1,3-DIPOLAR CYCLOADDITION OF C-BENZOYL-N-PHENYLNITRONE TO OXANORBORNADIENE AND OXANORBORNENE DERIVATIVES; *endo-exo* AND SITE SELECTIVITY*

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C-Benzoyl-N-phenylnitrone (*Ia*) and C,N-diphenylnitrone (*Ib*) react with 2,3-dimethoxycarbonyl-7-oxabicyclo[2,2,1]heptadiene (*II*) to give *endo*- and *exo*-adducts at both the substituted double bonds. The *endo-exo* and site selectivity of 1,3-dipolar cycloaddition is discussed. Cycloadditions of the nitrones *Ia* and *Ib* to 5,6-dimethoxycarbonyl-7-oxabicyclo[2,2,1]heptene and 2,3-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2-heptene are also described.

Our previous papers concerned 1,3-dipolar cycloaddition of C-benzoyl-N-phenylnitrone (*Ia*) to furan[1-4], condensed furan[5] or dihydrofuran derivatives[6]; in these reactions compound *Ia* reacted with high selectivity to give exclusively *endo*-adducts or a diastereoisomeric pair of *endo*- and *exo*- adducts in case of dihydrofurans. The present work investigates the *endo-exo* and site selectivity in 1,3-dipolar cycloadditions of the nitrone *Ia* and C,N-diphenylnitrone (*Ib*) to an oxanorbornadiene derivative, 2,3-dimethoxycarbonyl-7-oxabicyclo[2,2,1]heptadiene (*II*), and two oxanorbornene derivatives: 5,6-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2-heptene (*III*) and 2,3-dimethoxycarbonyl-7-oxabicyclo[2,2,1]-2-heptene (*IV*) (Scheme 1; indexes *a* for R = C_6H_5CO and *b* for R = C_6H_5). These systems were selected for their suitable model dihydrofuran skeleton and high reactivity of norbornene derivatives in 1,3-dipolar cycloaddition reactions[7]. Moreover, compound *II* represents a system suitable for study of relative reactivity of two unequally activated double bonds in reactions with the nitrones *Ia* and *Ib*.

Cycloadditions of the nitrones *Ia* and *Ib* to the derivatives *II*–*IV* were carried out in benzene in the molar ratio 1 : 1; the reaction with compound *II* did not give any bis-adducts. Elemental analyses, as well as mass, UV and IR spectra, indicated the formation of cycloadducts. Analysis of their ^1H NMR spectra gave the following results.

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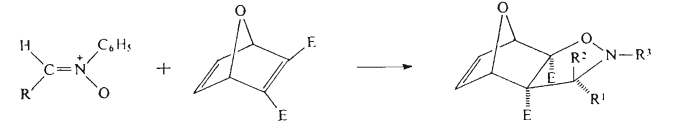
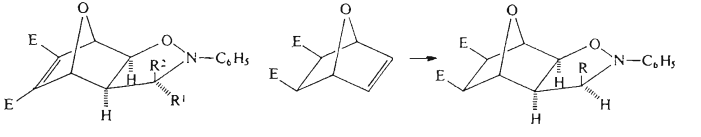
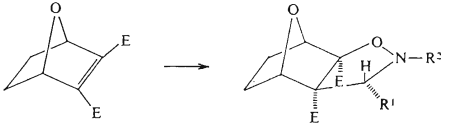
1,3-Dipolar cycloaddition of oxanorbornadiene *II* to nitrone *Ia* afforded three cycloadducts, two (*Va* and *VIa*) at the tetrasubstituted double bond and one (*VIIa*) at the disubstituted one. The multiplets of olefinic protons 7-H (6·81 ppm) and 8-H (6·39 ppm) in the ^{1}H NMR spectrum of compound *Va* shows cycloaddition at the deactivated double bond. All the hitherto described 1,3-dipolar cycloadditions with norbornene and norbornadiene derivatives[7,8], as well as their heterocyclic analogues[9,10], led exclusively to *exo*-adducts (relative to the bridge, see Scheme 1). Since



Ia, R = C_6H_5CO *II*, E = $COOCH_3$ *Va*, $R^1 = C_6H_5CO$, R^2 = H, $R^3 = C_6H_5$
Ib, R = C_6H_5 *Vb*, $R^1 = R^3 = C_6H_5$, R^2 = H
Vc, $R^1 = C_6H_5$, R^2 = H, $R^3 = CH_3$
VIa, R^1 = H, $R^2 = C_6H_5CO$, $R^3 = C_6H_5$
VIc, R^1 = H, $R^2 = C_6H_5$, $R^3 = CH_3$



VIIa, R^1 = H, $R^2 = C_6H_5CO$ *III* *IXa*, R = C_6H_5CO
VIIb, R^1 = H, $R^2 = C_6H_5$ *IXb*, R = C_6H_5
VIIIb, $R^1 = C_6H_5$, R^2 = H

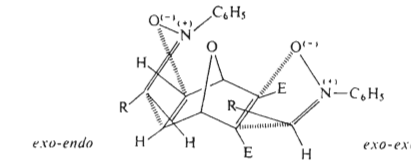


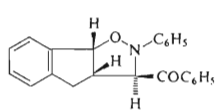
IV

Xa, $R^1 = C_6H_5CO$, $R^2 = C_6H_5$
Xb, $R^1 = R^2 = C_6H_5$
Xc, $R^1 = C_6H_5$, $R^2 = CH_3$

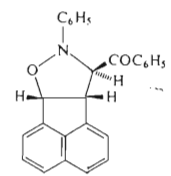
SCHEME 1

in cycloadditions of nitrones two *endo*- and *exo*-arrangements of transition states are possible[11,12] (Scheme 2), the asymmetric oxanorbornadiene can give rise to four cycloadducts (excluding the other four possible endo-cycloadducts): two at the tetrasubstituted (*exo-endo* (*V*) and *exo-exo* (*VI*)) and two at the disubstituted double bond (*exo-exo* (*VII*) and *exo-endo* (*VIII*), Scheme 1 and 2). Since there is no proton at the $C_{(4)}$ atom in the neighbourhood of the isoxazolidine proton 3-H (δ = 4·99 ppm), it is not possible to establish the configuration at $C_{(3)}$ from the coupling constants as we have done in our preceding study[6]. We determined the configuration on the basis of difference between the δ values of methoxycarbonyl signals ($\Delta\delta$ = 0·54 ppm, δ_4 = 3·79 ppm, δ_5 = 3·25 ppm) which corresponded to the *endo*-relation of the iso-





XI



XII

SCHEME 2

oxazolidine proton and the methoxycarbonyl groups. The different δ values can be explained by shielding with the benzoyl group, situated under the isoxazolidine ring plane. In the opposite diastereoisomer *VIa* this difference should be substantially smaller (for *VIa* $\Delta\delta$ = 0·28 ppm). The configurational assignment at the $C_{(3)}$ atom using the effect of the benzoyl group on chemical shift of the methoxycarbonyl groups was utilized in the study of compounds *Vc* and *Xc* (ref.[10]) as well as of diastereoisomeric adducts of the nitrones *Ia* and *Ib* with dimethyl maleate[13]. The signals of the methoxycarbonyl groups at $C_{(4)}$ and $C_{(5)}$ were assigned on the basis of greater influence of the benzoyl group on the methoxycarbonyl at $C_{(4)}$. For the isolated diastereoisomeric cycloadduct *VIa* the value of $\Delta\delta$ $COOCH_3$ is 0·28 ppm. The *exo*-

configuration at $C_{(3)}$ in compound *VIa* is also confirmed by a smaller solvation effect on the δ value of the isoxazolidine proton 3-*H* ($\Delta\delta(C_6{}^2H_6 - C^2HCl_3) = 0{\cdot}05$ ppm whereas for *Va* 0·11 ppm). It is obvious that in case of shielding of the 3-H proton by the ester groups the solvent-induced shift (SIS) will be smaller. The shift of the 3-H proton in *VIa* ($\delta = 5{\cdot}56$ ppm) due to shielding by the ester groups (for *Va* $\delta = 4{\cdot}99$ ppm) confirms the assigned structure. Interestingly, in deuteriochloroform the spectrum was simplified, the olefinic protons forming one strong singlet.

The absence of olefinic proton signals in ^{1}H NMR spectrum of the adduct *VIIa* indicates addition at the disubstituted double bond. The spectrum contains doublets of the bridge protons 6-H and 9-H with coupling constants $J_{5,6} = J_{4,9} = 1{\cdot}0$ Hz, confirming the *exo*-addition of nitrone *Ia* to oxanorbornadiene *II*. In case of an *endo*-addition the coupling constants should be much higher. Further two doublets due to 3-H (4·90 ppm; $J_{3-4} = 6{\cdot}4$ Hz) and 5-H (4·76 ppm; $J_{4-5} = 5{\cdot}1$ Hz) were assigned by decoupling resonance at 280·1 Hz, corresponding to the 4-H proton. The coupling constant $J_{3-4} = 6{\cdot}4$ Hz shows an *exo*-arrangement of the isoxazolidine proton relative to the bridge protons. The 4-H signal, present as an apparent triplet was simplified to a doublet on decoupling at 380·6 Hz (5-H). This decoupling served also for assignment of the bridge protons.

All the three adducts *Va*, *VIa* and *VIIa* which are formed in high yield (88%) show molecular peak in their mass spectra; the products of cycloaddition to tetrasubstituted double bond (*Va*, *VIa*) have fragments due to cycloreversion and loss of furan from their molecular ion; on the other hand, the adduct *VIIa* does not afford cycloreversion fragments.

Cycloaddition of the nitrone *Ib* gave somewhat different results. Addition of *Ib* to tetrasubstituted double bond in compound *II* gave solely the *exo-endo* adduct *Vb* (29%), whose structure was assigned analogously as described for reaction with *Ia*. The *endo*-arrangement of the isoxazolidine proton relative to the methoxycarbonyl groups is indicated by the large difference in their chemical shifts ($\Delta\delta = 0{\cdot}85$ ppm) which for steric reasons is naturally larger for the nitrone *Ib* than for the benzoyl group in *Ia*. Addition to the disubstituted double bond afforded the *exo-exo* adduct *VIIb* (15%) with coupling constant $J_{3-4} = 6{\cdot}0$ Hz and the *exo-endo* adduct *VIIIb* (3%) which was not formed with the nitrone *Ia*. The *endo*-arrangement of the isoxazolidine proton 3-H is proved by its singlet in ^{1}H NMR spectrum ($J_{3-4} = 0{\cdot}0$ Hz) as well as by signals of methoxycarbonyl groups at 3·61 and 3·76 ppm and a singlet at 5·04 ppm due to the bridge protons 6-H and 9-H.

DeMicheli and collaborators[10] studied recently site selectivity in reactions of 1,3-dipoles (aryl azides, benzonitrile oxides) with oxanorbornadiene *II*. Both the double bonds in compound *II* were attacked by these 1,3-dipoles; on the other hand, the site selectivity of C-phenyl-N-methylnitrone (*Ic*) was 100 : 0 and only products of addition to the deactivated tetrasubstituted double bond (*Vc* and *VIc*) were formed in the ratio 70 : 30. In our case, the nitrones *Ia* and *Ib* attacked also the disubstituted

double bond with formation of products *VIIa*, *VIIb* and *VIIIb*: with the first nitrone (*Ia*) the site selectivity was 59 : 41 and the ratio *Va* : *Vb* was 61 : 39, with the nitrone *Ib* the site selectivity was 62 : 38. The mentioned different site selectivities for *Ia* and *Ic* (61 : 39 *vs* 100 : 0) can be explained by application of the frontier orbital theory. 1,3-Dipolar cycloaddition reactions, controlled by the HOMO(1,3-dipole)-LUMO-(dipolarophile) frontier interaction should take place at the deactivated tetrasubstituted double bond, whereas additions to the disubstituted double bond should be controlled by the LUMO(1,3-dipole)-HOMO(dipolarophile) interaction. Whereas 1,3-cycloadditions of the nitrone behave according to the above-mentioned interaction, we have found[4] that cycloadditions of the nitrone *Ia* with heterocycles belong to the LUMO(*Ia*)-HOMO(heterocycle) type. In the case of the nitrones *Ia* and *II* both the frontier interactions operate which results in a site selectivity change. Similar reasoning holds also for the nitrone *Ib*. A solvent effect can be excluded since all the cycloadditions were done in benzene[10].

Since the structure of the products was assigned exclusively on the basis of ^{1}H NMR spectra without any X-ray analysis support, we chose as simpler model systems the partially hydrogenated derivatives *III* and *IV*. Addition of *Ia* to *III* gave only one *exo-exo* adduct *IXa*; its *exo*-configuration was proved by the coupling constant J_{3-4} (6·4 Hz), analogous to that for *VIa*. The isoxazolidine 3-H proton signal is a part of the apparent triplet with the 5-H proton which was confirmed by decoupling at 257·7 Hz (resonance of the 4-H proton). The small coupling constants J_{5-6} and J_{4-9} (both $<1{\cdot}0$ Hz) indicate an *exo*-addition of *Ia* relative to the oxygen bridge. Because of insolubility of *IXa* in hexadeuteriobenzene it was not possible to follow the solvent effect as in the case of the adducts *V*–*VIII* (see Experimental). Analogously, the nitrone *Ib* gave the *exo-exo* adduct *IXb*. In both cases of cycloadddition of nitrones *Ia* and *Ib* to the double bond in *III* the sterically more advantageous *exo*-transition state is preferred. The coupling constant J_{3-4} in *IXb* amounted to 7·0 Hz. It is interesting to compare the ^{1}H NMR spectra of *IXb* in deuteriochloroform and deuteriobenzene; in the latter the spectrum was simplified from four singlets, one multiplet and two doublets (in deuteriochloroform) to two singlets, a doublet-doublet and one multiplet. In deuteriobenzene, the bridge protons 6-H and 9-H, as well as both the ester groups, are equivalent.

Oxanorbornene *IV* was used as another model compound with deactivated double bond, destabilizing – for the LU_{1a}–HO_{1V} interaction – the *exo* transition state (relative to the methoxycarbonyl groups). Here the substituent effects are thus opposite to those in cycloadditions with furan[6], benzofuran[5] or furopyrrole[5] in which the *endo*-transition state was stabilized by secondary orbital interaction of the other multiple bond. We studied therefore the *endo-exo* stereoselectivity in the reaction of *Ia* with indene and acenaphthene in which a secondary orbital interaction can also be expected. Both these cycloadditions have been described by Huisgen[14]; however, he did not assign configuration to the isoxazolidine proton in the adducts. We charac-

terized the product *XI*, arising from indene and *Ia*, by its ^{1}H NMR spectrum in which the doublet of the 3-H isoxazolidine proton (δ = 5·04 ppm; J_{3-3a} = 2·5 Hz) clearly showed the *endo*-configuration. Similarly, we assigned configuration to the adduct *XII* from *Ia* and acenaphthene. Its spectrum displays a doublet of the 3-H proton at δ 5·54 ppm with J_{3-4} = 2·0 Hz. In both cases even a detailed study of the filtrate did not reveal any *exo*-adducts: this result represents a further support for the assumption of secondary orbital interactions between the π-bond and the nitrogen atom of the nitrone, mentioned in our previous paper[6]. Cycloaddition of the nitrone *Ia* to the compound *IV* in which the methoxycarbonyl groups destabilize the *exo*-transition state afforded only the *exo-endo* adduct *Xa*. The *endo*-configuration of the 3-H isoxazolidine proton follows from the great difference in chemical shift values of methoxycarbonyl groups ($\Delta\delta$ = 0·55 ppm), similar to that found for the adduct *Va* ($\Delta\delta$ = 0·54 ppm). The nitrone *Ib* reacted similarly (for reaction with *Xb* $\Delta\delta$ = = 0·79 ppm; for *Vb* $\Delta\delta$ = 0·85 ppm). Additions of the nitrones *Ia* and *Ib* with *IV* proceed thus *via* the *exo-endo* transition state (Scheme 2), although the *exo-exo* arrangement is sterically more advantageous. De Micheli with collaborators[10] reported that cycloaddition of nitrone *Ic* to compound *IV* gave as the main product the cycloadduct *Xc* which had also *exo-endo* configuration; moreover, they isolated ismall amounts of diastereoisomeric product.

EXPERIMENTAL

The melting points are uncorrected. Mass spectra were taken on an MS 902 S spectrometer (direct inlet, ionization energy 70 eV). ^{1}H NMR spectra were measured in deuteriochloroform and hexadeuteriobenzene on a Tesla BS 487C instrument with tetramethylsilane as internal standard. UV spectra were taken in methanol on a Specord UV VIS spectrometer in thermostated cells. The 7-oxabicyclic derivatives *II*, *III* and *IV* were prepared according to the literature[15-17]; in the preparation of *II* we got better yields (85%) working in an autoclave at 60°C; the reaction time was reduced to 30 h.

Cycloaddition of *Ia* to *II*

A mixture of *Ia* (3·1 g; 13·8 mmol) and *II* (2·9 g; 13·8 mmol) in benzene (30 ml) was kept at 40°C for 10 h in an autoclave. Evaporation *in vacuo* and chromatography on a silica gel column in benzene–ethyl acetate (2 : 1) afforded the following products: *Va* (2·0 g; 32%), m.p. 231–233°C (methanol). For $C_{24}H_{21}NO_7$ (435·4) calculated: 66·21% C, 4·83% H, 3·22% N; found: 66·73% C, 4·88% H, 3·34% N. ^{1}H NMR spectrum (C^2HCl_3): 7·00–8·30 (m, 10 H, aromatic protons), 6·81 (d, d, J_{7-8} = 6·0 Hz, J_{6-7} = 1·5 Hz, 1 H, 7-H), 6·39 (d, d, J_{8-9} = 1·5 Hz, 1 H, 8-H), 5·20 (d, 1 H, 6-H), 4·99 (d, 1 H, 9-H), 4·95 (s, 1 H, 3-H), 3·79 (s, 3 H, 5-CH_3), 3·25 (s, 3 H, 4-CH_3). UV spectrum λ_{max}, nm (log ε): 250 (4·28). Mass spectrum *m/z*: 367 ($M^+ - 68$), 68 (furan), cycloreversion fragments. *VIa* (1·2 g, 20·0%), m.p. 133–134°C (methanol). For $C_{24}H_{21}NO_7$ (435·4) calculated: 66·21% C, 4·83% H, 3·22% N; found: 66·75% C, 4·94% H, 3·50% N. ^{1}H NMR spectrum (C^2HCl_3): 6·92–8·12 (m, 10 H, aromatic protons), 6·54 (s, 2 H, 7-H and 8-H), 5·66 (s, 1 H, 3-H), 5·11 (s, 1 H, 6-H), 5·05 (s, 1 H, 9-H), 3·78 (s, 3 H, 5-CH_3), 3·50 (s, 3 H, 4-CH_3), (C_6 $^2H_6$)

6·75—8·37 (m, 10 H, aromatic protons), 6·43 (d, d, J_{7-8} = 2·0 Hz, J_{6-7} = 1·5 Hz, 1 H, 7-H), 6·21 (d, d, J_{8-9} = 1·5 Hz, 1 H, 8-H), 5·61 (s, 1 H, 3-H), 5·30 (d, 1 H, 6-H), 4·99 (d, 1 H, 9-H), 3·32 (s, 3 H, 5-CH_3), 3·12 (s, 3 H, 4-CH_3). UV spectrum λ_{max}, nm (log ε): 250 (3·65). Mass spectrum, *m/z*: cycloreversion fragments 367 ($M^{+\cdot}$ —68) and 68 (furan). *VIIa* (2·2 g, 36%), m.p. 165—167°C (methanol). For $C_{24}H_{21}NO_7$ (435·4) calculated: 66·21% C, 4·83% H, 3·22% N; found: 66·65% C, 5·02% H, 3·34% N. ^{1}H NMR spectrum (C^2HCl_3): 6·95—8·20 (m, 10 H, aromatic protons), 5·29 (d, J_{4-9} = 1·0 Hz, 1 H, 9-H), 5·21 (d, J_{5-6} = 1·0 Hz, 1 H, 6-H), 4·90 (d, J_{3-4} = 6·4 Hz, 1 H, 3-H), 4·76 (d, J_{4-5} = 5·1 Hz, 1 H, 5-H), 3·76 and 3·97 (s, s, 6 H, 2 × CH_3), 3·52 (apparent triplet, 1 H, 4-H), ($C_6{}^2H_6$): 6·82—8·12 (m, 10 H, aromatic protons), 4·91 and 5·04 (d, d, J_{5-6} = J_{4-9} = 1·5 Hz, 2 H, 6-H and 9-H), 4·69 (d, J_{3-4} = 6·4 Hz, 1 H, 3-H), 4·67 (d, J_{4-5} = 5·1 Hz, 1 H, 5-H), 3·50—3·69 (m, 1 H, 4-H), 3·25 and 3·31 (s, s, 6 H, 2 × CH_3). UV spectrum, λ_{max}, nm (log ε): 245 (4·39); mass spectrum, *m/z*: M + 435.

Cycloaddition of *Ib* to *II*

A mixture of *Ib* (1·97 g, 10 mmol), *II* (2·10 mmol) and ether (30 ml) was kept in an autoclave at 40°C for 2 h. After standing overnight, the crystalline product *Vb* was collected on filter, m.p. 138°C. Yield 1·1 g (29%). For $C_{23}H_{21}NO_6$ (407·4) calculated: 67·80% C, 5·16% H, 3·43% N; found: 68·40% C, 5·17% H, 3·28% N. ^{1}H NMR spectrum (C^2HCl_3): 7·00—7·50 (m, 10 H, aromatic protons), 6·68 (d, d, J_{6-7} = 2·0 Hz, J_{7-8} = 5·5 Hz, 1 H, 7-H), 6·44 (d, d, J_{8-9} = = 2·0 Hz, 1 H, 8-H), 4·95 and 5·20 (d, d, 2 H, 6-H, 9-H), 4·60 (s, 1 H, 3-H), 3·87 (s, 3 H, 5-CH_3), 3·02 (s, 3 H, 4-CH_3), ($C_6{}^2H_6$): 6·75—7·50 (m, 10 H, aromatic protons), 6·63 (d, d, J_{6-7} = 2·0 Hz, J_{7-8} = 5·5 Hz, 1 H, 7-H), 6·34 (d, d, J_{8-9} = 2·0 Hz, 1 H, 8-H), 4·82 and 5·11 (d, d, 2 H, 6-H, 9-H), 4.67 (s, 1 H, 3-H), 3·70 (s, 3 H, 5-CH_3), 2·74 (s, 3 H, 4-CH_3). UV spectrum λ_{max}, nm (log ε): 253 (3·73). Mass spectrum *m/z*: $M^{+\cdot}$ 407, cycloreversion fragments 339 (M^+ —68) and 68 (furan). Chromatography of the filtrate on a column of silica gel in benzene–ethyl acetate (2 : 1) afforded *VIIb* (0·6 g, 15%), m.p. 165—166°C (methanol). For $C_{23}H_{21}NO_6$ (407·4) calculated: 67·80% C, 5·16% H, 3·43% N; found: 68·61% C, 5·14% H, 3·28% N. ^{1}H NMR spectrum (C^2HCl_3): 6·87—7·50 (m, 10 H, aromatic protons), 5·22 and 5·32 (s, s, 2 H, 6 H and 9 H), 4·87 (d, J_{4-5} = 6·0 Hz, 1 H, 5 H), 4·14 (d, J_{3-4} = 6·0 Hz, 1 H, 3 H), 3·86 (s, 3 H, CH_3), 3·77 (s, 3 H, CH_3), 3·12 (apparent t, 1 H, 4-H), ($C_6{}^2H_6$): 7·00—7·25 (m, 10 H, aromatic protons), 5·02 and 5·17 (s, s, 2 H, 6-H and 9-H), 4·69 (d, J_{4-5} = 6·0 Hz, 1 H, 5-H), 4·13 (d, J_{3-4} = 6·0 Hz, 1 H, 3 H), 3·32 and 3·19 (s, s, 6 H, 2 × CH_3), 2·95 (apparent t, 1 H, 4 H), UV spectrum λ_{max}, nm (log ε): 2·51 (4·17), mass spectrum *m/z*: $M^{+\cdot}$ 407.

Cycloaddition of *Ia* to *III*

A mixture of *Ia* (2·25 g; 10 mmol), *III* (2·1 g, 10 mmol) and benzene (30 ml) was stirred at 40°C for 30 min and the precipitated *IXa*, m.p. 178—179°C (methanol), collected. Yield 2·3 g (62%). For $C_{24}H_{23}NO_7$ (437·3) calculated: 65·90% C, 5·26% H, 3·20% N; found: 65·72% C, 5·22% H, 3·45% N. ^{1}H NMR spectrum (C^2HCl_3): 6·97—8·17 (m, 10 H, aromatic protons), 4·90 and 4·97 (d, d, J_{5-6} = J_{4-9} = 1·0 Hz, 2 H, 6 H and 9 H), 4·55—4·70 (d, d, J_{3-4} = 6·4 Hz, J_{4-5} = = 7·0 Hz, 2 H, 3-H and 5-H), 3·70 and 3·65 (s, s, 6 H, 2 × CH_3), 3·20 (apparent t, 1 H, 4 H), 2·89 (s, 2 H, 7-H and 8-H). UV spectrum, λ_{max}, nm (log ε): 247 (4·35). Mass spectrum *m/z*: $M^{+\cdot}$ 437.

Cycloaddition of *Ib* to *III*

A mixture of *Ib* (1·97 g, 10 mmol), *III* (2·1 g, 10 mmol) and benzene (30 ml) was kept in an autoclave at 30°C for 6 h. After concentration *in vacuo*, the residue was triturated with ether, affording

2·9 g (71%) of *IXb*, m.p. 199–200°C (methanol). For $C_{23}H_{23}NO_6$ (409·3) calculated: 67·48% C, 5·62% H, 3·42% N; found: 67·85% C, 5·63% H, 3·26% N. ^{1}H NMR spectrum (C^2HCl_3): 6·87 to 7·50 (m, 10 H, aromatic protons), 4·88 and 4·98 (s, s, 2 H, 6-H and 9-H), 4·55 (d, $J_{4-5} = 7·0$ Hz, 1 H, 5-H), 3·94 (d, $J_{3-4} = 7·0$ Hz, 1 H, 3-H), 3·66 and 3·71 (s, s, 6 H, 2 × CH_3), 2·62–2·75 (m, 3 H, 4-H, 7-H and 8-H), ($C_6{}^2H_6$): 6·75–7·25 (m, 10 H, aromatic protons), 4·80 (s, 2 H, 6-H and 9-H), 3·87 (d, $J_{3-4} = J_{5-4} = 7·0$ Hz, 2 H, 3-H and 5-H), 3·37 (s, 6 H, 2 × CH_3), 3·30–3·70 (m, 3 H, 4-H, 7-H and 8-H). UV spectrum λ_{max}, nm (log ε): 247 (3·87). Mass spectrum *m/z*: $M^{+\cdot}$ 407.

Cycloaddition of *Ia* to *IV*

A mixture of *Ia* (2·25 g; 10 mmol), *IV* (2·1 g, 10 mmol) and benzene (30 ml) was kept in an autoclave at 40°C for 30 h. Evaporation *in vacuo* and trituration with ether afforded 2·8 g (66%) of compound *Xa*, m.p. 132–133°C (methanol). For $C_{23}H_{23}NO_6$ (409·3) calculated: 67·48% C, 5·62% H, 3·42% N; found: 67·57% C, 5·51% H, 3·40% N. ^{1}H NMR spectrum (C^2HCl_3): 7·00 to 8·25 (m, 10 H, aromatic protons), 4·99 (s, 1 H, 3-H), 4·62–4·87 (m, 2 H, 6-H and 9-H), 3·91 (s, 3 H, 5-CH_3), 3·36 (s, 3 H, 4-CH_3), 1·62–1·95 (m, 4 H, 7-H_2, 8-H_2); ($C_6{}^2H_6$): 6·62–8·25 (m, 10 H, aromatic protons), 5·09 (s, 1 H, 3-H), 4·47–4·80 (m, 2 H, 6-H and 9-H), 3·57 (s, 3 H, 5-CH_3), 2·99 (s, 3 H, 4-CH_3), 1·35–1·75 (m, 4 H, 7-H_2 and 8-H_2).

Cycloaddition of *Ib* to *IV*

A mixture of *Ib* (1·97 g; 10 mmol), *IV* (2·1 g; 10 mmol) and ether (30 ml) was heated to 60°C in an autoclave for 30 h. Evaporation *in vacuo* and trituration with ether gave *Xb* (3·3 g; 81%), m.p. 129–130°C (methanol). For $C_{23}H_{23}NO_6$ (409·3) calculated: 67·48% C, 5·62% H, 3·42% N; found: 67·31% C, 5·81% H, 3·47% N. ^{1}H NMR spectrum (C^2HCl_3): 7·00–7·50 (m, 10 H, aromatic protons), 4·86 (d, $J_{6-7} = 2·5$ Hz, 1 H, 6-H), 4·57 (s, 1 H, 3-H), 4·57 (d, $J_{8-9} = 5·0$ Hz, 1 H, 9-H), 3·90 (s, 3 H, 5-CH_3), 3·11 (s, 3 H, 4-CH_3), 1·55–2·13 (m, 4 H, 7-H_2 and 8-H_2): ($C_6{}^2H_6$): 6·75–7·50 (m, 10 H, aromatic protons), 4·67–4·80 (m, 2 H, 3-H and 6-H), 4·41 (d, $J_{8-9} = 5·0$ Hz, 1 H, 9-H), 3·57 (s, 3 H, 5-CH_3), 2·81 (s, 3 H, 4-CH_3), 1·37–2·00 (m, 4 H, 7-H_2, 8-H_2).

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