CONCLUSIONS

We have studied the thermal and boron trifluoride etherate catalyzed cyclopropyl-allyl isomerization of cyclopropanated norbornadine dimers leading to novel types of C_{15} and C_{16} carbocycles.

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PMR STUDY OF THE THREE-DIMENSIONAL STRUCTURE OF STEREOISOMERIC ADDUCTS OF CIS-ALLOOCIMENE WITH ACRYLONITRILE AND THEIR CYCLIZATION PRODUCTS WITH DICHLOROCARBENE

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Alloocimene (I) undergoes regioselective diene synthesis reaction at its C_4 - C_7 atoms, in which an unsymmetrically substituted atom in the dienophile is oriented toward the C_4 atom in (I) [1-4]. In the case of the reaction with acrylonitrile as the dienophile, the adduct has been shown [4] to have the structure 4,5-dimethyl-2-(2'-methyl-1'-propenyl)-1cyano-3-cyclohexene (II). The three dimensional structure of this adduct has not been established however. We assume that the adduct consists of a mixture of steroisomers [3, 5-8]. In the present paper we have investigated the three dimensional structure of adducts formed between triene (Ia) and acrylonitrile.

Addition of triene (I) (as a mixture of cis and trans isomers = 3.3/1) to acrylonitrile leads to the formation of a mixture of two stereoisomers (IIa, b) in a 1:1 ratio (based on GLC analysis), in 56% overall yield.

The methylene group protons attached to C⁶ in isomer (IIa) resonate in the 1.7 ppm region (Table 1), with a nonequivalene $\Delta\delta(\alpha e) = 0.18$ ppm and a geminal spin-spin coupling constant ${}^2J_{HH^1} = 13.2$ Hz. The H $_{\alpha}{}^6$ proton, which absorbs more downfield, interacts with the proton at C¹ with a larger vicinal coupling constant than that observed for proton H $_{e}{}^6$ (Table 2). These coupling constant values can be analyzed using known stereochemical relationships [9], which lead us to conclude that the H $_{\alpha}{}^6$ and H¹ protons are in an anti orientation relative to one another ($\theta = 180^{\circ}$), and that the H $_{e}{}^6$ and H¹ protons occupy a gauche orientation relative to one another ($\theta = 60^{\circ}$). Two conclusions may be drawn from these stereochemical assignments. First of all, the torsional cyclic angle around the C¹-C⁶ bond (Ψ_{1-6}) is close to 60°, and, secondly, the cyano group occupies a pseudoequatorial position relative to the ring. The values of the spin-spin coupling constants for the vicinal C⁵ and C⁶ protons indicate that they also are in a relative gauche orientation. Considering Newman projections along the C⁵-C⁶ bond the following ratios are deduced: $\Psi_{5-6} = \theta(H^5H_{a}{}^6) < \theta(H^5H_{e}{}^6)$, then we can also conclude that the cyclic angle Ψ_{5-6} is significantly less than 60°. This

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means that the methyl group at C¹ must be anti to the proton Ha⁶. The value of the vicinal spin-spin coupling constant ${}^{3}J_{H^{2}H_{e^{1}}} = 8.8$ Hz, taking into account the orientation of the CN-group, which was discussed above, suggests that the angle $\theta(H^{2}H^{1}) < 180^{\circ}$, which means that the torsional angle $\psi_{2-1} < 60^{\circ}$, and the substituent at C² must be in gauche orientation relative to both the H¹ proton and the cyano group. The small value of ${}^{3}J_{H^{2}H^{3}}$, together with the relative orientation of the substituent attached to C², which was determined above, suggest that the $\theta(H^{2}H^{3})$ dihedral angle is close to 90° and the cyclic angle along the C³-C² bond must be small. In this way, based on an analysis of vicinal coupling constants and a consideration of possible three-dimensional models, we conclude that isomer (IIa) exists in a half-chair conformation with a pseudoequatorial orientation of the cyano group.

The PMR spectrum of compound (IIb) differs significantly from that of isomer (IIa). The most noticeable changes are observed for the positions and (splitting) patterns of the resonance signals due to the methylene group protons and the proton located next to the cyano group. The resonance signal for the H¹ proton has undergone a downfield shift of 0.36 ppm. In addition, the value of ${}^{3}J_{H^{1}H^{2}}$ has been substantially reduced, although the values of ${}^{3}J_{H^{1}H^{6}}$ are practically identical. In contrast, the spin-spin coupling constants for the methylene group protons with the other vicinal proton at H⁵ has been increased by ~2 Hz, and the relative positions of the resonance signals for the H_a⁶ and H_e⁶ have been inverted: the Ha⁶ proton absorbs more downfield than the H_e⁶ proton. It should be noted here as well, that ${}^{3}J_{H^{3}H^{2}}$ has been increased almost by a factor of two. Analysis of this data and taking into account the α - and β -substituent effects on proton chemical shifts [10, 11] which accompany changes in their orientation lead us to conclude that isomers (IIa and b) differ in terms of the orientations of the substituents attached to C² and C⁵ relative to the ring. The cyano group has retained its pseudoequatorial orientation (in compound IIb). Thus, stereoisomer (IIb) exists in a half-chair conformation with a cis-configuration of substituents relative to the cyano group.

Com- pound	H2	H3	H²	Hı	Hå	H _e ⁶	H7	9-CH3	10-CH3	11-CH₃	12-CH₃
(II a) (II b) (III) (IV) (V) (VI) (VI) (VII)	2,07 1,96 2,25 1,49 1,47 1,39 -	4,98 5,11 5,15 - - 1,58	3,06 3,06 2,29 - 1,64 1,70 -	2.26 2.62 2.87 1.85 2.15 2.61	1,86 1,59 1,42 - 1,10 0,92 -	1,68 1,81 1,70 	4,76 4,98 0,87 0,65 	1,65 1,63 1,14 1,34 1,21 1,04 1,08	1,67 1,69 1,27 1,39 1,32 1,08 1,14	$\begin{array}{c} 0.95\\ 0.97\\ 0.91\\ 0.60\\ 0.57\\ 0.67\\ 0.64\end{array}$	1.58 1.55 1.67 0.91 0.87 1.39 1.23

TABLE 1. PMR Spectra of Compounds under Investigation, $\delta, \ensuremath{\mathsf{ppm}}$

TABLE 2. Spin-Spin Coupling Constants for the Compounds under Investigation

Com- pound	H⁵H ⁶ a	H⁵H ⁶ e	H3H2	H ² H ¹	H²H7	$\mathrm{H^{i}H}_{a}^{6}$	H ¹ H ⁶ _e	$H^6_a H^6_e$	Ħ₂Hıı	H3H15	H'H'	H7H10
(IIa) (IIb) (III) (IV) (V) (V) (VI) (VII)	$5.6 \\ 9.7 \\ 9.2 \\ - \\ 2.6 \\ 11.4 \\ - $	3.7 5.6 5 ,5 - - -	2.2 4.9 - 7.0 4.0 -	8.8 5.1 2,7 10.7 6.3 5,4	9.5 9,8 - 9.8 9.7 11,0 -	$ \begin{array}{c c} 11.0\\ 11.5\\ 3.7\\ -\\ 8.5\\ 9.2\\ 8.3 \end{array} $	3.2 2.9 5.5 7.0 6.3 5,4	-13.2 -13.1 -12.8 -11.8 -13.6 -	7.1 7.0 6.8 6.6 7.0 6,6	1.3 1.0 0.9 	1.5 1.2 - - - -	1,2 1,2 - - - -

The mutual cis orientation of substituents attached to C^2 and C^5 in adducts (IIa and b) suggests that both isomers are formed from cis-alloocimene (Ia). If acrylonitrile is added under analogous conditions to trans-alloocimene (Ib), which has been prepared by enrichment of the hydrocarbon fractions remaining after addition of acrylonitrile to cis-alloocimene, a complex mixture of products is obtained in low yield.

The lower reactivity of (Ib) and the lower yields of both $[4 \pm 2]$ and $[2 \pm 2]$ cycloaddition products formed from (Ib) has been noted previously in the case of the reaction of trans-alloocimene (Ib) with tetracyanoethylene [8]. The reactivity difference between (cisand trans-) alloocimenes (Ia and b) is associated with the fact that in (Ib) there is an unfavorable interaction of the CH₃ group at C⁷ and the hydrogen atom at C⁴ in the S-cis configuration of the 4,6-diene system, which disrupts the planarity of the diene system.

It is also expected that the stereoisomeric adducts (IIa) and (IIb) should also differ in reactivity, since in (IIb) there is steric hindrance to approach in the β -direction (all substituents are oriented cis relative to one another), and in compound (IIa) there is steric hindrance to approach in both the α - and β -directions (albeit to different degrees). The relationship between the reactivity of adducts (IIa, b) and their structures can be assessed by studying their cycloaddition products with dichlorocarbene, which is sensitive to steric effects.

Reaction of dichlorocarbene with adduct (IIa) gave a mixture of products (III), (IV), and (V), in a 6:2:1 ratio. The principal component (III), based on the results of IR, and ¹H- and ¹³C-NMR spectroscopic studies is the product of cycloaddition of dichlorocarbene to the C⁷-C⁸ exocyclic double bond in adduct (IIa).

The spectral parameters for compound (III) (Table 2) suggest that addition of a dichlorocarbene fragment to the trans isomer (IIa) produces a change in the orientation of substituents relative to the cyclohexene ring, with retention of configuration. The following facts support this conclusion. First of all, the vicinal coupling constants ${}^{3}J_{H^{1}H^{6}}$ have changed from 11.0 and 3.2 Hz to 3.7 and 5.5 Hz in compound (III) relative to compound (IIa); this is indicative of a change in the position of the cyano group, from pseudoequatorial to pseudoaxial (in III). Secondly, the small value of the ${}^{3}J_{H^{1}H^{2}}$ spin-spin coupling constant corresponds to a dihedral angle $\theta(H^{1}H^{2})$ of 70°, and, apparently, to an almost anti orientation of substituents at the C¹ and C² atoms ($\theta = \sim 170^{\circ}$). Finally, a significant increase in the value of the coupling constant between the methylene group protons and H⁵ (especially ${}^{3}J_{H^{5}Ha}{}^{6}$) leads us to conclude that the orientation of the 5-CH₃ group relative to the Ha⁶

TABLE 3. $^{13}\mbox{C-NMR}$ Spectra of the Compounds under Investigation, δ , ppm

						_				
Com- pound	Cı		C ² C ³		C4		C⁵	C.	C'	C*
(IIa) (IIb) (III) (IV) (V) (V1) (V1)	28,4 30,1 <td< td=""><td colspan="2">$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td><td>137, 136, 140, 30, 30, 30, 30, 30,</td><td>3 7 3 3 3 3 3 3 3 3 3 3</td><td>38,9 35.7 31.3 33.3 32.6 30,7 31,9</td><td>33,0 31,8 29,6 32,6 32,3 32,3 32,3 32,2</td><td>125,6 123,4 37,0 38,1 38,5 37,2 37,2</td><td>134,4 134,6 42,3 30,0 29,7 28.3 30,1</td></td<>		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		137, 136, 140, 30, 30, 30, 30, 30,	3 7 3 3 3 3 3 3 3 3 3 3	38,9 35.7 31.3 33.3 32.6 30,7 31,9	33,0 31,8 29,6 32,6 32,3 32,3 32,3 32,2	125,6 123,4 37,0 38,1 38,5 37,2 37,2	134 ,4 134 ,6 42 ,3 30 ,0 29 ,7 28.3 30,1
Com- pound	C ¹²		C"		C°		C ¹⁰	C ¹³	C14	C15
(IIa) (IIb) (III) (IV) (V) (V) (VI) (VI)	18,1 19 18,2 19 17,7 18 18,2 18 17,7 18 17,3 17 17,7 18 17,7 18 17,7 18 17,7 18 17,0 17		9.1 9.2 3.8 3.1 7.3 3.1 7.5	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		25,8 25,9 25,3 18,4 18,2 18,6 18,3	120,9 119.8 119.9 121,3 120,9 120,9 121,4	- 69.5 70,4 70.2 70.1	$ \begin{array}{c} - \\ 71.2 \\ 70.7 \\ 71.4 \\ 70.9 \end{array} $	

proton has been altered, from an anti orientation to a gauch orientation. The observed values of the coupling constants correspond to angles $\theta(H^5Ha^6) < 180^\circ$ and $\theta(H^5H_e^6) > 60^\circ$. An analogous conclusion regarding the three-dimensional orientation of the substituent at C^5 is reached based on a comparison of the ${}^3J_{\rm H}{}^5{\rm H}{}^6$ coupling constants in compounds (III) and (IIb). According to its PMR spectrum, therefore, the dichloromethylene derivative (III) exists in an inverted conformation relative to that in the trans-isomer (IIa) starting material (see Scheme 1).

Based on the results of elemental analysis, and IR and ¹H- and ¹³C-NMR spectroscopy, the two other reaction products, compounds (IV) and (V), are stereoisomeric products arising from addition of dichlorocarbene to both double bonds in compound (IIa). The observed value of ${}^{3}J_{H}{}^{3}H^{2} = 7$ Hz in compound (V) indicates that the cycloheptane ring exists in a chair conformation; the larger value of ${}^{3}J_{H}{}^{1}H^{2} = 10.7$ Hz implicates a cis orientation for the cyclopropane ring and the CN group [12-14].

In the case of the alternate stereoisomer (IV), its ¹H and ¹³C-NMR spectra are consistent with the proposed structure, but do not provide the necessary stereochemical information to establish its three-dimensional structure. The resonance signals due to the ring protons overlap one another, and the chemical shift changes relative to those observed in isomer (V) are in the 1 ppm range (Table 3).

Reaction of dichlorocarbene with adduct (IIb) gave two stereoisomeric addition products, at the two double bonds. Comparison of their δ^{13} C chemical shift values, which are presented in Table 3, reveals that in this case all of the resonance signals for corresponding carbon atoms are located in a very narrow interval, not exceeding 3 ppm. The observed spin-spin coupling constant values for the vicinal protons at the C¹ and C⁶ atoms in compounds (VI) and (VII) (Table 2) are the same as in compound (V), which suggests that they probably exist in either chair or tub conformations. In compound (VI), however, the ${}^{3}J_{H^{2}H^{3}}$ constants are considerably smaller than in isomer (V), which is an argument in favor of a tub-shaped form. The decreased coupling constants for the protons at C¹ and C² to 6.3 Hz, and the increased values of ${}^{3}J_{H^{5}Ha}{}^{6}$ to 11.4 Hz suggest a trans orientation of the cyclopropane ring relative to the cyano group.

It is not possible to reach unequivocal conclusions concerning the three dimensional structure of the second stereoisomer (VII).

It should be noted that in a previous paper [15] it was concluded, based on conformational calculations within the framework of atom-atom potential function model and electronographic studies, that 7,7-dichlorobicyclo[4.1.0]heptane exists in a structure with a half-chair conformation for the six-membered ring. The predominance of this form over chair and tub conformations was estimated to give a small value of 4 kcal/mole. The data obtained herein indicate that the conformation of a bicycloheptane ring system is influenced substantially not only by the introduction of substituents to the ring, but also by their configuration.

EXPERIMENTAL

IR spectra were recorded on a UR-10 spectrophotometer. PMR spectra were measured on a Bruker WM-250 spectrometer using 5% solutions in CCl₄. Spectral analysis was carried out using a separation method or resolution into sub-spectra, and using double resonance ${}^{1}H-{}^{1}H$. Resonance signal assignments were confirmed by analysis of spectra obtained upon addition of Eu(fod)₃. ${}^{13}C$ -NMR spectra were obtained on a Bruker WH-90 spectrometer using ${}^{1}D-20\%$ solutions in a mixture of CHCl₃ and CCl₄. Spectra with both complete and partial ${}^{13}C-{}^{1}H$ were also considered. Signal assignments in the ${}^{13}C$ -NMR spectra were made based on experiments with partial suppression of ${}^{13}C-{}^{1}H$ coupling and application of correlational tables for carbon-13 chemical shifts, according to previously outlined methods [16, 17].

UV spectra were recorded on a Specord UV-VIS spectrophotometer. Melting points were determined using a Kofler block. GLC analyses were carried out on a Khrom-4 chromatograph (5% polyethylene glycol sebacinate on Chromosorb G with Ge₂ carrier gas).

Chemapol grade L SiO, was used for adsorption chromatography, Silufol (Plates) for TLC.

Alloocimene was prepared according to [18], bp 74°C (12 mm), np²⁰ 1.5435, cis:trans ratio: 3.3:1. UV spectrum [isooctane, λ_{max} , nm (ϵ)]: 285 (33,544), 275 (41,772), 267 (32,911) [8].

<u>Preparation of a cis-Alloocimene Adduct with Acrylonitrile [4]</u>. A mixture of 6.5 g alloocimene, 3 g acrylonitrile, and 0.05 g of hydroquinone was heated in a sealed tube for 3 h at 115-120°C. Distillation of the product mixture gave 2 g of hydrocarbon which does not enter into the reaction with bp 69.5°C/8 mm Hg, $n_D^{2^0}$ 1.5390, and 5.08 g (56%) of adduct (bp 100-103°C/2 mm Hg, $n_D^{2^0}$ 1.4930). According to GLC analysis the mixture consists of two compounds in a 1:1 ratio. Chromatography of 1 g of adduct on 70 cm³ SiO₂ with elution with a mixture of petroleum ether-ether (9.5:0.5) gave 0.23 g of 4,5-dimethyl-2-(2'-methyl-1'-propenyl)-1-trans-cyano-3-cyclohexene (IIa), $n_D^{2^0}$ 1.4910. Found, %: C 82.15; H 10.55. C₁₃H₁₉N. Calculated, %: C 82.52; H 10.06. Also isolated from the mixture was 0.25 g 4,5-dimethyl-2-(2'-methyl-1'-propenyl)-1-cis-cyano-3-cyclohexene (IIb), $n_D^{2^0}$ 1.4870. Found, %: C 82.10; H 10.00. C₁₃H₁₉N. Calculated, %: C 82.52; H 10.06. IR spectra (ν , cm⁻¹): (IIa): 820, 840, 860, 970, 1010, 1055, 1075, 1105, 1120, 1170, 1380, 1460, 1660, 2740, 3030; (IIb): 820, 840, 870, 940, 990, 1030, 1050, 1105, 1130, 1385, 1460, 1660, 2240, 2740, 3030.

Addition of Dichlorocarbene to Adduct (IIa). A solution of 0.23 g (IIa) in 6 ml $CHCl_3$ was treated with 0.057 g of triethylbenzylammonium chloride, and 5.7 ml of 50% NaOH solution was then added, and the mixture was stirred for 3 days. The reaction mixture was diluted with water, extracted with ether, and the extract was washed with water and dried over $MgSO_4$. After solvent evaporation the reaction products (0.35 g) were subjected to chromatography on SiO_2 (35 cm³) and separated into three products: (III), (IV), and (V).

 $\frac{4,5-\text{Dimethyl}-2'(2'-\text{methyl}-1',2'-\text{dichloromethylenepropyl})-1-\text{cyano}-3-\text{cyclohexene (III)}.}{\text{The fraction which eluted with a mixture of hexane-ether (9.5:0.5) contained 0.17 g (III), mp 109-111°C (from hexane). Found, %: C 62.25; H 7.26; N 5.75. C₁₄H₁₉Cl₂N. Calculated, %: C 61.79; H 6.99; N 5.15. IR spectrum (<math>\nu$, cm⁻¹): 720, 780, 820, 850, 880, 890, 950, 970, 1020, 1060, 1080, 1100, 1150, 1195, 1655, 2240, 2735, 3010, 3030.

<u>4,5-Dimethyl-2-(2'-methyl-1',2'-dichloromethylenepropyl)-1-cyano-3,4-dichloromethylene-</u> <u>cyclohexane (IV)</u>. The fraction eluting with hexane-ether (9:1) gave 0.06 g (IV), mp 132-134°C (hexane). Found, %: C 50.74; H 5.40; N 4.15. C₁₅H₁₉Cl₄N. Calculated, %: C 50.74; H 5.36; N 3.95. IR spectrum (v, cm⁻¹): 810, 830, 840, 860, 870, 890, 960, 1000, 1010, 1040, 1080, 1090, 1120, 1150, 1250, 2240, 2985.

<u>4,5-Dimethyl-2-(2'-methyl-1',2'-dichloromethylenepropyl)-1-cyano-3,4-dichloromethylene-cyclohexane (V)</u>. The fraction eluting with hexane-ether (7:3) contained 0.03 g (V), mp 167-168°C (petroleum ether-ether). Found, %: C 51.24; H 5.61; N 3.98. $C_{15}H_{19}Cl_4N$. Calculated, %: C 50.74; H 5.35; N 3.95. IR spectrum (v, cm⁻¹): 810, 830, 870, 900, 1010, 1040, 1090, 1130, 1160, 2240, 3025.

Addition of Dichlorocarbene to Adduct (IIb). To a solution of 0.25 g (IIb) in 6.25 ml CHCl₃ was added 0.057 g triethylbenzylammonium chloride, followed by 5.7 ml of 50% aqueous NaOH solution; the mixture was then stirred for 3 days. The reaction mixture was diluted with water, extracted with ether, and the extract was washed with water and dried over $MgSO_4$. After solvent evaporation the reaction products (0.41 g) were subjected to chromatography on SiO₂ (40 cm³) and separated into two products (VI) and (VII).

 $\frac{4,5-\text{Dimethyl-2-}(2'-\text{methyl-1'2'-dichloromethylenepropyl)-1-cyano-3,4-dichloromethylene$ cyclohexane (VI). The fraction eluting with hexane-ether (9:1) contained 0.16 g (VI), mp142-145°C. Found, %: C 50.75; H 5.76; N 4.51. C₁₅H₁₉Cl₄N. Calculated, %: C 50.74; $H 5.36; N 3.95. IR spectrum (<math>\nu$, cm⁻¹): 830, 845, 870, 890, 940, 965, 1010, 1025, 1050, 1090, 1155, 1370, 2240, 3000, 3015.

<u>4,5-Dimethyl-2-(2'-methyl-1',2'-dichloromethylenepropyl)-1-cyano-3,4-dichloromethylene</u> <u>cyclohexane (VII)</u>. The fraction eluting with hexane-ether (9.5:0.5) consisted of 0.24 g (VII), mp 169-170°C (hexane-ether). Found, %: C 50.8; H 5.39; N 4.13; Cl 40.43. C₁₅H₁₉. Cl₄N. Calculated, %: C 50.74; H 5.35; N 3.94; Cl 39.96. IR spectrum (v, cm⁻¹): 830, 840, 900, 930, 1000, 1080, 1095, 1120, 1150, 1380, 2240, 3000, 3010.

CONCLUSIONS

1. cis-Alloocimene adds acrylonitrile to give two stereoisomeric adducts, which exist in a half-chair conformation. Based on PMR spectra, one of the stereoisomers has a quasiaxial methyl group and pseudoequatorial nitrile and isopropylidene groups, while the other stereoisomer has a quasi-axial isopropylidene substituent and equatorial nitrile and methyl groups.

2. Dichlorocyclopropanation of these adducts occurs from the sterically less hindered side of the molecules, with the formation, from one of the stereoisomers, of a cycloaddition product at the exocyclic double bond, and two stereoisomeric cycloaddition products at the two double bonds with a cis orientation of the cyclopropane ring and the CN group; the other stereoisomer, on the other hand, gives two stereoisomeric cycloaddition products at the two double bonds with a trans orientation of the cyclopropane ring and CN-group.

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