

Indene dimerization products

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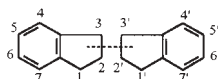
The reaction of 1*H*-indene (indene) in the presence of Friedel-Crafts acids was studied. As expected [M. Spiteller, J. Jovanović, *Fuel* **78**(1999)1263] there were dimers and trimers in the product mixture together with higher oligomers. Among products with double molecular weight relative to the molecular weight of indene, the structure of four compounds was determined: 6-(2',3'-dihydro-1'*H*-inden-1'-yl)-1*H*-indene, 2-(2',3'-dihydro-1'*H*-inden-1'-yl)-1*H*-indene, 1-(2',3'-dihydro-1'*H*-inden-2'-yl)-1*H*-indene and 2,3,1',3'-tetrahydro-[1,2']biindenylidene. It was shown that the first one represents an indene alkylation product and that the others were obtained by bonding of the indan-1-ylum ion and indene at the position 2, followed by acid catalyzed 1,2-hydride rearrangement in the case of the third and fourth one. Considering the indene dimerization products as components of pyrolysis oils and as interesting compounds to be used as model substances for NMR, MS and X-ray analysis, the reaction, separation and isolation parameters were optimized in this study.

Keywords: dimers of indene; structure elucidation; NMR spectroscopy; MS spectrometry; HPLC chromatography.

INTRODUCTION

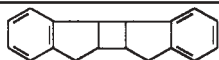
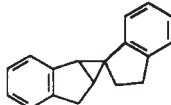
Derivatives of indene are among the major components of pyrolysis oils and their investigation could be useful for environmental research. During the investigation of the reaction of 1*H*-indene (indene) and naphthalene in the presence of boron trifluoride, significant quantities (intensive peaks in HPLC and GC-MS chromatograms) of dimers and trimers of indene, as well as alkylation products of naphthalene were found in the product mixture.¹ As shown in this study and according to expectations, the product mixture obtained by the reaction of indene in the presence of boron trifluoride contained compounds with double and triple molecular weights ($M = 232$ and 348) relative to the molecular weight of indene ($M = 116$). It was found, further, that their yield and relative quantity depended highly on the reaction temperature and the acid used.

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TABLE I. Possible products obtained by bonding two indene molecules arranged according to increasing values of their internal energies relative to the most stable structure **1**³

Nr	Structure	Name and remark
1		(<i>E</i>)-2,3,2',3'-Tetrahydro-[1,1']biindenylidene ^{4,5,6,7}
2		2,3,1',3'-Tetrahydro-[1,2']biindenylidene. ⁸ Isolated and analyzed by 2D-NMR
3		(<i>Z</i>)-2,3,2',3'-Tetrahydro-[1,1']biindenylidene ^{4,5,6,9}
4		2-(2',3'-Dihydro-1' <i>H</i> -inden-1'-yl)-1 <i>H</i> -indene. ^{6,10,11} Isolated and analyzed by 2D-NMR
5		2-(2',3'-Dihydro-1' <i>H</i> -inden-2'-yl)-1 <i>H</i> -indene
6		1,3,1',3'-Tetrahydro-[2,2']biindenylidene ^{12,13}
7		3-(2',3'-Dihydro-1' <i>H</i> -inden-2'-yl)-1 <i>H</i> -indene
8		3-(2',3'-Dihydro-1' <i>H</i> -inden-1'-yl)-1 <i>H</i> -indene ^{4,14}
9		5-(2',3'-Dihydro-1' <i>H</i> -inden-1'-yl)-1 <i>H</i> -indene
10		6-(2',3'-Dihydro-1' <i>H</i> -inden-1'-yl)-1 <i>H</i> -indene. Isolated and analyzed by 2D-NMR
11		7-(2',3'-Dihydro-1' <i>H</i> -inden-2'-yl)-1 <i>H</i> -indene
12		4-(2',3'-Dihydro-1' <i>H</i> -inden-1'-yl)-1 <i>H</i> -indene
13		1-(2',3'-Dihydro-1' <i>H</i> -inden-2'-yl)-1 <i>H</i> -indene. Isolated and analyzed by 2D-NMR
14		(1 <i>RS</i> , 1' <i>SR</i>)-1-(2',3'-Dihydro-1' <i>H</i> -inden-1'-yl)-1 <i>H</i> -indene ^{4,14}
15		(1 <i>RS</i> , 1' <i>RS</i>)-1-(2',3'-Dihydro-1' <i>H</i> -inden-1'-yl)-1 <i>H</i> -indene ^{4,14}
16		2,3-Benzo-5,6-(2',3'-dihydro)-1' <i>H</i> -indeno-bicyclo[2.2.1]heptane
17		<i>trans</i> -Truxane ¹⁵

TABLE I. Continued

Nr	Structure	Name and remark
18		<i>cis</i> -Truxane ¹⁵
19		Spiro-[1,1a,6,6a-Tetrahydrocyclopropa[a]indene-1,1'-2',3'-dihydro-1'H-indene] ¹⁶

By bonding two indene molecules it is theoretically possible to obtain numerous products as shown in Table I. They are arranged according to increasing values of internal energy relative to the most stable structure **1**, with the exception of structure **19** that was not calculated and hence is located at the end of Table I. The internal energy values, calculated using *Gaussian 98*,² applying the density functional B3LYP and the basis set of the Stuttgart group, were kindly given to us by Bleckmann *et al.*³ The compounds shown in Table I could be considered as interesting structures to be used as model substances for NMR, MS and X-ray analysis. For that purpose it was necessary to isolate them in pure enough form to make the unambiguous determination of their structures possible. Compounds **5**, **7**, **9**, **10**, **11**, **12**, **13** and **16** in Table I have not been described in the literature and the literature data for compound **2** were incorrect. Compounds **2**, **4**, **10** and **13** were isolated in this study and their structure could be determined (**10** and **13**) and confirmed (**2** and **4**).

The main component (compound **4**) of the dimer fraction of the product mixture was present in the quantity of over 90 % and the contents of the other, so called minor dimers, amounted to about 1 %. At the same time the components have similar chemical structures. Therefore, the isolation of the minor dimers proved to be an extremely difficult task. The separation and isolation of the minor dimers were made more difficult by the presence of higher oligomers which were actually the main reaction product when boron trifluoride was used (see Table IV). The reaction of indene in the presence of boron trifluoride was optimized to increase the portion of the dimer fraction and the content of minor dimers in it, but the effect was not satisfactory. The advantage of the reaction of indene in the presence of boron trifluoride was, however, that the product mixture could be obtained in a simple way in several minutes. The reactions of indene in the presence of H₂SO₄ and H₃PO₄ were also investigated in this study. It was shown that, regarding the separation and isolation of the minor dimers, the optimal composition of the product mixture was obtained if H₂SO₄ was used. Preparative GC and HPLC techniques were considered for isolation of the minor dimers. According to expectation, preparative glass capillary GC successfully separated the components of the dimer fraction. However, for the collection of quantities of 0.5 – 1.0 mg of each minor dimer, about three months of continuous work would be necessary. The HPLC technique, on the other hand, enabled the collection of 0.5 – 1.0 mg of the minor dimers of purity higher than 80 % only after the repeated separation and isolation. This technique was optimized in this study to accomplish the separation and isolation of the mi-

nor dimers in about ten days. At the end a reaction scheme is given explaining how the minor dimers were formed.

EXPERIMENTAL

Reaction of indene in the presence of boron trifluoride etherate

0.500 g of indene in a 25 ml single-neck open flask was heated to the reaction temperature (20, 40, 80, 120 and 150 °C) and 0.040 ml of boron trifluoride etherate were added into the liquid by a syringe. The reaction mixture was mixed manually. After a reaction time of 30 s, 10 ml of cold (5 °C) cyclohexane were added. The reaction mixture was neutralized with NaHCO₃ (5 %), washed with water and dried over CaCl₂.

Isolation of the higher oligomers

3 ml of the cyclohexane solution of the reaction product obtained at 120 °C were treated with an excess of acetonitrile or *n*-heptane. The obtained precipitate was isolated by filtration under vacuum and washed three times with acetonitrile.

Treatment of the higher oligomers with boron trifluoride etherate at 120 °C

30 mg of the higher oligomers (the washed precipitate of the previous experiment) were dissolved in 50 µl of decalin and heated to 120 °C in a 5 ml single-neck open flask. 1.6 µl of boron trifluoride etherate were added into the solution by a syringe. The reaction mixture was mixed manually. After a reaction time of 30 s, 500 µl of cold (5 °C) cyclohexane were added. The reaction mixture was neutralized with NaHCO₃ (5 %), washed with water and dried over CaCl₂.

Reaction of indene in the presence of H₂SO₄

The general procedure was the one described by Dansi and Pasini.¹⁷ 10 g of indene (> 99.0 % purity) and 40 ml 48 % H₂SO₄, as a two-phase mixture, were refluxed (oil-bath temperature 125–130 °C) with vigorous stirring for 8 hrs. After cooling to room temperature, 100 ml cyclohexane were added. The reaction mixture was neutralized with NaHCO₃ (5 %), washed with water and dried over Na₂SO₄. After evaporating the cyclohexane, 8.7 g of brown viscous oil (the product mixture) were obtained.

Reaction of indene in the presence of H₃PO₄

The general procedure was the one described by Noland, Lauducci and Darling.¹⁰ 2 g of indene (> 99.0 % purity), 2 ml of 85 % H₃PO₄ and 2 ml of water, as a two-phase mixture, were refluxed (oil-bath temperature 117 °C) with vigorous stirring for 23 h. After cooling to room temperature, 20 ml of cyclohexane were added. The reaction mixture was neutralized with NaHCO₃ (5 %), washed with water and dried over Na₂SO₄. After evaporating the cyclohexane, 1.96 g of brown viscous oil were obtained.

GC analysis

Gas chromatography (Carlo Erba, GC 6000 VEGA SERIES); on-column injection; column DB-5 30 m, 0.25 µm i.d.; flow 3 ml H₂/min; temperature 80 °C (2 min) – 10 °C/min – 280 °C (20 min); FID detector. Indene was used as the standard for the quantitative work.

GC-MS analysis

Gas chromatography (Shimadzu GC 17A); on-column injection (temperature 60–295 °C); column DB-5, 30 m, 0.25 µm i.d.; µm i.d. FT; flow 0.8 ml He/min; temperature program 60 °C (5 min) – 4 °C/min – 300 °C (30 min); interface 280 °C.

Mass spectrometry Shimadzu QP 5000; electron impact ionization energy: 70 eV; vacuum: 1.5 × 10⁻³ Pa; ion source 200 °C; detector gain was set to 1.75 kV; mass range 45 – 700 u.

HPLC – procedure

Liquid chromatography was carried out with a Gynotek (Germering, Germany) model P 580 pump. The analytes were chromatographed on a preparative normal phase column VP 250/10 Nucleosil 100 – 7.

Isocratic LC elution was performed using *n*-hexane + 0.1 % tetrahydrofuran for the isolation of dimers from group II and *n*-hexane + 0.3 or 1.0 % tetrahydrofuran for the isolation of GC peak 5 (HPLC peak 1 in Fig. 2) and group II from the product mixture, at a flow rate of 3 ml/min. 40 to 100 μ l of a 6 % solution of group II and the product mixture, were injected, respectively.

NMR analysis

Instrument: VARIAN UNITY 600 and Bruker AMX 600; Solvent: CDCl_3 ; Frequency: $^1\text{H} = 600.13$ MHz; $^{13}\text{C} = 150.94$ MHz; Calibration $^{13}\text{C} = 77.7$ ppm; $^1\text{H} = 7.26$ ppm.

RESULTS AND DISCUSSION

GC and GC-MS analysis

The TIC-GC chromatogram obtained by GC-MS analysis of the product mixture of the reaction of indene in the presence of boron trifluoride at 120 °C is shown in Fig. 1. Three groups of peaks can easily be seen. The first group includes 2,3-dihydro-1*H*-indene (indane) – an impurity in indene – and unreacted indene and has a retention time of 13–14 min. The second group contains compounds with double molecular weight ($M = 232$) relative to the molecular weight of indene ($M = 116$) and has a retention time of 45–52 min.

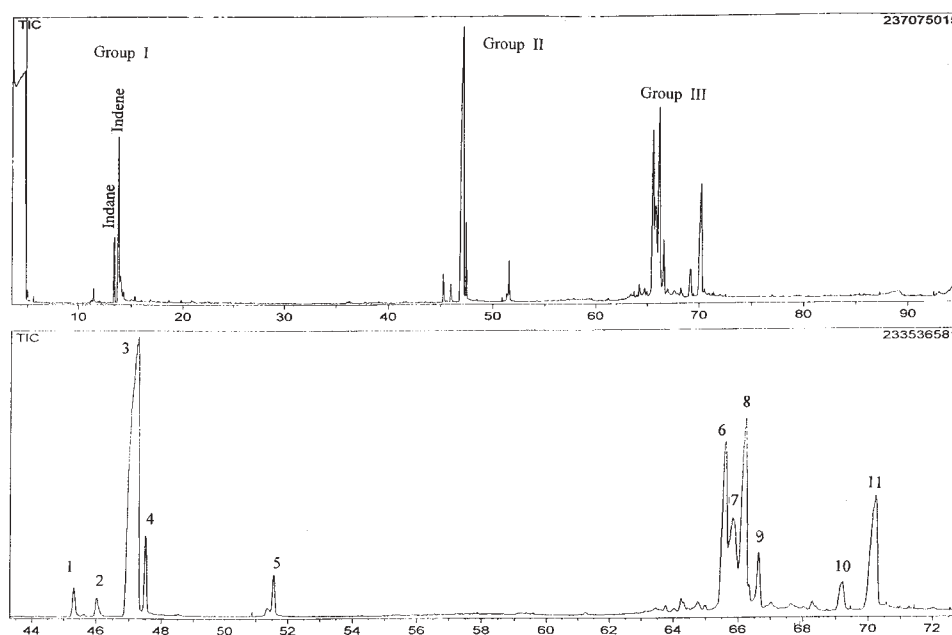


Fig. 1. TIC-GC chromatogram of the product mixture.

The third group contains compounds with triple molecular weight ($M = 348$) relative to the molecular weight of indene ($M = 116$) and has a retention time of 65–71 min. The lower chromatogram in Fig. 1 represents the expanded part covering the retention times of 44–72 min. That is the region of groups II and III with peaks designated as 1–5 and 6–11,

respectively. The mass spectra of GC peaks 1 – 5 are shown in Table II. All GC peaks have the molecular ion 232 indicating dimers of indene.

The mass spectra of GC peaks 1 – 5 could be divided into those having the MS base peak m/z 116 (peaks 1 and 4) and those having the MS base peak m/z 117 (peaks 2, 3 and 5). The other m/z values are typical for aromatic structures and are present in each spectrum of GC peaks 1 – 5 in similar quantities. Consequently, they can not be used for structural elucidation. The MS base peak m/z 117 represents a benzylic type carbonium ion and indicates structures from which it could originate. The MS base peak m/z 116 indicates structures that could not easily form a benzylic type carbonium ion. In that case rearrangement fragmentation with hydrogen transfer could take place giving m/z 116.

TABLE II. Relative intensities (%) of the characteristic peaks of the mass spectra of GC peaks 1 – 5 (group II in Fig. 1)

m/z	232	231	215	202	117	116	115
GC peak 1	16	4	9	7	52	100	45
GC peak 2	75	26	25	22	100	48	53
GC peak 3	47	9	25	16	100	20	50
GC peak 4	12	1	10	6	35	100	32
GC peak 5	27	6	18	10	100	12	32

Group III in Fig. 1 contained compounds with triple molecular weight ($M=348$) relative to the molecular weight of indene ($M=116$). The GC peaks of group III are designated in Fig. 1 by numbers 6 – 11. Their mass spectra are shown in Table III.

TABLE III. Relative intensities (%) of the characteristic peaks of the mass spectra of GC peaks 6 – 11 (group III in Fig. 1)

m/z	348	233	232	231	230	215	202	117	116	115
GC peak 6	7	3	18	50	42	26	11	100	35	54
GC peak 7	3	1	20	48	3	13	7	100	49	45
GC peak 8	8	2	18	45	60	30	13	100	35	57
GC peak 9	5	1	10	23	17	14	8	100	17	32
GC peak 10	20	28	10	31	3	14	4	100	37	44
GC peak 11	13	1	3	10	1	7	2	100	1	30

All of them have m/z 117 as the MS base peak. The compounds of group III were not investigated further in this study.

To determine the structures of dimer GC peaks 1 – 5, it is obviously necessary to isolate them in pure form and use other methods of identification than MS, such as NMR and X-ray for instance.

TABLE IV. Yields of groups I (indene and indane), II (dimers), III (trimers) and oligomers obtained by the reaction of indene at 120 °C in presence of boron trifluoride and sulfuric acid

Components of the product mixture	Yield/%, BF ₃	Yield/%, H ₂ SO ₄
Group I (Indene + Indane)	1.5	0.5
Group II (Dimers; peaks 1 – 5)	9.2	88.1
Group III (Trimers; peaks 6 – 11)	5.6	6.1
Sum of small peaks	0.8	–
Oligomers	69.5	2.3
Lost	13.4	3.0

TABLE V. Composition of group II (GC peaks 1 – 5)

Components of Group II	Yield/%, BF ₃	Yield/%, H ₂ SO ₄
Peak 1	0.78	1.80
Peak 2	1.11	1.48
Peak 3	95.44	93.64
Peak 4	1.77	1.82
Peak 5	0.90	1.25

The reaction of indene in the presence of boron trifluoride was studied at temperatures of 20; 80; 120 and 150 °C. The highest yield and purity of the GC peaks 1 – 11 were obtained at 120 °C. Hence, this temperature was chosen as optimal. During the reaction of indene in the presence of boron trifluoride higher oligomers with 7 – 32 monomer moieties were obtained together with dimers, trimers and alkylation products.¹ They could be isolated from the cyclohexane solution of the product mixture by precipitation with *n*-heptane or acetonitrile (see Experimental). To determine whether there was an equilibrium between dimers, trimers and higher oligomers, which could be established during the reaction, the precipitate was washed with acetonitrile or *n*-heptane until it no longer contained dimers, trimers and alkylation products (GC-MS control). Afterwards it was dissolved in decalin and heated to 120 °C, boron trifluoride etherate was added and the reaction was performed as described in the experimental part. Decalin had to be used as the higher oligomers were

still a solid at 120 °C. GC-MS analysis of the product mixture showed that no trace of dimers, trimers and alkylation products was present. Consequently, it was proved that dimers, trimers and alkylation products could not be obtained by degradation of the higher oligomers at 120 °C in the presence of boron trifluoride etherate.

As already mentioned at the beginning, we concentrated our work in this study to determine the structure of GC peaks 1–5, especially the minor dimers (peaks 1, 2, 4 and 5). Table IV shows the yields of groups I, II and III determined by GC analysis (See Fig. 1) and the precipitated oligomers. Table V shows the composition of group II. When boron trifluoride was used (Tables IV and V), the contents of the minor dimers amounted to 0.1 % and 1.0 % in the product mixture and group II, respectively. To isolate them in quantities of 0.5 – 1.0 mg and purities over 80 %, several months of work would be required, if preparative GC were used, and several weeks of work would be necessary and several tens of liters of solvent consumed if preparative HPLC were used for that purpose. Therefore, we tried the reaction of indene in presence of other acids hoping to obtain higher yields and more convenient distributions of dimers in the product mixture. Much better results were obtained when H_2SO_4 ¹⁷ was used instead of boron trifluoride (see Tables IV and V). The product mixture, still having practically the same qualitative composition, contained essentially lower quantities of the oligomers and about ten times higher quantities of the dimers. In this case 2-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene (compound 4 in Table I; GC peak 3 in Fig. 1) dominated in the product mixture, instead of oligomers. Similar results were obtained when H_3PO_4 ¹⁰ was used, but in that case the reaction time was longer – 24 h compared to 8 h in the case of H_2SO_4 . By reacting indene in the presence of H_2SO_4 , 8.7 g of the product mixture was produced. It was used as the starting material for the isolation of minor dimers in the quantities and purity necessary for NMR analysis.

Isolation of the components of group II

As the content of the main component (GC peak 3 in Fig. 1) amounted to more than 90 % and the contents of the minor dimers (GC peaks 1, 2, 4 and 5 in Fig. 1) amounted to 1 – 2 %, their isolation represented a difficult experimental task. As mentioned before, we used the preparative HPLC technique. It could be applied easily for the isolation of GC peak 5 (HPLC peak 1 in Fig. 2) and groups II (HPLC peak 2 in Fig. 2) and III (HPLC peaks 3, 4 and 5 in Fig. 2) as a whole, but not for the isolation of their components (GC peak 5 was an exception), in the first step. We accomplished the isolation of GC peaks 1, 2 and 3 through a second HPLC step using group II, not containing GC peak 5, as the starting material. GC peak 4 was, however, not isolated in a satisfactory pure form and its structure could not be determined by NMR analysis. It was only possible to concentrate it from 1.82 % to 5.1 % (HPLC peak 3 in Fig. 3) and 7.9 % (HPLC peak 4 in Fig. 3). Normal phase HPLC gave better separation in a shorter time compared to the inverse phase, and it was chosen for use in this study. Group II minus GC peak 5 was isolated in the first step working isocratically with the solvent mixture *n*-hexane + 0.3 – 1.0 % of tetrahydrofuran (THF). Fig. 2 shows the HPLC chromatogram obtained using *n*-hexane + 0.3 % THF as the solvent. It was possible to shorten the analysis time to 15 min by using *n*-hexane + 1 % THF as the solvent.

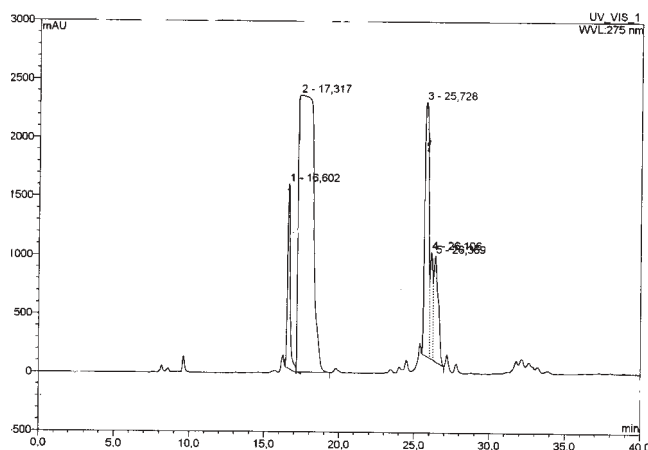


Fig. 2. HPLC chromatogram of the product mixture obtained using *n*-hexane and 0.3 % THF as the solvent.

GC-MS analysis identified HPLC peak 1 (r.t. 16.60 min in Fig. 2) as the minor dimer **5** (GC peak 5 in Fig. 1) and it was isolated successfully in the first step. HPLC peak 2 (r.t. 17.32 min in Fig. 2) contained the minor dimers **1**, **2** and **4** (GC peaks 1, 2 and 4 in Fig. 1) and the main dimer **3** (GC peak 3 in Fig. 1). HPLC peaks 3, 4 and 5 (r.t. 25.73, 26.11 and 26.37 min in Fig. 2) were a mixture of trimers (GC peaks 6–11 in Fig. 1). Three fractions were isolated in the first step: HPLC peak 1, HPLC peak 2 and HPLC peaks 3, 4 and 5 (Fig. 2). Fig. 3 shows the HPLC chromatogram obtained by separating, in the second step, HPLC peak 2 (Fig. 2) using *n*-hexane + 0.1 % THF as solvent.

GC-MS analysis identified HPLC peak 1 (r.t. 12.85 min in Fig. 3) as the minor dimer **2** (GC peak 2 in Fig. 1), HPLC peak 2 (r.t. 13.09 min in Fig. 3) as the main dimer **3** (GC peak 3 in Fig. 1) and HPLC peak 5 (r.t. 14.27 min in Fig. 3) as the minor dimer **1** (GC peak 1 in Fig. 1). The minor dimer **4** (GC peak 4 in Fig. 1) was found in the parts of the main HPLC peak with retention times 13.586 and 13.794 min. Through 140 HPLC cycles it was possible to collect about 0.5 and 0.8 mg with the purity of 96.5 and 80.0 % of the minor

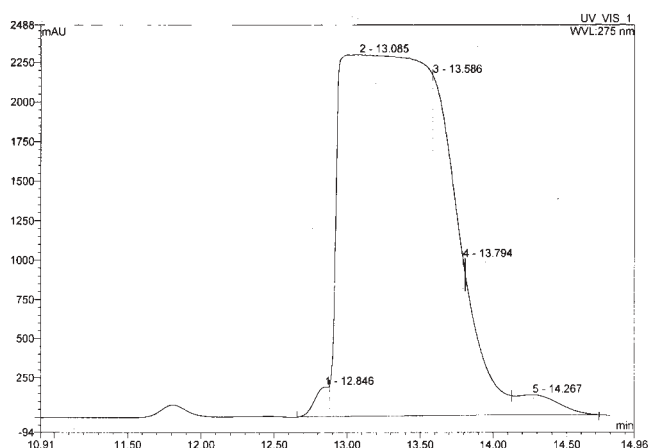


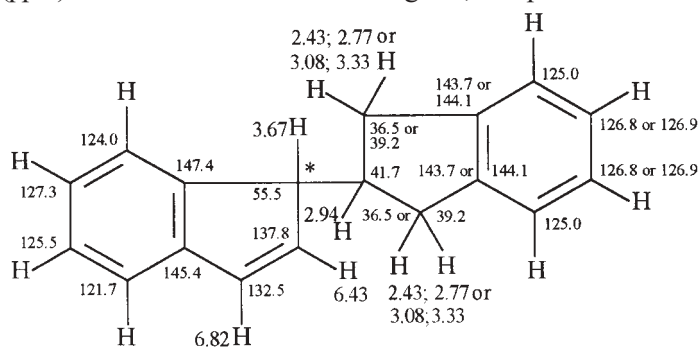
Fig. 3. HPLC chromatogram of HPLC peak 2 in Fig. 2 obtained using *n*-hexane and 0.1 % THF as the solvent.

dimers **2** and **1** (HPLC peaks 1 and 5 in Fig. 3), respectively, and about 75 mg of the main dimer **3** (HPLC peak 2 in Fig. 3) and to elucidate their structure by NMR analysis. Consequently NMR analysis of GC peaks 1, 2, 3 and 5 (see Fig. 1) could be performed and their structure was determined in this study. NMR analysis of the mixture that contained GC peak 4, however, gave some information about its structure that was not sufficient for the structural elucidation.

NMR and MS analysis

The isolated GC peaks 1, 2, 3 and 5 were analyzed by the NMR technique. ^1H , ^{13}C and two-dimensional NMR correlation spectra were obtained. They gave sufficient data for structure determination. MS spectra of GC peaks 1–5, shown in Table II, gave insufficient information for that purpose.

GC peak 1. Its NMR spectra corresponded to the structure shown in Fig. 4. The chemical shifts (ppm) of the H and C atoms are also given, except for aromatic H atoms.



The resolution of NMR spectra was not good enough to make the arrangement of eight H - atoms possible (1H at 7.50 ppm; 1H at 7.36 ppm; 1H at 7.27 ppm; 2H at 7.22 ppm; 3H at 7.14 - 7.08 ppm).

Fig. 4. Chemical shifts (ppm) of the H and C atoms of 1-(2',3'-dihydro-1'H-inden-2'-yl)-1H-indene (GC peak 1 in Fig. 1).

Two other possible compounds of indene substituted on C-1, structures **14** and **15** in Table I, are described in the literature,^{4,14} but their NMR and MS spectra were clearly different from the spectra of GC peak 1.

The MS spectrum of GC peak 1 shows as the base peak m/z 116, which could be obtained by the migration of H from the methylene groups of the indane structural element to the olefinic bond of the indene structural element, followed by the cleavage of the C-1 – C-2' bond, and the high intensity peaks m/z 115 and 117 (about 50 % of relative abundance), which could be obtained by allylic cleavage.

Hence, GC peak 1 in Fig. 1 is: 1-(2',3'-dihydro-1'H-inden-2'-yl)-1H-indene.

GC peak 2. Its NMR spectra corresponded to 6-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene.¹⁸ The MS spectrum of GC peak 2 (see Table II) shows as the base peak a benzylic type

carbonium ion m/z 117, which could be obtained by the cleavage of the C-6–C-1' bond. The other part of the dimer (m/z 115; r.a. 53 %) is also present. m/z 231 (r.a. 27 %) could be a benzylic type carbonium ion obtained by the cleavage of the C-1' – H bond.

Hence, GC peak 2 in Fig. 1 is: 6-(2',3'-dihydro-1'*H*-inden-1'-yl)-1*H*-indene.

GC peak 3. Its NMR spectra corresponded to 2-(2',3'-dihydro-1'*H*-inden-1'-yl)-1*H*-indene.¹⁹

The structural data obtained by X-ray analysis confirmed this structure.¹¹

The MS spectrum of the GC peak 3 (see Table II) shows as the base peak the benzylic type carbonium ion m/z 117, which could be obtained by the cleavage of the C-2 – C-1' bond.

Hence, GC peak 3 in Fig. 1 is: 2-(2',3'-dihydro-1'*H*-inden-1'-yl)-1*H*-indene.

GC peak 4. We did not succeed to isolate it in a purity that would be sufficient for NMR analysis. It was contaminated by GC peaks 1 and 3 to such an extent that its structure could not be determined. The MS spectrum of GC peak 4 was different from all the structures that were shown in Table I and described in the literature. NMR analysis proved only one signal to be from GC peak 4, that is the olefinic sp^2 CH at 6.2 ppm. A signal from another olefinic sp^2 CH was not present.

The MS spectrum of the GC peak 4 (see Table II) shows as the base peak m/z 116, which could be obtained from the structure shown in Fig. 5 by steric convenient migration of H from the methylene groups of the indane structural element to C-2 of the olefinic bond of the indene structural element followed by the cleavage of the C-3 – C-2' bond. On the basis of its MS spectrum, and the reaction scheme to be shown later (see Fig. 7), a possible structure for GC peak 4 is given in Fig. 5 and it corresponds to 3-(2',3'-dihydro-1'*H*-inden-2'-yl)-1*H*-indene.

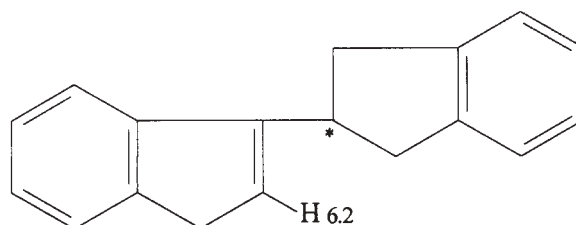


Fig. 5. Possible structure of GC peak 4 in Fig. 1.

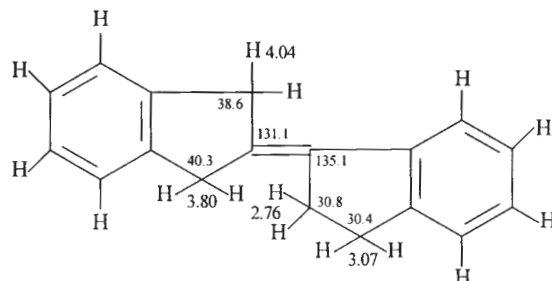
GC peak 5. Its NMR spectra corresponded to the structure shown in Fig. 6. The chemical shifts (ppm) of the H and C atoms are also given, except for aromatic C and H atoms.

The following data proved this structure:

- two + four quaternary C atoms, four sp^3 CH₂, eight aromatic sp^2 CH, no olefinic sp^2 CH;
- H – H coupling (ppm) between H (4.04 and 3.80), H (4.04 and 2.76), H (3.80 and 2.76), H (3.07 and 2.76).

Due to the rigid structure and no chiral C atom, the H atoms of each sp^3 CH₂ group are equivalent. The structure shown in Fig. 6 was confirmed by the DFT calculation, giving four H couples, each with two identical values of the natural charge.³

The other biindenylidene structures 1⁴⁻⁷ and 3^{4-6,9} (see Table I) have been described in the literature. Their NMR and MS spectra clearly differ from the spectra of GC peak 5. The



Eight aromatic H: 7.1 - 7.5

Four quaternary aromatic C: 147.3; 142.9; 141.9; 141.6

Eight aromatic CH C-atoms: 126.8; 126.7; 126.65; 126.6 125.4; 125.0; 124.8; 123.9

Fig. 6. Chemical shifts (ppm) of the H and C atoms of 2,3,1',3'-tetrahydro-[1,2']biindenylidene (GC peak 5 in Fig. 1).

biindenylidene structure **6** (see Table I) represents a highly symmetrical compound with four equivalent sp^3 CH_2 . DFT calculation for the structure **6** gave eight H atoms with the same natural charge.³ The compound with the structure **6** (see Table I) has been described in the literature.¹² Its NMR and MS spectra clearly differ from the appropriate spectra of GC peak 5.

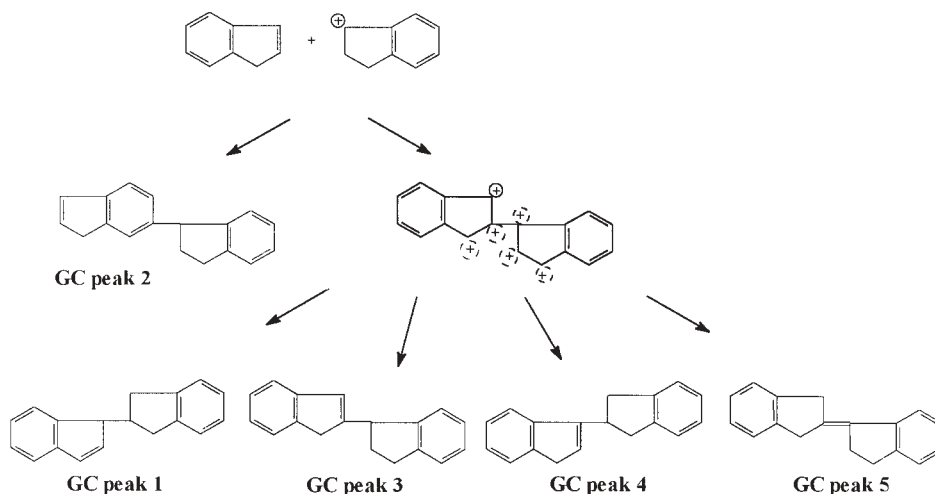


Fig. 7. The reaction scheme of indene dimerization in presence of acids.

The MS spectrum of GC peak 5 (see Table II) shows practically no m/z 116 as the olefinic bond makes difficult the cleavage of this dimer into two equal parts. It is not, however, to be seen explicitly how the base peak m/z 117 was formed. The structure shown in Fig. 6 is of the compound **2** in Table I and it was described in the literature.⁸ We prepared it following the description and proved that it was not the compound **2** but the compound **19**.¹⁶ Its mass spectrum differs slightly from the spectrum of compound **2** and NMR spectra differ essentially.

Hence, GC peak 5 in Fig. 1 is: 2,3,1',3'-tetrahydro-[1,2']biindenylidene.

Reaction scheme

It is well known that indene, in the presence of acids, could form the indan-1-ylidene ion which reacts with another indene molecule giving 2-(2',3'-dihydro-1'H-inden-1'-yl)-1H-indene^{6,14,20,21,22} (the main dimer, GC peak 3 in Fig. 1). It was the main product (over 90 %) in the product mixture obtained using H₂SO₄ and H₃PO₄. It is reasonable to assume that the minor dimers (peaks 1, 2, 4 and 5 in Fig. 1) were also formed by the reaction of the indan-1-ylidene ion with indene. There is no doubt that the minor dimer **2** (GC peak 2 in Fig. 1) was formed by alkylation of the benzene ring. The other minor dimers (GC peaks 1, 4 and 5 in Fig. 1) could be formed by the known acid catalyzed 1,2-hydride rearrangement, as shown in the scheme (Fig. 7).

This scheme has the disadvantage that the structure of the minor dimer **4** (GC peak 4 in Fig. 1) could not be unambiguously proved in this study.

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ИЗВОД

ПРОИЗВОДИ ДИМЕРИЗАЦИЈЕ ИНДЕНА

ЈОВАН ЈОВАНОВИЋ, МИХАЕЛ ШПИТЕЛЕР и ВИЛХЕЛМ ЕЛИНГ

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Испитивана је реакција 1H-индена у присуству Фридел-Крафтсових киселина. Као што је и очекивано, смеша производа је садржала димере, тримере и више олигомере. Међу производима са двоструком молском масом, у односу на молску масу индена, одређена је структура четири једињења: 6-(2',3'-дихидро-1'H-инден-1'-ил)-1H-индена, 2-(2',3'-дихидро-1'H-инден-1'-ил)-1H-индена, 1-(2',3'-дихидро-1'H-инден-2'-ил)-1H-индена и 2,3,1',3'-тетрахидро-[1,2]биинденилидена. Показано је да је прво једињење производ алкилације индена, а да су преостала три добивена повезивањем индена у положају 2 са индан-1-илијум јоном, при чему је у случају трећег и четвртог једињења дошло и до 1,2-хидридног премештања. Узимајући у обзир да су производи димеризације индена компоненте пиролитичких уља и интересантна једињења као модели за NMR и MS анализе и анализе помоћу X-зрака, у овом раду је оптимизовано њихово добијање, раздвајање и изоловање.

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