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NMR analysis of (1*S*,1a*R*,6a*R*)-2',3',6,6a-tetrahydro-spiro[cycloprop[*a*]indene-1(1a*H*),1'-[1*H*]indene]

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Abstract: The aldol condensation product of 1*H*-indan-1-one, (2*E*)-2-(2,3-dihydro-1*H*-inden-1-ylidene)-2,3-dihydro-1*H*-inden-1-one, subjected to Huang–Minlon reduction conditions was shown, *via* 1D and 2D NMR analysis, to be a mixture of (1*S*,1a*R*,6a*R*)-2',3',6,6a-tetrahydro-spiro[cycloprop[*a*]indene-1(1a*H*),1'-[1*H*]indene] and its 1*R*,1a*S*,6a*S* enantiomer and not 2,3,1',3'-tetrahydro-[1,2']-biindenylidene as originally expected. The full NMR assignment, the coupling constants in the proton NMR, and the couplings in the HMBC and NOESY of the title compound are summarized in the Table.

Keywords: dimer of indene, NMR assignment, J_{HH}, HMBC, NOESY.

INTRODUCTION

Pyrolysis oil from petroleum and coal contains usually several percent of indene. Therefore, condensation and dimerization products of indene are often found in the pyrolysis oil, generally at concentrations of 0.001 – 0.05 % or even more if it has been in contact with acidic materials.[1] By bonding two indene molecules it is theoretically possible to obtain at least 19 isomers and we have analysed these over the last few years, especially the group of tetrahydro-biindenylidene isomers.[2,3] During this investigation we attempted to synthesize 2,3,1',3'-tetrahydro-[1,2']-biindenylidene (**1**). According to Bell and Spanswick,[4] **1** can be prepared *via* (2*E*)-2-(2,3-dihydro-1*H*-inden-1-ylidene)-2,3-dihydro-1*H*-inden-1-one (**2**),[5] obtained by aldol condensation of 1*H*-indan-1-one followed by a reduction of the carbonyl function to the corresponding CH_2 group under Huang–Minlon reduction conditions.[4] The compound we obtained following this procedure had the same

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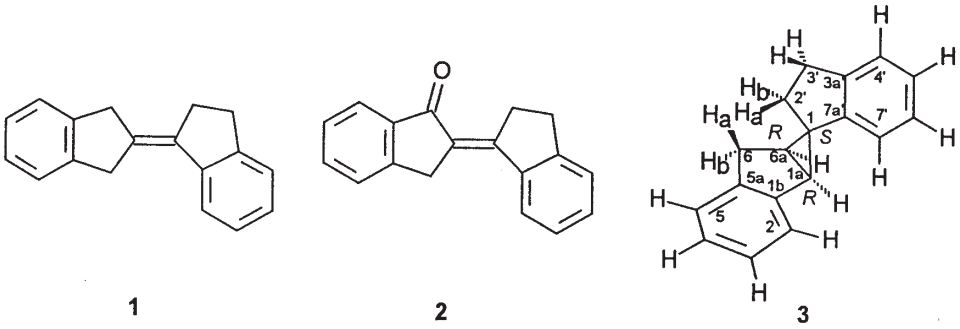
melting point and molecular weight as reported.[4] However, its GC retention time and ^{1}H and ^{13}C-NMR parameters clearly distinguished the obtained compound **3** from **1**. The biindenylidene **1** has already been isolated and characterized from the product mixture obtained from the reaction of 1*H*-indene with H_2SO_4.[6] Therefore, the structure of the thus far unknown compound **3** was elucidated by NMR experiments to be a racemic mixture of (1*S*,1a*R*,6a*R*)-2',3',6,6a-tetrahydro-spiro[cycloprop[*a*]indene-1(1a*H*),1'-[1*H*]indene] (**3**) and its 1*R*,1a*S*,6a*S* enantiomer. This proposal is confirmed by an X-ray analysis.[7] Obviously, a cyclization reaction occurred during the Huang–Minlon reduction, as has also been reported, for instance, during the reduction of cinnamic aldehyde, which has been described to give cyclopropylbenzene.[8]

Recently, **3** was used as model compound to establish a new NMR technique for the determination of relative configurations of small organic molecules.[9]



EXPERIMENTAL

*(1S,1a*R*,6a*R*)-2',3',6,6a-Tetrahydro-spiro*[*cycloprop*[a]*indene-1(1a*H*),1'-*[*1*H]*indene*] (**3**) was syntehsized in racemic form together with its 1*R*,1a*S*,6a*S* enantiomer according to the method of Bell and Spanswick.[4] After aldol condensation of 1*H*-indan-1-one, the carbonyl product **2** was reduced applying Huang–Minlon reduction conditions. The resulting product **3** was isolated by crystallization from propan-2-ol (m.p. 367 K).

Spectra

The ^{1}H and ^{13}C-NMR spectra were measured in $CDCl_3$ on Bruker AMX 600, DMX 600, and Varian INOVA 600 NMR spectrometers. ^{1}H-NMR spectra were calibrated to the residual $CHCl_3$ signal (7.26 ppm) and the ^{13}C-NMR spectra to the $CDCl_3$ signal (77.00ppm). A 5 mm triple probe with a z-gradient was used for standard 1D and 2D experiments. For 2D NOESY experiments, a mixing time between 800 and 1000 ms was used.

RESULTS AND DISCUSSION

Via 1D and 2D NMR analysis, using COSY, NOESY, HSQC and HMBC measurements, it was possible to assign all protons and carbons of **3**, despite the fact that several of the aromatic ring protons were not resolved clearly in the ^{1}H-NMR at 600 MHz. Therefore, J_{HH} for some of the aromatic protons could only be determined by measuring these coupling constants in the HSQC spectrum. Since the resolution of

the J_{HH} coupling constants was limited to 1 – 2 Hz in the HSQC, $^4J_{HH}$ couplings are not shown in Table I. The full assignment of **3**, the coupling constants in the proton NMR, and the couplings in the HMBC and NOESY are summarized in Table I.

The ^{1}H-NMR spectrum showed some interesting details. The H-6a proton is represented as a doublet of doublets with $^3J_{HH}$ 6.7 and 6.5 Hz. Taking into account that H-6a is coupling with H-1a and the two, chemically non-equivalent H-6 protons, a more complex pattern could be expected. Obviously, the dihedral angle between H-6a and H_a-6 amounts practically to $\Phi = 90^o$, giving, in that case, $^3J_{(Ha\text{-}6,\ H\text{-}6a)} = 0$ and thus meaning that the values for the other $^3J_{(Hb\text{-}6,\ H\text{-}6a)}$ and $^3J_{(H\text{-}1a,\ H\text{-}6)}$ must be similar (they amounted to 6.7 and 6.5 Hz, respectively). As the H_a-6 proton with δ_H 3.011 ppm is represented as a doublet (H_b-6 with δ_H 3.365 ppm is represented as a doublet of a doublet), $^3J_{(Ha\text{-}6,\ H\text{-}6a)} = 0$. Some of the long range HC couplings (HMBC experiment) could not be assigned unambiguously, since C-6a and C-3' possess both the same chemical shift δ_C at 30.71 in the ^{13}C-NMR. Also several signals in the aromatic region show nearly identical chemical shifts in the ^{13}C or the ^{1}H-NMR. Only by separately acquiring HSQC and HMBC measurements from the region at δ_H 6.7 – 7.4 ppm and δ_C 110 – 130 ppm, the resolution necessary to assign these signals could be achieved.

TABLE I. NMR-Data of **3** ($CDCl_3$, 600 MHz, 293 K)

Atom	δ_C	δ_H	*J* / Hz	HMBC	NOESY
1 = 1'	37.65	–	–	–	–
1a	39.44	2.692 (*d*, 1H)	6.5 ($^3J_{H\text{-}1a,\ H\text{-}6a}$)	C-1', C-6, C-6a, C-2, C-5a, C-7a'	H-2, H-6a, H-7'
1b	143.55	–	–	–	–
2	124.51	7.247 (*d*, 1H)	7.2 ($^3J_{H\text{-}2,\ H\text{-}3}$)	C-1a, C-4, C-5a	H-1a, H-3
3	126.08	7.135 (*dd*, 1H)	7.2 ($^3J_{H\text{-}3,\ H\text{-}2}$), 6.5 ($^3J_{H\text{-}3,\ H\text{-}4}$)	C-5, C-1b	H-2, H-4
4	125.61	7.123 (*dd*, 1H)	7.0 ($^3J_{H\text{-}4,\ H\text{-}5}$), 6.5 ($^3J_{H\text{-}4,\ H\text{-}3}$)	C-2, C-5a	H-3, H-5
5	124.44	7.178 (*d*, 1H)	7.0 ($^3J_{H\text{-}5,\ H\text{-}4}$)	C-1b, C-3, C-6,	H-4, H_a-6, H_b-6
5a	143.72	–	–	–	–
6 (H_a)	33.19	3.011 (*d*, 1H)	17.8 ($^2J_{Ha\text{-}6,\ Hb\text{-}6}$)	C-1, C-1a, C-1b, (C-3), C-5, C-6a	H-5, H_b-6, H-6a, H_a-2'
6 (H_b)		3.365 (*dd*, 1H)	17.8 ($^2J_{Ha\text{-}6,\ Hb\text{-}6}$), 6.7 ($^3J_{Hb\text{-}6,\ H\text{-}6a}$)	C-1, C-1b, (C-3), C-5, C-6a	H-5, H_a-6, H-6a
6a	30.01	2.207 (*d*, 1H)	6.7 ($^3J_{H\text{-}6a,\ Hb\text{-}6}$), 6.5 ($^3J_{H\text{-}6,\ H\text{-}1a}$)	C-1, C-1a, C-1b, C-5a, C-6, C-7a'	1a-H, 6-H_a, 6-H_b, 7'-H
2' (H_a)	23.76	1.758 (*ddd,* 1H)	13.8 ($^2J_{Ha\text{-}2',\ Hb\text{-}2'}$), 9.4 ($^3J_{Ha\text{-}2',\ H\text{-}3'}$), 7.1 ($^3J_{Ha\text{-}2',\ H\text{-}3'}$)	C-1, C-1a, C-6a, C-3'?, C-3a', C-7a	H_b-2', H-3', H_a-6
2' (H_b)		1.305 (*ddd*, 1H),	13.8 ($^2J_{Ha\text{-}2',\ Hb\text{-}2'}$), 8.6 ($^3J_{Hb\text{-}2',\ H\text{-}3'}$), 6.1 ($^3J_{Hb\text{-}2',\ H\text{-}3'}$)	C-1, C-1a, C-6a, C-3'?, C-3a', C-7a'	H_a-2', H-3'

TABLE I. Continued

Atom	δ_C	δ_H	J / Hz	HMBC	NOESY
3’	30.01	2.929 (*m,* 2H)	–	C-1, C-2’, C-3a', C-4', (C-6'), C-7a'	Ha-2', Hb-2', Ha-6
3a’	143.43	–	–	–	–
4’	124.24	7.187 (*d*, 1H)	7.6 ($^3J_{H\text{-}4', H\text{-}5'}$)	C-3’, C-6’, C-7a’	H-3’, H-5'
5’	126.00	7.150 (*dd*, 1H)	7.6 ($^3J_{H\text{-}5', H\text{-}4'}$), 7.0 ($^3J_{H\text{-}5', H\text{-}6'}$)	C-3a’, C-7’	H-4’, H-6’
6’	126.57	7.188 (*dd*, 1H)	7.0 ($^3J_{H\text{-}6', H\text{-}7'}$), 7.0 ($^3J_{H\text{-}6', H\text{-}5'}$)	C-4’, C-7a’	H-5’, H-7’
7’	118.63	6.795 (*dd*, 1H)	7.0 ($^3J_{H\text{-}7', H\text{-}6'}$)	C-1, C-3a’, C-5’	H-1a, H-6a, H-6’
7a’	147.59	–	–	–	–

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ИЗВОД

NMR АНАЛИЗА (1*S*,1a*R*,6a*R*)-2´,3´,6,6a-ТЕТРАХИДРО-СПИРО[ЦИКЛОПРОП[*a*]ИНДЕН-1(1a*H*),1’-[1*H*]ИНДЕНА]

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Показано је помоћу 1D и 2D NMR анализе да (2*E*)-2-(2,3-дихидро-1*H*-инден-1-илиден)-2,3-дихидро-1*H*-инден-1-он, добивен алдолном кондензацијом 1*H*-индан-1-она, подвргнут Хуанг–Минлоновој редукцији даје смешу (1*S*,1a*R*,6a*R*)-2’,3’,6,6a-тетрахидро-спиро[циклопроп[*a*]инден-1(1a*H*),1’-[1*H*]индена] и његовог 1*R*,1a*S*,6a*S* енантиомера, а не 2,3,1’,3’-тетрахидро-[1,2’]-бииденилиден како се првобитно очекивало. Потпуни NMR распоред, константе куповања протона и HMBC и NOESY куповање једињења у наслову дати су збирно у табели.

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