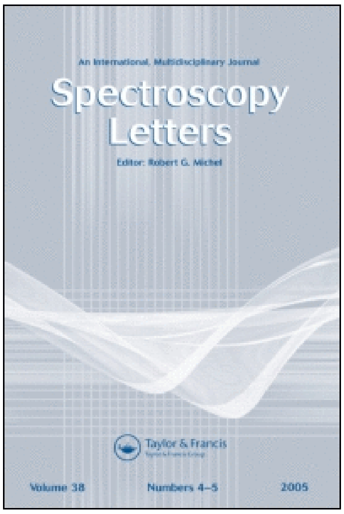

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Configurational Assignments of 5-Norbornene-2,3-dicarboximide and N-Phenyl-5-norbornene-2,3-dicarboximide by One- and Two- Dimensional NMR Spectroscopy

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CONFIGURATIONAL ASSIGNMENTS OF 5-NORBORNENE-2,3-DICARBOXIMIDE AND N-PHENYL-5-NORBORNENE-2,3-DICARBOXIMIDE BY ONE- AND TWO- DIMENSIONAL NMR SPECTROSCOPY

KEY WORDS: norbornene, dicarboximide, NMR spectroscopy

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ABSTRACT

The ^{1}H, ^{13}C, and two-dimensional both homonuclear (H,H-Cosy) and heteronuclear (H,C-Cosy) correlated NMR spectra of *endo*- and *exo*-isomers of 5-norbornene-2,3- dicarboximide and N-phenyl-5-norbornene-2,3- dicarboximide have been examined. Two-dimensional spectra gave evidence for configurations based on long-range couplings. ^{13}C resonances of carbons 1,4 and carbons 2,3 were ultimately assigned by means of gated decoupled spectra from which the coupling constants ($^{1}J_{C,H}$) were determined. The literature assignments of the ^{1}H NMR spectrum of N-phenyl-5-norbornene- *endo*-2,3-dicarboximide have been revised. The spectra of the imides were compared with the spectra of *endo*- and *exo*-isomers of 5-norbornene-2,3-dicarboxylic anhydride in order to examine the stereochemical effects of imide ring on the proton and carbon shieldings in 5-norbornene skeleton. When the imide ring is at *endo*-position of norbornene skeleton the protons of carbons 2 and 3 resonate at higher field than the protons of carbons 1 and 4. The order is opposite with the *endo*-anhydride. The carbonyl carbons resonate clearly at lower field in imides than in anhydrides.

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INTRODUCTION

Several substituted bicyclo[2.2.1]heptene derivatives have been investigated by NMR spectroscopy in order to evaluate the influence of molecular geometry and substituents on ^1H and ^{13}C chemical shifts and coupling constants.[1-8] The chemical shifts of the protons at carbons 2 and 3 have been used in determination of the *endo/exo* configurations of the bicyclic Diels-Alder adducts. The magnetically anisotropic double bond shifts the signals of *exo*- protons downfield and the *endo*-protons upfield.[9,10] Similarly, substituents in the 2- and 3-positions affect the chemical shifts of the protons at the double bond. Another characteristic feature is that the bridge carbon 7 in bicyclic Diels-Alder adducts resonate at higher field in the *exo*-isomer than in the *endo*-isomer.[6,7]

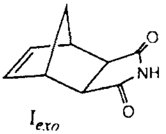
In this study the influence of imide ring on the chemical shifts of the ^1H and ^{13}C NMR spectra of norbornene skeleton has been investigated and compared with the spectra of corresponding anhydrides. Hasan[11] has investigated ^{13}C NMR spectra of some amides, anhydrides and imides and found the imide carbonyl mostly resonate at lower field than amide carbonyl and anhydride carbonyl. Two-dimensional spectra (H,H-Cosy and H,C-Cosy) have been proven useful in determination the *endo*- and *exo*-configurations. In the *endo*-isomers the protons 1, 4 and 2, 3 resonate quite near to each other, however the signals can be assigned by using two-dimensional both homonuclear (H,H-Cosy) and heteronuclear (H,C-Cosy) correlation spectra together with the coupling constants ($^1J_{C,H}$).

EXPERIMENTAL

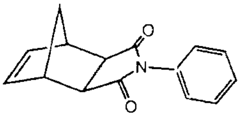
Most of the one and two-dimensional NMR spectra were obtained on a Varian Gemini 200 NMR-spectrometer operating at 199.89 MHz for ^1H, 50.29 MHz for ^{13}C and some one-dimensional spectra on a Jeol PFT-100 with Texas Instr. EC-100 data system, memory capacity 20 k. The NMR samples were 0.4 - 0.5 M in $CDCl_3$ and some also in $(CD_3)_2CO$. ^1H and ^{13}C NMR measurements were carried out at room temperature in 5 mm diameter NMR tubes (or some ^{13}C NMR measurements in 10 mm diameter tubes). The ^1H and ^{13}C chemical shifts in δ ppm were referenced to the signal of internal TMS.

Compounds

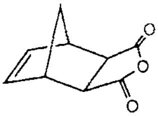
The compounds, 5-norbornene-2,3-dicarboximides (I_{endo} and I_{exo}), N-phenyl-5-norbornene-2,3-dicarboximides (II_{endo} and II_{exo}), and 5-norbornene-2,3-dicarboxylic anhydrides (III_{endo} and III_{exo}) were synthesized according to literature.[12,13]



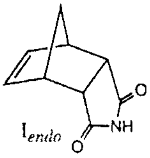
I_{exo}



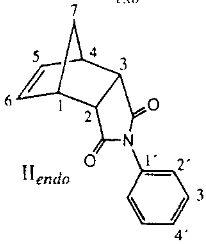
II_{exo}



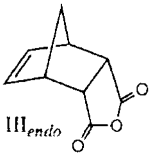
III_{exo}



I_{endo}



II_{endo}



III_{endo}

The purities of the compounds were checked by the melting points, by the mass spectra and by the NMR spectra, which did not show any impurity signals.

RESULTS AND DISCUSSION

Molecular mechanics calculations (with Sybyl program) showed the *endo*-isomers are energetically about 3.2-4.2 kJ/mol more stable than the *exo*-isomers. The imide ring is nearly planar in both cases and the bond lenghts between C(sp^2) and O are about 1.22 Å and between N - C(sp^2) are about 1.34 Å. Although the resonance is not very significant the C(sp^2) - O bond is a little bit longer than the normal double bond between carbon and oxygen and similarly the N - C(sp^2) bond is shorter than the normal single bond between carbon and nitrogen. The bond between nitrogen and carbon atom of aromatic ring is also little shorter than the normal single N - C single bond. The resonance between the free electron pair of nitrogen and the π-electrons of aromatic ring can not be very significant, because the bond angle between aromatic and imide ring is unfavorable (about 42° calculated by Sybyl and 45° calculated by Macromodel).

TABLE 1

^{1}H Chemical Shifts (in ppm from internal TMS) of *Endo*- and *Exo*-Isomers of Compounds I, II and III.

H	I_{endo}	I_{exo}	II_{endo}	II_{exo}	III_{endo}	III_{exo}
7a	1.52	1.46	1.59	1.47	1.59	1.42
			1.62*	1.50*	1.68¤	1.40¤
7s	1.74	1.57	1.77	1.61	1.77	1.65
			1.79*	1.61*	1.70¤	1.60¤
2 & 3	3.32	2.74	3.42	2.85	3.56-3.62	3.03
			3.51*	2.87*	3.78¤	3.13¤
1 & 4	3.35	3.29	3.47	3.36-3.43	3.47-3.55	3.39-3.47
			3.45*	3.42*	3.43¤	3.34¤
5 & 6	6.20	6.28	6.25	6.34	6.30	6.33
			6.27*	6.36*	6.28¤	6.37¤
NH	8.41	8.91				
arom H			7.07-7.52	7.20-7.57		

*values from ref. 4

¤measured in aceton-D_6

^{1}H NMR Spectra (Table 1): The effect of imide ring on chemical shifts is larger than the effect of N-phenylimide ring. The norbornene skeleton protons of imides and N-phenylimides resonate mainly at higher field than the corresponding protons of anhydrides, except proton 7a of *exo* I and II isomers which resonates at lower field than in anhydrides. Earlier it has been found that the protons 1,4 of the *endo*-isomer of N-phenylimide (II_{endo}) resonate at higher field than the protons 2,3.[4] However, the present study clearly shows, protons 1 and 4 of *exo*-imides I and II resonate at lower field than the protons 2 and 3 but in *endo*-anhydrides the order is opposite, the difference is due to the different effects of nitrogen and oxygen.

The two hydrogen atoms (7a and 7s) of the methylene bridge are not equivalent and they give an AB type spectrum. The geminal coupling constant between the protons 7a and 7s is larger at *endo*-isomers:J = -8.8 Hz (I_{endo}), J = -9.9 Hz (I_{exo}); J = -8.9 Hz (II_{endo}), J = -9.8 Hz (II_{exo}), J = -9.0 Hz (III_{endo}); J = -10.2 Hz (III_{exo}).

^{13}C NMR Spectra (Table 2): Compared with norbornene all carbons of imides I and II resonate at lower field except the double bond carbons 5 and 6 of *endo*-imides. The carbons 1,4 and 2,3 of *endo*-N-phenyl-5-norbornenedicarboximide (II_{endo}) resonate quite near to each other and the assignment has been difficult.[4] Our study shows that carbon 1 and 4 appear upfield from carbons 2 and 3 both in imides and anhydrides. The ultimate assignment of the carbons 1,4 and 2,3 is possible by the gated decoupling experiment (Table 3) as $^1J_{CH}$-coupling is larger at bridgehead (carbons 1 and 4) than in etylene bridge (carbons 2 and 3).[14] Carbons 1 and 4 are at γ-position with respect to nitrogen and oxygen. In imides these carbons resonate at higher field than in the N-phenylimides and especially the carbons 1 and 4 of imides are shifted to higher field compared with anhydrides. The carbons 2 and 3 in N-phenylimides resonate at higher field than in imides and anhydrides.

Endo- and *exo*-configurations can be assigned based on the chemical shifts of carbons 5 and 6 or based on the chemical shift of carbon 7. In *endo*-isomers the carbons 5 and 6 resonate at higher field than at *exo*-isomers. The carbons 5 and 6 of the *endo*-imides (I_{endo} and II_{endo}) resonate 3.17 and 3.45 ppm at higher field than the carbons 5 and 6 of *exo*-imides. The corresponding difference between *endo*- and *exo*- anhydrides is only 2,3 ppm. In *endo*-isomers the chemical shift of carbon 7 is at lower field than in *exo*- isomers. The difference between the chemical shifts of carbon 7 of *endo*- and *exo*-imides is 9,4 ppm, of *endo*- and *exo*-N-phenylimides 9,2 ppm and of *endo*- and *exo*-anhydrides only 8.6 ppm.

Two-dimensional H,H-correlated Spectra (H,H-Cosy spectra) of compounds show the couplings between protons of the compounds I, II and III (Fig. 1 and Table 4).

Kamezawa et al[2] have measured the coupling constants of anhydrides III_{endo} and III_{exo} using a decoupling technique and from the present H,H-Cosy spectra it's

TABLE 2

^{13}C Chemical Shifts (in ppm from internal TMS) of *Endo*- and *Exo*-Isomers of Compounds I, II and III.

C	I_{endo}	I_{exo}	II_{endo}	II_{exo}	III_{endo}	III_{exo}
1 & 4	44.92	45.12	45.36 45.8*	45.77 45.8*	46.1 47.1*	46.8 46.8*
2 & 3	47.32	49.19	45.65 45.5*	47.81 47.8*	47.1 46.1*	48.8 48.7*
7	52.27	42.91	52.08 52.2*	42.91 44.6*	52.7 52.8*	44.1 44.1*
5 & 6	134.54	137.71	134.45 134.6*	137.90 138.0*	135.5 135.5*	137.8 137.9*
C=O	178.28	178.62	176.63	176.87	171.5	171.7
2'			126.56	126.27		
4'			128.39	128.50		
3'			128.89	129.04		
1'			131.86	131.83		

* values from ref.4

TABLE 3

Selected Coupling Constants $^{1}J_{CH}$ in Hz.

$^{1}J_{CH}$	I_{endo}	I_{exo}	II_{endo}	II_{exo}	III_{endo}	III_{exo}
$C_{1,4}H$	153.1	152.4	152.8	152.6	152.7	152.6
$C_{2,3}H$	142.5	146.6	142.4	147.1	144.0	147.1
$C_{7}H$	131.9	134.4	132.2	132.9	132.9	134.3
$C_{5,6}H$	172.2	172.1	172.2	172.1	170.3	173.9

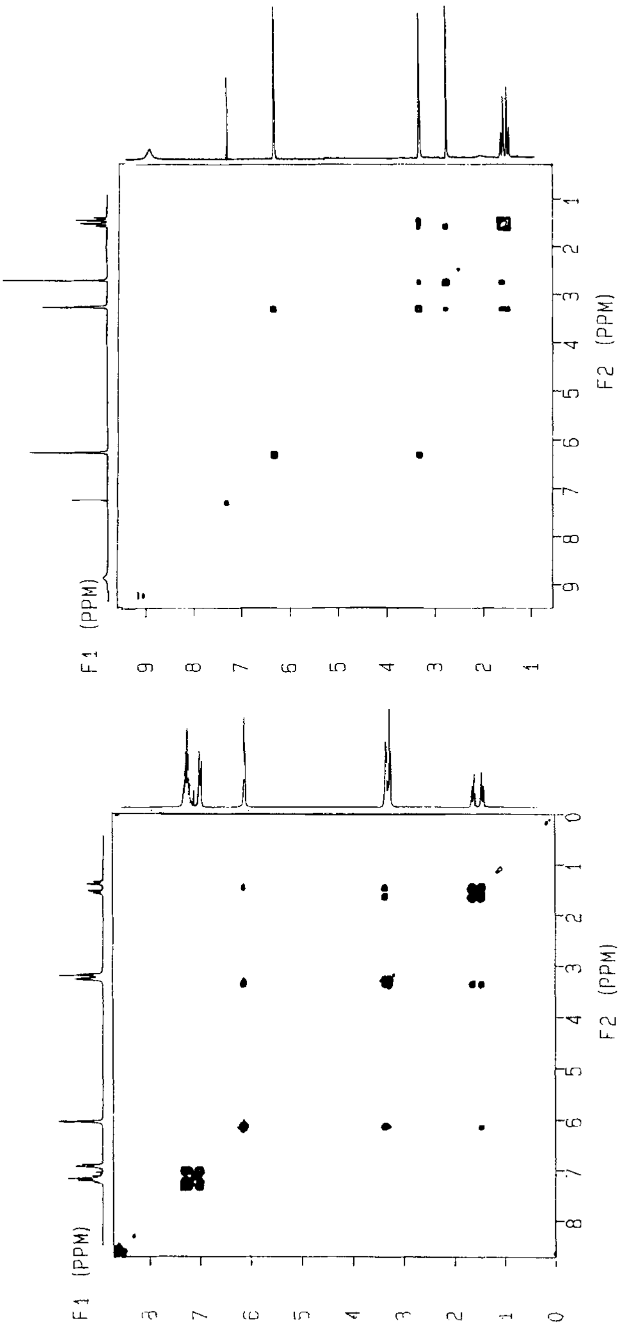


FIG. 1. The H,H-Cosy spectrum of a) II$_{endo}$ and b) I$_{exo}$.

TABLE 4

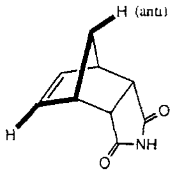
The H,H-Cosy Spectra Show the Following Couplings Between the Protons of Compounds I, II and III.

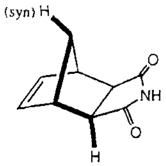
J_{HxHy}	I_{endo}	I_{exo}	II_{endo}	II_{exo}	III_{endo}	III_{endo*}	III_{exo}	III_{exo*}
7a;7s	+	+	+	+	+	9.0	+	10.2
7a;1,4	+	+	+	+	+	1.3	+	1.7
7s;1,4						1.4		1.5
7a;5,6	+	-	+	+	+	0.4	+	0.7
1,4;5,6	+	+	+	+	+	1.8	+	1.9
1,4;2,3	+	+	+	+	+	2.2	+	0.5
7s;2,3	-	+	-	+	-	0.7	+	1.8

+ the couplings found, - the couplings not found

* III_{endo} and III_{exo} measured by Kamezawa et al[2]

possible to see the same couplings except that the proton 7a of *exo*-imides is not coupled to the protons at carbons 5 and 6 although the coupling constant 0,7 Hz has been measured for III_{exo}. In order to find this coupling the H-relayed (H,H)-Cosy experiment should have been used. Instead *endo*-imides this coupling can be seen. The characteristic feature for *exo*-isomers I, II and III is the long range coupling (W-type) of the proton 7s to the protons on C-2 and C-3. This coupling may be used to identify the *exo*- configurations. The same coupling is not visible in H,H-Cosy spectra of *endo*-isomers although a coupling constant of 0.7 Hz has been reported for it.[2] The bonds linking the coupled nuclei 7a and 5(or 6) of both *endo*- and *exo*-isomers or 7s and 2(or 3) of *exo*-isomers are in sterically fixed W configuration, but for the bonds linking the protons 7s and 2 or 3 of *endo*-isomers this is not possible.





Moreover, the protons on the carbons 1 and 4 are coupled to the both protons on carbon 7. Thus H,H-Cosy allows easy assignment of protons 1,4 and 2,3.

Two-dimensional H,C-correlated Spectra (H,C-Cosy) are useful in assignment of chemical shifts in ^1H and ^{13}C spectra. (Fig.2) This spectrum ultimately confirm that in the ^{13}C spectra of imides I and II and anhydrides III the carbons 2 and 3 resonate at lower field than the carbons 1 and 4. We can also confirm that in the ^1H spectra of imides I and II the protons 1 and 4 resonate at lower field than the protons 2 and 3 but at *endo*-anhydride the order is opposite.

CONCLUSION

The ^1H and ^{13}C NMR spectra of norbornene-2,3- dicarboximides (I and II) have been determined and the assignment of chemical shifts of protons and carbons 2,3 and 1,4 in the spectra of II_{endo} have been revised. Characteristic for *endo*-imides (I and II) is that the chemical shifts of the protons 1 and 4 are at lower field than the chemical shifts of the protons 2 and 3, opposite to *endo*-anhydrides. Both imides and anhydrides the chemical shifts of carbons 2 and 3 are at lower field than the chemical shifts of the carbons 1 and 4.

The usefulness of two-dimensional H,H- and H,C- correlation spectroscopy in assigning the spectra has been shown. The *endo*/*exo*-configuration can be assigned reliably by using H,H-Cosy spectra: the proton 7s is coupled to the protons on the carbon 2 and 3 of *exo*-isomers. The bridgehead protons 1 and 4 can be distinguished from the protons on carbons 2 and 3 based on the couplings, which may be seen from H,H-Cosy spectra. The protons 1 and 4 are coupled with the protons 7a and 7s. Altogether the coupling constants $^1J_{C,H}$ of the bridgehead carbons is larger than the same coupling constant of the carbons 2 and 3. When the carbons 1,4 and 2,3 have

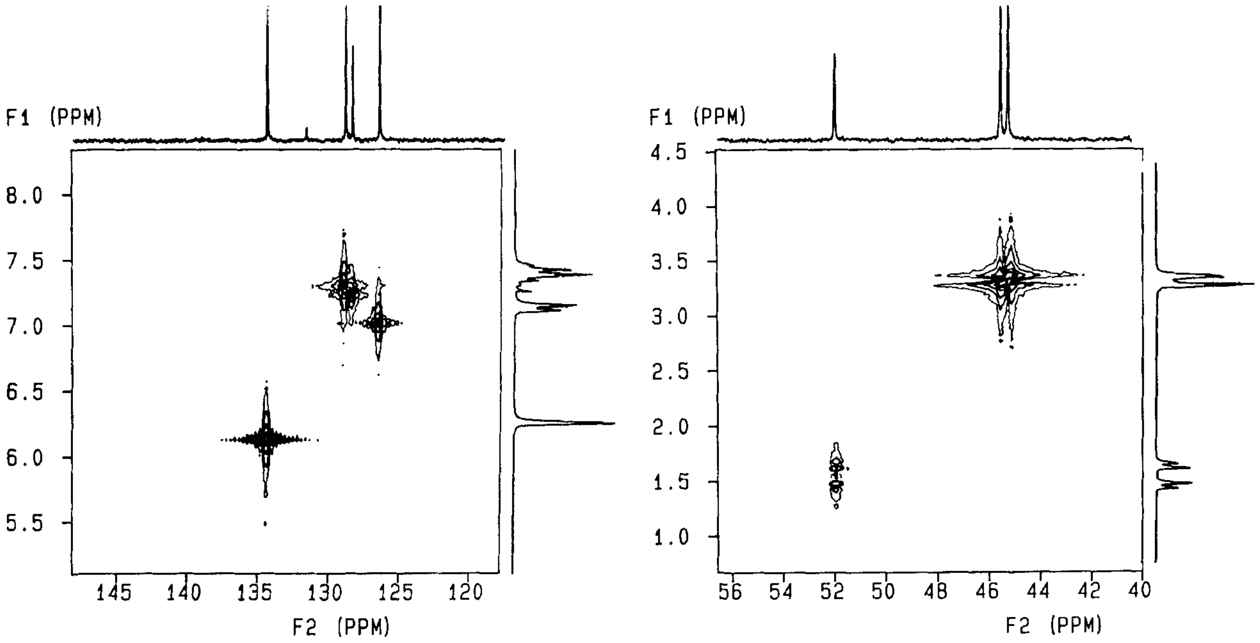


FIG. 2. The H,C-Cosy Spectrum of II_{endo}.

been assigned the chemical shifts of the corresponding protons may be identified by H,C-Cosy spectra.

Endo/exo assignments can also be made on the basis of coupling constant. In *endo*-isomers the $^2J_{7a,7s}$ is larger than in *exo*-isomers. The characteristic feature for *exo*-isomers is also that the chemical shift of carbon 7 is at higher field than at *endo*-isomers.

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REFERENCES

1. P. M. Subramanian, M. T. Emerson and N. A.LeBel, Nuclear Magnetic Resonance Studies of 5,6-Dihalo-2-norbornenes and 2,3-Dihalonorbornenes, *J. Am. Chem. Soc. 30* (1965) 2625-2634.

2. N. Kamezawa, K. Sakashita and K. Hayamizu, Nuclear Magnetic Resonance Studies of 5,6-Dicarboxy-2-norbornene Derivatives, *Org. Magn. Res. 1* (1969) 405-414.

3. S. M. Verma and A. K. Singh, Configurational Assignments of Cyclopentadiene-Maleic Anhydride Diels-Alder Adducts Through Conformational Studies by NMR Spectroscopy, *Indian J. Chem. 15B* (1977) 700-702.

4. A. C. Wong and W. M. Ritchey, The Endo-Exo Isomerization of N-Phenyl-5-norbornene-2,3-dicarboximide, *Spectroscopy Letters 13* (1980) 503-508.

5. N. H. Werstiuk, R. Taillefer, R. A. Bell and B. Sayer, ^{13}C-H Coupling Constants in Cyclic Systems; a Probe for Hyperconjugation and Homoconjugation?, *Can. J. Chem. 51* (1973) 3010-3014.

6. E. Lippmaa, T. Pehk, J. Paasivirta, N. Belikova and A. Plate, Carbon-13 Chemical Shifts of Bicyclic Compounds, *Org. Magn. Res. 2* (1970) 581-604.

7. H. Brouwer, J. B. Stothers and C. T. Tan, Carbon-13 N.m.r. Studies, Part 66 - ^{13}C Spectra of Several Methyl, Hydroxymethyl and Carboxylic Acid Derivatives of Bicyclo[2.2.1]heptane and Bicyclo[2.2.2]octane *Org. Magn. Res. 9* (1977) 360-366 and ref. therein.

8. J. B. Stothers, C. T. Tan and K. C. Teo, ^{13}C Nuclear Magnetic Resonance Studies. 55. A Comparison of the Stereochemical Dependence of γ- and δ-substituent Effects on ^{13}C Shieldings in Several Norbornanols and Norbornenols, *Can. J. Chem. 54* (1976) 1211 - 21.

9. R. S. Fraser, The Establishment of Configuration in Diels-Alder Adducts by N.M.R. Spectroscopy, *Can. J. Chem. 40* (1962) 78-84

10. A. P. Marchand and J. E. Rose, On the Question of Bridge-Proton Absorptions in the Nuclear Magnetic Resonance Spectra of Norbornene and Related Systems, *J. Am. Chem. Soc. 90 (1968) 3724-3731.*

11. M. u Hasan, ^{13}C NMR Spectra of Some Amides and Imides. Effect of Inductive and Mesomeric Interactions, Cyclization and Hydrogen Bonding on ^{13}C NMR Chemical Shifts, *Org. Magn. Res. 14* (1980) 447-450.

12. L. Fieser, Organic Experiments, D.C.Heath and Company, 1964, Boston, p. 83.

13. A. Vogel, Eds. B.S. Firnis, A. J. Hanaford, P.W.G. Smith and A. R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, Including Qualitative Organic Analysis, 4th ed, Longman, 1978, London, p.828.

14. K. Tori, T. Tsushima, H. Tanida, K. Kushida and S. Satoh, NMR Studies of Bridged Ring Systems XIX ^{13}C-^{1}H Spin Coupling and ^{13}C Chemical Shift of the Bridge Methylene in Benzonorbornene and Benzonorbornadiene, *Org. Magn. Res. 6* (1974) 324-326.

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