3-triazoles isomeric with the desired triazolines are produced in the initial reaction of the synthetic sequence.



(1)

Table I
^{13}C Spectra of Triazoles[a]

Compd	Tr-4	Tr-5	*N*-Ph	*o*-Ph	*m*-Ph	*p*-Ph
3	134.0	121.7	136.6	120.2	129.4	128.4
2a	144.6	120.3	136.8	120.3	129.6	128.6
2b	146.9	119.4	137.0	120.2	129.5	128.4

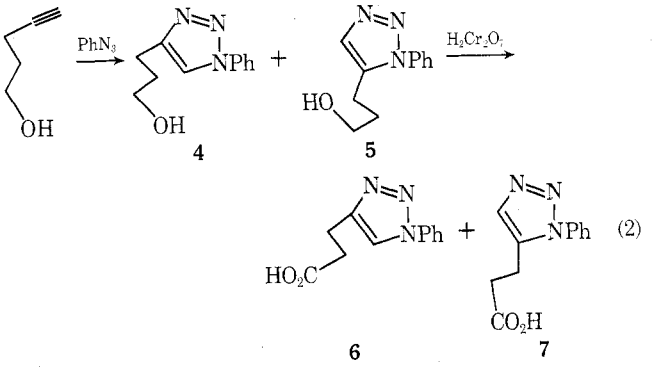
[a] Chemical shifts in parts per million relative to Me_4Si internal standard.

The reaction of phenyl azide with 2,3-dicarbomethoxymethylenecyclopropane (**1a**) led to a white, crystalline solid subsequently identified as 1-phenyl-4-(1,2-dicarbomethoxyethyl)-1,2,3-triazole (**2a**). This material shows an ABX pattern in the aliphatic hydrogen region of its NMR spectrum with coupling constants J_{AX} = 6, J_{BX} = 8, and J_{AB} = 17 Hz, in addition to a one-proton singlet at δ 7.98. In a similar fashion, 2-carbethoxymethylenecyclopropane (**1b**) gave 1-phenyl-4-(2-carbethoxyethyl)-1,2,3-triazole (**2b**). The NMR spectrum of **2b** shows a sharp singlet at δ 7.75 for the triazole ring proton as well as a pair of triplets for the aliphatic side chain. Ir and NMR spectral data were also obtained for the incompletely characterized 1-phenyl-4-(2-carbethoxypropyl)-1,2,3-triazole (**2c**) produced from the addition of phenyl azide to 2-carbethoxy-2-methylmethylenecyclopropane (**1c**). The methyl group of **2c** appears as a doublet at δ 1.24 in the NMR spectrum and the triazole ring proton gives a sharp singlet at δ 7.74. (Compound **1c** was obtained in a mixture with its isomer, 1-carbethoxyethylidenecyclopropane, by photochemical decomposition of the pyrazoline resulting from addition of diazomethane to ethyl 2-methyl-2,3-butadienoate.)

The uv spectra of **2a** and **2b** evidence intense maxima at 251 and 248 nm, respectively. Under the same conditions, 1-phenyl-1,2,3-triazole (**3**) exhibits a 245-nm band arising from conjugation of the phenyl and triazole rings. The observed bathochromic shift of the absorption bands for **2a** and **2b** supports assignment as 4-substituted 1-phenyl-1,2,3-triazoles. Substitution at the 5 position of the triazole ring would be expected to disrupt interaction between the two aromatic rings shifting the maximum to shorter wavelength.[4]

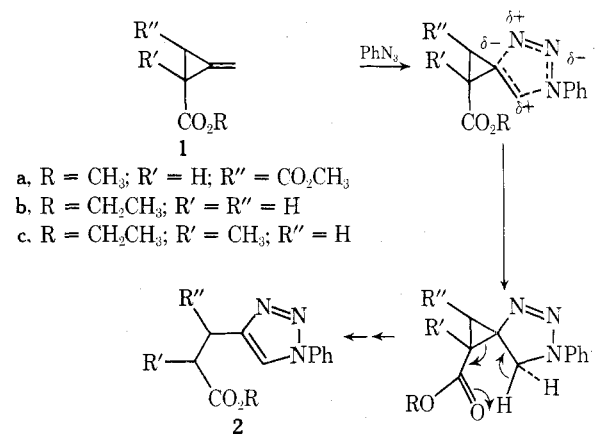
The structural assignments of **2a** and **2b** were confirmed by ^{13}C NMR. Table I gives the chemical shifts of the triazole and phenyl ring carbons for **3**, **2a**, and **2b**. Substitution at the 4 position of **3** gives rise to a ca. 10-ppm downfield shift at that carbon along with a slight upfield shift of C-5 of the triazole. The ortho carbons of the phenyl ring prove to be an important indicator for the triazole ring-substitution pattern. The presence of a substituent on C-4 of the triazole ring leaves the ortho carbons of the phenyl relatively unaffected, whereas substitution at C-5 moves these carbons downfield to ca. 124.5 ppm. In this case, the triazole C-4 carbon moves upfield slightly as well.[5] The ^{13}C spectra of **2a** and **2b** given in Table I behave as expected for 4-substituted 1-phenyl-1,2,3-triazoles, supporting the structural assignments given.

Finally, an authentic sample of the free acid derived from **2b** was obtained by an independent synthetic route. Phenyl azide reacted with 4-pentyn-1-ol to yield a 2:1 mixture of 4- and 5-(3-hydroxypropyl)-1,2,3-triazole (**4** and **5**). Each of the NMR signals of the major isomer appears at lower field than the corresponding one of the minor isomer.[6] The triazole ring protons are particularly characteristic of this situation, appearing at δ 7.76 and 7.53 for **4** and **5**, respectively. Chromic acid oxidation of the mixture of alcohols gave a mixture of carboxylic acids **6** and **7**. The NMR signals for the two isomers bore the same relationship as for the alcohols, with the triazole ring protons appearing at δ 7.78 and 7.58 for **6** and **7**, respectively. The major isomer of this mixture was isolated and shown to be identical in all respects with a sample obtained from hydrolysis of **2b**.



The formation of triazoles **2a**, **2b**, and **2c** is rationalized by the addition of phenyl azide to the methylenecyclopropane substrate as shown in Scheme I. The substituent-bearing nitrogen of phenyl azide ordinarily bonds to the olefinic carbon best able to bear a positive charge.[7] In this case, the cyclopropyl ring apparently directs the addition of phenyl azide onto the *exo*-methylene carbon in the fashion indicated, because of the interaction of the cyclopropyl ring with the double bond. A similar orientational preference has been proposed for the triazolines arising from reaction of phenyl azide with methylenecyclopropane and its phenyl-substituted analogs.[2] The intermediate triazolines from **1a**, **1b**, and **1c** are all unstable under the reaction conditions and undergo rearrangement[8] to the aromatic triazole isomers. This hydrogen transfer probably occurs with the assistance of the proximal ester carbonyl as shown below.

Scheme I



Experimental Section

General. NMR spectra were recorded for $CDCl_3$ solutions on a Varian HR-220 spectrometer. Ir spectra were obtained on neat samples or $CHCl_3$ solutions using a Perkin-Elmer 137 Infracord. Carbon-13 spectra were obtained on $CHCl_3$ solutions using a Varian XL-100-15 NMR spectrometer operating in Fourier-transform mode; chemical shifts are given in parts per million relative to internal Me_4Si. Mass spectra (70 eV) were obtained on Varian MAT CH-7 and AEI MS-9 spectrometers. Gas chromatography (GLC) was performed on an Aerograph A-700 preparative instrument. Analyses were run by Midwest Microlab, Inc. Anhydrous $MgSO_4$ was routinely used as a drying agent.

Reaction of Phenyl Azide with 1a. A mixture of 2 g of **1a** and 10 ml of phenyl azide was heated on a steam bath for 12 hr. The reaction mixture was cooled and hexane was added to dissolve remaining phenyl azide. The supernatant layer was decanted and the

resulting brown solid was recrystallized from acetone–cyclohexane to yield 3.1 g (91%) of **2a**. A pure sample of **2a** was obtained by recrystallization from ethyl acetate: mp 114–115°; ir 5.68, 8.0, and 9.6 μ; uv (ethanol) λ_{max} 251 nm (log ϵ 3.22); NMR (ABX pattern for three protons) δ_A 3.06, δ_B 3.21, δ_X 4.39 (J_{AB} = 17, J_{AX} = 6, J_{BX} = 8 Hz), 3.69 (s, 3), 3.74 (s, 3), 7.5 (m, 3), 7.71 (d, 2, J = 6 Hz), and 7.98 (s, 1); ^{13}C NMR δ 35.7, 39.1, 51.9, 52.6, 120.3, 128.6, 129.6, 136.8, 144.6, 171.5, and 171.7; mass spectrum *m/e* (rel intensity) 289 (7), 258 (15), 247 (10), 203 (13), 202 (100), 201 (27), 188 (20), 170 (17), 160 (13), 143 (18), 142 (20), 104 (17), 77 (87), 59 (17), and 51 (35).

Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.13; H, 5.23; N, 14.53. Found: C, 57.7; H, 5.1; N, 14.5.

Reaction of 1b with Phenyl Azide. A mixture of 770 mg of **1b**[9] and 2.75 g of phenyl azide was heated on a steam bath under nitrogen for 24 hr. The reaction was cooled and pentane was added to dissolve the remaining phenyl azide. The supernatant layer was decanted and the resulting crystalline material was dissolved in ethyl acetate. Precipitation with pentane gave 730 mg (50%) of tan crystals. Recrystallization from ethyl acetate–pentane gave pure **2b**: mp 61.5–63°; ir 5.81, 9.7, 13.2, and 14.8 μ; uv (ethanol) λ_{max} 248 nm (log ϵ 3.46); NMR δ 1.18 (t, 3, J = 7 Hz), 2.74 (t, 2, J = 7.5 Hz), 3.02 (t, 2, J = 7.5 Hz), 4.08 (q, 2, J = 7 Hz), 7.3–7.7 (m, 5) and 7.75 (s, 1); ^{13}C NMR δ 14.2, 21.0, 33.6, 60.5, 119.4, 120.2, 128.4, 129.5, 137.0, 146.9, and 172.5; mass spectrum *m/e* (rel intensity) 245 (1), 217 (3), 200 (18), 188 (13), 144 (10), 131 (10), 130 (100), 104 (10), 77 (62), and 51 (16).

Anal. Calcd for $C_{13}H_{15}N_3O_2$: C, 63.66; H, 6.16; N, 17.13. Found: C, 63.4; H, 6.2; N, 17.2.

Hydrolysis of 2b. A 218-mg sample of **2b** was refluxed for 4 hr in 10 ml of methanol with one KOH pellet. The solvent was removed and the residue was dissolved in ether, washed with water, and dried. The ether was removed to yield 50 mg (26%) of 1-phenyl-4-(2-carboxyethyl)-1,2,3-triazole (**6**), mp 125–126°.

2-Carbethoxy-2-methylmethylenecyclopropane (1c). Ethyl 2-methyl-2,3-butadienoate[10] (2.9 g, 23 mmol) in 60 ml of ether was combined with 42 ml of a 0.58 *M* solution of diazomethane in ether (23 mmol) and the foil-wrapped flask was stored at 0° for 48 hr.[11] The colorless solution was concentrated and the resulting oily pyrazoline was dissolved in enough benzene to make a 2% solution. Photolysis for 5 hr in a Rayonet photochemical reactor with 3130-Å bulbs gave 2.5 g (78%) of a 55:45 mixture of two products which were separated by GLC. Compound **1c** showed ir 5.83 (br), 7.82, 8.79, 9.73, and 11.2 μ; NMR (CCl_4) δ 1.20 (t of m, 4, J = 7.5 Hz), 1.33 (s, 3), 1.89 (d of t, 1, J = 9, 2 Hz), 4.01 (q, 2, J = 7.5 Hz), 5.33 (t of m, 1, J = 2 Hz), and 5.39 (t of m, 1, J = 2 Hz); NMR (benzene-d_6) δ 0.89 (t, 3, J = 7 Hz), 1.00 (d of t, 1, J = 8.5, 2.5 Hz), 1.35 (s, 3), 2.00 (d of t, 1, J = 8.5, 2.5 Hz), 3.88 (q, 2, J = 7 Hz), 5.73 (t of m, 1, J = 2.5 Hz), and 5.77 (t of m, 1, J = 3 Hz); mass spectrum *m/e* (rel intensity) 140 (0.1), 125 (1), 112 (100), 97 (12), 95 (16), 69 (17), 67 (25), 43 (18), 41 (27), and 39 (24).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.7; H, 8.5.

1-Carbethoxyethylidenecyclopropane showed ir 5.87, 7.78, 8.89, and 11.6 μ; NMR (CCl_4) δ 1.09 (t of m, 2, J = 7 Hz), 1.27 (t, 3, J = 7 Hz), 1.37 (t of m, 2, J = 7 Hz), 1.96 (m, 3) and 4.10 (q, 2, J = 7 Hz); NMR (benzene-d_6) δ 0.71 (t of q, 2, J = 8.5, 1.5 Hz), 1.01 (t, 3, J = 7 Hz), 1.21 (t of q, 2, J = 9, 2 Hz), 2.06 (m, 3) and 4.07 (q, 2, J = 7 Hz); mass spectrum *m/e* (rel intensity) 140 (1), 112 (100), 111 (20), 97 (18), 95 (24), 83 (18), 69 (31), 67 (38), 43 (38), 41 (41), and 39 (40).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.5; H, 8.6.

Reaction of 1c with Phenyl Azide. A mixture of 103 mg (0.7 mmol) of **1c** and 265 mg (2.2 mmol) of phenyl azide was heated on a steam bath under nitrogen for 22 hr. The reaction mixture was cooled and pentane was added to dissolve remaining phenyl azide. The supernatant layer was decanted and NMR and ir examination of the residue showed only **2c**: ir 5.79, 6.86, 8.2, 8.6, and 9.6 μ; NMR δ 1.20 (t, 3, J = 7 Hz), 1.24 (d, 3, J = 7 Hz), 2.91 (m, 2), 3.14 (m, 1), 4.08 (q, 2, J = 7 Hz), 7.3–7.7 (m, 5), and 7.74 (s, 1).

1-Phenyl-1,2,3-triazole (3). Compound **3** synthesized by the method of El Khadem[12] showed uv (EtOH) λ_{max} 245 nm (log ϵ 4.02); NMR (60 MHz) δ 7.3–7.8 (m, 5), 7.81 (d, 1, J = 1 Hz), and 8.12 (d, 1, J = 1 Hz); NMR (220 MHz) δ 7.35–7.55 (m, 3), 7.68–7.78 (m, 2), 7.83 (s, 1), and 8.00 (s, 1); ^{13}C NMR δ 120.2, 121.7, 128.4, 129.4, 134.0, and 136.6; mass spectrum *m/e* (rel intensity) 145 (15), 117 (24), 90 (5), 77 (100), and 51 (43).

1-Phenyl-4-(2-carboxyethyl)-1,2,3-triazole (6). Phenyl azide (2.3 g, 16.5 mmol) was stirred with 800 mg (9.5 mmol) of 4-pentyn-1-ol at 100° for 15 hr. The resulting mixture was cooled and hexane was added to dissolve remaining phenyl azide. The supernatant layer was decanted, leaving 1.82 g (94%) of a dark oil. NMR examination showed a 67:33 mixture of **4** and **5**. Compound **4** showed NMR δ 1.94 (p, 2, J = 7 Hz), 2.84 (t, 2, J = 7 Hz), 3.68 (t, 2, J = 7 Hz), 4.99 (s, 1), 7.25–7.65 (m, 5), and 7.76 (s, 1). Compound **5** showed NMR δ 1.81 (p, 2, J = 7 Hz), 2.72 (t, 2, J = 7 Hz), 3.59 (t, 2, J = 7 Hz), 4.99 (s, 1), 7.25–7.50 (m, 5), and 7.53 (s, 1).

A 2.38-g (1.06 mmol) sample of the crude mixture of **4** and **5** was dissolved in 50 ml of acetone and cooled to 0° and 6 ml of 8 *N* chromic acid was added over 15 min. After stirring for an additional 15 min, the layers were separated and the aqueous layer was extracted several times with ether. The extract was washed with saturated NaCl and dried. Solvent removal gave 1.26 g (46%) of tan crystals. NMR examination showed a 67:33 mixture of 4- and 5-(2-carboxyethyl)-1-phenyl-1,2,3-triazole (**6** and **7**). Compound **6** showed NMR δ 2.63 (t, 2, J = 7 Hz), 2.96 (t, 2, J = 7 Hz), 7.25–7.50 (m, 5), and 7.58 (s, 1).

Pure **6** crystallized from a benzene solution of the mixture: mp 125–126° (no melting point depression was observed on mixing with material obtained from hydrolysis of **2b**); ir 3.0 (br), 5.85, 9.5, 13.1, and 14.5 μ; NMR δ 2.81 (t, 2, J = 7 Hz), 3.08 (t, 2, J = 7 Hz), 7.3–7.5 (m, 3), 7.64 (d, 2, J = 9 Hz), and 7.78 (s, 1); mass spectrum *m/e* (rel intensity) 143 (1), 131 (2), 130 (61), 77 (54), and 51 (18).

Treatment of **6** with ethereal diazomethane gave 1-phenyl-4-(2-carbomethoxyethyl)-1,2,3-triazole, mp 95–98°. A 100-mg sample of the methyl ester was stirred and refluxed for 24 hr in 5 ml of ethanol and 10 drops of concentrated H_2SO_4. The reaction mixture was diluted with water and extracted with chloroform. The organic layer was washed with water and dried and the solvent was removed to give 105 mg (100%) of **2b**, mp 62–63°, which was spectroscopically identical with material obtained from the reaction of **1b** with phenyl azide.

Acknowledgment. We thank Dr. Anibal C. Rojas for obtaining the ^{13}C NMR spectra.

Registry No.—**1a,** 55281-54-4; **1b,** 18941-94-1; **1c,** 55281-55-5; **2a,** 55281-56-6; **2b,** 55281-57-7; **2c,** 55281-58-8; **3,** 1453-81-2; **4,** 4600-03-7; **5,** 55281-59-9; **6,** 55281-60-2; **7,** 55281-61-3; phenyl azide, 622-37-7; ethyl 2-methyl-2,3-butadienoate, 5717-41-9; 1-carbethoxyethylidenecyclopropane, 55281-62-4; 4-pentyn-1-ol, 5390-04-5; 1-phenyl-4-(2-carbomethoxyethyl)-1,2,3-triazole, 55281-63-5.

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