

**1,3-DIPOLAR CYCLOADDITIONS
TO 2,3-DIMETHOXYCARBONYL-7-OXABICYCLO[2,2,1]-2,5-HEPTADIENE,
1,4-EPOXY-1,4-DIHYDRONAPHTHALENE, AND *exo-endo*-
-1,6-DIMETHOXYCARBONYL-11,12-DIOXATETRACYCLO-
[4,4,0,1^{2,5},1^{7,10}]-3,8-DODECADIENE***

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The paper deals with site-selectivity of 1,3-dipolar cycloadditions of ethyl azidoformate, azidoacetate, and diazo acetate to 2,3-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2,5-heptadiene. The *exo-endo* stereoselectivity has been studied of the reactions of 1,4-epoxy-1,4-dihydronaphthalene with C-benzoyl-N-phenyl- and C,N-diphenylnitrones, 5-azido-2-furanecarbaldehyde, 4-nitrophenyl azide, benzenenitril oxide, ethyl azidoformate, azidoacetate, and diazo acetate. The cycloadditions to the bis-adduct of furane with dimethyl acetylenedicarboxylate and thermolyses of some of the adducts prepared have also been studied.

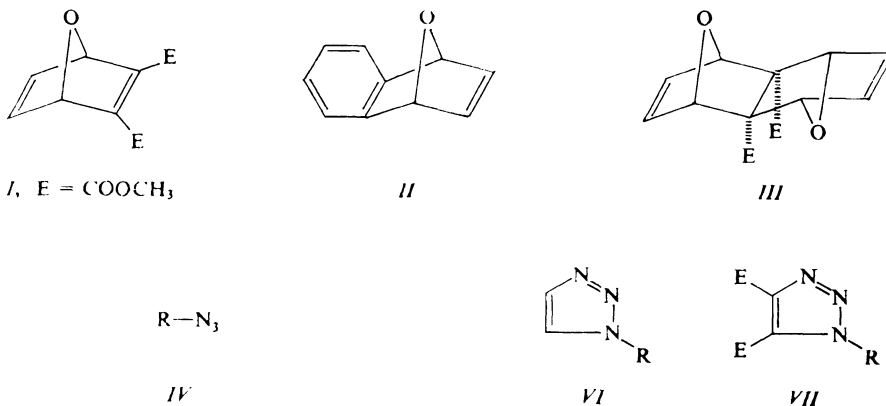
The 1,3-dipolar cycloadditions of 2,3-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2,5-heptadiene (*I*) exhibit various degrees of site-selectivity¹⁻⁴, and the intermediate cycloadducts undergo the Diels-Alder cycloreversion to give furane or 3,4-dimethoxycarbonylfurane and the corresponding five-membered heterocycles. In the previous paper⁴ we found that compound *I* is an excellent synthetic equivalent of acetylenes, and we investigated its applications to the synthesis of β -substituted furane derivatives. The aim of the present communication is to study the site-selectivity of *I* with some further 1,3-dipoles containing the electron-acceptor ethoxycarbonyl group, as well as to investigate the *exo-endo* stereoselectivity of the derivatives containing the oxabicyclo[2,2,1]heptene grouping.

The 1,3-dipolar cycloaddition of ethyl azidoformate (*IVc*) with *I* gives (in analogy with the previous works^{2,4}) a mixture of cycloreversion products: 1-ethoxycarbonyl-1,2,3-triazole (*VIc*) and 1-ethoxycarbonyl-4,5-dimethoxycarbonyl-1,2,3-triazole (*VIIc*) in the ratio of 65 : 35 in favour of the cycloaddition to the non-substituted double bond. The structure of adduct *VIc* was assigned on the basis of the presence of signals of the triazole protons at 7.75 and 8.23 ppm, and that of *VIIc* by the signals of the methoxycarbonyl groups at 3.96 and 4.04 ppm. Triazole *VIIc* was

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only prepared under drastic conditions⁵ by the cycloaddition of *IVc* to dimethyl acetylenedicarboxylate at 150°C, and triazole *VIc* was prepared by the cycloaddition to 2,3-dimethoxycarbonyl-7-isopropylidenebicyclo[2,2,1]-2,5-heptadiene with the yield of 20% under even more drastic reaction conditions⁶. In this case, too, the usefulness of *I* as a synthetic equivalent for acetylene derivatives can be seen⁴.

Compound *I* also reacts with ethyl azidoacetate (*IVd*) already at room temperature to give a 86 : 14 mixture of 1-ethoxycarbonylmethyl-4,5-dimethoxycarbonylmethyl-1,2,3-triazole (*VIIId*) and 1-ethoxycarbonylmethyl-1,2,3-triazole (*VId*). The triazole *VIIId* prepared by us in high yield (85%) was prepared⁷ by the cycloaddition of the azide *IVd* to dimethyl acetylenedicarboxylate at 100°C, and the triazole *VId* was prepared by addition to acetylene under severe conditions⁸ (100°C, 1.1 MPa). Compared with the azide *IVc*, the ethoxycarbonylmethyl group does not lower the LUMO_{IV} energy so much as the ethoxycarbonyl group (due to the presence of the methylene group acting as insulant of the inductive effect), whereby the frontier orbital interaction HOMO_{IVd}-LUMO becomes dominant, which results in a change of the site-selectivity in favour of the cycloaddition to the deactivated double bond in *I*.

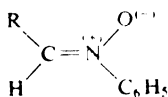


In formulae *IV*, *VI* and *VII*:



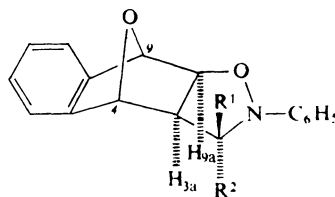
The cycloaddition of ethyl diazoacetate to compound *I* gives exclusively⁹ 5-ethoxycarbonyl-3,4-dimethoxycarbonylpyrazole (*XVII*) in an almost quantitative yield: in this case the reaction is only controlled by the frontier orbital interaction HOMO_{dipole}-LUMO_I, although it is known that the both frontier orbital interactions are significant in the cycloadditions of ethyl diazoacetate¹⁰.

One of frequently studied phenomena in the 1,3-dipolar cycloaddition reactions is the exclusive *exo* selectivity of norbornene and norbornadiene derivatives (with respect to the methylene bridge)¹¹. We observed³ the exclusive *exo* stereoselectivity of the oxa norbornadiene analogue *I* in the 1,3-dipolar cycloadditions of nitrones with *I*. As another model system we chose its benzo derivative, 1,4-epoxy-1,4-dihydronaphthalene (*II*) which represents an oxabicyclo[2,2,1]heptadiene system, too. Although its larger dipolarophilicity can be expected because of the ring strain (as compared with 1,4-dihydronaphthalene) and the presence of the free electron pair at oxygen (as compared with 1,4-dihydro-1,4-methylenenaphthalene), the available literature only gives one example of its participation in 1,3-dipolar cycloaddition. Sasaki and coworkers¹² obtained the *exo* adduct *Xb* from the reaction with benzoylnitroxide, the triazoles *IX* from *IVc* and phenyl azide, and the iminoderivative type *XIII* from *p*-toluenesulphonyl azide.



Va, R = C₆H₅CO

Vb, R = C₆H₅



VIIIa, R¹ = C₆H₅CO, R² = H

VIIIb, R¹ = H, R² = C₆H₅CO

VIIIc, R¹ = C₆H₅, R² = H

VIIId, R¹ = H, R² = C₆H₅

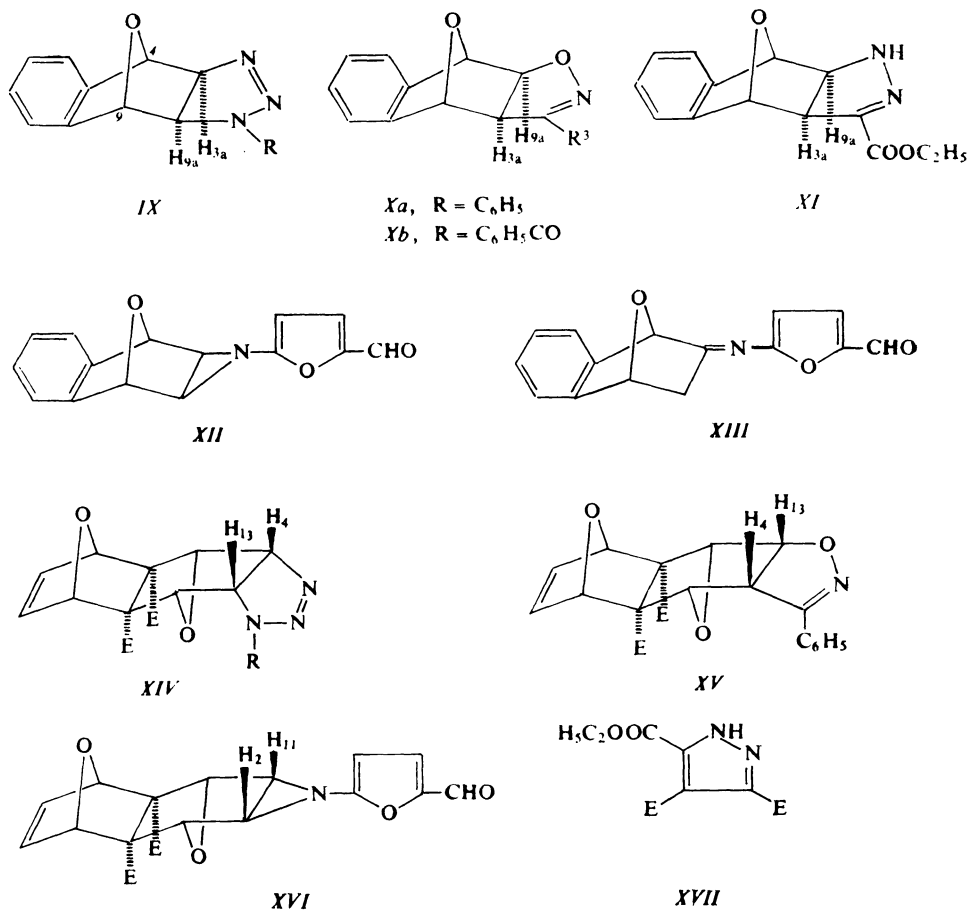
The 1,3-dipolar cycloadditions of C,N-diphenylnitrone (*Vb*), C-benzoyl-N-phenylnitrone (*Va*), 5-azido-2-furanecarbaldehyde (*IVa*), 4-nitrophenyl azide (*IVb*), azides *IVd*, ethyl diazoacetate, and benzenenitril oxide gave high yields of 1 : 1 *exo*-adducts which are stable at room temperature. After the reaction of *Vb* with *II*, we isolated the adduct *VIIIc* (M⁺, *m/z* 341) to which we assigned the *exo-exo* structure (the first prefix refers to the arrangement with respect to the oxygen bridge, the second prefix concerns the arrangement of nitrone and double bond³) on the basis of zero value of the coupling constant $J_{3a,4} = J_{9-9a}$ as well as the 3a-H multiplicity, and the value $J_{3,3a} = 7.0$ Hz. In the *endo* arrangement with respect to the bridge the 4-H and 9-H protons could not give singlets but they would give doublets due to interactions with the bridge protons 3a-H and 9a-H. In the case of the second *exo-endo* diastereoisomer *VIIId* the value of the coupling constant $J_{3,3a}$ should be smaller or zero, as it was found in our previous works³ dealing with the cycloadditions to *I*.

The ¹H NMR spectrum of the mother liquor indicates the presence of a mixture of the *exo-endo* adduct *VIIId* and compound *VIIIc* which could not be separated.

The *exo-endo* structure of the former derivative, however, could be reliably determined from the presence of a doublet with the coupling constant $J_{3a,9a} = 6.0$ Hz (3a-H, δ 3.42). The *anti* arrangement with respect to the isoxazolidine proton 3-H follows from the zero value of $J_{3,3a}$. The ratio of the adducts is 82 : 18 in favour of the *exo-exo* adduct *VIIIc*. The diastereoisomer of the same *exo-exo* arrangement *VIIIa* was obtained as a dominant product of the cycloaddition of *Va* to *II*. The influence of the electron-acceptor benzoyl group makes itself felt in the increased δ value of the 3-H proton of the isoxazolidine ($\Delta\delta = 0.56$ ppm). The mother liquor contains the diastereoisomeric *exo-endo* adduct *VIIIb* whose isolation failed similarly as that in the previous case. The *exo-endo* arrangement was also confirmed on the basis of ^1H NMR spectrum: the 3-H proton gives a singlet. The ratio of the two adducts is 62 : 38 in favour of the *exo-exo* adduct. The increase of proportion of the *exo-endo* adduct from the cycloaddition of the nitrone *Va* as compared with that of *Vb* was also observed³ in the cycloadditions to *I*. In the case of oxabicyclo[2,2,1]-heptene derivatives the *exo-exo* adducts only were formed due probably to the through-space interactions between the two multiple bonds in the derivatives *I* and *II*. From the results obtained in the 1,3-dipolar cycloadditions of nitrones with *II* it can be presumed that the reaction is controlled by the frontier orbital interaction $\text{LUMO}_{1,3\text{-dipole}}\text{-HOMO}_{\text{II}}$. As it follows from our previous communications^{3,4} the nitrone *Va* has a higher reactivity than *Vb* in this type of reactions, which was proved experimentally.

Although reactivity and properties of *IVa* are very similar to those of *p*-toluenesulphonyl azide¹³, the cycloaddition of *IVa* to *II* gave the stable 1 : 1 *exo*-adduct *IXa* in the yield of 89%. The bridgehead protons 4-H and 9-H do not interact with the triazoline protons 3a-H and 9a-H, which determines the *exo* arrangement *IXa*. The cycloadduct *IXa* decomposes at its melting point, its mass spectrum lacks the molecular ion of the 1 : 1 cycloadduct and only contains the fragment m/z ($M^+ - 28$) formed by elimination of nitrogen from the molecule *IXa*. With the azide *IVb* the 1 : 1 *exo*-adduct *IXb* also is formed (71%) which loses nitrogen under the conditions of the mass spectrum measurement, too (m/z 280, $M^+ - 28$). The basic peak is that of the fragment m/z 118 (isobenzofurane) formed by the Diels-Alder cycloreversion. Hence, the reactions with the azides *IVa* and *IVb* produce the relatively stable 4,9-epoxy-3a,4,9,9a-tetrahydro-1-aryl-1H-naphtho[2,3-*d*]triazoles *IXa* and *IXb*, respectively, in contrast to the reactions with *p*-toluenesulphonyl azide which give the imino derivatives type *XIII* with simultaneous splitting off of nitrogen. The behaviour of *IXa* and *IXb* in the mass spectrum initiated our investigation of their thermal reactions. The thermolysis of *IXa* liberates nitrogen as low as at 110°C, the reaction being finished within 30 min. The ^1H NMR spectrum of the raw reaction mixture indicates the presence of two compounds whose ratio does not change on further heating, the two derivatives being formed independently. The molar ratio 36:37 of the aziridine derivative *XII* and the imine product *XIII* was determined

from the integral intensities of the signals of the aldehydic protons at 9.25 and 9.21 ppm, respectively. The structure *XII* was assigned on the basis of a higher symmetry of the ^1H NMR spectrum: the aziridine protons 2-H and 9-H absorb as one singlet at 3.08 ppm, and the bridgehead protons 3-H and 8-H also absorb as one singlet at 5.34 ppm. In the imino derivative *XIII* these protons already give two singlets at 5.38 and 5.41 ppm, and the methylene protons give a doublet at 3.80 ppm. As further evidence we can give the value of the chemical shift δ 5.53 for 4'-H of the furane nucleus which is lower than that of the aziridine derivative *XII* (δ 5.75) due to higher conjugation in the imino derivative *XIII*. In the case of the tosyl adduct *IX*, the imino derivative of the type *XIII* only is formed¹².



Compound *IXb* shows an entirely different behaviour. It does not split off nitrogen on heating at 160°C, but instead, it undergoes the Diels–Alder cycloreversion to give 1-(4-nitrophenyl)-1,2,3-triazole (*VIIb*).

The comparable character of the ^1H NMR spectra of the *IXd* adduct obtained by the cycloaddition of *IVd* to *II* with that of the previous products spectroscopically proved indicates the formation of the 1 : 1 *exo*-adduct *IXd* (88%). Due to the non-equivalency of the protons, the signal of the methylene group is of the *d,d* type with high geminal constant $^2J = 19$ Hz. The compound *XI* obtained by the cycloaddition of ethyl diazoacetate to *II* represents a product of 1,3-dipolar cycloaddition and subsequent 1,3-sigmatropic rearrangement, which was proved by the ^1H NMR spectrum. The reaction is a typical conversion of unstable 1-pyrazolines into 2-pyrazolines. The *exo*-configuration of *XI* was determined from the value $J_{3a,4} = J_{9,9a} = 0$ Hz. The adduct *IXd* is stable up to the temperature of 160°C. The cycloaddition with benzenenitriloxide also gave a stable 1 : 1 *exo*-adduct (*Xa*).

Furthermore, we studied the stereoselectivity of the 1,3-dipolar cycloadditions of the azides *IVa* and *IVb* as well as benzenenitriloxide to *exo-endo*-1,6-dimethoxycarbonyl-11,12-dioxatetracyclo[4,4,0,1^{2,5},1^{7,10}]-3,8-dodecadiene (*III*) which contains the oxabicyclo[2,2,1]heptene skeleton. In all the cases we isolated the stable *exo* 1 : 1 cycloadducts *XIVa* (73%), *XIVb* (73%), and *XV* (28%) without the expected aromatization. The *exo*-cycloaddition follows from the ^1H NMR spectrum in which all bridgehead hydrogen atoms in the neighbourhood of oxygen (5-H, 7-H, 10-H, 12-H) absorb as singlets. Compound *XIVa* liberates nitrogen on heating in benzene at 100°C (autoclave). By the Diels–Alder cycloreversion the compound *XIVa* can be decomposed down to furane, 3,4-dimethoxycarbonylfuran, and 1-(5-formyl-2-furyl)-1,2,3-triazole, or – by elimination of nitrogen – it can produce the aziridine and imine derivatives as in the case of *IXa*. The thermolysis of *XIVa*, however, produces the aziridine derivative *XVI* as a single product (54%), and the presence of the molecular peak M^+ , m/z 387 excludes the decomposition of *XIVa* by the Diels–Alder cycloreversion. The structure of *XVI* was proved from the ^1H NMR spectrum in analogous way as that of *XII*. The cycloadduct *XIVb* is stable up to 200°C. Its mass spectrum contains the peaks with m/z 190, 184, 68 indicating the Diels–Alder cycloreversion induced by an electron impact, because compound *XIVb* is stable at the temperatures of measurement of the mass spectrum.

The structure of the derivatives prepared is confirmed by the ^{13}C NMR spectra as well. To assign the signals of compound *IXa*, we measured the ^{13}C NMR spectra of the compounds *VIa* and *VIIa* prepared earlier⁴. The signals of quaternary carbon atoms of benzo grouping of the derivatives *VIIIa,c*, *IXa,d*, and *Xa* are found in the region from 141.34 to 146.71 ppm, the doublets of $C_{(5)}-C_{(8)}$ in the region from 119.75 to 130.11 ppm, the doublets of the oxabicyclic skeleton $C_{(4)}$ and $C_{(9)}$ in the region from 80.97 to 85.82 ppm, and the doublets of the bridgehead carbon atoms $C_{(3a)}$ and $C_{(9a)}$ in the regions about 60 ppm or about 85 ppm depending on the nature of the heteroatom.

EXPERIMENTAL

The melting points are not corrected. The mass spectra of the derivatives synthesized were measured with a MS 902 S apparatus with a direct inlet system, ionisation energy of 70 eV. The ^1H NMR spectra were measured with a Tesla BS 487 C apparatus, the ^{13}C NMR spectra were measured with a JEOL apparatus in deuteriochloroform with tetramethylsilane as the internal standard. The UV spectra were measured with a Specord UV VIS apparatus with tempered cells in methanol. 2,3-Dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2,5-heptadiene (*I*) was prepared according to ref.⁴, the bisadduct *III* was prepared by cycloaddition of furane with dimethyl acetylenedicarboxylate by standing at room temperature for 100 days. 1,4-Epoxy-1,4-dihydro-naphthalene (*II*) was prepared by cycloaddition of dehydrobenzene with furane¹⁴.

Cycloaddition of *IVc* to *I*

A mixture of 1.15 g (10 mmol) azide *IVc*, 2.1 g (10 mmol) *I*, and 15 ml ether was left to stand at room temperature 16 h. The mixture was concentrated and distilled in vacuum, and the fraction obtained at 50–60°C/0.66 kPa was submitted to freezing out to give 0.3 g (21%) ethyl 1,2,3-triazole-1-carboxylate (*VIc*), m.p. 40–42°C (ref.⁶ does not give m.p.). ^1H NMR spectrum: 7.75 and 8.23 (d, d 2 H, the triazole protons), 4.60 (q, $J = 7.0$ Hz, 2 H, $\text{CH}_2\text{—CH}_3$), and 1.50 (t, 3 H, CH_2CH_3). The distillation residue contains the unreacted starting substances besides 1-ethoxycarbonyl-3,4-dimethoxycarbonyl-1,2,3-triazole (*VIIc*). ^1H NMR spectrum: 4.62 (q, 2 H, $\text{CH}_2\text{—CH}_3$), 3.96 and 4.04 (s, s, 6 H $2 \times \text{COOCH}_3$), 1.50 (t, $J = 7.0$ Hz, 3 H, $\text{CH}_2\text{—CH}_3$).

Cycloaddition of *IVd* to *I*

A mixture of 1.5 g (10 mmol) azide *IVd*, 2.1 g (10 mmol) *I*, and 20 ml ether was left to stand at room temperature 16 h to give 1.9 g (64%) 1-ethoxycarbonyl-4,5-dimethoxycarbonyl-1,2,3-triazole (*VIII d*) (m.p. 122–123°C, ref.⁷ m.p. 124°C). ^1H NMR spectrum: 5.46 (s, 2 H, CH_2), 4.28 (q, $J = 7.0$ Hz, 2 H, $\text{CH}_2\text{—CH}_3$), 4.0 (s, 6 H, $2 \times \text{COOCH}_3$), and 1.30 (t, 3 H, $\text{CH}_2\text{—CH}_3$), and 0.16 g (11%) 1-ethoxycarbonylmethyl-1,2,3-triazole (*VI d*). ^1H NMR spectrum: 7.71 and 7.89 (d, d, $J = 2.0$ Hz, 2 H, the triazole protons), 5.24 (s, 2 H, CH_2), 4.25 (q, $J = 7.0$ Hz, 2 H, $\text{CH}_2\text{—CH}_3$)₁ and 1.26 (t, 3 H, $\text{CH}_2\text{—CH}_3$).

Cycloaddition of Ethyl Diazoacetate to *I*

A mixture of 1.14 g (10 mmol) ethyl diazoacetate, 2.1 g (10 mmol) *I*, and 20 ml ether was left to stand at room temperature 16 h. The mixture was concentrated to one half of its original volume to give 2.5 g (97%) 5-ethoxycarbonyl-3,4-dimethoxycarbonylpyrazole (*XVII*), m.p. 97–98°C (ref.⁹ m.p. 98°C). ^1H NMR spectrum: 4.41 (q, $J = 7.0$ Hz, 2 H, $\text{CH}_2\text{—CH}_3$), 3.94 (s, 6 H, $2 \times \text{COOCH}_3$), and 1.35 (t, 3 H, $\text{CH}_2 \times \text{CH}_3$).

Cycloaddition of *Va* to *II*

A mixture of 1.13 g (5 mmol) nitron *Va*, 0.72 g (5 mmol) *II*, and 30 ml benzene was left to stand at room temperature 48 h. After concentrating in vacuum and trituration with 30 ml ether, a practically quantitative yield of the mixture 62 : 38 of the two adducts *VIII a* and *VIII b* was obtained. The former adduct *VIII a* was isolated by crystallization from dichloromethane, m.p. 184–186°C. For $\text{C}_{24}\text{H}_{19}\text{NO}_3$ (369.4) calculated: 78.03% C, 5.18% H, 3.79% N; found: 78.14% C, 5.19% H, 3.83% N. UV spectrum, λ_{max} (log ϵ): 247 nm (3.34). Mass spectrum, m/z 369 (M^+). ^1H NMR spectrum: 8.03–8.28 and 6.90–7.23 (m, 14 H, aromatic), 5.33 and 5.38 (s, s, 2 H,

4-H and 9-H), 4.73 (d, $J_{3a,9a} = 7.0$ Hz, 1 H, 9a-H), 4.70 (d, $J_{3a,3} = 7.0$ Hz, 3-H), and 3.28 (apparent t, 1 H, 3a-H).

The mother liquid contains the *exo-endo* stereoisomer *VIIIb*. ^1H NMR spectrum: 6.90–8.20 (m, 14 H, aromatic), 5.43 (s, 1 H, 3-H), 5.23 (s, 2 H, 4-H and 9-H), 5.00 (d, $J_{3a,9a} = 8.0$ Hz, 1 H, 9a-H), and 3.40 (d, 1 H, 3a-H).

Cycloaddition of *Vb* to *II*

A mixture of 1.0 g (5 mmol) nitrene *Vb*, 0.72 g (5 mmol) *II*, and 65 ml ether was treated as in the previous case to give 0.6 g (35%) *VIIIc*, m.p. 159–161°C (cyclohexane–ether, 1 : 2). For $\text{C}_{23}\cdot\text{H}_{19}\text{NO}_2$ (341.4) calculated: 80.91% C, 5.61% H, 4.10% N; found: 80.82% C, 5.60% H, 4.30% N. UV spectrum λ_{max} (log ϵ): 253 nm (3.06). Mass spectrum, m/z 341 (M^+). ^1H NMR spectrum: 6.93–7.48 (m, 14 H, aromatic), 5.30 and 5.39 (s, s, 2 H, 4-H and 9-H), 4.64 (d, $J_{3a,9a} = 7.0$ Hz, 1 H, 9a-H), 4.15 (d, $J_{3a,3} = 7.0$ Hz, 1 H, 3-H), and 2.96 (apparent t, 1 H, 3a-H). ^{13}C NMR spectrum: 149.11, 145.15, 141.44, 139.49, 129.03, 128.38, 128.12, 127.86, 127.54, 127.21, 124.10, 121.04, 119.81, and 119.22 (aromatic carbon atoms), 82.77 (d, $\text{C}_{(9a)}$), 82.12 (d, $\text{C}_{(9)}$), 80.43 (d, $\text{C}_{(4)}$), 74.26 (d, $\text{C}_{(3)}$), 62.95 (d, $\text{C}_{(3a)}$).

Cycloaddition of *IVa* to *II*

A mixture of 0.68 g (5 mmol) azide *IVa*, 0.77 g (5 mmol) *II*, and 20 ml ether was left to stand at room temperature 18 h to give 1.30 g (89%) *IXa*, m.p. 120–122°C (ether). For $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}_3$ (281.3) calculated: 64.05% C, 3.94% H, 14.94% N; found: 64.14% C, 4.12% H, 14.83% N. UV spectrum, λ_{max} (log ϵ): 341 nm (3.37). Mass spectrum, m/z 253 ($\text{M}^+ - \text{N}_2$). ^1H NMR spectrum, 9.43 (s, 1 H, CHO), 7.25–7.50 (m, 5 H, 3'-H, furane and aromatic protons), 6.28 (d, $J_{3',4'} = 3.8$ Hz, 1 H, 4'-H (furane)), 5.63 and 5.75 (s, s, 2 H, 4-H and 9-H), 5.18 (d, $J_{3a,9a} = 8.0$ Hz, 1 H, 3a-H), and 4.36 (d, 1 H, 9a-H). ^{13}C NMR spectrum: 174.71 (d, CHO), 153.98 (s, $\text{C}_{(2')}$), 146.71 and 142.35 (s, the aromatic bridgehead carbon atoms), 128.38, 128.25, 127.41, 121.37, and 120.76 (d, $\text{C}_{(5)}$, $\text{C}_{(6)}$, $\text{C}_{(7)}$, $\text{C}_{(8)}$, $\text{C}_{(3')}$, and $\text{C}_{(4')}$), 93.04 (s, $\text{C}_{(5')}$), 89.79 (d, $\text{C}_{(3a)}$), 82.77 and 82.51 (d, $\text{C}_{(4)}$ and $\text{C}_{(9)}$), 60.23 (d, $\text{C}_{(9a)}$). ^{13}C NMR spectrum of compound *VIa*, the figures with apostrophes refer to the furane rings: 176.85 (d, CHO), 149.05 (s, $\text{C}_{(2')}$), 134.36 (s, $\text{C}_{(5')}$), 123.84 (d, triazole), 121.82 (d, $\text{C}_{(3')}$), 100.32 (d, $\text{C}_{(4')}$). ^{13}C NMR spectrum of compound *VIIa*: 177.05 (d, CHO), 159.44 and 158.14 (s, COOCH_3), 150.34 (s, $\text{C}_{(2')}$), 144.82 (s, $\text{C}_{(4)}$), 138.40 (s, $\text{C}_{(5)}$), 131.74 (s, $\text{C}_{(5')}$), 121.68 (d, $\text{C}_{(3')}$), 105.48 (d, $\text{C}_{(4')}$), 54.38 and 53.08 (q, CH_3).

Cycloaddition of *IVb* to *II*

A mixture of 0.81 g (5 mmol) azide *IVb*, 0.72 g (5 mmol) *II*, and 25 ml tetrahydrofuran was left to stand at room temperature 9 h to give 1.10 g (81%) *IXb*, m.p. 202–204°C (tetrahydrofuran). For $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_3$ (308.3) calculated: 62.33% C, 3.92% H, 18.18% N; found: 62.12% C, 4.01% H, 18.27% N. UV spectrum, λ_{max} (log ϵ): 353 nm (3.22) and 293 nm (sh, 2.90). Mass spectrum, m/z 280 ($\text{M}^+ - \text{N}_2$). ^1H NMR spectrum: 7.19–7.75 and 8.13–8.41 (m, 8 H, aromatic), 5.69 and 5.80 (s, s, 2 H, 4-H and 9-H), 5.26 (d, $J_{3a,9a} = 9.0$ Hz, 1 H, 3a-H), and 4.43 (d, 1 H, 9a-H).

Cycloaddition of *IVd* to *II*

A mixture of 0.65 g (5 mmol) azide *IVd*, 0.72 g (5 mmol) *II*, and 15 ml ether was left to stand at room temperature 16 h to give 1.25 g (88%) *IXd*, m.p. 121–122°C (dichloromethane). For $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_3$ (273.3) calculated: 61.53% C, 5.53% H, 15.38% N; found: 61.35% C, 5.51% H,

15.49% N. ^1H NMR spectrum: 7.23–7.48 (m, 4 H, aromatic), 5.48 and 5.73 (s, s, 2 H, 4-H and 9-H), 5.06 (d, $J_{3a,9a} = 9.0$ Hz, 1 H, 3a-H), 4.38 and 4.83 (d, d, $J = 19$ Hz, 2 H, $\text{CH}_2\text{—CO}$), 4.25 (q, $J = 8.0$ Hz, 2 H, $\text{CH}_2\text{—CH}_3$), 3.89 (d, 1 H, 9a-H), and 1.3 (t, 3 H, $\text{CH}_2\text{—CH}_3$).

Cycloaddition of Ethyl Diazoacetate to II

A mixture of 0.57 g (5 mmol) ethyl diazoacetate, 0.72 g (5 mmol) II, and 30 ml ether was left to stand at room temperature 72 h to give 0.45 g (36%) XI, m.p. 153–156°C (dichloromethane). For $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_3$ (258.3) calculated: 65.10% C, 5.46% H, 10.85% N; found: 65.23% C, 5.49% H, 11.00% N. UV spectrum, λ_{max} (log ϵ): 298 nm (3.02). ^1H NMR spectrum: 7.08–7.43 (m, 4 H, aromatic), 6.50 (s, br, 1 H, NH), 5.39 and 5.63 (s, s, 2 H, 4-H and 9-H), 4.15–4.50 (m, 3 H, 9a-H and $\text{CH}_2\text{—CH}_3$), 3.68 (d, $J_{3a,9a} = 9.0$ Hz, 1 H, 3a-H), and 1.36 (t, $J = 9.0$ Hz, 3 H, $\text{CH}_2\text{—CH}_3$). ^{13}C NMR spectrum: 192.59 (s, $\text{C}=\text{O}$), 145.32 (s, $\text{C}_{(3)}$), 142.39 and 138.59 (s, aromatic), 127.71, 127.30, 120.22, and 120.04 (d, $\text{C}_{(5)}$, $\text{C}_{(6)}$, $\text{C}_{(7)}$, and $\text{C}_{(8)}$), 86.64 (d, $\text{C}_{(9)}$), 82.31 (d, $\text{C}_{(4)}$), 68.56 (d, $\text{C}_{(9a)}$), 61.07 (d, $(3a)$), 55.52 (t, CH_2), 14.39 (q, CH_3).

Cycloaddition of Benzenenitril Oxide to II

During 1 h, 2.5 ml (18 mmol) triethylamine was added to a mixture of 2.50 g (16 mmol) benzenehydroxamic acid chloride, 2.3 g (16 mmol) II, and 20 ml ether at 0–5°C. The mixture was stirred overnight at room temperature, the separated triethylammonium chloride was collected by filtration, and the filtrate gave 3.2 g (77%) Xa, m.p. 170–172°C. For $\text{C}_{17}\text{H}_{13}\text{NO}_2$ (263.3) calculated: 77.55% C, 4.98% H, 5.32% N; found: 77.61% C, 5.14% H, 5.51% N. UV spectrum λ_{max} (log ϵ): 267 nm (3.39). ^1H NMR spectrum: 7.25–7.84 (m, 5 H, aromatic), 5.50 and 5.62 (s, s, 2 H, 4-H and 9-H), 5.06 (d, $J_{3a,9a} = 8.0$ Hz, 1 H, 9a-H), and 4.01 (d, 1 H, 3a-H). ^{13}C NMR spectrum: 153.98 (s, $\text{C}=\text{N}$), 144.85 and 141.34 (s, aromatic bridgehead carbon atoms), 130.11, 128.94, 128.64, 127.88, 127.59, 126.71, 121.00, and 119.75 ($\text{C}_{(5)}$, $\text{C}_{(6)}$, $\text{C}_{(7)}$, $\text{C}_{(8)}$, and C_6H_5), 87.63 (d, $\text{C}_{(9a)}$), 85.82 (d, $\text{C}_{(9)}$), 80.97 (d, $\text{C}_{(4)}$), 58.55 (d, $\text{C}_{(3a)}$).

Cycloaddition of Benzenenitril Oxide to III

A mixture of 1.0 g (3.6 mmol) III, 0.9 g (5.8 mmol) benzenehydroxamic acid chloride, 20 ml dioxane was treated with 1.0 ml (7.2 mmol) triethylamine as in the previous case, and the reaction mixture was submitted to column chromatography (silica gel; chloroform–ether 1 : 2 as eluent, to give 0.05 g dimer of benzenenitril oxide besides 0.4 g (28%) XV, m.p. 222–224°C. For $\text{C}_{21}\text{H}_{19}\text{.NO}_7$ (397.4) calculated: 63.47% C, 4.82% H, 3.53% N; found: 63.51% C, 5.04% H, 3.42% N. UV spectrum λ_{max} (log ϵ): 268 nm (3.15). ^1H NMR spectrum (hexadeuteriodimethyl sulphoxide), 7.38–7.58 and 7.75–7.93 (m, 5 H, aromatic), 6.60 (s, 2 H, 8-H and 9-H), 5.13 (d, $J_{4,13} = 7.0$ Hz: 1 H, 13-H), 5.14 and 5.35 (s, s, 2 H, 5-H and 12-H), 4.84 and 4.98 (s, s, 2 H, 7-H and 10-H), 4.35 (d, 1 H, 4-H), 3.51 and 3.56 (s, s, 6 H, $2 \times \text{COOCH}_3$).

Cycloaddition of IVa to III

A mixture of 1.4 g (5 mmol) III, 0.7 g (5 mmol) azide IVa, and 20 ml chloroform was left to stand at room temperature 16 h. The reaction mixture was evaporated, and the evaporation residue was crystallized from acetone to give 1.5 g (73%) XIVa, m.p. 124–126°C. For $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_8$ (415.3) calculated: 54.94% C, 4.13% H, 10.12% N; found: 54.81% C, 4.22% H, 10.21% N. UV spectrum λ_{max} (log ϵ): 348 nm (3.31). ^1H NMR spectrum: 9.38 (s, 1 H, CHO), 7.28 (d, $J_{3',4'} = 3.8$ Hz, 1 H, 3'-H furane), 6.56 and 6.74 (d, d, $J_{8,9} = 6.0$ Hz, 2 H, 8-H and 9-H), 6.21 (d, 1 H, 4'-H furane), 5.29 (d, $J_{4,13} = 0$ Hz, 1 H, 4-H), 5.23 and 5.28 (s, s, 2 H, 5-H and 12-H), 4.95 and 5.03 (s, s, 2 H, 7-H and 10-H), 4.49 (d, 1 H, 13-H), and 3.68 (s, 6 H, $2 \times \text{COOCH}_3$).

Cycloaddition of *IVb* to *III*

A mixture of 0.3 g (1.1 mmol) *III*, 0.18 g (1.1 mmol) azide *IVb*, and 10 ml chloroform was treated in the same way as above, and 0.35 g (73%) *XIVb* was obtained, m.p. 220–222°C (acetone). For $C_{20}H_8N_4O_8$ (432.3) calculated: 55.57% C, 1.87% H, 12.96% N; found: 55.61% C, 1.91% H, 13.08% N. UV spectrum, λ_{max} (log ϵ): 357 nm (3.35). 1H NMR spectrum (hexadeuteriodimethyl sulphoxide): 7.61 and 7.99 (d, d, $J = 10$ Hz, 4 H, aromatic), 6.54 and 6.73 (d, d, $J = 6.5$ Hz, 2 H, 8-H and 9-H), 5.38 (d, $J_{4,13} = 9.0$ Hz, 1 H, 4-H), 5.26 and 5.43 (s, s, 2 H, 5-H and 12-H), 4.93 and 5.13 (s, s, 2 H, 7-H and 10-H), 4.50 (d, 1 H, 13-H), 3.53 and 3.56 (s, s, 6 H, $2 \times COOCH_3 \times COOCH_3$).

Thermolysis of *IXa*

Adduct *IXa* (0.27 g, 1 mmol) was heated in benzene at 110°C (the bath temperature) in a glass autoclave 30 min (until the end of liberation of nitrogen). Evaporation in vacuum and trituration (ether) gave 0.20 g (81%) mixture of *XII* and *XIII* in the ratio 63 : 37. The column chromatography of the mixture (silica gel; cyclohexane–ethyl acetate 3 : 5 as eluent) gave pure *XII* in the yield 0.10 g (50%), m.p. 65–67°C. For $C_{15}H_{11}NO_3$ (253.2) calculated: 71.14% C, 4.37% H, 5.33% N; found: 71.16% C, 4.41% H, 5.61% N. 1H NMR spectrum: 9.25 (s, 1 H, CHO), 7.05 to 7.43 (m, 5 H, aromatic protons and 3'-H furane), 5.75 (d, $J_{3',4'} = 4.0$ Hz, 1 H, 4'-H furane), 5.34 (s, 2 H, 3-H and 8-H), and 3.08 (s, 2 H, 2-H and 9-H). Furthermore, compound *XIII* was obtained which was contaminated with *XII*. 1H NMR spectrum: 9.21 (s, 1 H, CHO), 7.25 to 7.37 (m, 4 H, aromatic), 7.21 (d, $J_{3',4'} = 3.5$ Hz, 1 H, 3'-H furane), 5.53 (d, 1 H, 4'-H furane), 5.38 and 5.41 (s, s, 2 H, the bridgehead protons), and 3.8 (d, $J = 1.5$ Hz, 2 H, CH_2).

Thermolysis of *IXb*

0.2 g (0.64 mmol) *IXb* in 10 ml toluene was heated at 160°C (autoclave) 4 h. Evaporation in vacuum and subsequent sublimation in vacuum (120°C/0.33 kPa) gave 0.1 g (81%) 1-(4-nitrophenyl)-1,2,3-triazole, m.p. 205–207°C (ref.² m.p. 207°C).

Thermolysis of Adduct *XIVa*

Adduct *XIVa* (0.5 g, 1.2 mmol) was heated in benzene (100°C, 1 h), the solvent was evaporated, and the residue was crystallized from dichloromethane–ether to give 0.2 g (53.7%) *XVI*, m.p. 158–161°C. For $C_{19}H_{17}NO_8$ (387.3) calculated: 58.91% C, 4.42% H, 3.62% N; found: 58.74% C, 4.53% H, 3.79% N. 1H NMR spectrum: 9.18 (s, 1 H, CHO), 7.10 (d, $J_{3',4'} = 4.0$ Hz, 1 H, 3'-H furane), 6.65 (s, 2 H, 6-H and 7-H), 5.59 (d, 1 H, 4'-H furane), 4.95 (s, 4 H, 3-H), 5-H, 8-furane), 6.65 (s, 2 H, 6-H and 7-H), 5.59 (d, 1 H, 4'-H furane), 4.95 (s, 4 H, 3-H, 5-H, 8-H, and 10-H), 3.63 (s, 6 H, $2 \times COOCH_3$), and 3.08 (s, 2 H, 2-H and 11-H).

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