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MOLECULAR REARRANGEMENTS OF 5-AZIDO SUBSTITUTED 1,2,3-TRIAZOLES

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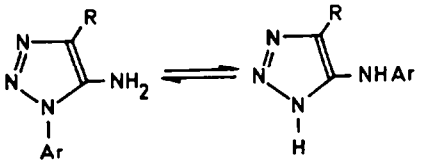
Abstract. 5-Azido-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (8a) and its phenyl substituted derivatives 8b,c rearrange at 60-80°C to give tetrazolyldiazoacetates 9, which have been isolated. When the reactions are allowed to go to completion, products derived from the diazo compounds are obtained; i.e. norcaradienes (10) from benzene solutions and imidazotetrazoles (12) from nitrile solutions. The latter decompose photochemically into diazacyclopentadienonimines (13). A kinetic study of the rearrangement 8 → 9 has been carried out and the mechanism (Scheme VI) is discussed in comparison with the Dimroth rearrangement.

Considerable work has already been carried out in the field of 1,2,3-triazoles[1] and one of the earliest highlights is the discovery by O. Dimroth in 1909 of the thermal interconversion of 5-amino-1-aryl-1,2,3-triazoles and 5-anilino-1,2,3-triazoles (1 ⇄ 2).[2] This type of rearrangement has proved to occur frequently in heterocyclic chemistry and is conveniently classified as a rearrangement involving one side-chain atom.[3]

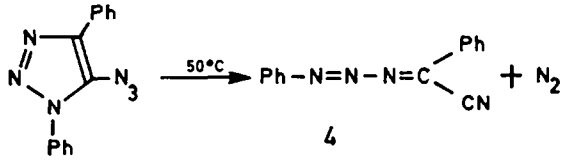


1 2

Although 5-amino-substituted 1,2,3-triazoles are easily accessible from the reactions of active methylene nitriles and organic azides in the presence of a strong base,[4] only two publications are concerned with their conversion into azidotriazoles. Thus, Smith et al.[5] prepared 5-azido-1,4-diphenyltriazole 3 and reported its thermal decomposition at 50°C with loss of nitrogen to give 1-phenyl-3-(α-cyano)-benzylidenetriazene 4. Sutherland and Tennant[6] synthesized 5-azido-4-methoxycarbonyl-1-phenyl-1,2,3-triazole and further transformed it to a triazolo[4,5-d]pyrimidine derivative without observing any rearrangement during the condensation reaction.

We have now prepared a number of 5-azidotriazoles bearing an ester function at the 4-position in order to study their thermal behaviour. This work was inspired by a recent discovery that 5-azido-4-ethoxycarbonyl-1,2,3-thiadiazole 5 undergoes

a spontaneous rearrangement into ethyl α-thiatriazolyldiazoacetate 6.[7] The same behaviour was predicted to occur in the triazole field. A full account of our findings is described in this paper.[8]



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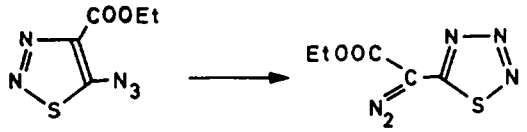


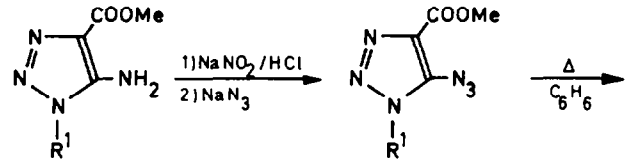
5 6

REACTION PRODUCTS

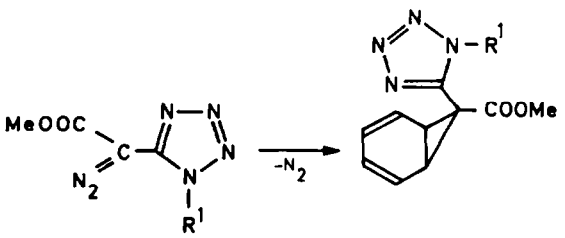
The azidotriazoles 8a-c were prepared from the aminotriazoles 7a-c[4] by diazotization at 0-5°C, followed by treatment of the diazonium salts with an excess of sodium azide at about -30°C.

When 8a was heated at 70°C in benzene solution, two products were formed which were identified as the diazoalkyltetrazole 9a and the norcaradiene 10a (Scheme I).

Scheme I



7 8



9 10

8-10	R^1
a	C_6H_5
b	p-$CH_3OC_6H_4$
c	p-Cl C_6H_4

The latter results from 9a via carbene addition onto the solvent. In order to isolate the products under appropriate reaction conditions, the concentrations at several time intervals were determined directly by integration of the methyl proton signals in the ^{1}H NMR spectra. The results, shown in Fig. 1, indicate that the diazo compound 9a reaches a maximum concentration of 60% after 23 h and then decomposes in favour of the norcaradiene 10a. Similar results were obtained with the azidotriazoles 8b and 8c.

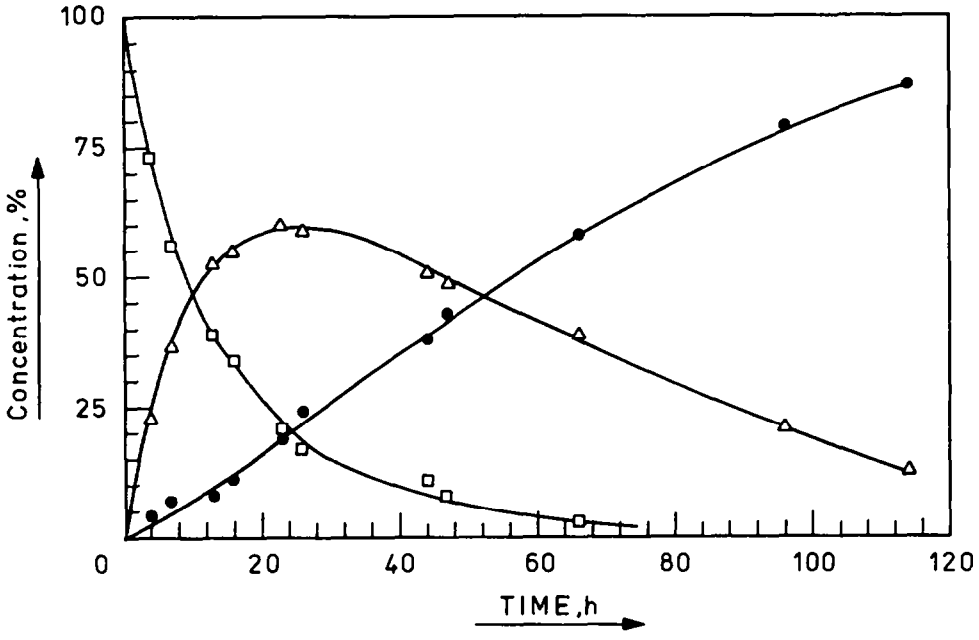


Fig. 1. Decomposition of 8a (□) to 10a (●) via 9a (△) at 70°C

Compound 8a was also thermolyzed in acetonitrile and benzonitrile solutions and yielded the imidazotetrazoles 12a,b. Thus, the intermediate iminocarbene 11 reacted as a 1,3-dipole towards the nitriles (Scheme II), a reaction which has been described recently for open-chain derivatives.[9] When the reaction in acetonitrile was followed by ^{1}H NMR spectroscopy at 70°C, curves similar to those in Fig. 1 were obtained with a maximum concentration for the diazo 9a of 37% after 38 h.

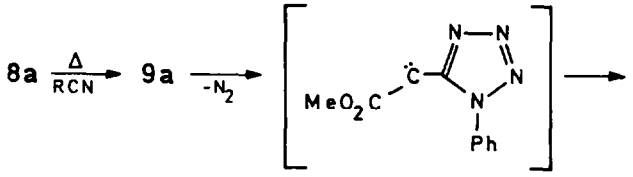
The azapentalenes 12a,b proved to be unstable in the presence of sunlight or upon irradiation with 350 nm light, yielding the diazacyclopentadienonimines 13a,b by loss of nitrogen. All attempts to isolate 13a in the pure state failed,[10] but its existence has been established by ^{1}H and ^{13}C NMR analyses of a solution containing the product in more than 90% purity (vide infra). Compound 13b, on the contrary, has been isolated as a red brown solid and further characterized by spectral methods. It did not react in a Diels-Alder fashion with diethylaminopropyne or with dimethyl acetylenedicarboxylate.[11]

NMR ANALYSIS

That rearrangement occurred during the thermolysis of 8 can be recognized easily by a consideration of the ^{13}C NMR spectra of the products. For instance, the ring carbon absorptions of 8a at δ 129 (C_4) and 139 (C_5) have shifted to δ 56 and 144 respectively in 9a. The high field resonance at δ 56 is diagnostic for a diazo compound.[12]

For the carbene adducts to benzene, two possible structures are conceivable; namely the norcaradiene 10 and the valence isomeric cycloheptatriene 14.[13] The room temperature ^{1}H NMR spectrum of the adduct (R^1 = Ph) shows absorptions for H_1

Scheme II



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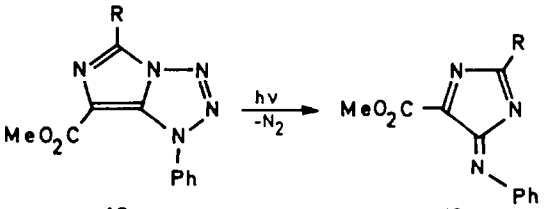


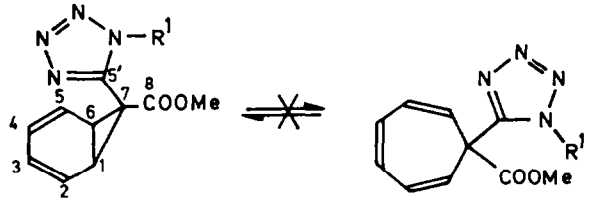
12 13

a: R=Me ; b: R=Ph

and H_6 at δ 3.25, characteristic of cyclopropyl hydrogens in norcaradienes carrying electronegative groups at C_7. The olefinic protons in the cycloheptatriene 14a would be expected to absorb in the region δ 5-7. The ^{13}C NMR spectrum also points to this conclusion, since the C_1 and C_6 carbon atoms absorb at δ 38.4 with a typical cyclopropyl coupling constant $^1J_{CH}$ of 172.5 Hz.

Of interest also are the ^3J coupling constants between the cyclopropyl hydrogens and the $C_{5'}$ and C_8 carbon atoms: $^3J_{C5'-H}$ = 1.75 Hz; $^3J_{C8-H}$ = 4.5 Hz. The larger value of $^3J_{C8-H}$ indicates that the ester function is located cis to the cyclopropyl hydrogens,[14] thus occupying the exo-7 position. This has been confirmed by a crystal structure X-ray analysis.[8]

It is noteworthy that no equilibrium between 10 and 14 (R^1 = Ph) is observed by lowering the temperature to -95°C, although a significant splitting of the H_1 and H_6 signals occurs in the ^1H NMR spectrum. This has been attributed to restricted rotation of the tetrazole nucleus, which is located at the endo-7 position (see ref. 8 for details).



10 14

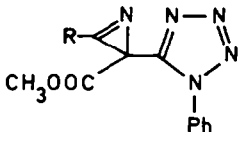
Three possible structures (15, 16 and 12) can a priori be formulated for the carbene adducts to nitriles, depending on whether the carbene is considered to react as a free entity or with participation of either the ester or the heterocyclic group. A distinction between these possibilities can be made on the basis of the chemical shift values in the ^{13}C NMR spectra. Indeed, no absorptions are found which correspond to the quaternary aliphatic carbon atom (expected value δ 35-45 ppm)[15] and the C=N carbon atom (expected value δ 165-170 ppm)[15] of the azirine 15. The only low field resonance at δ 162 is attributed to the ester C=O carbon, since

it shows a long range quartet multiplicity in the proton coupled spectrum of both adducts.

Also the oxazole structure 16 is refuted since it should exhibit two (instead of one) sp^2-carbon absorptions at about δ 160 ppm,[16] i.e. for the C_2 and C_5 atoms.

On the contrary, the C=N carbon atoms of the original nitrile functions are found at δ 126.8 (q) and 129.5 (t) ppm in the methyl and phenyl adducts respectively. The data are in agreement with the structures 12a and 12b, and the signals are attributed as shown in Scheme III.[17]

Scheme III



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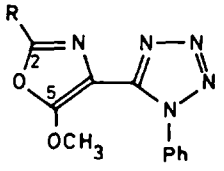

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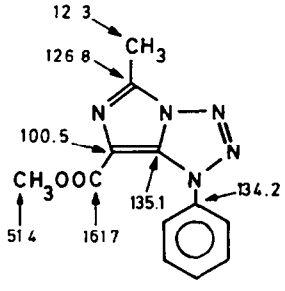
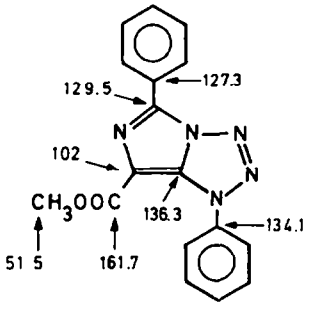


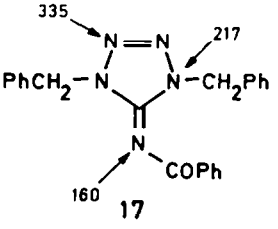
12 a



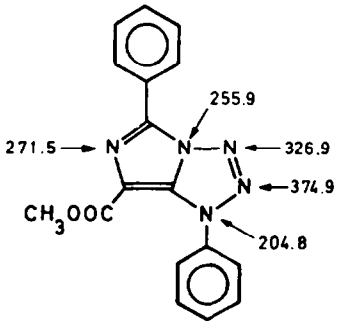
12 b

Further confirmation of structure 12b is provided by the ^{15}N NMR spectrum in chloroform solution, which shows only two (instead of three) resonances downfield 300 ppm (i.e. at δ 326.9 and 374.9 ppm relative to liq. ammonia). For the 1,5-disubstituted tetrazoles 15 and 16, three absorptions downfield 300 ppm are to be expected, corresponding to the three pyridine-type nitrogen atoms.[18] Structure 12b is consistent with the observed absorptions (see Scheme IV) and the signals are attributed by comparison with our model compound 17 and with known values for imidazoles and tetrazoles.[18] This was done by considering the following empirical increments in going from a monocyclic to a bicyclic azole: (i) the ^{15}N atom is

Scheme IV



17

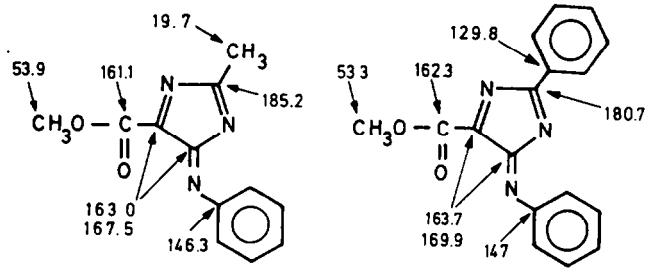


12 b

shifted downfield by 30 à 40 ppm when it is present at a ring junction; (ii) the ^{15}N atoms in the α-positions to a junction are shielded by 15 à 25 ppm, and, (iii) the ^{15}N atoms in the β-positions to a junction are deshielded by 5 à 15 ppm.

When the NMR tube containing 12a in $CDCl_3$ solution was irradiated with UV light, a deep red colour appeared corresponding to a product with downfield shifts for the methyl ester (from δ 3.8 to 4.05 ppm) and phenyl absorptions in the ^1H NMR spectrum. The ring carbon atoms in the ^{13}C NMR spectrum also manifested a considerable shift to lower field. The results are interpreted in terms of structure 13a as shown in Scheme V.

Scheme V



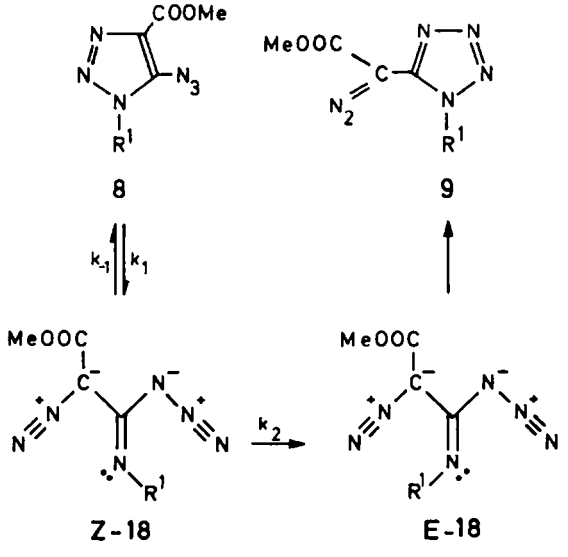
13a 13b

Irradiation of 12b in $CDCl_3$ also produced a red product with similar spectral data as 13a (see Scheme V); hence corresponding to structure 13b. Its ^{15}N NMR spectrum shows three resonances which are attributed to the ring nitrogen (δ 330 and 350 ppm) and exocyclic nitrogen atoms (δ 247.5 ppm). No ^{13}C and ^{15}N NMR data on diazacyclopentadienonimines are available from the literature for comparison.

KINETICS AND MECHANISM

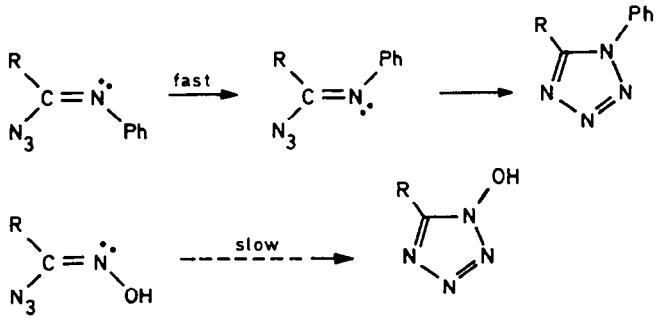
Mechanistically, the novel rearrangement 8 → 9 is closely related to the Dimroth rearrangement[3] (1 → 2) and involves the sequence of ring-opening of the triazole 8, syn-anti isomerization of the azido-imine 18, and ring-closure to the tetrazole 9 (Scheme VI).

Scheme VI



Contrary to what has been concluded for the Dimroth rearrangement of the parent compound (hydrogen substituents) on the basis of ab initio calculations,[19] we consider the syn-anti isomerization of 18 as the fast process compared with ring-cleavage of the triazole. This is deduced from the fact that N-phenyl substituted imidoyl azides cannot be isolated in the Z-configuration when they are generated from imidoyl chlorides; instead rapid nitrogen inversion occurs, followed by spontaneous ring-closure to tetrazoles (Scheme VII).[20] When nitrogen inversion is slowed down by introducing an OH function at the nitrogen atom, the azidoximes (generated from nitrile oxides) can indeed be isolated, although the corresponding tetrazoles are thermodynamically more stable (Scheme VII).[21] Furthermore, our intermediates 18a-c are comparable with N-phenyl substituted guanidines, which are known to undergo a fast syn-anti isomerization at low temperature.[22]

Scheme VII



From this knowledge we conclude that ring-opening of 8 is the rate-determining step in Scheme VI. Since the first step is reversible, the experimentally determined first-order rate constant is given by the equation:

$$k = k_1 \frac{k_2}{k_{-1} + k_2}$$

The term $k_2/(k_{-1} + k_2)$ is the partition coefficient which gives the fraction of Z-18 undergoing further conversion to 9 via E-18.

The introduction of an electron-withdrawing substituent at the 1-position is expected to increase k_1 and k_2, so that the overall rate increases. This is confirmed experimentally as shown in Table I. Thus, the half-life times at 70°C are 7.6 h for a phenyl, 20 h for a p-methoxyphenyl, and 3.2 h for a p-chlorophenyl substituent. The same order of reactivity is reported for the Dimroth rearrangement,[23] and the temperature at which rearrangement occurs is also comparable with that for 5-amino-4-ethoxycarbonyl-1-aryl substituted 1,2,3-triazoles (50-70°C).[24]

Table I. Substituent effect on the rearrangement 8 → 9 in C_6D_6 at 70°C

Azide	8a	8b	8c
10^5 k, s^{-1}	2.53	0.96	8.17

The dependence of the rate on the solvent polarity is shown in Table II. The results indicate that the reactions are faster in non-polar solvents, but the effect is very small. For instance, the rate constant is only 3.6 times larger in benzene than in acetonitrile at 70°C. The solvent is not expected to have a large influence on the syn-anti isomerization of 18 (when it proceeds by an inversion

mechanism),[22] but its small (and retarding) effect on the ring-opening of 8 is rather surprising.

Table II. Solvent effect on the rearrangement 8a → 9a at 70°C

Solvent	CCl_4	C_6D_6	CD_3OD	CD_3CN
10^5 k, s^{-1}	4.8	2.53	0.93	0.70

EXPERIMENTAL[25]

The ^1H NMR spectra were recorded at 90 MHz with a Varian EM-390 (CW), or at 250 MHz with a Bruker WM (FT) spectrometer. The ^{13}C NMR spectra were determined at 62.9 MHz with a Bruker WM-250 instrument, using 5 mm sample tubes. TMS was used as internal reference.

The ^{15}N NMR spectra of chloroform solutions in 10 mm sample tubes were taken with a Bruker WM-250 spectrometer, operating at 25.35 MHz. $Cr(Acac)_3$ was added as relaxation reagent. The spectra were determined without proton decoupling (since 12b and 13b contain only tertiary nitrogen atoms) at a spectral width of 10 kHz, applying a 60° pulse with a repetition time of 5 s for 30.000 to 40.000 accumulations. The chemical shifts were determined with respect to external nitromethane contained in a 4 mm capillary held concentrically in the sample tube. This reference was given the δ-value of 380 ppm, thus converting the N-chemical shifts to the liquid ammonia shielding scale.

Synthesis of the 5-azidotriazoles 8a-c. 5-Amino-4-methoxycarbonyl-1-phenyl-1,2,3-triazole was diazotized by slow addition of 2.5 g sodium nitrite to a water solution of 7a (2.18 g, 0.01 mol) containing 75 mL of concentrated hydrochloric acid at 0-5°C. Then, a tenfold excess of sodium azide in water was added dropwise at about -30°C. The reaction mixture was extracted with ether and the ether extracts were dried over $MgSO_4$. After evaporation of the ether in vacuo, a yellow oil of 8a was obtained, which solidified (yield 82%).

5-Azido-4-methoxycarbonyl-1-phenyl-1,2,3-triazole (8a) was crystallized from ether and then recrystallized from methanol to give pale yellow crystals, mp 86°C (dec.); IR (KBr) 2145 (s, N_3), 1710 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.03 (s, 3 H, CH_3), 7.4-7.7 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 52.3 (CH_3), 128.6 (C_4), 138.8 (C_5), 161.2 (CO); mass spectrum, m/e (relative intensity) 244 (22, $M^{+\cdot}$), 129 (45, $M^{+\cdot}$ - 2 N_2 - COOMe), 103 (33, $PhNC^{+\cdot}$), 91 (17, $PhN^{+\cdot}$), 77 (100, $C_6H_5^+$). Anal. Calcd for $C_{10}H_8N_6O_2$ (mol wt 244): C, 49.18; H, 3.27. Found: C, 49.22; H, 3.40.

Compound 8a was converted into the corresponding iminophosphorane upon treatment with triphenylphosphine in dry ether at room temperature; yield 75%, mp 248-250°C (ether-chloroform). Anal. Calcd for $C_{28}H_{23}N_4O_2P$ (mol wt 478): C, 70.25; H, 4.84. Found: C, 70.05; H, 4.69.

5-Azido-4-methoxycarbonyl-1-(p-methoxyphenyl)-1,2,3-triazole (8b) was similarly prepared and purified by column chromatography on silica gel with CCl_4-ethyl acetate as the eluent; yield 21%, mp 140°C (dec.)(ether-chloroform); IR (KBr) 2125 (s, N_3), 1710 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 3.88 (s, 3 H, CH_3OAr), 4.0 (s, 3 H, CH_3OCO), 7.0 (d, 2 aromatic H), 7.45 (d, 2 aromatic H); ^{13}C NMR ($CDCl_3$) δ 52.3 (CH_3), 128.4 (C_4), 138.7 (C_5), 161.2 (CO); mass spectrum, m/e (relative intensity) 274 (28, $M^{+\cdot}$), 159 (100, $M^{+\cdot}$ - 2 N_2 - COOMe), 133 (73, $MeOC_6H_4NC^{+\cdot}$), 121 (31, $MeOC_6H_4N^{+\cdot}$), 107 (78, $MeOC_6H_4^+$). Anal. Calcd for $C_{11}H_{10}N_6O_3$ (mol wt 274): C, 48.19; H, 3.68. Found: C, 48.09; H, 3.76.

Compound 8b was converted into the iminophosphorane upon treatment with triphenylphosphine in ether at room temperature; yield 51%, mp 195°C (ether-chloroform). Anal. Calcd for $C_{29}H_{25}N_4O_3P$ (mol wt 447): C, 68.48; H, 4.95. Found: C, 68.24; H, 5.02.

5-Azido-1-(p-chlorophenyl)-4-methoxycarbonyl-1,2,3-triazole (8c) was similarly prepared and extracted from the reaction mixture with chloroform. It was purified by column chromatography on silica gel with dichloromethane as the eluent; yield 13.5%, mp 117°C (dec.)(EtOH); IR (KBr) 2120 (s, N_3), 1710 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 4.0 (s, 3 H, CH_3O), 7.55 (s, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 52.3 (CH_3O), 128.7 (C_4), 138.8 (C_5), 161.1 (CO); mass spectrum, m/e (relative intensity) 278 (23, $M^{+\cdot}$), 163 (39, $ClC_6H_4NC\text{-}CN^+$), 137 (31, $ClC_6H_4NC^{+\cdot}$), 111 (100, $ClC_6H_4^+$). Anal. Calcd for $C_{10}H_7ClN_6O_2$ (mol wt 278): C, 42.89; H, 2.53. Found: C, 42.65; H, 2.69.

Thermolysis of 8 in benzene. When 8a (1 g) was heated in 5 mL of benzene at 70°C for 5 days, the ^{1}H NMR spectrum indicated the presence of 10a in 95% yield. The solvent was evaporated in vacuo and the residual red oil was purified by column chromatography on silica gel with CCl_4-ethyl acetate as the eluent. 7-Methoxycarbonyl-7-(1-phenyltetrazol-5-yl)-norcaradiene 10a was isolated in 25% yield, mp 175°C (ether-chloroform); IR (KBr or $CDCl_3$) 1730 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.25 (t, 2 H, H_1 and H_6), 3.85 (s, 3 H, CH_3O), 5.66 and 5.74 (two m, 4 vinyl H), 7.3-7.7 (m, 5 aromatic H); ^{13}C NMR ($CDCl_3$) δ 14.65 (C_7), 38.4 (C_1 and C_6), 53.6 (CH_3O), 123.1 and 125.3 (vinyl C), 148.0 (tetrazole C), 173.4 (CO); mass spectrum, m/e (relative intensity) 294 (27, $M^{+\cdot}$), 251 (34, $M^{+\cdot}$ - CH_3-N_2), 235 (9, $M^{+\cdot}$ - COOMe), 207 (33, $M^{+\cdot}$ - COOMe - N_2), 103 (100, $PhNC^{+\cdot}$), 91 (10, $PhN^{+\cdot}$), 77 (59, $C_6H_5^+$). Anal. Calcd for $C_{16}H_{14}N_4O_2$ (mol wt 294): C, 65.28; H, 4.79. Found: C, 65.16; H, 4.70.

When the reaction was stopped after 66 h, the mixture contained 9a (39%), 10a (58%) and unreacted 8a (3%). The products were separated by column chromatography on silica gel.

5-(Methoxycarbonyl-diazomethyl)-1-phenyl-1,2,3,4-tetrazole (9a) was obtained in 20% yield, mp 57°C (dec.)(yellow crystals from ether-chloroform); IR ($CHCl_3$) 2105 (s, CN_2), 1715 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.53 (s, 3 H, CH_3O), 7.57 (s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 52.7 (CH_3), 56.07 (weak, br, CN_2), 144.4 (tetrazole C), 161.8 (CO); mass spectrum, m/e (relative intensity) 244 (20, $M^{+\cdot}$), 188 (12, $M^{+\cdot}$ - 2 N_2), 103 (92, $PhNC^{+\cdot}$), 91 (13, $PhN^{+\cdot}$), 77 (100, $C_6H_5^+$). Anal. Calcd for $C_{10}H_8N_6O_2$ (mol wt 244): C, 49.17; H, 3.30. Found: C, 49.11; H, 3.40. The triphenylphosphine adduct melts at 200-202°C (ether-chloroform).

7-Methoxycarbonyl-7-(1-p-methoxyphenyltetrazol-5-yl)-norcaradiene (10b) was similarly obtained by thermolysis of 8b in benzene at 80°C for 42 h; yield 50%, mp 185°C (ether-chloroform); IR (KBr) 1725 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.2 (br, 2 H, H_1 and H_6), 3.8 (s, 3 H, CH_3OAr), 3.9 (s, 3 H, CH_3OCO), 5.7 (br s, 4 vinyl H), 7.0 and 7.3 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 14.7 (C_7), 38.6 (C_1 and C_6), 53.5 and 55.7 (CH_3), 123.2 and 125.3 (vinyl C), 148.0 (tetrazole C), 173.4 (CO); mass spectrum, m/e (relative intensity) 324 (34, $M^{+\cdot}$), 237 (23, $M^{+\cdot}$ - N_2 - COOMe), 149 (28, $MeOC_6H_4N_3^{+\cdot}$), 133 (100, $MeOC_6H_4NC^{+\cdot}$), 121 (10, $MeOC_6H_4N^{+\cdot}$), 107 (11, $MeOC_6H_4^+$). Anal. Calcd for $C_{17}H_{16}N_4O_3$ (mol wt 324): C, 62.94; H, 4.97. Found: C, 62.80; H, 5.03.

When the reaction was stopped after 15 h, the mixture contained 9b (40%), 10b (35%) and unreacted 8b (25%). The products were separated by column chromatography on silica gel with dichloromethane as the eluent.

5-(Methoxycarbonyl-diazomethyl)-1-(p-methoxyphenyl)-1,2,3,4-tetrazole (9b) was isolated in 20% yield, mp 102°C (dec.)(ether-chloroform); IR (KBr) 2130 (s, CN_2), 1720 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 3 H, CH_3OCO), 3.87 (s, 3 H, CH_3OAr), 7.0 and 7.4 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 52.8 and 55.7 (CH_3), 144 (tetrazole C), 161.9 (CO), no CN_2 observed; mass spectrum, m/e (relative intensity) 274 (32, $M^{+\cdot}$), 218 (3, $M^{+\cdot}$ - 2 N_2), 159 (100, $M^{+\cdot}$ - 2 N_2 - COOMe), 133 (69, $MeOC_6H_4NC^{+\cdot}$), 121 (34, $MeOC_6H_4N^{+\cdot}$), 107 (90, $MeOC_6H_4^+$), 77 (89, $C_6H_5^+$). Anal. Calcd for $C_{11}H_{10}N_6O_3$ (mol wt 274): C, 48.16; H, 3.67. Found: C, 48.18; H, 3.73.

7-Methoxycarbonyl-7-(1-p-chlorophenyltetrazol-5-yl)-norcaradiene (10c) was similarly obtained by thermolysis of 8c in benzene at 70°C for 72 h and then isolated by crystallization from methanol; yield 34%, mp 215°C (MeOH); IR (KBr) 1720 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 3.2 (br t, 2 H, H_1 and H_6), 3.75 (s, 3 H, CH_3O), 5.7 (s, 4 vinyl H), 7.3-7.6 (two d, 4 aromatic H); ^{13}C NMR ($CDCl_3$) δ 14.6 (C_7), 38.5 (C_1 and C_6), 53.7 (CH_3O), 123.1 and 125.5 (vinyl C), 148 (tetrazole C), 172.0 (CO); mass spectrum, m/e (relative intensity) 328 (21, $M^{+\cdot}$), 285 (31, $M^{+\cdot}$ - N_2 - Me or $M^{+\cdot}$ - HN_3), 269 (18, $M^{+\cdot}$ - COOMe), 241 (28, $M^{+\cdot}$ - COOMe - N_2), 137 (100, $ClC_6H_4NC^{+\cdot}$). Anal. Calcd for $C_{16}H_{11}ClN_4O_2$ (mol wt 328): C, 58.44; H, 3.98. Found: C, 58.46; H, 4.05.

Thermolysis of 8 in nitriles. The azide 8a was heated in a threefold excess of acetonitrile at 80°C for 2 days. Then, the solvent was removed in vacuo and the residue was triturated with ether to give 7-methoxycarbonyl-5-methyl-1-phenylimidazo[1,5-d]tetrazole (12a) in 42% yield; mp 210-212°C (dec.) (ether-chloroform); UV ($CHCl_3$) λ_{max} (log ε) 317 (3.6), 268.5 nm (4.05); IR (KBr) 1725 cm^{-1} (s, CO); ^{1}H NMR ($CDCl_3$) δ 2.75 (s, 3 H, ring CH_3), 3.8 (s, 3 H, CH_3OCO), 7.4-7.7 (m, 5 aromatic H); ^{13}C NMR ($CDCl_3$) see Scheme III; mass spectrum, m/e (relative intensity) 257 (22, $M^{+\cdot}$), 229 (4, $M^{+\cdot}$ - N_2), 103 (100, $PhNC^{+\cdot}$), 77 (31, $C_6H_5^+$). Anal. Calcd for $C_{12}H_{11}N_5O_2$ (mol wt 257): C, 56.01; H, 4.28; N, 27.23. Found: C, 55.86; H, 4.34; N, 27.11.

When 12a in $CDCl_3$ solution was exposed to sunlight for 12 h, 5-methoxycarbonyl-3-methyl-2,4-diazacyclopentadienon-N-phenylimine (13a) was formed as a red product in 15% (NMR) yield. This product decomposed upon further standing. Alternatively, when a solution of 12a (50 mg) in dry $CDCl_3$ (treated with alumina to remove traces of acid) was irradiated with 350 nm light for 100 min under nitrogen and ice-cooling, the ^1H and ^{13}C NMR spectra indicated the presence of 13a in 90% yield; ^1H NMR ($CDCl_3$) δ 2.69 (s, 3 H, ring CH_3), 4.05 (s, 3 H, CH_3OCO), 7.3-7.5 (m, 3 aromatic H), 7.75 (m, 2 aromatic H); ^{13}C NMR ($CDCl_3$ at -40°C) see Scheme V.

7-Methoxycarbonyl-1,5-diphenylimidazo[1,5-d]tetrazole (12b) was similarly obtained by heating 8a in benzonitrile at 80°C for 2 days; yield 51%, mp 205°C (dec.)(ether-chloroform); UV ($CHCl_3$) λ_{max} (log ε) 335 (3.97), 278 nm (4.29); IR (KBr) 1700 cm^{-1} (s, CO); ^1H NMR ($CDCl_3$) δ 3.8 (s, 3 H, CH_3O), 7.4-7.8 and 8.35 (two m, 8 + 2 aromatic H); ^{13}C NMR ($CDCl_3$) see Scheme III; mass spectrum, m/e (relative intensity) 319 (19, $M^{+\cdot}$), 291 (19, $M^{+\cdot} - N_2$), 259 (21, $M^{+\cdot} - N_2$ - MeOH), 103 (100, $PhNC^{+\cdot}$), 77 (25, $C_6H_5^+$). Anal. Calcd for $C_{17}H_{13}N_5O_2$ (mol wt 319): C, 63.93; H, 4.10; N, 21.94. Found: C, 63.75; H, 4.12; N, 21.84.

When a solution of 12b (100 mg) in dry $CDCl_3$ (treated with alumina) was irradiated with 350 nm light for 2 h under nitrogen and ice-cooling, the ^1H and ^{13}C NMR spectra indicated the presence of 5-methoxycarbonyl-3-phenyl-2,4-diazacyclopentadienon-N-phenylimine (13b) in ca 98% yield. After evaporation of the solvent, a red-brown solid was obtained which was crystallized from ether in 55% yield, mp 117°C; IR (KBr) 1740 (s, CO), 1600 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 4.1 (s, 3 H, CH_3O), 7.4-7.7, 8.0 and 8.5 (three m, 6 + 2 + 2 aromatic H); ^{13}C NMR ($CDCl_3$) see Scheme V; mass spectrum, m/e (relative intensity) 291 (71, $M^{+\cdot}$), 260 (12, $M^{+\cdot}$ - OMe), 232 (12, $M^{+\cdot}$ - COOMe), 103 (100, $PhNC^{+\cdot}$). Anal. Calcd for $C_{17}H_{13}N_3O_2$ (mol wt 291): C, 70.08; H, 4.50. Found: C, 70.09; H, 4.60.

Kinetic measurements. Solutions of the azides 8a-c (1 mmol in 3 mL of solvent) were placed in NMR tubes at 70°C (± 0.1°) for decomposition. At several time intervals, the NMR tubes were cooled to 0°C and analyzed by ^1H NMR spectroscopy. The rates of decomposition were followed by integration of the ester methyl singlets in the spectra, i.e. at δ 4.0 for the azides 8, δ 3.5-3.6 for the diazo compounds 9, and δ 3.7-3.9 for the norcaradienes 10. By plotting log [azide](%) vs time, linear plots were obtained up to a high degree of conversion (> 80%), all having a correlation coefficient of at least -0.993. The first order rate constants were determined from the slopes of the linear plots and the results are given in Tables I and II.

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