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¹³C-NMR SPECTRA OF POLYCYCLIC COMPOUNDS AND THE
STEREOCHEMISTRY OF UNSATURATED DERIVATIVES OF
BICYCLO[2.2.1]HEPT(EN)ANE AND RELATED STRUCTURES

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¹³C-NMR spectroscopy has been used extensively to study bicyclo[2.2.1]-hept(en)ane derivatives [1-5]. For instance, the stereochemistry of isomeric dicyclopentadienes (DCPD) has been established by ¹³C-NMR [4].

The signals due to the bridging C atoms are particularly characteristic and thus useful in identifying stereoisomers; these signals differ by more than 10 ppm in the transition from endo- to exo-DCPD.

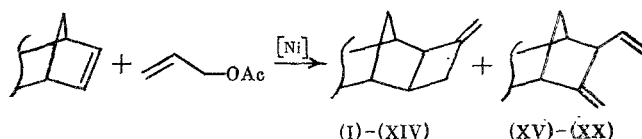
In the first paper in this series, we examined in detail the ¹³C-NMR spectra of norbornadiene dimers and carried out the stereochemical assignments [6]. In the present paper we have used ¹³C-NMR to determine the structure and stereochemistry of a series of unsaturated derivatives of norbornane and norbornene, which were prepared by the reactions of allyl acetate with norbornene, norbornadiene, and their derivatives via catalysis by metal complexes [7].

EXPERIMENTAL

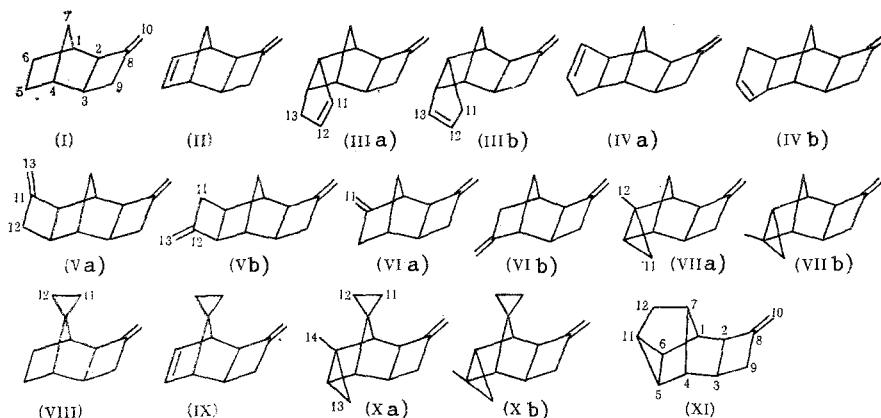
¹³C-NMR spectra were recorded on a Jeol FX-90Q spectrometer (22.5 MHz, in CDCl₃ versus TMS), both in the proton decoupling and monoresonance modes.

RESULTS AND DISCUSSION

According to [6], the catalytic reaction of allyl acetate with norbornene derivatives leads to the formation of two types of structures, namely (I)-(XIV) and (XV)-(XX).



The ¹³C-NMR spectral parameters of compounds (I)-(XIV) are summarized in Table 1.



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TABLE 1. ^{13}C -NMR Spectral Characteristics of Methylenecyclo-

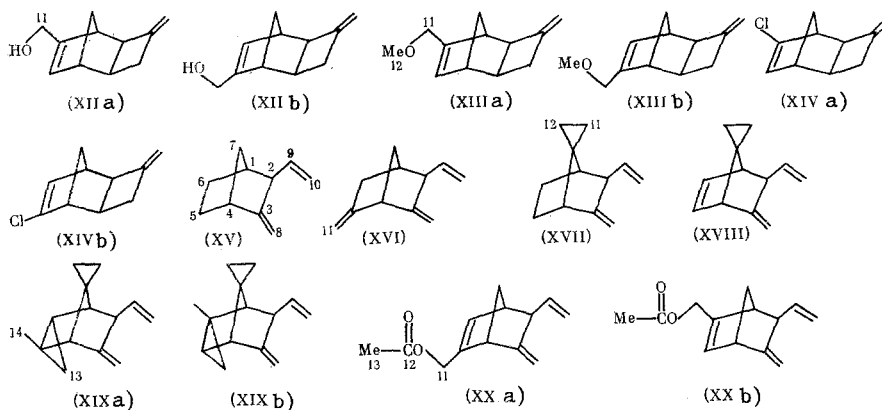
Compound	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ⁷
(I)	39.89 d [+3.1]	51.86 d [+21.8]	37.23 d [+7.1]	39.55 d [+2.8]	28.54 t [-1.6]	27.20 t [-2.9]	32.14 t [-6.6]
(II)	44.99 d [+3.0]	48.13 d [+22.6]	33.64 d [+8.1]	45.21 d [+2.8]	136.86 d [+1.4]	135.21 d [-0.3]	40.37 t [-8.4]
(III a)	42.15 d (42.9)	47.94 d (47.2)	30.21 d (29.2)	44.08 d (44.2)	42.59 d (41.1)	51.64 d (50.2)	35.22 t (34.8)
(III b)	45.06 d (44.5)	44.47 d (43.9)	33.14 d (32.5)	42.09 d (42.6)	53.05 d (51.5)	41.20 d (39.8)	35.22 t (34.8)
(IV a)	43.89 d (43.7)	54.83 d (51.1)	37.32 d (36.1)	46.75 d (46.1)	41.42 d (42.5)	51.32 d (53.1)	25.49 t (25.2)
(IV b)	46.57 d (46.4)	53.42 d (50.8)	36.65 d (36.4)	44.04 d (43.4)	51.82 d (54.4)	42.80 d (41.2)	25.49 t (25.2)
(Va)	43.37 d (43.0)	49.48 d (49.0)	36.06 d (35.5)	42.69 d (42.4)	36.06 d (35.6)	49.48 d (49.0)	25.85 t (25.5)
(Vb)	43.13 d (42.7)	50.73 d (50.3)	34.87 d (34.3)	43.13 d (42.7)	50.73 d (50.3)	34.87 d (34.3)	25.85 t (25.5)
(VI a)	48.78 d (48.4)	51.06 d (50.1)	36.39 d (36.7)	40.20 d (39.5)	37.21 d (36.5)	150.58 s (151.1)	32.60 t (32.3)
(VI b)	40.46 d (39.8)	50.97 d (51.4)	35.95 d (35.4)	48.61 d (48.1)	151.58 s (152.4)	36.71 t (35.2)	32.48 t (32.3)
(VII a)	44.73 d (46.4)	49.28 d (47.5)	35.59 d (34.1)	40.74 d (39.9)	27.48 d (31.6)	23.97 s (26.9)	44.43 t (43.2)
(VII b)	40.57 d (40.2)	50.06 d (48.8)	34.81 d (32.8)	44.73 d (46.1)	24.10 s (28.2)	28.61 d (30.3)	44.43 t (43.2)
(VIII)	45.99 d (45.0)	53.27 d (51.7)	39.62 d (37.0)	44.43 d (44.7)	28.78 t (28.3)	27.70 t (27.0)	30.64 s (27.9)
(IX)	51.54 d (50.3)	49.80 d (48.0)	36.24 d (33.4)	50.02 d (50.1)	137.14 d (136.7)	135.67 d (135.0)	38.27 d (36.2)
(X a)	51.71 d (51.5)	48.76 d (47.3)	38.01 d (33.9)	44.95 d (45.0)	28.43 d (31.4)	27.96 s (26.7)	43.95 s (40.0)
(X b)	46.46 d (45.3)	50.06 d (48.6)	37.19 d (32.6)	50.80 d (51.2)	28.74 s (28.0)	27.61 d (30.1)	43.95 s (40.0)
(XI)	46.70 d (46.10)	51.08 d (48.24)	37.02 d (35.30)	46.42 d (45.27)	13.52 d (130.42)	13.07 d (150.23)	35.72 d (40.37)
(XII a)	45.58 d (46.36)	49.85 d (48.11)	34.00 d (35.22)	45.95 d (45.51)	151.00 d (132.76)	128.87 d (146.33)	40.37 t (40.31)
(XII b)	45.77 d (45.3)	49.74 d (48.6)	32.83 d (32.6)	46.21 d (51.2)	148.67 s (28.0)	131.08 d (30.1)	40.31 t (40.0)
(XIII a)	47.94 d (46.29)	51.93 d (49.89)	35.37 d (33.90)	46.16 d (47.94)	131.08 d (139.48)	137.96 d (129.56)	40.09 t (40.09)
(XIII b)					s	d	t

Note: The increments due to the methylenecyclobutane fragment
Calculated data are given in parentheses.

butane Derivatives of Norbornane and Norbornene (δ , ppm, CDCl_3 , TMS)

C^8	C^9	C^{10}	C^{11}	C^{12}	C^{12}	C^{14}	Peak ratio
152.48 s	33.95 t	106.30 t					
149.73 s	29.91 t	106.56 t					
153.50 s	34.03 t	105.91 t	131.48 d	130.64 d	31.55 t		3:5
153.00 s	33.85 t	105.74 t	31.88 t	130.64 d	131.44 d		5:3
151.98 s	33.33 t	106.39 t	132.20 d	132.00 d	39.29 t		8:9
152.16 s	33.14 t	106.39 t	39.40 t	132.00 d	132.00 d		9:8
152.16 s	33.90 t	106.48 t	152.16 s	33.90 t	106.90 t		1:1
152.25 s	33.90 t	106.52 t	33.90 t	152.25 s	106.52 t		1:1
152.35 s	33.98 t	107.36 t	103.18 t				7:4
153.46 s	33.09 t	106.69 t	102.68 t				4:7
151.59 s	33.12 t	106.28 t	21.98 t	22.32 q			3:4
151.58 s	33.12 t	106.19 t	21.98 t	22.45 q			4:3
152.75 s	33.64 t	106.15 t	0.69 t	9.10 t			
148.41 s	28.35 t	106.80 t	0.78 t	12.05 t			
151.71 s	32.60 t	106.24 t	0.87 t	8.67 t	21.07 t	22.71 q	5:6
151.68 s	32.79 t	106.11 t	0.87 t	8.67 t	21.07 t	23.06 q	6:5
152.94 s	34.16 t	106.00 t	14.52 d	31.23 t			
149.28 s	30.64 t	106.82 t	60.79 t				1:1
149.84 s	30.19 t	106.45 t	60.68 t				1:1
149.80 s	30.60 t	106.80 t	70.35 t	57.82 q			3:2
150.15 s	30.17 t	106.45 t	70.26 t	57.82 t			2:3
148.07 s	30.34 t	107.80 t					3:1
148.97 s	29.56 t	107.19 t					1:3

relative to norbornane and norbornene (I) are given in brackets.

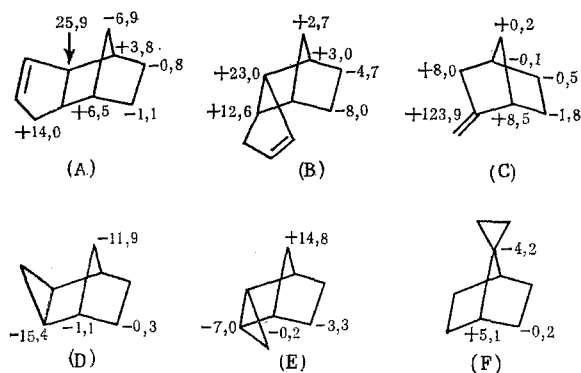


In order to simplify comparisons between the same types of carbon atoms, the atomic designations used in this paper follow the numbering system of the norbornane skeleton in each molecule.

The spectrum of (I) exhibits 10 signals, of which 7 are assigned to the norbornane skeleton; the doublet signals at 51.86 and 37.23 ppm correspond to C^2 and C^3 , respectively. The exo-methylene group gives rise to the singlet at 152.48 and the triplet at 106.30 ppm. The methylene group triplet at 33.96 ppm completes the spectrum of the cyclobutane fragment. In order to establish the orientation of the cyclobutane fragment relative to the norbornane skeleton, the chemical shifts (CS) of the bridging carbon C^7 were utilized. It is known that the CS of the C^7 bridge is 38.7 ppm in the parent molecule, norbornane [1]. In the case of unsaturated DCPD derivatives, the corresponding signal for the endo-isomer occurs at 41.4 ppm, and that of the exo-isomer at 31.8 ppm [4]. The CS of the bridging carbon C^7 in (I) (32.14 ppm) indicates therefore that this compound belongs to the exo-stereochemical series. The diamagnetic shift of the C^7 signal can be explained in terms of steric interactions involving the syn-bridging proton and the exo- $C=C$ double bond of the cyclobutane fragment.

Compound (II) is characterized by downfield signals for C^5 and C^6 (136.86 and 135.21 ppm). The diamagnetic shift of the C^7 signal by 8 ppm relative to the analogous signal in norbornene [1] is indicative of the exo-orientation of the methylenecyclobutane fragment.

Comparison of the spectra of (I), (II), norbornane, and norbornene [1] has yielded incremental values for the effect of an exo-methylenecyclobutane group on the CS of the norbornane skeleton. The values of these increments are given in Table 1 in brackets. Incremental values for the effect of a cyclopentenyl group on the CS of the norbornane skeleton in exo-(A) and endo-(B) DCPD were calculated in a similar manner [4].



Using the data reported previously [4, 5], incremental values for the methylene group in compound (C) and the cyclopropane rings in the annelated derivatives (D) and (E) and in the 7,7-spiroderivative (F) were determined. Based on these incremental values, the spectra of mixtures of isomers of (IIIa, b) and (VIIa, b) were analyzed, and the relative positions of the double bonds and methyl groups, as well as the orientations of the cyclopentenyl, methylcyclobutane, and cyclopropane fragments relative to the norbornane skeleton, were established.

TABLE 2. ^{13}C -NMR Spectral Parameters for 2-exo-Methylene-3-vinyl Derivatives of Norbornane and Norbornene (δ , ppm, CDCl_3 , TMS)

Compound	C ¹	C ²	C ³	C ⁴	C ⁵	C ⁶	C ⁷	C ⁸	C ⁹	C ¹⁰	C ¹¹	C ¹²	C ¹³	C ¹⁴	Peak ratio
(XV)	45.34 d	157.38 s	52.92 d	42.48 d	29.52 t	28.65 t	35.95 t	103.96 t	140.28 d	113.43 t					
(XVI)	[+3.4] 54.96 d	154.39 s	[+14.8] 51.60 d	[+5.8] 42.43 d	[0.0] 37.15 t	[+0.3] 151.83 s	[-3.0] 36.67 t	103.31 t	140.02 d	113.97 t	104.87 t				
(XVII)	(53.3) 50.89 d	(154.6) 157.99 s	(52.4) 55.22 d	(41.5) 48.29 d	(37.2) 29.13 t	(150.3) 29.26 s	(36.4) 33.42 s	103.77 t	140.78 d	113.35 t	3.47 t	7.06 t			
(XVIII)	(50.4) 56.70 d	(157.1) 152.87 s	(52.7) 51.93 d	(47.6) 53.83 d	(28.4) 137.05 d	(29.3) 134.89 d	(32.7) 43.39 s	105.15 t	140.22 d	114.60 t	3.77 t	9.15 t			
(XIX a)	(55.8) 57.34 d	(152.6) 154.56 s	(48.1) 52.27 d	(53.0) 48.11 d	(134.4) 28.65 d	(133.5) 29.00 s	(42.8) 46.60 s	105.28 t	140.83 d	113.65 t	3.77 q	6.11 q	23.10 t	22.02 q	5:6
(XIX b)	(56.9) 52.70 d	(152.8) 155.26 s	(49.6) 51.49 d	(47.9) 53.54 d	(32.4) 29.39 s	(28.1) 27.91 d	(43.8) 46.60 s	105.72 t	140.91 d	113.65 t	3.34 q	6.24 q	23.10 t	22.93 q	6:5
(XX a)	(50.7) 52.03 d	(154.1) 152.36 s	(48.3) 49.32 d	(54.1) 48.04 d	(29.0) 133.75 d	(31.7) 144.65 s	(43.8) 46.02 t	106.07 t	140.70 d	114.69 t	64.69 t	170.74 s	20.85 q		4:3
(XX b)	51.34 d	153.40 s	49.09 d	48.78 d	145.66 s	132.25 d	46.21 t	105.71 t	140.51 d	114.92 t	62.01 t	170.79 s	20.86 q		3:1

Note. Incremental values for the vinyl group relative to 2-methylenenorbornane [5] are shown in brackets; calculated data are given in parentheses.

For the 7,7-spirocyclopropane derivatives (VIII)-(X), in addition to the signal due to the quaternary carbon atom C⁷, the CS difference for the CH₂ group of the spirocyclopropane ring is also informative; this difference arises due to steric shielding of the syn-methylene group by the exo-oriented cyclobutane fragment. The exo-orientation of the methylenecyclobutane fragment in polycycle (XI) was established by comparison with the corresponding norbornadiene dimers, namely, hexacyclo[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]tetradecane stereoisomers [6]. Disturbing the planar symmetry of the starting norbornadiene molecule by the presence of functional groups such as CH₂OH (XII), CH₂OMe (XIII), and Cl (XIV) leads to the formation of mixtures of isomers, with the fraction of isomers with the functional groups located at C⁶ increasing in this series. Analysis of the spectra of (XVI)-(XX) was carried out using the incremental values of the vinyl group, which were obtained from the spectrum of (XV) relative to 2-methylenenorbornane (C) [5], and which are given in Table 2. The exo-configuration of the vinyl group follows from the shielding of C⁷. The presence of one isomer (XVI) with 2,6-dimethylene groups reflects its greater stability as a result of conjugation effects, compared to the other possible isomers having a 2,5-distribution of double bonds. In the 7,7-spirocyclopropane derivatives, a vinyl group in the exo-orientation has a much weaker influence on the methylene group of the cyclopropane ring than a methylene-cyclobutane group, which also supports the steric nature of the interaction.

CONCLUSIONS

Structures of a series of unsaturated bicyclo[2.2.1]hept(en)ane derivatives and related compounds have been established by analysis of their ¹³C-NMR spectra, which has also permitted stereochemical assignments of cyclopropane, cyclobutane, and cyclopentene fragments and vinyl groups, relative to the norbornane backbone in each molecule. In the case of 7,7-spirocyclopropane derivatives of norbornane and norbornene, the chemical shift difference for the methylene groups of the cyclopropane fragment proved to be stereochemically informative.

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