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SYNTHESIS AND THERMAL REARRANGEMENT OF 5-DIAZOMETHYL-1,2,3-TRIAZOLES

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Abstract. 5-Diazomethyl-4-methoxycarbonyltriazoles are capable of undergoing ring-degenerate rearrangements (19 → 20) when a strong electron-withdrawing substituent (e.g. p-nitrophenyl or o,p-dinitrophenyl) is located at the N-1 position. Whereas the unrearranged diazomethyltriazole 19a decomposes thermally in benzene to give the cycloheptatriene 21a, the rearranged diazo compound 20b yields the norcaradiene 22b. Several methods are described for preparing the aldehydes 11 which are the precursors of the diazomethyltriazoles.

Molecular rearrangements of five-membered heterocycles which furnish the same ring system, are denoted as ring-degenerate rearrangements.[1] A typical example is the interconversion of 1-aryl-5-amino-1,2,3-triazoles (1, $R^5 = NH_2$) and 5-anilino-1,2,3-triazoles (3), known as the Dimroth rearrangement.[1] This reaction involves the exchange of an endocyclic with an adjacent exocyclic nitrogen atom via a diazoimine (2) as intermediate (Scheme I).

Ring-degenerate rearrangements of triazoles may also occur with the participation of two side-chain atoms if the R^4-substituent is an imine function. Thus, Becher et al.[2] reported the thermal isomerization of 4-iminomethylene-5-hydroxy-1,2,3-triazoles (1, R^4 = CH=NR, R^5 = OH) into triazole-4-carboxamides (4).

We now describe a third case of ring-degenerate rearrangement of triazoles where three side-chain atoms are incorporated into the newly formed triazole. As shown in Scheme I, this is possible by introducing a diazomethyl function at the 5-position (1 → 2 → 5).

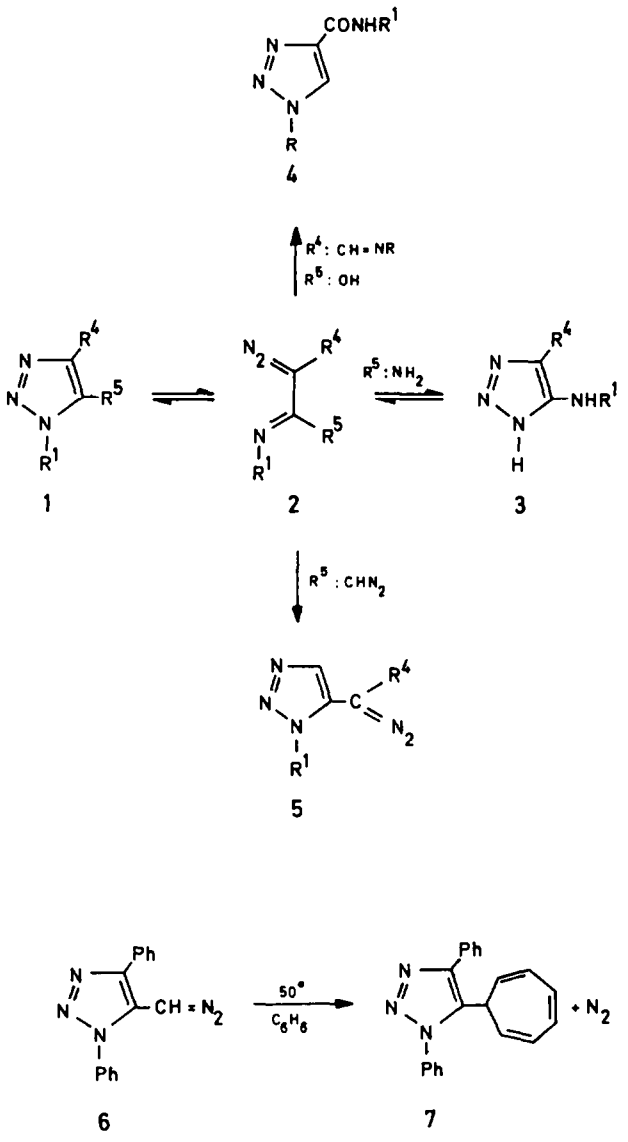
Smith et al.[3] have already investigated the chemistry of 5-diazomethyl-1,4-diphenyltriazole 6 but did not observe any rearrangement. Indeed, in benzene at 50°, the diazo function decomposes, and the resulting carbene adds to the solvent with formation of the cycloheptatriene 7. Thus, decomposition of the diazo function occurs more rapidly than ring-opening of the triazole.

In order to stabilize the diazo substituent and to facilitate triazole cleavage, we have placed an ester function at the 4-position of 1. Also, the R^1-substituent was varied from phenyl to nitro-substituted phenyls. These groups are known to promote the Dimroth rearrangement of 5-aminotriazoles[4] and were expected to have a similar effect on our compounds.

RESULTS AND DISCUSSION

Since the 5-formyltriazoles 11 are the key intermediates in the synthesis of the diazo compounds 19, several approaches have been devised to prepare them. For instance, the 1,3-dipolar cycloaddition of methyl 4-hydroxy-2-butynoate (8)[5] with

Scheme I

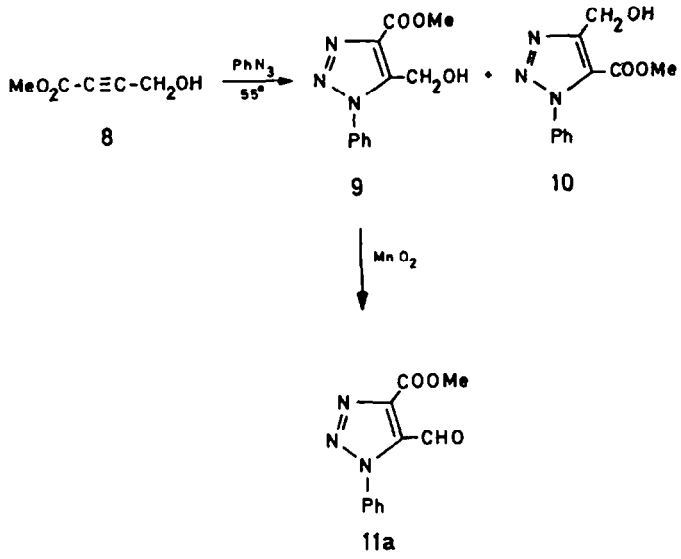


phenyl azide yields 9 as the major product (49%), together with 10 (8%). Oxidation of 9 with freshly prepared manganese dioxide furnishes the aldehyde 11a in 48% yield (Scheme II).

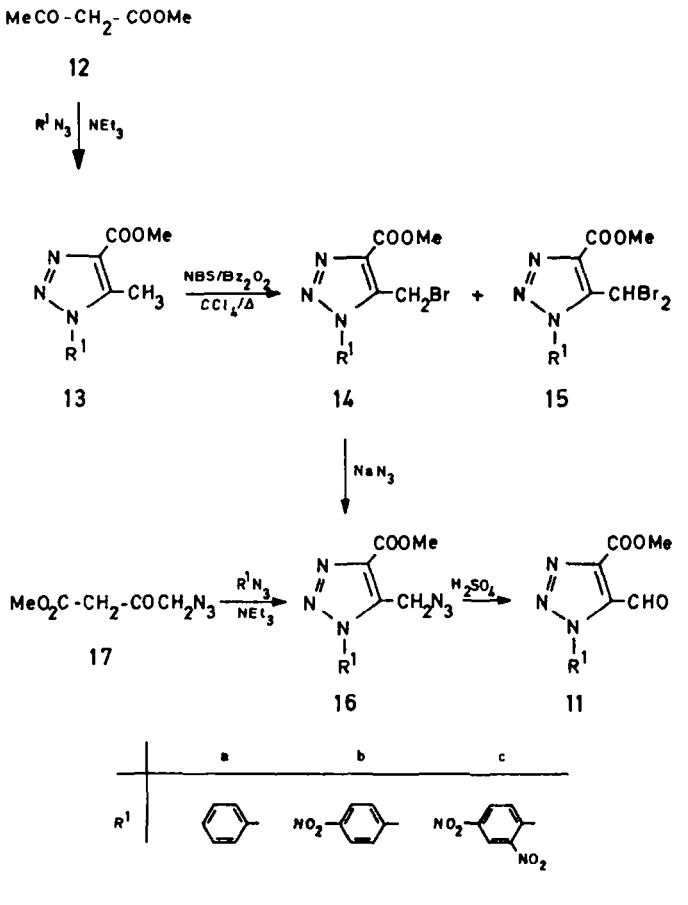
The two regioisomers 9 and 10 are easily distinguished by the NMR spectra. Indeed, the methylene hydrogens of 9 (δ 4.85) are shielded compared with those of 10 (δ 5.00), due to the anisotropic effect of the phenyl ring. This effect is unimportant in ^{13}C NMR spectroscopy, but there the phenyl substituent causes an upfield shift of the C-atoms in γ-position. Thus, for 9, the methylene carbon resonates at higher field (δ 53.3) and the ester carbon at lower field (δ 162.9) than for 10 (δ 56.8 and 158.8).

A more convenient method for the synthesis of 11a starts with the readily available methyl acetoacetate 12, which is first transformed into the triazole 13a and then brominated with N-bromosuccinimide under free-radical conditions. This yields a mixture of two brominated products, 14a and 15a, with a preponderance of 14a.

Scheme II



Scheme III

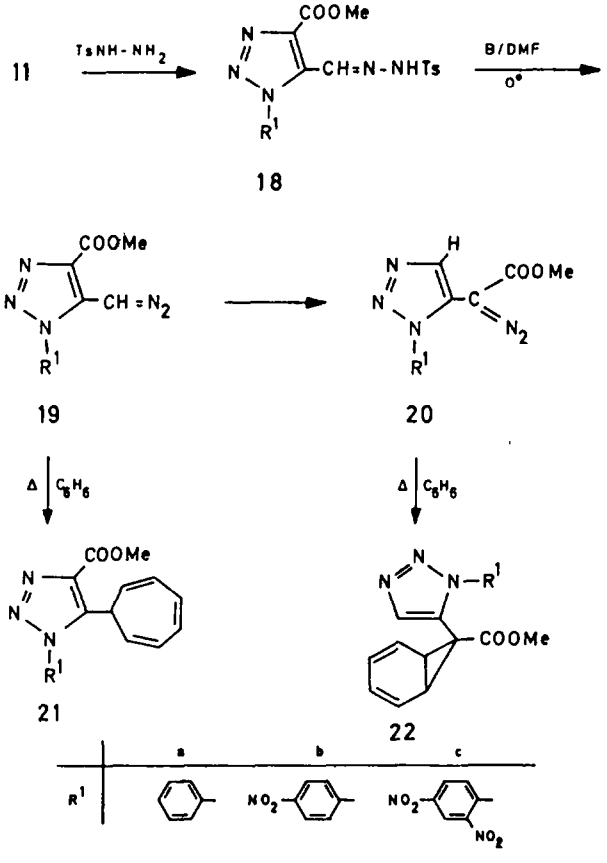


Since dimethyl sulfoxide failed to oxidize 14a to 11a, we have utilized a novel route based on a publication of Tashiro.[6] This involves conversion of 14a to the azide 16a and decomposition of the latter in concentrated sulfuric acid. The overall yield of 11a by Scheme III was 28%. The p-nitrophenyl derivative 11b was similarly prepared in 40% overall yield.

This reaction sequence could not be used to prepare 11c since bromination of 13c failed. Therefore, we explored an alternative method and found that the condensation of methyl 4-azido-3-oxobutanoate 17 with o,p-dinitrophenyl azide yields directly the azidomethyltriazole 16c in reasonably good yield (63%). The reaction was carried out under mild conditions (NEt_3, 0°C) to prevent a base-induced decomposition of 17.[7] There is advantage to synthesize 16b also by this procedure (yield 66%), but 16a could not be obtained.

The tosylhydrazones 18a-c, derived from the aldehydes 11, were subjected to the Bamford-Stevens reaction by treatment with piperidine in dimethylformamide at 0°C (Scheme IV). In the cases of 18a and 18b, the unrearranged diazo compounds 19a,b were obtained and characterized, inter alia, by a singlet at δ 5-6 in the ^{1}H NMR spectra and a doublet at about δ 40 in the ^{13}C NMR spectra, attributable to the diazomethyl function.[8] The tosylhydrazone 18c, on the contrary, yielded a mixture of 19c and 20c in a ratio of 16:84. The rearranged diazo derivative 20c exhibits an aromatic singlet at δ 7.9 in the ^{1}H NMR spectrum, as well as a doublet at δ 134 for the C-4 ring atom in the coupled ^{13}C NMR spectrum. Upon warming in benzene at 40° for 1 h, the ratio of isomeric diazo compounds remained unchanged.

Scheme IV



In benzene at 70°C, the diazo 19a decomposes with a half-life of 7.0 h (k_1 = 2.73 x 10^{-5} s^{-1}) to give the cycloheptatriene 21a as the sole reaction product. Under similar conditions, the more electronegatively substituted 19b yields the norcaradiene 22b as a result of rearrangement to 20b, followed by decompostion. When this reaction was followed by ^{1}H NMR spectroscopy, 20b could not be detected, indicating that it only occurs as a transient intermediate. Since the overall rate constant of the reaction 19b → 20b → 22b is 9.63 x 10^{-5} s^{-1} at 70°C (half-life 2.0 h), we conclude that 20b is less stable than 19a. Finally, the diazo 20c was also decomposed in benzene solution, but furnished a product whose structure could not be fully elucidated (see Exp. Section for spectral data).

The structures 21 and 22 are differentiated by their ^{1}H and ^{13}C NMR spectra. Whereas the olefinic protons of the cycloheptatriene 21a absorb in the region δ 5.3-6.6, the cyclopropyl hydrogens of 22b,c resonate at higher field (δ 3.2) in the ^{1}H NMR spectra. Also in the ^{13}C NMR spectra, the corresponding cyclopropyl carbon atoms C-1 and C-6 resonate at high field (δ 39) with a typical cyclopropyl coupling constant $^1J_{CH}$ of 172 Hz. Furthermore, the triazole substituent in 22b,c is located at the endo-7 position since the ^{3}J-coupling constant between the cyclopropyl hydrogens and the triazole C-5 atom is only 1.8 Hz.[9] This is in agreement with the statement of Günther et al.[10] that 7-aryl-7-ester substituted norcaradienes adopt the endo-aryl/exo-ester configuration.

EXPERIMENTAL

Synthesis of the hydroxymethyltriazoles 9 and 10. Methyl 4-hydroxy-2-butynoate (8)(9.6 g, 84 mmol) and phenyl azide (10.5 g, 88 mmol) in 5 mL of toluene were heated at 55°C for one week. Then, an additional amount of 8 (1 mL) was added and heating was continued at 55°C until the azide absorption peak had disappeared from the IR spectrum (1 week). The reaction mixture was dissolved in warm methanol and cooled to 0°C, giving 9 as white crystals in 44% yield. The filtrate was evaporated and the residue was subjected to column chromatography on silica gel with EtOAc/CCl_4 (ratio 3:4) as the eluent. This furnished another crop of 9 (5%) and 10 (8%).

5-Hydroxymethyl-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (9): mp 92°C; IR (KBr) 3395 (br, OH), 1735 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 4.0 (t, 1H, OH), 4.05 (s, 3H, CH_3), 4.85 (d, 2H, CH_2), 7.6 (s, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 52.6 (CH_3), 53.3 (CH_2), 125.1, 129.7, 130.3, 135.0 (Ph C-atoms), 137.4 (C-4), 141.6 (C-5), 162.9 (CO). Anal. Calcd for $C_{11}H_{11}N_3O_3$ (mol wt 233): C, 56.65; H, 4.72. Found: C, 56.55; H, 4.80.

4-Hydroxymethyl-5-methoxycarbonyl-1-phenyl-1,2,3-triazole (10): mp 80°C; IR (KBr) 3395 (br, OH), 1735 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.2 (t, 1H, OH), 3.80 (s, 3H, CH_3), 5.00 (d, 2H, CH_2), 7.5 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 52.8 (CH_3), 56.8 (CH_2), 125.8 (C-5), 125.8, 128.9, 130.1, 136.8 (Ph C-atoms), 151.5 (C-4), 158.8 (CO). Anal. Calcd for $C_{11}H_{11}N_3O_3$ (mol wt 233): C, 56.65; H, 4.72. Found: C, 56.42; H, 4.69.

4-Methoxycarbonyl-5-methyl-1-phenyl-1,2,3-triazole (13a). A solution of methyl acetoacetate (12) (18.9 g, 163 mmol), phenyl azide (19.4 g, 163 mmol) and triethylamine (16.5 g, 163 mmol) in 150 mL of methanol was heated at 70°C for 10 days. The solvent was replaced by chloroform (300 mL), washed with an aqueous solution of NaOH and dried over $MgSO_4$. After removal of the solvent, the remaining oil was crystallized from ether to give 13a in 68% yield; mp 79°C; IR (KBr) 1720 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 3H, CH_3), 4.00 (s, 3H, CH_3O), 7.6 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 9.7 (CH_3), 51.7 (CH_3O), 125.1, 129.4, 129.8, 135.2 (Ph C-atoms), 136.2 (C-4), 138.7 (C-5). Anal. Calcd for $C_{11}H_{11}N_3O_2$ (mol wt 217): C, 60.83; H, 5.07. Found: C, 60.82; H, 5.18.

4-Methoxycarbonyl-5-methyl-1-(p-nitrophenyl)-1,2,3-triazole (13b). A solution of methyl acetoacetate (12)(5.8 g, 50 mmol), p-nitrophenyl azide (8.2 g, 50 mmol) and triethylamine (5.05 g, 50 mmol) in 100 mL of methanol was heated at reflux temperature for 2 days. The reaction mixture was cooled and the crystals were filtered off and recrystallized from chloroform, yield 95%, mp 154°C (lit.[11] 152°C); IR (KBr) 1710 cm^{-1} (s, CO); ^{1}H NMR (DMSO-d_6) δ 2.6 (s, 3H, CH_3), 3.9 (s, 3H, CH_3O), 8.0 and 8.5 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 9.8 (CH_3), 51.8 (CH_3O), 125.0, 126.5, 139.9,

147.9 (aromatic C-atoms), 136.2 (C-4), 139.8 (C-5), 161.3 (CO). Anal. Calcd for $C_{11}H_{10}N_4O_4$ (mol wt 262): C, 50.38; H, 3.82. Found: C, 50.35; H, 3.69.

1-(o,p-Dinitrophenyl)-4-methoxycarbonyl-5-methyl-1,2,3-triazole (13c). A solution of methyl acetoacetate (12)(4.3 g, 37 mmol), o,p-dinitrophenyl azide (7.8 g, 37 mmol) and triethylamine (3.7 g, 37 mmol) in 100 mL of methanol was left overnight at 0°C. Then, the crystals were filtered off and recrystallized from methanol, yield 57%, mp 153°C; IR (KBr) 3080 (m, CH), 1720/1730 cm^{-1} (s, CO); ^1H NMR (DMSO-d_6) δ 2.55 (s, 3H, CH_3), 3.95 (s, 3H, CH_3O), 8.30 (d, 1 aromatic H), 8.85 (dd, 1 aromatic H), 9.10 (d, 1 aromatic H); ^{13}C NMR (DMSO-d_6) δ 9.1 (CH_3), 51.9 (CH_3O), 121.6, 129.3, 131.1, 131.6, 145.1, 148.6 (aromatic C-atoms), 135.8 (C-4), 141.3 (C-5), 161.0 (CO). Anal. Calcd for $C_{11}H_9N_5O_6$ (mol wt 307): C, 43.00; H, 2.93. Found: C, 42.94; H, 2.84.

Bromination of 13a. Compound 13a (20 g, 92 mmol), N-bromosuccinimide (2.2 equiv., 36 g) and dibenzoyl peroxide (2 g, 8 mmol) were heated with stirring in 1500 mL of CCl_4 for 24 h. The warm mixture was filtered into 2 L of water and the CCl_4 layer was washed three times with 750 mL of water and dried over $MgSO_4$. After removal of the solvent, the oil was crystallized from ether (200 mL) to give a first crop of 14a in 45.5% yield. The filtrate was concentrated and chromatographed on silica gel with dichloromethane as the eluent. This furnished 15a (14.5% after crystallization from $CHCl_3$/ether) and a second crop of 14a (20% after crystallization from $CHCl_3$/ether).

5-Bromomethyl-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (14a): mp 87°C; IR (KBr) 1710 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.02 (s, 3H, CH_3), 4.74 (s, 2H, CH_2), 7.65 (s, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.3 (CH_2), 52.4 (CH_3), 125.2, 129.8, 130.7, 136.5 (Ph C-atoms), 134.7 (C-4), 138.2 (C-5), 161.1 (CO). Anal. Calcd for $C_{11}H_{10}BrN_3O_2$ (mol wt 296): C, 44.59; H, 3.38. Found: C, 44.66; H, 3.39.

5-Dibromomethyl-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (15a): mp 135°C; IR (KBr) 1735 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.05 (s, 3H, CH_3), 7.6-7.8 (m, 6H, $CHBr_2$ + Ph); ^{13}C NMR ($CDCl_3$) δ 20.5 (CH), 52.7 (CH_3), 127.0, 129.2, 131.1, 135.6 (Ph C-atoms), 133.1 (C-4), 139.9 (C-5), 161.1 (CO). Anal. Calcd for $C_{11}H_9Br_2N_3O_2$ (mol wt 375): C, 35.20; H, 2.40. Found: C, 35.10; H, 2.40.

Bromination of 13b. Compound 13b (5.24 g, 20 mmol), N-bromosuccinimide (7.12 g, 40 mmol) and dibenzoylperoxide (350 mg, 1.45 mmol) was heated in 750 mL of CCl_4 for 24 h. The warm mixture was filtered and the filtrate was evaporated. The residue was dissolved in chloroform, washed three times with 500 mL of water and dried over $MgSO_4$. The solution was concentrated and then chromatographed on silica gel with dichloromethane as the eluent to give 14b and 15b.

5-Bromomethyl-4-methoxycarbonyl-1-(p-nitrophenyl)-1,2,3-triazole (14b) was crystallized from $CHCl_3$/ether in 69% yield, mp 119°C; IR (KBr) 1720 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.05 (s, 3H, CH_3), 4.85 (s, 2H, CH_2), 7.9 and 8.5 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 15.9 (CH_2), 52.6 (CH_3), 125.4, 126.0, 139.6, 148.8 (aromatic C-atoms), 137.2 (C-4), 138.5 (C-5), 160.2 (CO). Anal. Calcd for $C_{11}H_9BrN_4O_4$ (mol wt 341): C, 38.71; H, 2.60. Found: C, 38.81; H, 2.52.

5-Dibromomethyl-4-methoxycarbonyl-1-(p-nitrophenyl)-1,2,3-triazole (15b) was crystallized from $CHCl_3$/ether in 15% yield, mp 167°C; IR (KBr) 1720 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.1 (s, 3H, CH_3), 7.7 (s, 1H, $CHBr_2$), 8.05 and 8.50 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 20.3 ($CHBr_2$), 53.0 (CH_3), 124.7, 128.4, 140.4 or 140.7, 149.3 (aromatic C-atoms), 133.3 (C-4), 140.4 or 140.7 (C-5), 161.0 (CO). Anal. Calcd for $C_{11}H_8Br_2N_4O_4$ (mol wt 420): C, 31.43; H, 1.90. Found: C, 31.46; H, 1.82.

Synthesis of the azidomethyltriazoles 16a-c. Method A. Compound 14a (12.3 g, 42 mmol) was allowed to react with sodium azide (13 g, 200 mmol) in 200 mL of acetone containing a catalytic amount of sodium iodide. After one day at room temperature, the iodide was neutralized with $Na_2S_2O_3$ and the solution was extracted three times with 100 mL of chloroform. The extracts were dried over $MgSO_4$, the solvent removed and the residue crystallized from ether at 0°C.

5-Azidomethyl-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (16a) was obtained in 90% yield, mp 65°C; IR (KBr) 2125 (s, N_3), 1735 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.02 (s, 3H, CH_3), 4.70 (s, 2H, CH_2), 7.61 (s, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 41.6 (CH_2), 52.4 (CH_3), 125.0, 129.8, 130.6, 134.8 (Ph C-atoms), 136.1 (C-5), 137.6 (C-4), 161.4 (CO). Anal. Calcd for $C_{11}H_{10}N_6O_2$ (mol wt 258): C, 51.16; H, 3.88. Found: C, 51.04; H, 3.75.

5-Azidomethyl-4-methoxycarbonyl-1-(p-nitrophenyl)-1,2,3-triazole (16b) was similarly prepared from 14b in 90% yield, mp 115°C; IR (KBr) 2120 (s, N_3), 1720 and 1740 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.05 (s, 3H, CH_3), 4.80 (s, 2H, CH_2), 7.95 and 8.50 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 41.5 (CH_2),

52.6 (CH_3), 125.3, 125.6, 139.5, 148.5 (aromatic C-atoms), 138.2 (C-4), 136.3 (C-5), 161.1 (CO). Anal. Calcd for $C_{11}H_9N_7O_4$ (mol wt 303): C, 43.56; H, 2.97. Found: C, 43.70; H, 2.86.

Method B. To a solution of methyl 4-azido-3-oxobutanoate (17) (7.75 g, 50 mmol) and o,p-dinitrophenyl azide (10.45 g, 50 mmol) in 200 mL of dry methanol an equimolar amount of triethylamine (5.05 g) was added dropwise at 0/-5°C. The solution was left overnight at room temperature and then cooled to give crystals, which were filtered off and recrystallized from methanol.

5-Azidomethyl-1-(o,p-dinitrophenyl)-4-methoxycarbonyl-1,2,3-triazole (16c) was obtained in 66% yield, mp 138°C; IR (KBr) 2115 and 2100 (s, N_3), 1730 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.05 (s, 3H, CH_3), 4.85 (s, 2H, CH_2), 7.90 (d, 1 aromatic H), 8.70 (dd, 1 aromatic H), 9.05 (d, 1 aromatic H); ^{13}C NMR ($CDCl_3$) δ 42.1 (CH_2), 52.8 (CH_3), 121.6 , 128.6, 131.3, 133.0, 145.4, 149.1 (aromatic C-atoms), 137.4 and 138.4 (C-4 and C-5), 160.9 (CO). Anal. Calcd for $C_{11}H_8N_8O_6$ (mol wt 348): C,37.93; H, 2.30; N, 32.18. Found: C, 37.84; H, 2.23; N, 32.08.

Note: Compound 16b was similarly prepared in 63% yield.

Synthesis of the 5-formyltriazoles 11a-c. Method A. A solution of 9 (1.28 g, 5.5 mmol) in 100 mL of benzene was stirred with activated MnO_2 (9.9 g, 114 mmol) at 60°C for 3 h. Then, another amount of MnO_2 (3.3 g, 38 mmol) was added and heating was continued at 60°C for another one day. The warm reaction mixture was filtered and the filtrate was concentrated. Addition of ether precipitated crude 11a in 48% yield. This compound was converted, without further purification, into the hydrazone 18a.

Method B. A solution of 16a (8.4 g, 32.5 mmol) in 30 mL of concentrated sulfuric acid was stirred at 40°C for 5 days. Then the mixture was poured into 250 mL of ice-cooled water and the whole was extracted three times with 100 mL of chloroform. The extracts were washed with an aqueous solution of $NaHCO_3$, dried over $MgSO_4$ and evaporated. The residue was crystallized from ether.

5-Formyl-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (11a) was obtained in 70.6% yield. An analytical sample was obtained by column chromatography on silica gel with dichloromethane as the eluent, mp 98°C; IR (KBr) 1695 (s, CHO), 1735 cm^{-1} (s, COOMe); ^1H NMR ($CDCl_3$) δ 4.05 (s, 3H, CH_3), 7.6 (m, 5H, Ph), 10.5 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 53.0 (CH_3), 125.6, 129.2, 130.7, 135.8 (Ph C-atoms), 134.8 (C-5), 142.3 (C-4), 160.6 (CO), 179.6 (CHO). Anal. Calcd for $C_{11}H_9N_3O_3$ (mol wt 231): C, 57.14; H, 3.90. Found: C, 57.08; H, 4.00.

5-Formyl-4-methoxycarbonyl-1-(p-nitrophenyl)-1,2,3-triazole (11b) was similarly prepared from 16b in 67% yield, mp 175°C; IR (KBr) 3080 (m, CH), 1695 and 1720 cm^{-1} (s, CO); ^1H NMR (DMSO-d_6) δ 4.05 (s, 3H, CH_3), 8.0 and 8.5 (two d, 4 aromatic H), 10.35 (s, 1H, CHO); ^{13}C NMR (DMSO-d_6) δ 52.8 (CH_3), 124.5, 127.2, 140.4, 148.3 (aromatic C-atoms), 135.6 (C-5), 141.1 (C-4), 160.0 and 180.1 (CO). Anal. Calcd for $C_{11}H_8N_4O_5$ (mol wt 276): C, 47.87; H, 2.90. Found: C, 47.68; H, 2.84.

1-(o,p-Dinitrophenyl)-5-formyl-4-methoxycarbonyl-1,2,3-triazole (11c) was prepared by stirring a solution of 16c (6.8 g, 19.5 mmol) in 15 mL of sulfuric acid overnight at room temperature. After work-up as described above, 11c was obtained in 88% yield, mp 143°C; IR (KBr) 3080 (m, CH), 1695 and 1740 cm^{-1} (s, CO); ^1H NMR (DMSO-d_6) δ 4.05 (s, 3H, CH_3), 8.20 (s, 1 aromatic H), 8.85 (dd, 1 aromatic H), 9.10 (d, 1 aromatic H), 10.30 (s, 1H, CHO); ^{13}C NMR (DMSO-d_6) δ 53.0 (CH_3), 121.2, 129.4, 131.6, 132.9, 144.1, 148.7 (aromatic C-atoms), 135.8 (d, ^2J = 33 Hz, C-5), 140.9 (C-4), 159.6 and 180.6 (CO). Anal. Calcd for $C_{11}H_7N_5O_7$ (mol wt 321): C, 41.12; H, 2.18. Found: C, 41.08; H, 2.18.

Synthesis of the tosylhydrazones 18a-c. A solution of 11a (4.1 g, 18 mmol), p-toluenesulfonhydrazide (3.03 g, 18 mmol) and 1 mL of acetic acid in 20 mL of ethanol was refluxed for 3 h. Upon cooling to -20°C, 18a crystallized out in 77% yield.

4-Methoxycarbonyl-1-phenyl-1,2,3-triazole-5-carbaldehyde p-tosylhydrazone (18a): mp 139°C; IR (KBr) 3180 (s, NH), 1725 cm^{-1} (s, CO); ^1H NMR (DMSO-d_6) δ 2.40 (s, 3H, CH_3), 3.90 (s, 3H, CH_3O), 7.3 (m, 4H, Ts), 7.4-7.7 (m, 5H, Ph), 8.40 (s, 1H, CH=N), 12.1 (s, NH); ^{13}C NMR (DMSO-d_6) δ 20.9 (CH_3), 52.2 (CH_3O), 126.3, 126.9, 128.9, 129.5, 130.0, 135.4, 136.5, 143.6 (aromatic C-atoms), 132.6 (C=N), 134.3 (C-5), 137.1 (C-4), 160.7 (CO). Anal. Calcd for $C_{18}H_{17}N_5O_4S$ (mol wt 399): C, 54.14; H, 4.26. Found: C, 54.05; H, 4.34.

4-Methoxycarbonyl-1-(p-nitrophenyl)-1,2,3-triazole-5-carbaldehyde p-tosylhydrazone (18b) was similarly prepared from 11b in 78% yield (reflux time 1 day), mp 154°C; IR (KBr) 3110 (m, CH), 1720 cm^{-1} (s, CO); ^1H NMR (DMSO-d_6) δ 2.35 (s, 3H, CH_3), 3.90 (s, 3H, CH_3O), 7.3 (s, 4H, Ts), 7.85 and 8.30

(two d, 4 aromatic H), 8.40 (s, 1H, CH=N), 12.35 (s, NH); ^{13}C NMR (DMSO-d_6) δ 20.9 (CH_3), 52.3 (CH_3O), 124.2, 126.7, 127.7, 129.4, 135.5, 141.4, 143.6, 147.7 (aromatic C-atoms), 132.2 (C=N), 135.0 (C-5), 137.2 (C-4), 160.5 (CO). Anal. Calcd for $C_{18}H_{16}N_6O_6S$ (mol wt 444): C, 48.65; H, 3.60. Found: C, 48.45; H, 3.55.

1-(o,p-Dinitrophenyl)-4-methoxycarbonyl-1,2,3-triazole-5-carbaldehyde p-tosylhydrazone (18c) was prepared by stirring a solution of 11c (3.21 g, 10 mmol), p-toluenesulfonylhydrazide (1.86 g, 10 mmol) and one drop of acetic acid in water/methanol (100 mL, 1:1) at room temperature for one day. The precipitate was filtered off and crystallized from ethanol, yield 82%, mp 135°C (dec.); IR (KBr) 3180 (m, NH), 3100 (m, CH), 1720 cm^{-1} (s, CO); ^{1}H NMR (DMSO-d_6) δ 2.40 (s, 3H, CH_3), 3.95 (s, 3H, CH_3O), 7.20 and 7.30 (two d, 4 aromatic H), 8.15 (d, 1 aromatic H), 8.40 (s, 1H, CH=N), 8.75 (dd, 1 aromatic H), 8.95 (d, 1 aromatic H); ^{13}C NMR (DMSO-d_6) δ 21.0 (CH_3), 52.5 (CH_3O), 121.1, 129.4, 131.8, 139.5, 143.9, 148.2 (dinitrophenyl C-atoms), 126.5, 129.6, 135.3, 143.9 (tosyl C-atoms), 131.5 (C=N), 135.9 (C-5), 136.8 (C-4), 160.3 (CO). Anal. Calcd for $C_{18}H_{15}N_7O_8S.1/2$ EtOH: C, 44.51; H, 3.50. Found: C, 44.45; H, 3.59.

Synthesis of the diazo compounds 19a,b and 20c. Piperidine (0.425 g, 5 mmol) was added dropwise and with stirring to an ice-cooled solution of 18a (2 g, 5 mmol) in 5 mL of DMF and the yellow solution was left overnight at 0°C. After addition of 40 mL of water, the solution was extracted six times with 40 mL of ether. The ether extracts were combined, washed with water and dried over Na_2SO_4. The ether was distilled off and the residue was crystallized from $CHCl_3$/ether.

5-Diazomethyl-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (19a) was obtained in 75% yield, mp 124°C (dec.); IR (KBr) 3100, 3060 and 2940 (w, CH), 2080 (s, CN_2), 1720 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 3H, CH_3), 5.52 (s, 1H, CHN_2), 7.6 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 39.8 (CHN_2, $^1J_{CH}$ = 203.5 Hz), 52.0 (CH_3), 125.9, 129.7, 130.6, 134.9 (Ph C-atoms), 131.4 (C-4), 133.6 (C-5), 161.8 (CO). Anal. Calcd for $C_{11}H_9N_5O_2$ (mol wt 243): C, 54.32; H, 3.70. Found: C, 54.21; H, 3.83.

5-Diazomethyl-4-methoxycarbonyl-1-(p-nitrophenyl)-1,2,3-triazole (19b) was similarly prepared from 18b in 78% yield, mp 138°C (dec.); IR (KBr) 3095 (m, CH), 2100 (s, CN_2), 1700 cm^{-1} (s, CO); ^{1}H NMR (DMSO-d_6) δ 3.85 (s, 3H, CH_3), 6.05 (s, 1H, CHN_2), 7.95 and 8.45 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 40.1 (CHN_2, $^1J_{CH}$ = 202 Hz), 52.3 (CH_3), 125.4, 126.4, 139.9, 148.5 (aromatic C-atoms), 132.1 (C-4), 133.7 (C-5), 161.6 (CO). Anal. Calcd for $C_{11}H_8N_6O_4$ (mol wt 288): C, 45.83; H, 2.78. Found: C, 45.79; H, 2.74.

1-(o,p-Dinitrophenyl)-5-(methoxycarbonyl-diazomethyl)-1,2,3-triazole (20c) was similarly prepared as described above. The residue, after removal of the ether, was chromatographed on silica gel with dichloromethane/ethyl acetate as the eluent, and then crystallized from $CHCl_3$/ether. This furnished a mixture of 19c and 20c in a ratio of 16:84 in 18% yield.
Spectral data of 19c: ^{1}H NMR ($CDCl_3$) δ 4.00 (s, CH_3), 5.45 (s, CHN_2), 7.88 (d), 8.70 (dd), 8.02 (d); ^{13}C NMR ($CDCl_3$) δ 52.3 (CH_3), 40.2 (CHN_2, $^1J_{CH}$ = 200 Hz).
Spectral data of 20c: IR (KBr) 2110 (s, CN_2), 1715 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.70 (s, CH_3), 7.9 (s, triazole CH), 7.9 (d), 8.65 (dd), 8.97 (d); ^{13}C NMR ($CDCl_3$) δ 52.9 (CH_3), 55.2 (CN_2, recorded at -30°C), 125.9 (C-5, $^2J_{CH}$ = 15.3 Hz), 134.3 (C-4, $^1J_{CH}$ = 199.2 Hz).

5-Cycloheptatrienyl-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (21a). A benzene solution of 19a (0.93 g, 3.8 mmol in 50 mL) was refluxed for two days. After removal of the solvent, the residue was chromatographed on silica gel with dichloromethane as the eluent. This furnished 21a in 65% yield after crystallization from $CHCl_3$/ether, mp 168°C; IR (KBr) 1730 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.15 (t, 1H), 3.95 (s, 3H, CH_3), 5.35 (dd, 2H), 6.22 (dm, 2H), 6.62 (t, 2H), 7.3-7.6 (two m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 36.3, 123.2, 125.0, 130.9 (cycloheptatriene C-atoms), 52.2 (CH_3), 125.6, 129.5, 130.2, 135.2 (Ph C-atoms), 136.5 (C-4), 143.9 (C-5), 161.8 (CO). Anal. Calcd for $C_{17}H_{15}N_3O_2$ (mol wt 293): C, 69.62; H, 5.12. Found: C, 69.44; H, 5.18.

7-Methoxycarbonyl-7-(1-p-nitrophenyl-1,2,3-triazol-5-yl)-norcaradiene (22b). Compound 19b (300 mg, 1 mmol) was heated in 75 mL of dry benzene for one day. After removal of the solvent, the residue was dissolved in dichloromethane and purified by preparative thin layer chromatography (SiO_2, CH_2Cl_2). This furnished 22b in 49% yield after crystallization from $CHCl_3$, mp 219°C; IR (KBr) 1730 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.2 (m, 2H, H_1 and H_6), 3.85 (s, 3H, CH_3), 5.8 (br, 4 vinyl H), 7.50

(s, 1H, triazole H), 7.70 and 8.40 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 13.6 (cyclopropyl C-7), 39.1 (cyclopropyl C-1 and C-6, $^1J_{CH}$ = 172 Hz), 53.6 (CH_3), 122.8 and 124.7 (vinyl H), 124.7, 126.3, 141.7, 147.6 (aromatic C-atoms), 130.0 (triazole C-5), 138.8 (triazole C-4, $^1J_{CH}$ = 195.5 Hz), 170.7 (CO). Anal. Calcd for $C_{17}H_{14}N_4O_4$ (338): C, 60.36; H, 4.14. Found: C, 60.19; H, 4.16.

Thermolysis of 20c. Compound 20c (40 mg, contaminated with 19c) was heated in 100 mL of dry benzene for 1 day. After removal of the solvent, the residue was crystallized from $CHCl_3$/ether to give a pale yellow product (20 mg, mp 178°C) with the following spectral data: IR (KBr) 1770 and 1755 cm^{-1}; ^{1}H NMR (DMSO-d_6 + $CDCl_3$) δ 3.90 (s, 3H), 8.45 (d, 1H), 8.63 (dd, 1H), 8.72 (s, triazole CH), 8.86 (d, 1H); ^{13}C NMR (DMSO-d_6 + $CDCl_3$) δ 54.5 (CH_3O), 123.1, 123.8, 126.2 (aromatic CH), 129.8, 137.5, 147.0 (aromatic quat. C-atoms), 128.1 (d, J = 12 Hz, triazole C-5), 141.4 (^{1}J = 202 Hz, triazole C-4), 151.8 (q), 158.9 (s).

Kinetic measurements. A solution of 19a in deuterated benzene was placed in an NMR tube at 70°C (± 0.1°) for decomposition. At several time intervals, the NMR tube was cooled to 0°C and analyzed by ^{1}H NMR spectroscopy. The rate of decomposition was followed by integration of the CHN_2 singlet at δ 5.1, using the ester methyl singlets at δ 3.7 as reference. By plotting log diazo |%| vs time, a linear plot was obtained with a correlation coefficient of -0.9975. The first-order rate constant was determined from the slope of the linear plot: $k_1 = 2.73 \times 10^{-5}$ s^{-1}.

In the case of 19b, a series of benzene solutions were placed in a thermostat at 70°C. At several time intervals, the solutions were cooled, evaporated and analyzed by ^{1}H NMR spectroscopy. The rate of decomposition was followed by integration of the ester methyl singlets in the spectra. The first order rate constant, determined graphically, was $k_1 = 9.63 \times 10^{-5}$ s^{-1} (correlation coefficient -0.996).

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