SITE-SELECTIVITY OF 1,3-DIPOLAR CYCLOADDITIONS TO 2,3-DIMETHOXYCARBONYL-7-OXABICYCLO[2,2,1]-HEPTADIENE*

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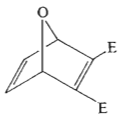
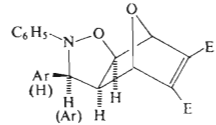
Site-selectivity of dipolar cycloaddition to the title compound was studied. Azomethine *X* afforded a 1 : 1 cycloadduct *XI* at the deactivated double bond at room temperature; upon thermolysis at 110°C it afforded the acetylated enamine *XIII*, which was formed *via* a direct cycloaddition at the mentioned temperature. The cycloaddition course was investigated in various solvents; the enamine *XIV* formed by solvolysis of *XIII* was the final product in methanol. Cycloaddition of the title compound to azides, benzoylnitrile N-oxide and C-acetyl-N-phenylnitrilimine furnished the product of cycloreversion instead of the not isolable 1 : 1 cycloadducts. 5-Azido-2-furancarbaldehyde and 4-nitrophenylazide yielded cycloaddition products to both multiple bonds in an approximately 1 : 1 ratio; HN_3, tosylazide, benzoylnitrile N-oxide and C-acetyl-N-phenylnitrilimine gave the addition products to the deactivated double bond. The solvent-effect of site-selectivity of 1,3-dipolar cycloaddition was investigated and the title compound was found to be an excellent synthetic equivalent for acetylene and dimethyl butinedioate.

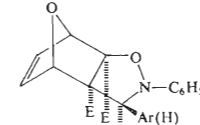
1,3-Dipolar cycloadditions of 2,3-dimethoxycarbonyl-7-oxabicyclo[2,2,1]heptadiene (*I*) to arylazides, benzonitrile N-oxide, diphenylnitrilimine and nitrones show various site-selectivity[1-3]. Arylazides and benzonitrile N-oxides attack preferentially electron deficient double bond[1,2] and the intermediate cycloadducts *IV*, *V* undergo the Diels-



I



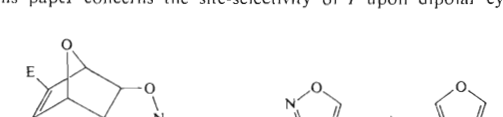
II



III

* Part XI in the series 1,3-Dipolar Cycloaddition to Heterocycles; Part X; Chem. Zvesti, in press.

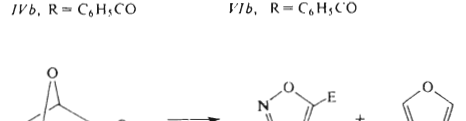
-Alder cycloreversion (Scheme 1) to form the furan derivative *IX*, 3,4-dimethoxycarbonylfuran (*VIII*), or heterocycles *VI*, *VII*. Our preceding paper[3] dealt with cycloadditions of C-benzoyl-N-phenyl-, and C,N-diphenylnitrone to *I* resulting in the stable *endo*- and *exo*-adducts *II* and *III* (addition to the first or second the double bond). This paper concerns the site-selectivity of *I* upon dipolar cycloadditions



IVa, R = C_6H_5
IVb, R = C_6H_5CO

VIa, R = C_6H_5
VIb, R = C_6H_5CO

VIII



Va, R = C_6H_5
Vb, R = C_6H_5CO

VIIa, R = C_6H_5
VIIb, R = C_6H_5CO

IX

E = $COOCH_3$

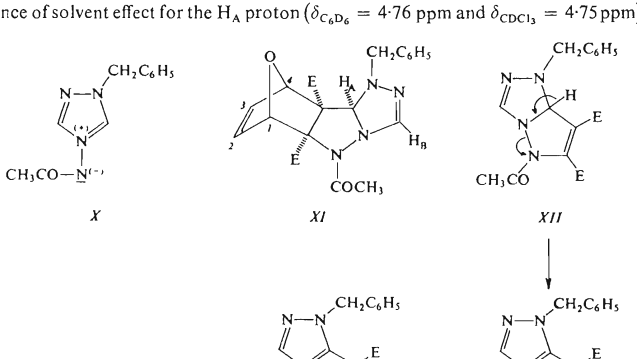
SCHEME 1

to 1-benzyl-4-N-acylimino-1,2,4-triazolylbetaine (*X*), electron deficient azides *XVa–XVd*, benzoylnitrile N-oxide and C-acetyl-N-phenylnitrilimine (*XX*). This paper was aimed to find a suitable 1,3-dipole directing the cycloaddition to the unsubstituted double bond of *I* in order to obtain β-substituted furan derivatives difficulty preparable by routine synthetic methods.

Although cycloadditions were carried out in a molar ratio, formation of any bis-adduct has not been observed. Azomethine *X* reacted with *I* yielding the cycloadduct *XI* (Scheme 2), whereas other reactants afforded five-membered heterocycles arising from an immediate cycloreversion.

Formation of the cycloadduct *XI* was proved by the mass spectrum and elemental analysis. The ^1H NMR spectrum provided evidence for the cycloaddition to proceed exclusively to the deactivated double bond by the presence of two olefinic proton doublets at 6·77 and 6·31 ppm interacting with the bridge-head protons $J_{1,2}$ = 1·8 Hz,

this being backed by a decoupling experiment at 448 Hz (1-H and 4-H). The triazoline proton H_B was located in the aromatic region as a distinguished singlet at 7·01 ppm. The little difference between chemical shifts of methoxycarbonyl groups (3·71 and 3·61 ppm) indicated the *exo*-arrangement of the H_A proton. Another argument was the absence of solvent effect for the H_A proton ($\delta_{C_6D_6}$ = 4·76 ppm and δ_{CDCl_3} = 4·75 ppm).

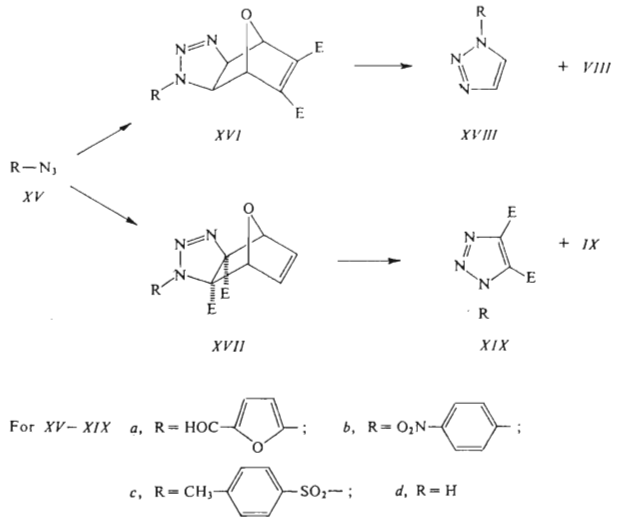


SCHEME 2

The ^{1}H NMR spectrum of the crude reaction mixture did not contain any signal indicative of cycloaddition to the unsubstituted double bond in *I*. Formation of an isolable cycloadduct *XI* during the reaction with *I* is the second known case. The only stable cycloadducts hitherto reported were those prepared from nitrones as 1,3-dipoles[1-3]. The mass spectrum of compound *XI* showed also fragments arising from cycloreversion at m/z 358 ($M^{+\cdot} - 68$ and 68 (protonated furan). Therefore, the thermal stability of *XI* was of interest; compound *XIII*, identical with that obtained by cycloaddition of the azomethine imine *X* with dimethyl butinedioate[4] was synthesized by heating *XI* in an autoclave under nitrogen in a 6% yield. That is why the cycloaddition of azomethine imine *X* with *I* was studied in more detail employing various solvents and elevated temperature. High yield (50–61%) of *XIII* was achieved in toluene, acetonitrile, tetrachloromethane, nitromethane, and *n*-butanol; its formation could be rationalized as follows: Adduct *XI*, originating from the primary 1,3-dipolar cycloaddition, afforded *via* an allowed cycloreversion the heterocycle *XII*, which, upon a subsequent 1,3-sigmatropic transition restored the aromatic

1,2,4-triazole system. An alternative pathway, *i.e.* the primary cycloreversion of *I* followed by a cycloaddition to the originating dimethyl butinedioate was not presumed, since yields of this reaction are much higher than those of *X* with dimethyl butinedioate itself, and, at 70°C the intermediate cycloadduct was even isolated and thermolyzed to yield *XIII*. The oxabicyclic derivative *I* can be, however, employed as a synthon with masked triple bond which is much more reactive than dimethyl butinedioate due to a tension. Moreover, the reaction course is more selective, since only 1 : 1 products were obtained; dimethyl butinedioate gave 1 : 2 and 1 : 3 adducts as by-products.

Reaction of *X* with *I* in methanol had an anomalous course; instead of the expected enamine *XIII* compound *XIV* was obtained in a 74% yield; its structure was adduced from mass, IR and ^{1}H NMR data. Signals in the ^{1}H NMR spectrum are indicative of aromatic protons (singlet at 7·27 ppm), methylene protons at the benzyl group (singlet at 5·13 ppm) and two methoxycarbonyl groups (singlets at 3·50 and 3·43 ppm). The triazole system was evidenced by the presence of the triazole

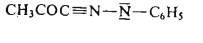


SCHEME 3

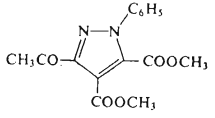
proton at 7·89 ppm (ring current effect). The IR spectrum showed two stretching vibrations of the NH_2 group at 3 477 and 3 322 cm^{-1}. The formation of *XIV* was explained by solvolysis of the ethinamine *XIII* by methanol and proved by heating of *XIII* in methanol affording *XIV* in a 85% yield.

Considering the results of cycloaddition of *I* with nitrones[3] and with azomethine imine *X*, and also those[1,2] reporting the cycloadditions with nitrile oxides, azides and nitrilimines, the site-selectivity to *I* can be rationalized by a simple qualitative perturbation theory for cycloaddition reactions[5,6]. The 1,3-dipolar cycloaddition to the substituted (deactivated) double bond in *I* is controlled by the limit HOMO(1,3-dipole)-LUMO(*I*) interaction, and the cycloaddition to the unsubstituted double bond in *I* by limit LUMO-(1,3-dipole)-HOMO(*I*) interaction. The benzoyl group in C-benzoyl-N-phenylnitrone lowers its LUMO energy in comparison with C-phenyl-N-methylnitrone and therefore, also the unsubstituted double bond is attacked[3]. Propargyl-type 1,3-dipoles (nitrile oxides, nitrilimines, azides) gave unstable cycloadducts, which cycloreversed to the corresponding five-membered heterocycles and furan or 3,4-dimethoxycarbonylfuran. For a dipole preferentially attacking the unsubstituted double bond azides were taken as model substrances, as well (*cf.* Scheme 3). Since Reinhoudt and coworkers[1] reported only addition to the substituted deactivated double bond when reacting phenylazide with *I*, we employed azides substituted by an electron-accepting group, which lowers their LUMO energy and consequently, favourizes the limit interaction LUMO(azide)–HOMO(*I*). Reaction of 5-azido-2-furancarbaldehyde (*XVa*) with *I* gave at an ambient temperature 1-(5-formyl-2-furyl)-1,2,3-triazole (*XVIIIa*, 43%), formed from the product of cycloaddition *XVI* to the unsubstituted double bond in *I*, and 1-(5-formyl-2-furyl)-4,5-dimethoxycarbonyl-1,2,3-triazole (*XIXa*, 54%), originating from the cycloaddition product *XVII* to the deactivated double bond in *I*. The structure of triazoles was deduced from the ^{1}H NMR signals appearing at 8·25 and 7·88 ppm (for *XVIIIa*), which are indicative of triazole system and those of methoxycarbonyl groups for *XIXa*. Triazole *XVIIIa* was prepared[7] from azide *XVa* and acetylene at 6 MPa and 20°C in a 11% yield only. The ratio of triazole *XVIIIa* to *XIXa* was found to be 43 : 57 (ether) in favour of cycloaddition to the deactivated double bond. The influence of solvent on their mutual ratio was investigated and results are listed in Table I. The enhanced polarity of the solvent favourizes, as expected, the attack to the unsubstituted double bond; in acetone, however, both derivatives were formed in a virtually equal ratio (51 : 49) in favour of *XVIIIa*. *para*-Nitrophenylazide (*XVb*) afforded triazoles *XVIIIb* and *XIXb* in a 50 : 50 ratio. Simultaneously De Micheli and Gandolfi[2] reported the ratio 51·6 : 48·4 as determined by gas chromatography; our results were obtained from the integrated intensities of the ^{1}H NMR spectrum of the unpurified reaction mixture. The use of azides with electron-accepting substituents (*XVa*, *XVb*) changed the ratio 17·6 : 82·4 for phenylazide (paper[1] reported the ratio 0 : 100) in favour of the cycloaddition to the deactivated double bond to approximately 50 : 50 thus proving

the above-mentioned perturbation theory for 1,3-dipolar cycloadditions to *I*. Cycloaddition of tosylazide (*XVc*) proceeded to the deactivated double bond at room temperature. Isolated were 1-tosyl-4,5-dimethoxycarbonyl-1,2,3-triazole (*XIXc*) in a 65% yield and the unreacted starting tosylazide. The triazole *XIXc* was prepared[8] in a 75% yield (in toluene at 80°C for 192 h) by cycloaddition of tosylazide with dimethyl butinedioate. At room temperature and 150 h of treatment only unreacted tosylazide was isolated[8]. Triazole *XIXb* was synthesized by the same authors by a 24-h reflux of *XVb* with dimethyl butinedioate in benzene. This comparison of cycloaddition to *I* and to dimethyl butinedioate evidenced the already mentioned enhanced reactivity of *I* in reactions with 1,3-dipoles. Cycloaddition of the fundamental azide HN_3 afforded in a 61% yield the cycloaddition product to the deactivated double bond *XIXd* only, which was already obtained by reaction of HN_3 with butinedioate and esterification[9].



XX



XXI

The site-selectivity 100 : 0 in favour of the deactivated double bond of *I* was published[2] for cycloaddition to C,N-diphenylnitrilimine. Therefore, C-acetyl-N-phenylnitrilimine (*XX*), having its LUMO energy[10] lowered by the acetyl group was chosen for the 1,3-dipole. We likewise isolated the cycloaddition product of nitrilimine to the deactivated double bond, namely 1-phenyl-3-acetyl-4,5-dimethoxycarbonylpyrazole (*XXI*, 81%), prepared already by Gotthard and coworkers[11] in two ways.

TABLE I

Ratio of cycloaddition products (%) obtained from *XVc* and *I* in various solvents

Solvent	E_T	*XVIIIa*	*XIXa*
Benzene	34·5	42	58
Ether	34·6	43	57
Tetrahydrofuran	37·4	44	56
Chloroform	39·3	42	58
Dichloromethan	41·1	50	50
Acetone	42·2	51	49

A site-selectivity 75 : 25 was observed upon cycloaddition of benzenenitrile N-oxide[1,2]. Aiming to get the cycloaddition shifted in the required direction, benzoylnitrile N-oxide was selected as the 1,3-dipole; the 3-benzoyl-4,5-dimethoxycarbonylisoxazole (*VIIb*) to 3-benzoylisoxazole (*VIb*) ratio was found to be 55 : 45 in favour of the cycloaddition to deactivated double bond. In contrast to sulfo group in tosylazide, the directly bound carbonyl group in benzoylnitrile N-oxide lowered the site-selectivity from 75 : 25 to 55 : 45; electron-accepting carbonyl, or nitro groups on arylated and heteroarylated azides shifted the ratio to 50%. The exclusive cycloaddition to unsubstituted double bond to *I* would require at least two deactivating groups. This paper showed the advantage of the oxabicyclic derivative *I* as a synthetic equivalent of acetylene and dimethyl butinedioate in organic synthesis.

EXPERIMENTAL

Melting points were uncorrected. Electron impact mass spectra were measured with an MS 902 S apparatus at a 70 eV ionizing energy. The ^{1}H NMR spectra in deuteriochloroform or deuteriobenzene containing tetramethylsilane were recorded with a Tesla BS 487 C spectrometer operating at 80 MHz. UV spectra of methanolic solution were taken with Specord UV VIS spectrophotometer in temperated cells, and IR spectra of chloroform solutions with Unicam SP 100 apparatus. Derivative *I* was prepared according to[3], azomethine imine (*X*) according to[12], 5-azido-2-furancarbaldehyde (*XVa*) according to[7], 4-nitrophenylazide (*XVb*) according to[13], tosylazide (*XVc*) according to[14], C-acetyl-N-phenylnitrilimine (*XX*) according to[15], benzoylnitrile N-oxide according to[16].

Cycloaddition of *I* to *X*

a) Compound *I* (2·1 g, 10 mmol) and azomethine imine (*X*) (2·1 g, 10 mmol) in toluene were stirred at 60°C in a stoppered flask for 60 h. The unreacted *X* (1·2 g, 57%) was filtered off the next day, the filtrate was concentrated and separated on a silica gel-packed column with cyclohexane–ethyl acetate 6 : 1. Yield 1·6 g (83%) of *X* to the azomethine imine, m.p. 129—130°C. For $C_{21}H_{22}N_4O_6$ (426·3) calculated: 59·19% C, 5·16% H, 13·14% N; found: 59·31% C, 5·27% H, 13·45% N. ^{1}H NMR spectrum (C^2HCl_3): 7·30—7·40 (m, 5 H, aromatic protons), 7·01 (s, 1 H, H_B), 6·77 (d, d, $J_{2,3}$ = 5·5 Hz, $J_{1,2}$ = 1·8 Hz, 1 H, 2-H), 6·31 (d, d, $J_{2,3}$ = 5·5 Hz, $J_{3,4}$ = = 1·8 Hz, 1 H, 3-H), 5·60 (d, $J_{1,2}$ = 1·8 Hz, 1 H, 1-H), 4·58 (d, $J_{3,4}$ = 1·8 Hz, 1 H, 4-H), 4·75 (s, 1 H, H_A), 4·20 (d, d, 2 H, CH_2), 3·61 and 3·71 (s, s, 6 H, 2 × $COOCH_3$), 1·96 (s, 3 H, $COCH_3$). ($C_6^2H_6$) 7·07—7·25 (m, 5 H, aromatic protons), 6·89 (s, 1 H, H_B), 6·74 (d, d, 1 H, 2-H), 6·12 (d, d, 1 H, 3-H), 5·90 (d, 1 H, 1-H), 4·56 (d, 1 H, 4-H), 4·76 (s, 1 H, H_A), 4·08 (d, d, 2 H, CH_2), 3·26 and 3·51 (s, s, 6 H, 2 × $COOCH_3$), 2·16 (s, 3 H, $COCH_3$). UV spectrum λ_{max}, nm (log ε): 252 (3·63). Mass spectrum *m/z*: 426 ($M^{+\cdot}$), base peak 91 ($C_6H_5CH_2^+$), fragments of cycloreversion 358 ($M^{+\cdot}$-furan) and 68 (furan)$^+$.

b) The mixture obtained by procedure *a* was heated in a glass autoclave at 110°C for 24h. The unreacted *X* (1·1 g, 52%) was filtered off and the residue was crystallized from ether. Yield 1·2 g (61%) of the triazole *XIII*. This product was also obtained under the same reaction conditions, but using acetonitrile, tetrachloromethane, nitromethane and n-butanol in 55, 60, 55 and 50% yield, respectively.

c) A solution of *X* (1 g, 4·6 mmol), and (1 g, 4·7 mmol) in methanol was heated in a glass autoclave at 110°C for 14 h. The product *XIV* was filtered off after cooling; yield 1·39 g (74%), m.p. 182–184°C. For $C_{15}H_{16}N_4O_4$ (316·3) calculated: 56·95% C, 5·09% H, 17·71% N; found: 17·82% N. ^{1}H NMR spectrum (C^2HCl_3): 7·89 (s, 1 H, triazole proton), 7·27 (s, 5 H, aromatic protons), 5·13 (s, 2 H, CH_2), 3·50 and 3·43 (s, s, 6 H, 2 × $COOCH_3$). Mass spectrum *m/z*: 316 ($M^{+\cdot}$), base peak 91 ($C_6H_5CH_2^+$). IR spectrum (chloroform): 3 477 and 3 322 cm^{-1} (NH_2). Triazole *XIV* was obtained by heating the methanolic solution (6 ml) of *XIII* (0·2 g, 0·56 mmol) under pressure at 110°C for 20 h. Yield 0·15 g (85%).

Thermolysis of Adduct *XI*

Monoadduct *XI* (0·1 g, 0·23 mmol) was heated in a glass autoclave at 100°C for 1 h under nitrogen atmosphere. The triazole derivative *XIII*, m.p. 127–128°C, (ref.[4] 129–130°C) was obtained in 59% yield by chromatography over silica gel with benzene as an eluent. ^{1}H NMR spectrum (C^2HCl_3): 11·13 (s, br, 1 H, NH), 7·93 (s, 1 H, triazole proton), 7·28 (s, 5 H, aromatic protons), 5·26 (s, 2 H, CH_2), 3·63 and 3·40 (s, s, 6 H, 2 × $COOCH_3$), 2·24 (s, 3 H, $COCH_3$) is consistent with that of *XIII* prepared by another procedure[4].

Cycloaddition of Benzoylnitrile N-Oxide to *I*

Triethylamine (0·48 g, 0·67 ml) was added during 1 h to a stirred and ice-cooled solution of 2-phenyl-2-oxoethanehydroxamoyl chloride (0·82 g, 4·9 mmol) and *I* (2·1 g, 10 mmol) in ether (50 ml). The separated triethylammonium chloride was filtered off after 16 h, washed with ether and the filtrate was evaporated to give an oil (2·67 g), the ^{1}H NMR spectrum of which indicated the 55 : 45 ratio of adducts *VIIb* and *VIb*. Column chromatography (SiO_2, 100 g, eluent cyclohexane–ethyl acetate 8 : 3) afforded:

3-*Benzoylisoxazole* (VIb), yield 0·25 g (30%). For $C_{10}H_7NO_2$ (173·2) calculated: 69·36% C, 4·07% H, 8·09% N; found: 69·91% C, 3·88% H, 8·14% N. ^{1}H NMR spectrum (C^2HCl_3): 8·50 (d, J = 2·0 Hz, 1 H, 5-H), 8·27 (d, d, 2 H, aromatic protons), 7·43 (m, 3 H, aromatic protons), 6·83 (d, J = 2·0 Hz, 1 H, 4-H).

3-*Benzoyl*-4,5-*dimethoxycarbonylisoxazole* (VIIb), yield 0·45 g (32%), m.p. 91–92°C. For $C_{14}H_{11}NO_6$ (289·2) calculated: 58·13% C, 3·83% H, 4·84% N; found: 58·34% C, 4·01% H, 4·62% N. ^{1}H NMR spectrum (C^2HCl_3): 8·15 (d, d, 2 H, *o*-aromatic protons), 7·53 (m, 3 H, aromatic protons), 3·87 and 3·99 (s, s, 6 H, 2 × $COOCH_3$). Mass spectrum *m/z*: 289 ($M^{+\cdot}$). In addition, the unreacted *I* (0·35 g) and the furan derivative *VIII* (0·36 g, 41%) were isolated.

Cycloaddition of Azide *XVa* to *I*

The mixture of *XVa* (1·37 g, 10 mmol), *I* (2·10 g, 10 mmol) and ether (20 ml) was left to stand at room temperature and in the dark for 16 h. The separated 1-(5-formyl-2-furyl)-1,2,3-triazole (*XVIIIa* 0·5 g, 31%), had m.p. 127–128°C (ref.[7] 131°C). ^{1}H NMR spectrum (C^2HCl_3): 9·66 (s, 1 H, CHO), 8·25 and 7·88 (d, d, J = 1·0 Hz, 2 H triazole protons), 7·43 (d, $J_{3,4}$ = 3·8 Hz, 1 H, 4-H), 6·95 (d, 1 H, 3-H). The filtrate was concentrated and washed with hexane (6 × 20 ml). The residue was purified by a fractional crystallization from ether to yield another crop of *XVIIIa* (0·2 g, 43% total), and 1-(5-formyl-2-furyl)-4,5-dimethoxycarbonyl-1,2,3-triazole (*XIXa*), m.p. 84–86°C. Yield 1·50 g (54%). ^{1}H NMR spectrum (C^2HCl_3): 9·69 (s, 1 H, CHO), 7·46 (d, $J_{3,4}$ = = 3·5 Hz, 1 H, 4-H), 7·00 (d, $J_{3,4}$ = 3·5 Hz, 1 H, 3-H), 4·05 and 4·01 (s, s, 6 H, 2 × $COOCH_3$). For $C_{11}H_9N_3O_6$ (279·2) calculated: 47·32% C, 3·25% H, 15·05% N; found: 47·51% C, 3·50% H, 14·95% N. Mass spectrum, *m/z*: 279 ($M^{+\cdot}$).

Estimation of the solvent effect: A solution of *XVa* (1 mmol) and *I* (1 mmol) in the respective solvent (10 ml) was allowed to stand at room temperature in the dark for 24 h. The solvent was removed under diminished pressure and the *XVIIIa* to *XIXa* ratio was adduced from the integrated intensities of ^{1}H NMR signals; the results are listed in Table I.

Cycloaddition of *XVb* to *I*

The solution of *XVb* (1·64 g, 10 mmol) and *I* (2·1 g, 10 mmol) in tetrahydrofuran (30 ml) was left to stand at an ambient temperature in the dark for 16 h. The residue, obtained by evaporation of the solvent under reduced pressure and washing with hexane, was chromatographed (SiO_2) with cyclohexane–ethyl acetate (1 : 1). Yield of *XIXb* (1·22 g 39%), m.p. 116—117°C, (ref.[8] 117—118°C). ^{1}H NMR spectrum (C^2HCl_3): 8·45 and 7·80 (d, d, J = 9·0 Hz, 4 H, aromatic protons), 4·02 and 3·97 (s, s, 6 H, 2 × $COOCH_3$) and triazole *XVIIIb*, yield 0·76 g (40%), m.p. 205—207°C (ref.[2] 207°C). ^{1}H NMR spectrum (C^2HCl_3): 8·45 and 8·01 (d, d, J = 9·0 Hz, 4 H, aromatic protons), 8·13 and 7·27 (s, s, 2 H, triazole protons). The *XVIIb* to *XIXb* ratio was found to be 50 : 50, as adduced from ^{1}H NMR data.

Cycloaddition of Azide *XVc* to *I*

The solution of tosylazide (*XVc*, 1·8 g, 9·1 mmol) and *I* (2 g, 9·5 mmol) in ether was allowed to stand at room temperature in the dark for 5 days. The residue obtained by removal of the solvent *in vacuo* was chromatographed (SiO_2, cyclohexane–ethyl acetate 5 : 3) to furnish 1-tosyl--4,5-dimethoxycarbonyl-1,2,3-triazole (*XIXc*), 2·20 g (65%), m.p. 137—139°C (ref.[8] 133—134°C) and the unreacted azide *XVc* (0·2 g, 22%).

Cycloaddition of *XVd* to *I*

Compound *I* (2·1 g, 10 mmol) and the ethereal 0·1M azoimine (*XVd*, 0·43 g, 10 mmol) were allowed to stand at room temperature overnight, the solvent was distilled off *in vacuo* and the residue was triturated with trichloromethane. The product, 2,3-dimethoxycarbonyl-1,2,3-triazole (*XIXd*), m.p. 133°C, (ref.[9] 133—134°C) was obtained in a 61% (1·1 g) yield. ^{1}H NMR spectrum (C^2HCl_3): 10·53 (s, br, 1 H, NH), 4·02 (s, 6 H, 2 × $COOCH_3$).

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REFERENCES

1. Reinhoudt D. N., Kouwenhoven C. G : Rec. Trav. Chim. Pays-Bas *95*, 67 (1976).
2. Cristina D., De Amici M., De Micheli C., Gandolfi R.: Tetrahedron *37*, 1349 (1981).
3. Fišera Ľ.; Kováč J., Patúš J., Pavlovič D.: This Journal *48*, 1048 (1983).
4. Zálupský P., Birošová M., Fišera Ľ.: This Journal, in press.
5. Sustmann R.: Pure Appl. Chem. *40*, 569 (1974).
6. Houk K. N., Sims J., Duke R. E. jr, Strozier R. W., George J. K.: J. Amer. Chem. Soc. *95*, 7287 (1973).
7. Lieb F., Eiter K.: Justus Liebigs Ann. Chem. *761*, 130 (1972).
8. Huisgen R., Knorr R., Moebius L., Szeimes G.: Chem. Ber. *98*, 4014 (1965).
9. Yamada S., Mizoguchi T., Ayata A.: Yakugaku Zasshi *77*, 452 (1957); Chem. Abstr. *51*, 14 697 (1957).

10. Fišera Ľ., Kováč J., Leško J., Šmahovský V.: Chem. Zvesti *35*, 93 (1981).
11. Gotthardt H., Reiter F.: Chem. Ber. *112*, 1206 (1979).
12. Becker H. G. O., Sauder N., Timpe H.-J.: J. Prakt. Chem. *311*, 897 (1969).
13. Hodgson H. H., Norris W. H. H.: J. Chem. Soc. *1949*, 762.
14. Doering W. E., De Puy C. H.: J. Amer. Chem. Soc. *75*, 5955 (1953).
15. Neber P. W., Wörner H.: Justus Liebigs Ann. Chem. *526*, 173 (1936).
16. Otsuji Y., Tsuji Y., Yoshida A., Imoto E.: Bull. Chem. Soc. Jap. *44*, 223 (1971).

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