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Thermally Induced Tandem Cycloaddition of 2-Alkyl-3-phenylcyclopropenones to 6-Aryl-1,5-diazabicyclo[3.1.0]hexanes

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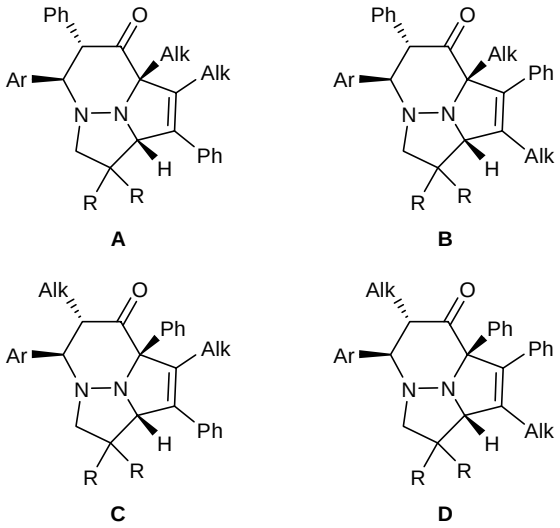
Abstract—Thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in the presence of 2-alkyl-3-phenylcyclopropenones gives fused polycyclic systems of the 4a,7b-diazacyclopenta[*cd*]inden-7-one series as a result of addition of two cyclopropenone molecules and extrusion of CO molecule. The first step of the process is characterized by 100% regioselectivity, leading to the adduct with vicinal arrangement of the aryl groups, while the regioselectivity of the second step is likely to be determined by spatial interactions between substituents in the cyclopropenone molecule and trimethylene bridge of the diazabicyclohexane. Steric hindrances in the second step could eliminate formation of stable products.

Cyclopropenones are known to react with a large number of organic compounds having a C=N bond, e.g., imines, diimines, amidines, guanidines, etc., to give mono- and polycyclic structures which may be regarded as formal [2+3]-cycloaddition products at the C–C(O) bond of the three-membered ring [1, 2]. Cycloaddition at the double carbon–carbon bond of cyclopropenones occurs more rarely; it is typical of nitrogen-containing 1,3-dipoles such as ylides and azomethine imines [2, 3]. Here, the initially formed fused system consisting of three- and five-membered rings undergoes expansion to six-membered ring [4]. As a result, stable zwitterionic cyclic structure may be obtained provided that appropriate stabilizing substituents are present [5].

We recently showed that thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in the presence of diphenylcyclopropenone leads to formation of fused tricyclic systems, 4a,7b-diazacyclopenta[*cd*]inden-7-ones as a result of unusual successive cycloadditions of two cyclopropenone molecules [6]. It was presumed that in the first step diphenylcyclopropenone adds to unstable azomethine imine which is generated by thermally induced opening of the diaziridine fragment in 6-aryl-substituted diazabicyclohexanes [7–9]; the subsequent ring expansion gives azomethine ylide which is stabilized via addition of the second diphenylcyclopropenone molecule and extrusion of one carbon(II) oxide molecule.

In the present work we studied the regio- and stereoselectivity and the role of electronic and steric factors in the reactions of unsymmetrically substituted cyclopropenones, 2-methyl-3-phenylcyclopropenone (**Ia**) and 2-isopropyl-3-phenylcyclopropenone (**Ib**), with 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **IIa**–**IIe**. In keeping with the mechanism proposed previously, formation of four regioisomeric adducts **A–D** might be expected and their relative configuration should be analogous to the configuration of adducts with diphenylcyclopropenone [6].



However, thermolysis of 3,3-dimethyl-substituted diazabicyclohexanes **IIa** and **IIb** in the presence of cyclopropenone (**Ia**) afforded only adducts **IIIa** and **IIIb**, respectively, whose structure corresponds to regioisomer **A** (Scheme 1). The products were isolated

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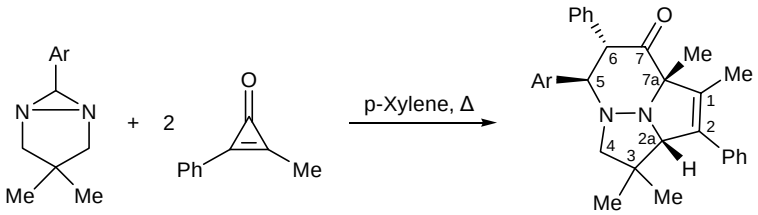
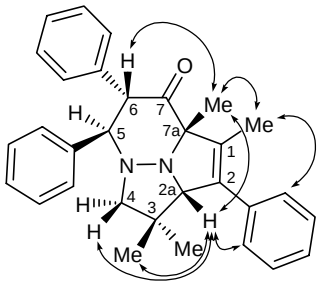
Scheme 1.



IIa, **IIb** **Ia** **IIIa** (44%), **IIIb** (63%)

Ar = 4-$MeOC_6H_4$ (**a**), Ph (**b**).

by column chromatography in 44 and 63% yield, respectively. The ^{1}H NMR spectrum of adduct **IIIb** contained signals from 15 aromatic protons in the region δ 7.17–7.60 ppm and a quartet δ 4.60 ppm (*J* = 1.7 Hz) due to the 2a-H proton. The observed long-range coupling is likely to originate from interaction between 2a-H and methyl group in position *1*; such interaction is typical of allyl-type systems; analogous coupling in the spectrum of adduct **IIIa** is characterized by a constant *J* of 2.1 Hz. Two doublets at δ 4.45 and 4.35 ppm (*J* = 6.7 Hz) belong to protons in positions *6* and *5*, respectively; protons on C^4 give rise to two doublets at δ 2.36 (pseudoequatorial) and 2.17 ppm (pseudoaxial), *J* = 8.9 Hz. Protons of the methyl group on C^1 resonate at δ 2.03 ppm (*J* = 1.7 Hz), the singlet at δ 1.64 ppm belongs to the 7a-CH_3 group, and signals from the methyl groups on C^3 appear at δ 1.01 ppm (psevdoequatorial) and 0.79 ppm (pseudoaxial).



IIIb

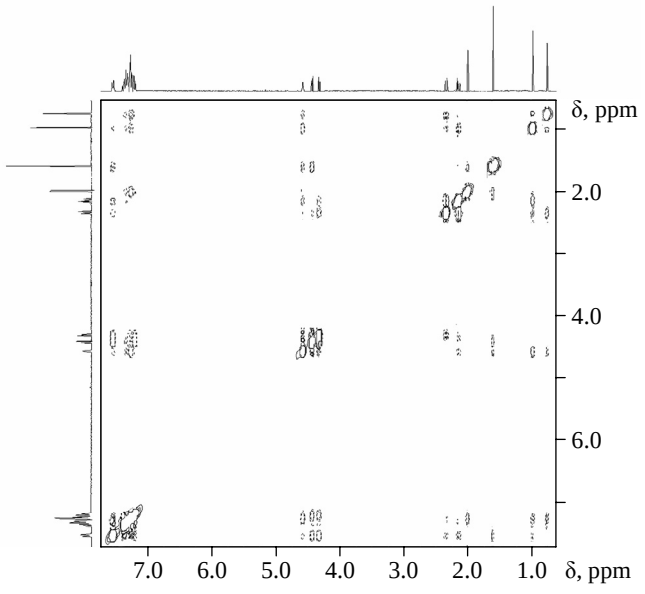
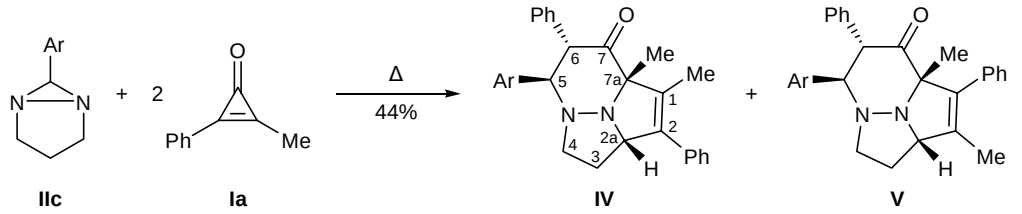


Fig. 1. 2D ^{1}H NMR spectrum (NOESY) of compound **IIIb** and scheme of NOEs.

The signals in the ^{1}H NMR spectra of compounds **IIIa** and **IIIb** were assinged, and the relative configuration of the adducts was determined, on the basis of the two-dimensional ^{1}H NMR spectrum of **IIIb**. Figure 1 shows the observed nuclear Overhauser effects (NOE) and the NOESY spectrum of **IIIb**. The proton on C^{2a} (δ 4.60 ppm, *J* = 1.7 Hz) gives cross peaks with protons of the methyl group on C^{7a} (δ 1.64 ppm), *ortho* protons of the phenyl group on C^2, pseudoequatorial methyl group on C^3 (δ 1.01 ppm), and pseudoaxial proton at C^4 (2.17 ppm). The methyl group in position *1* (δ 2.03 ppm) shows NOEs with *ortho*-protons of the 2-phenyl ring and methyl group in position *7a*. The 5-H and 6-H protons give cross peaks with *ortho*-protons of the corresponding aromatic rings, which are typical of their *trans* arrangement. The 6-H proton also interacts with protons of the 7a-methyl group oriented *cis* with respect to the former. A cross peak is observed for the 7a-methyl protons and *ortho*-protons of the aromatic ring on C^5 (*cis* arrangement). The pseudoaxial 4-H proton, in addition to the cross peaks noted above, gives those with *ortho*-protons of the 5-phenyl ring and pseudoequatorial methyl group on C^3, while the pseudoequatorial 4-H proton is coupled with 5-H and pseudoaxial methyl group on C^3. The relative configuration of adduct **IIIb** is fully consistent with that found by X-ray analysis for the adducts with diphenylcyclopropenone [6].

The ^{1}H NMR spectra of the reaction mixtures obtained from compounds **IIIa** and **IIIb** contained

Scheme 2.



IIc **Ia** **IV** **V**

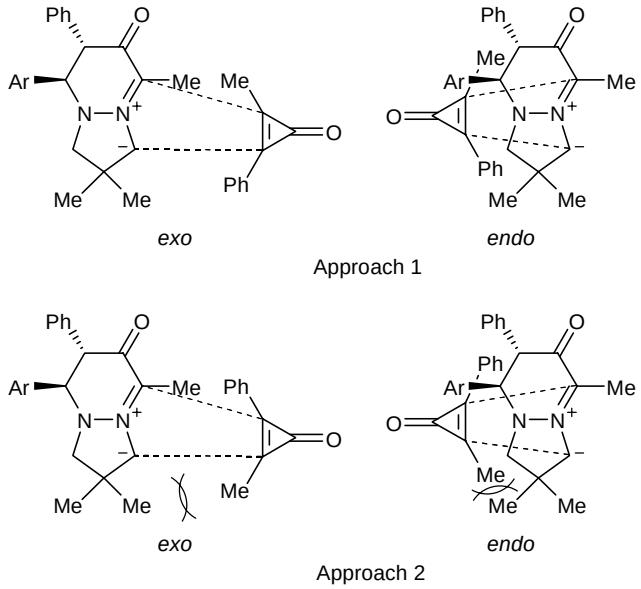
Ar = 4-$MeOC_6H_4$.

neither signals assignable to 4,5-dihydropyrazole derivatives formed by thermolysis of 1,5-diazabicyclo[3.1.0]hexanes in the absence of dipolarophiles nor those belonging to other products.

Unlike compounds **IIa** and **IIb**, thermolysis of 6-(4-methoxyphenyl)-1,5-diazabicyclohexane (**IIc**) in the presence of 2 equiv of 2-methyl-3-phenylcyclopropenone (**Ia**) (*p*-xylene, 138°C, 20 min) gave 44% of a mixture of two substances which were not isolated in the pure state because of their similar chromatographic mobilities. As with **IIa** and **IIb**, the ^{1}H NMR spectrum of the reaction mixture contained no signals assignable to the corresponding 4,5-dihydropyrazole or other products. The elemental composition of the product mixture corresponded to the expected formula $C_{30}H_{30}N_2O_2$, and analysis of the methyl proton signals in the ^{1}H NMR spectrum (singlets at δ 1.63, 1.64, and 1.75 ppm and a doublet at δ 2.07 ppm with a long-range coupling constant *J* of ~2 Hz, see above) revealed no coupling between any methyl group and the 6-H proton which should be observed in possible regioisomers **C** and **D**. Therefore, products **IV** and **V** were assigned structures **A** and **B** (Scheme 2). The ratio of regioisomers **IV** and **V** was estimated from the intensity ratio of the methyl protons signals at δ 2.07 and 1.75 ppm, respectively (~1:1). Unfortunately, we failed to completely assign signals in the spectrum of an equimolar mixture of **IV** and **V**. The overall preparative yield of products **IV** and **V** was relatively low (44%), presumably due to their decomposition during the isolation process. By column chromatography we isolated a fraction containing unidentified compounds whose signals were absent in the ^{1}H NMR spectrum of the reaction mixture.

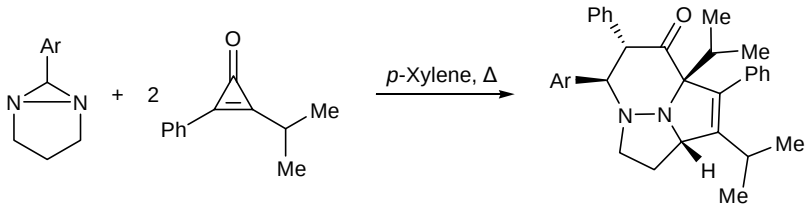
Obviously, the regioselectivity observed in the addition of the second cyclopropenone **Ia** molecule to intermediate ylide in the thermolysis of diazabicyclohexanes **IIa** and **IIb** and the lack of regioselectivity in the thermolysis of diazabicyclohexane **IIc** are determined by the presence in molecules **IIa** and **IIb** of two methyl groups in position *3*, i.e., the formation of one or another regioisomer is governed by spatial interactions upon reactant approach to each other. As shown in Scheme 3, in all cases approach of the second cyclopropenone molecule to intermediate ylide should give rise to spatial interactions between one methyl group in the trimethylene bridge and substituent in the cyclopropenone molecule (phenyl or methyl group). On the other hand, the structure of the products suggest that approach 1, according to which the phenyl group in cyclopropenone **I** and methyl group in the trimethylene bridge of the ylide appear in close proximity, is preferable to approach 2 which implies proximity of the methyl groups.

Scheme 3.



By thermolysis of diazabicyclohexanes **IId** and **IIe** in the presence of 2-isopropyl-3-phenylcyclopropenone (**Ib**) we obtained only isomers **VIa** and **VIb** in 24 and 20% yield, respectively (Scheme 4); the products had the structure of regioisomer **B**. Their structure was confirmed by the analytical data, and the relative configuration was established by analysis of the two-dimensional ^{1}H NMR spectrum of **VIa**. Its

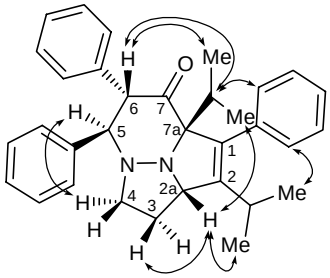
Scheme 4.



IId, **IIe** **Ib** **VIa** (24%), **VIb** (20%)

IId, **VIa**, Ar = Ph; **IIe**, **VIb**, Ar = 4-FC_6H_4.

^{1}H NMR spectrum contained signals from aromatic protons (15H) in the region δ 6.95–7.37 ppm; a multiplet at δ 4.54–4.59 ppm belongs to the 2a-H proton (as in **VIb**); two doublets at δ 4.55 and 4.02 ppm with a coupling constant *J* of 9.8 Hz correspond to 5-H and 6-H, respectively; multiplets at δ 2.88–3.00 and 2.79–2.88 ppm arise from the pseudoequatorial and pseudoaxial 4-H protons, respectively; septets at δ 2.74 (*J* = 7.1 Hz) and 2.64 ppm (*J* = 6.8 Hz) are typical of the isopropyl groups in positions *2* and *7*a, respectively; the pseudoaxial 3-H proton gives a multiplet at δ 2.24–2.38 ppm, and the pseudoequatorial 3-H proton gives a multiplet at δ 2.02–2.20 ppm; two doublets at δ 1.18 and 1.06 ppm (3H each) with a coupling constant of 7.1 Hz belong to the isopropyl group on C^2; and signals from methyl protons in the isopropyl group on C^{7a} appear as doublets at δ 1.16 and 0.97 ppm (3H each) with a coupling constant of 6.8 Hz.



IVa

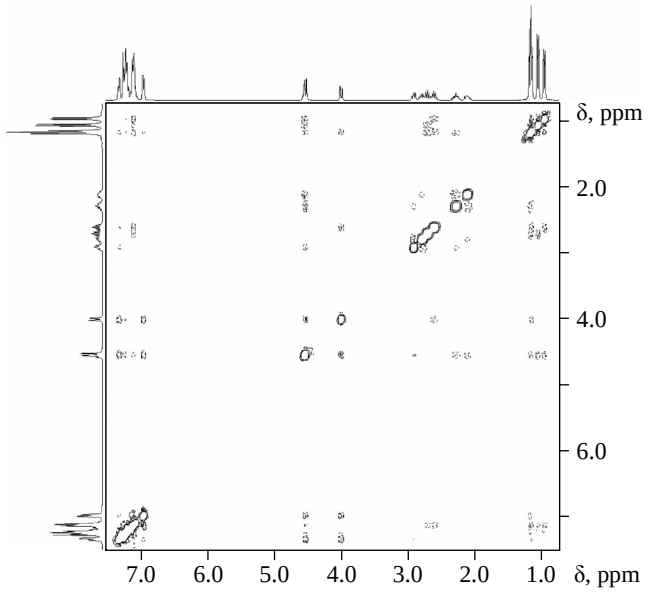


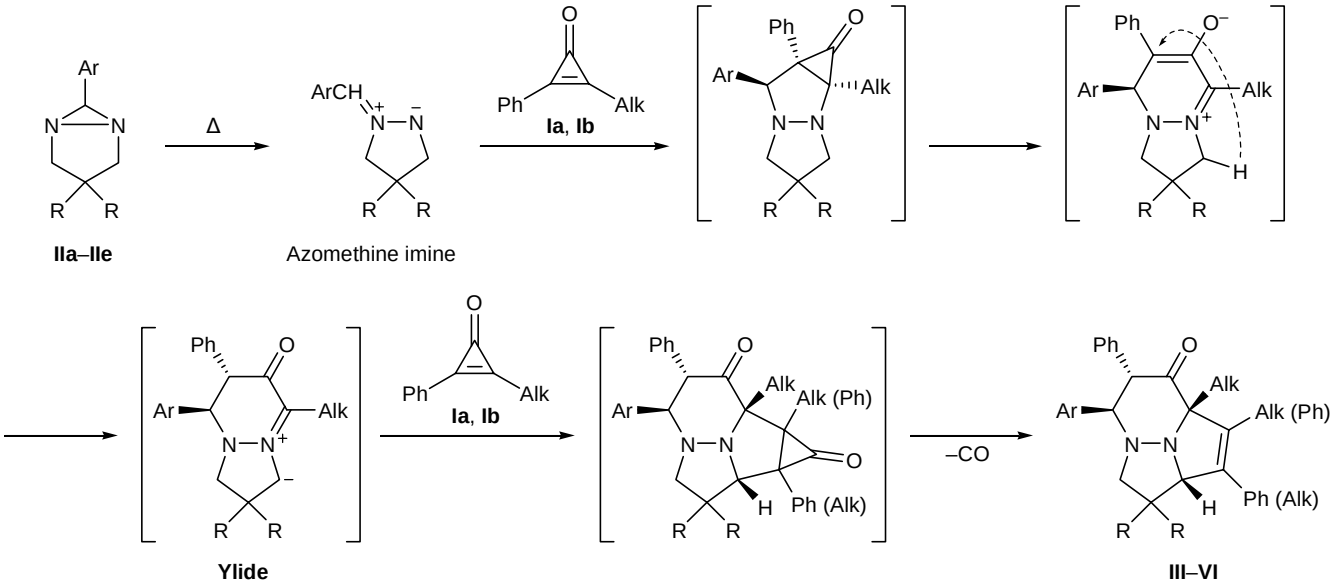
Fig. 2. 2D ^{1}H NMR spectrum (NOESY) of compound **VIa** and scheme of NOEs.

Figure 2 illustrates the main nuclear Overhauser effects observed in the 2D NOESY spectrum of compound **VIa**. The 5-H and 6-H protons give cross peaks with *ortho* protons of the aromatic rings in the geminal and vicinal positions, which is characteristic of *trans* orientation of 5-H and 6-H. The latter in turn interacts with protons of one methyl group (δ 1.16 ppm) and CH proton of the isopropyl group on C^{7a}, indicating their *cis* orientation with respect to each other. The 5-H proton gives a cross peak with the pseudoequatorial 4-H proton. *ortho*-Protons in the benzene ring attached to C^1 interact with the 7a-isopropyl group and protons of one methyl group in the isopropyl substituent on C^2. Cross peaks are observed between 2a-H, on the one hand, and one methyl group of the 2-isopropyl substituent, one methyl group of the 7a-isoptopyl substituent (*cis*), and pseudoequatorial 3-H proton, on the other.

In addition to signals belonging to tricyclic compounds **VIa** and **VIb**, the reaction mixtures contained those corresponding to 4,5-dihydropyrazole derivatives and cyclopropenone **Ib**, which were isolated in 24–31 and 43–53% yield, respectively; also, signals from unidentified products were present in the regions δ 0.6–1.2 and 6.9–7.5 ppm.

The formation of 4,5-dihydropyrazole derivatives via concurrent isomerization of intermediate azomethine imines and low yields of the target products indicate reduced reactivity of 2-isopropyl-3-phenylcyclopropenone (**Ib**) as compared to 2,3-diphenyl- and

Scheme 5.



R = H, Me.

2-methyl-3-phenylcyclopropenones, both in the first and in the second cycloaddition steps. We believe that the reason is primarily increased effective size of the substituent (isopropyl group), which hampers approach of the reagent to the substrate. Just that factor is responsible for the inverse regioselectivity in the addition of the second cyclopropenone **Ib** molecule, while the regioselectivity in the first cycloaddition step remains the same as in the reaction with **Ia**. Here, approach of the reagent molecule to intermediate ylide implies close proximity of two isopropyl groups, which is strongly unfavorable for steric reason.

It might be expected that introduction of two methyl groups into the trimethylene bridge of the initial diazabicyclohexane should increase steric hindrances to the second cycloaddition step even more strongly. In fact, we failed to isolate stable products of successive cycloaddition of two cyclopropenone molecules in the thermolysis of diazabicyclohexane **IIb** in the presence of cyclopropenone **Ib**. In this case, the ^{1}H NMR spectrum of the reaction mixture contained signals of the corresponding 4,5-dihydropyrazole and initial cyclopropenone **Ib** which were isolated in 35 and 66% yield, respectively, as well as signals at δ 0.6–1.2 and 6.0–7.5 ppm from unidentified products.

Our results led us to draw the following conclusion. In the thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]-hexanes in the presence of unsymmetrically substituted cyclopropenones, 1,3-dipolar cycloaddition of the first cyclopropenone molecule to azomethine imine generated by opening of the diaziridine ring in the substrate occurs equally regioselectively to give adducts with vicinal arrangement of the aromatic substituents. An analogous pattern was observed in the reactions of pyridinium *N*-imines with 2-methyl-3-phenylcyclopropenone [10], where the ring carbon atom bearing an alkyl group in unsymmetrically substituted cyclopropenone added to the "anionic" nitrogen atom. It should be noted that reactions of soft nucleophiles, azomethine imines among these, at the double carbon–carbon bond of cyclopropenones are governed by orbital control [11] which is sensitive to steric factor.

The regioselectivity in the addition of the second unsymmetrically substituted cyclopropenone molecule to intermediate ylide is determined by steric factors. The absence of steric hindrances leads to complete loss of regioselectivity (thermolysis of compound **IIc** in the presence of cyclopropenone **Ia**), while increase in steric hindrances eliminates formation of stable cycloaddition products (thermolysis of diazabicyclohexane **IIb** in the presence of cyclopropenone **Ib**). In keeping with the presumed mechanism (see above), the reaction of 6-aryl-1,5-diazabicyclohexanes **IIa**–**IIe** with unsymmetrically substituted cyclopropenones **Ia** and **Ib** may be illustrated by Scheme 5. In all cases where the relative configuration of the resulting adducts was established it was the same. The high stereoselectivity is likely to indicate a concerted mechanism of the entire process, in agreement with the proposed scheme.

Our attempts to obtain cycloaddition products by thermolysis of 6-aryl-1,5-diazabicyclohexanes in the presence of unsymmetrically substituted cyclopropenes, such as methyl 2,3-diphenylcyclopropenecarboxylate, 2,3,3-triphenylcyclopropenecarbonitrile, and 2,3-diphenylcyclopropenecarbonitrile, resulted in exclusive formation of the corresponding 4,5-dihydropyrazole derivatives. Presumably, the reactivity of these compounds as 1,3-dipolarophiles is insufficient to trap unstable short-lived azomethine imines generated from 6-aryl-1,5-diazabicyclo[3.1.0]hexanes.

EXPERIMENTAL

The IR spectra were recorded from 2% solutions in chloroform on a UR-20 spectrometer. The ^{1}H NMR spectra and the 2D NOESY spectra were obtained from 5% solutions in $CDCl_3$ on a Bruker DPX-300 instrument (300 MHz).

2-Methyl-3-phenylcyclopropenone (**Ia**) was synthesized by the procedure reported in [12], and 2-isopropyl-3-phenylcyclopropenone (**Ib**) was obtained in a similar way. Initial 6-aryl-1,5-diazabicyclo-[3.1.0]hexanes **IIa**, **IIc**, and **IId** were prepared by condensation of the corresponding aldehyde and 1,3-diamine, followed by oxidation of intermediate hexahydropyrimidine according to the procedures described in [6–8].

6-Aryl-1,5-diazabicyclo[3.1.0]hexanes IIb and IIe (*general procedure***).** A solution of the corresponding aromatic aldehyde in aqueous ethanol or methanol was added dropwise under stirring and cooling with ice water to 1.1–2 equiv of 1,3-propanediamine or 2,2-dimethyl-1,3-propanediamine, maintaining the temperature below 40°C. The mixture was stirred for at least 1 h at 18–20°C, and ethanol or methanol was distilled off on a rotary evaporator at a temperature not exceeding 40°C. An alkaline solution of sodium hypochlorite was added dropwise to the residue, maintaining the temperature below 40°C, and the mixture was stirred for 1 h at 18–20°C. The organic phase was separated, the aqueous phase was extracted with benzene, and the extracts were combined with the organic phase, dried over sodium sulfate, and evaporated on a rotary evaporator at a temperature not exceeding 45°C. The residue was recrystallized from appropriate solvent.

3,3-Dimethyl-6-phenyl-1,5-diazabicyclo[3.1.0]-hexane (IIb) was obtained from 4.6 g (0.044 mol) of 2,2-dimethyl-1,3-propanediamine and 4.1 ml (0.04 mol) of benzaldehyde dissolved in a mixture of 30 ml of methanol and 15 ml of water; the oxidation was performed with the use of 19.2 ml (0.048 mol) of a 2.5 N solution of sodium hypochlorite. Recrystallization from ether with a small addition of hexane gave 3.5 g (46%) of compound **IIb** as colorless crystals with mp 89–90°C. IR spectrum, ν, cm^{-1}: 960, 1000, 1130, 1080, 1135, 1260, 1285, 1310, 1365, 1385, 1460, 2880, 2970 s, 3030. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 s (3H), 1.35 s (3H), 2.99 d (2H, J = 11.0 Hz), 3.27 d (2H, J = 10.6 Hz), 3.43 s (1H), 7.27–7.38 (5H). Found, %: C 76.64, 76.35; H 8.79, 8.76; N 15.09, 14.59. $C_{12}H_{16}N_2$. Calculated, %: C 76.55; H 8.57; N 14.88.

6-(4-Fluorophenyl)-1,5-diazabicyclo[3.1.0]-hexane (IIe) was obtained from 7.3 ml (0.088 mol) of 1,3-propanediamine and 8.4 ml (0.08 mol) of 4-fluorobenzaldehyde dissolved in a mixture of 60 ml methanol and 30 ml of water; the oxidation was performed using 38 ml (0.088 mol) of a 2.3 N solution of sodium hypochlorite. Recrystallization from a mixture of benzene with diethyl ether and hexane gave 8.7 g (61%) of compound **IIe** as colorless crystals with mp 99–100°C. IR spectrum, ν, cm^{-1}: 960, 977, 1020, 1093, 1160, 1190, 1260, 1295, 1340, 1383, 1435, 1455, 1475, 1520, 1615, 2880, 2960, 2985 s, 3030. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.80–1.97 m (2H), 3.05–3.20 m (2H), 3.10 s (1H), 3.51–3.63 m (2H), 6.95–7.06 (2H), 7.27–7.35 (2H). Found, %: C 67.03; H 6.10; N 15.66. $C_{10}H_{11}FN_2$. Calculated, %: C 67.40; H 6.22; N 15.72.

Thermolysis of 1,5-diazabicyclo[3.1.0]hexanes IIa–IIe in the presence of cyclopropenones Ia and Ib (*general procedure***).** A mixture of 1,5-diazabicyclo-[3.1.0]hexane **IIa**–**IIe** and 2 equiv of cyclopropenone **Ia** or **Ib** in *p*-xylene was stirred at 138°C for 20 (**IIa**, **IIc**), 25 (**IIb**, **IId**), or 30 min (**IIe**). The reaction time was determined by kinetic study of the thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in the presence and in the absence of dipolarophiles [9]. The solvent was distilled off, and the residue was recrystallized from appropriate solvent or subjected to chromatographic separation.

***rel*-(2a*R*,5*R*,6*S*,7a*S*)-5-(4-Methoxyphenyl)-1,3,3,7a-tetramethyl-2,6-diphenyl-3,4,5,6,7,7a-hexahydro-2a*H*-4a,7b-diazacyclopenta[*cd*]inden-7-one (IIIa)** was obtained from 0.65 g (3 mmol) of compound **IIa** and 0.86 g (6 mmol) of cyclopropenone **Ia** in 8 ml of *p*-xylene. Recrystallization from a mixture of diethyl ether with hexane gave 0.5 g of adduct **IIIa**.

An additional amount of **IIIa** (0.13 g) was isolated from the mother liquor by column chromatography on silica gel L (160–200 μm, substrate-to-sorbent weight ratio 1:20, gradient elution with hexane–ethyl acetate, 6:1 to 3:1). Overall yield 0.63 g (44%), mp 174–175°C. IR spectrum, ν, cm^{-1}: 1010, 1040, 1060, 1130, 1180, 1260, 1290, 1305, 1360, 1460, 1520, 1620, 1735 s, 2840, 2880, 2940, 2960, 3040. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.79 s (3H), 1.02 s (3H), 1.62 s (3H), 2.02 d (3H, *J* = 2.1 Hz), 2.16 d (1H, *J* = 9.1 Hz), 2.34 d (1H, *J* = 9.1 Hz), 3.83 s (3H), 4.30 d (1H, *J* = 6.6 Hz), 4.42 d (1H, *J* = 6.6 Hz), 4.59 q (1H, *J* = 2.1 Hz), 6.88 d (2H, *J* = 8.4 Hz), 7.20–7.40 (12H), 7.48 d (2H, *J* = 8.4 Hz). Found, %: C 80.30, 80.26; H 7.12, 7.09; N 5.54, 5.99. $C_{32}H_{34}N_2O_2$. Calculated, %: C 80.30; H 7.16; N 5.85.

***rel*-(2a*R*,5*R*,6*S*,7a*S*)-1,3,3,7a-Tetramethyl-2,5,6-triphenyl-3,4,5,6,7,7a-hexahydro-2a*H*-4a,7b-diazacyclopenta[*cd*]inden-7-one (IIIb)** was obtained from 0.47 g (2.5 mmol) of compound **IIb** and 0.72 g (5 mmol) of cyclopropenone **Ia** in 6 ml of *p*-xylene. The product was isolated by column chromatography on silica gel L (100–200 μm, substrate-to-sorbent weight ratio 1:34, eluent hexane–ethyl acetate, 6:1), followed by recrystallization from acetone–diethyl ether–hexane. Yield 0.52 g (63%), mp 173–175°C. IR spectrum, ν, cm^{-1}: 1005, 1010, 1038, 1058, 1079, 1090, 1115, 1280, 1360, 1458, 1497, 1610, 1735 s, 2840, 2875, 2930, 2970, 3040. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.79 s (3H), 1.01 s (3H), 1.64 s (3H), 2.03 d (3H, *J* = 1.7 Hz), 2.17 d (1H, *J* = 8.9 Hz), 2.36 d (1H, *J* = 8.9 Hz), 4.35 d (1H, *J* = 6.7 Hz), 4.45 d (1H, *J* = 6.7 Hz), 4.60 q (1H, *J* = 1.7 Hz), 7.17–7.60 (15H). Found, %: C 82.85, 83.24; H 7.29, 7.46; N 5.99, 6.26. $C_{31}H_{32}N_2O$. Calculated, %: C 83.00; H 7.19; N 6.24.

5-(4-Methoxyphenyl)-1,7a-dimethyl-2,6-diphenyl-3,4,5,6,7,7a-hexahydro-2a*H*-4a,7b-diazacyclopenta[*cd*]inden-7-one (IV) and 5-(4-methoxyphenyl)-2,7a-dimethyl-1,6-diphenyl-3,4,5,6,7,7a-hexahydro-2a*H*-4a,7b-diazacyclopenta[*cd*]-inden-7-one (V) were obtained from 0.19 g (1 mmol) of compound **IIc** and 0.29 g (2 mmol) of cyclopropenone **Ia** in 4 ml of *p*-xylene. The product was isolated by column chromatography on silica gel L (160–200 μm, substrate-to-sorbent weight ratio 1:84, eluent hexane–ethyl acetate, 3:1). It was a mixture of regioisomers **IV** and **V** at a ratio of 1:1. Yield 0.2 g (44%), colorless crystals. IR spectrum, ν, cm^{-1}: 1020, 1040, 1080, 1097, 1115, 1135, 1160, 1180, 1240, 1260, 1290, 1310, 1340, 1365, 1380, 1450, 1500, 1520, 1740 s, 2840, 2860, 2940, 2980, 3040. ^1H NMR spectrum ($CDCl_3$) (regioisomer mixture), δ, ppm: 1.63 s (3H), 1.64 s (3H), 1.75 s (3H), 1.85–1.95 (1H), 2.07 d (3H, *J* ≈ 2 Hz), 2.10–2.20 (3H), 2.30–2.44 (2H), 2.68–2.79 (1H), 2.82–3.01 (1H), 3.807 s (3H), 3.810 s (3H), 4.31–4.42 (4H), 4.46 d (1H, *J* = 7.5 Hz), 4.82–4.91 (1H), 6.82–6.92 (4H), 7.10–7.50 (24H). Found, % (regioisomer mixture): C 80.07, 79.88; H 6.87, 6.89; N 6.33, 6.39. $C_{30}H_{30}N_2O_2$. Calculated, %: C 79.97; H 6.71; N 6.22.

***rel*-(2a*R*,5*S*,6*R*,7a*R*)-2,7a-Diisopropyl-1,5,6-triphenyl-3,4,5,6,7,7a-hexahydro-2a*H*-4a,7b-diazacyclopenta[*cd*]inden-7-one (VIa)** was obtained from 0.4 g (2.5 mmol) of compound **IId** and 0.86 g (5 mmol) of cyclopropenone **Ib** in 6 ml of *p*-xylene. The product was isolated by column chromatography on silica gel L (160–200 μm, substrate-to-sorbent weight ratio 1:50, gradient elution with hexane–ethyl acetate, 10:1 to 3:1). Yield 0.28 g (24%), mp 157–158°C. IR spectrum, ν, cm^{-1}: 1005, 1025, 1030, 1060, 1080, 1120, 1160, 1240, 1280, 1360, 1380, 1460, 1490, 1610, 1720 s, 2875, 2940, 2960 s, 3040. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.97 d (3H, *J* = 6.8 Hz), 1.06 d (3H, *J* = 7.1 Hz), 1.16 d (3H, *J* = 6.8 Hz), 1.18 d (3H, *J* = 7.1 Hz), 2.02–2.20 m (1H), 2.24–2.38 m (1H), 2.64 sept (1H, *J* = 6.8 Hz), 2.74 sept (1H, *J* = 7.1 Hz), 2.79–2.88 m (1H), 2.88–3.00 m (1H), 4.02 d (1H, *J* = 9.8 Hz), 4.55 d (1H, *J* = 9.8 Hz), 4.54–4.59 m (1H), 6.95–7.37 (15H). Found, %: C 82.77, 83.25; H 7.36, 7.73; N 5.95, 6.12. $C_{33}H_{36}N_2O$. Calculated, %: C 83.15; H 7.61; N 5.88.

In addition, 0.1 g (24%) of 1-phenylmethyl-4,5-dihydropyrazole and 0.46 g (53%) of initial cyclopropenone **Ib** were isolated from the reaction mixture by column chromatography.

***rel*-(2a*R*,5*S*,6*R*,7a*R*)-2,7a-Diisopropyl-1,6-diphenyl-5-(4-fluorophenyl)-3,4,5,6,7,7a-hexahydro-2a*H*-4a,7b-diazacyclopenta[*cd*]inden-7-one (VIb)** was obtained from 0.45 g (2.5 mmol) of compound **IIe** and 0.86 g (5 mmol) of cyclopropenone **Ib** in 6 ml of *p*-xylene. The product was isolated by column chromatography on silica gel L (160–200 μm, substrate-to-sorbent weight ratio 1:60, gradient elution with hexane–ethyl acetate, 9:1 to 1:1). Yield 0.25 g (20%), mp 144–145°C. IR spectrum, ν, cm^{-1}: 1005, 1040, 1060, 1080, 1120, 1160, 1240, 1280, 1295, 1340, 1360, 1380, 1457, 1470, 1515, 1540, 1560, 1610, 1720 s, 2880, 2940, 2970 s, 3040. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.98 d (3H, *J* = 7.0 Hz), 1.08 d (3H, *J* = 7.0 Hz), 1.16 d (3H, *J* = 7.0 Hz), 1.20 d (3H, *J* =

7.0 Hz), 2.07–2.21 m (1H), 2.23–2.35 m (1H), 2.63 sept (1H, J = 7.0), 2.73 sept (1H, J = 7.0 Hz), 2.78–2.85 m (1H), 2.87–2.96 m (1H), 3.96 d (1H, J = 9.1 Hz), 4.52 d (1H, J = 9.1 Hz), 4.53–4.61 m (1H), 6.90–7.36 (14H). Found, %: C 79.93; H 7.34; N 5.85. $C_{33}H_{35}FN_2O$. Calculated, %: C 80.13; H 7.13; N 5.66.

In addition, 0.14 g (31%) of 1-(4-fluorophenylmethyl)-4,5-dihydropyrazole and 0.38 g (44%) of initial cyclopropenone **Ib** were isolated from the reaction mixture by column chromatography.

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