Polymer Communication

A Model study for Diels–Alder reaction of biscyclopentadienyl monomer with bismaleimides. Benzylcyclopentadiene: synthesis, characterization and Diels–Alder reaction with *N*-(4-benzoyl)-phenylmaleimide

H. Ben Romdhane[a], M.R. Chaâbouni[a], M.F. Grenier-Loustalot[b], F. Delolme[b], P. Mison[b], B. Sillion[b,*]

[a]*Laboratoire de Synthèse et Analyse de Matériaux, Ecole Nationale d'Ingénieur de Tunis, Département de Génie Industriel, BP 37, Le Belvédère 1002 Tunis, Tunisia*
[b]*Service Central d'Analyses, CNRS, BP 22, 69390 Vernaison, France*

Abstract

Reaction between benzylbromide and sodium cyclopentadienide leads to a mixture of dienes. These can be identified by several techniques such as size exclusion chromatography, mass spectroscopy (MS) and high performance liquid chromatography/MS coupling. Their structure is confirmed by analysis of adducts obtained after reaction of *N*-(4-benzoyl)-phenylmaleimide with these dienes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Diels–Alder; Cyclopentadiene; Maleimide

1. Introduction

The Diels–Alder cycloaddition, a very interesting approach for the synthesis of linear polyimides has been previously used [1]. The reaction proceeds smoothly when the diene is electron rich and the dienophile is electron deficient [2]. This theoretical aspect and also the low cost of the bismaleimides make them good candidates for Diels–Alder polyadditions with different bisdienes. Furanes [3], isobenzofuranes [4], cyclohexadienes [5], cyclopentadienones [6] and α-pyrones [7] have been used as dienes and in most cases the thermally unstable cycloadduct can lead up to a thermally stable aromatic system after extrusion of a small molecule (water, carbon monoxide or carbon dioxide when furanes, cyclopentadienones or pyrones are, respectively, implied).

However, the reverse reaction of a polyadduct could also be a source of technical interest. The chemistry and reverse Diels–Alder of the nadimide—a bicyclo compound—obtained by the reaction of a maleimide with cyclopentadiene is well documented [8]. For example, the reverse reaction is the first step taking place during the thermal polymerization of bismaleimide thermosetting resins [8]. The synthesis of two types of polynadimide have been previously published. Stille and Blummer [9] used condensation of bismaleimides with unsubstituted bis cyclopentadiene. These authors described biscyclopentadienyl-(hexane, nonane and *p*-xylene) as waxy materials containing mono substituted derivatives and oligomers. Kiselev et al. [10,11] compared the reactivities of different cyclopentadienes with and without a methyl substituent, and they pointed out that polymethyl cyclopentadiene would be more reactive than the unsubstituted one.

However, in these articles, the formation of alkyl or benzylcyclopentadiene by reaction of an unsubstituted cyclopentadienyl carbanion with the corresponding alkyl or benzylbromide was not clearly demonstrated.

This work is a model study to reinvestigate the synthesis of the benzylcyclopentadiene, by using the described reaction of benzylbromide with sodium cyclopentadienide. The reaction products were analyzed by size exclusion chromatography (SEC), high performance chromatography and mass spectroscopy (MS) and then reacted with *N*-(4-benzoyl)-phenylmaleimide.

2. Experimental

Sodium cyclopentadienide solution in tetrahydrofuran (THF, 2.0 mol), benzylbromide, 4-amino-benzophenone,

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* Corresponding author. Tel.: +33-7802-2222; fax: +33-7802-7187.
E-mail address: sillion@sca.cnrs.fr (B. Sillion)

Table 1
Temperature and time used in the synthesis of cyclopentadiene

	Run 1	Run 2	Run 3
Temperature (°C)	0	25	65
Time (min)	60	180	60

maleic anhydride and anhydrous THF were purchased from Aldrich and were used as received.

2.1. Attempt to synthesize benzylcyclopentadiene

10 ml of sodium cyclopentadienide solution (20 mmol of Cp^-) is added with a syringe and septum to 3.104 g (18.1 mmol) of benzylbromide in 15 ml of anhydrous THF, stirred under nitrogen atmosphere. Temperatures and reaction time are given in Table 1. The immediate formation of a white precipitate is observed. At the end of the reaction, the latter is filtered and then washed with $3 \times$ 10 ml of diethylether. The extracts are added to the filtrate which is washed in turn several times with 15 ml of distilled water until neutral pH. Following this, the organic layer is dried over sodium sulfate. Finally, the solvent is stripped off, and a brown viscous oil is obtained. The latter is stored at cold temperature (less then 0°C). Sodium bromide is dried in vacuum and isolated in quantitative yield ($\approx 100\%$).

2.2. Preparation of N-(4-benzoyl) phenylmaleimide

2.2.1. N-(4-benzoyl)phenylmaleamic acid

In a three necked flask provided with a reflux condenser, maleic anhydride (8.66 g, 0.088 mol) is dissolved in diethylether (100 ml). Under mechanical stirring, a solution of 4-aminobenzophenone (17.35 g, 0.088 mol) in ether (40 ml) is added dropwise through a dropping funnel. After the addition, the thick suspension is stirred at room temperature for 1 h and then cooled in an ice bath. The product is obtained by filtration. The yellow colored powder (m.p. 178°C) is used in the next step without purification (21.8 g, 0.086 mol, 98%).

2.2.2. N-(4-benzoyl)phenylmaleimide

In a three necked flash equipped with a reflux condenser are added acetic anhydride (120 ml, 1.152 mol), anhydrous potassium acetate (12.6 g, 0.091 mol) and N-(4-benzoyl)-phenylmaleamic acid (22.01 g, 0.087 mol). The reaction mixture is heated at 100°C for 30 min under stirring. After cooling at room temperature, the reaction mixture is poured into ice cold water (100 ml). The precipitate is obtained by suction filtration, washed with cold water (3×60 ml) and then with petroleum ether (50 ml). After drying the crude
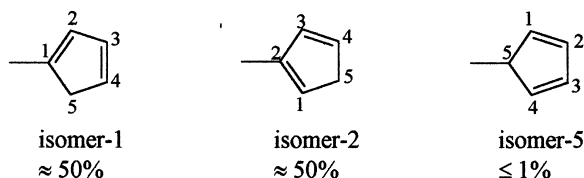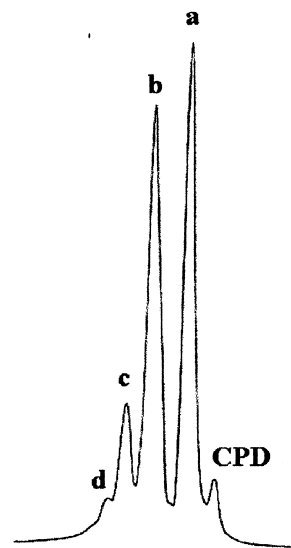

Fig. 2. The different isomers of monosubstituted cyclopentadiene.

(CPD) : 28.5 min, (a) : 27.3 min, (b) : 25.8, (c) : 24.9 min, (d) : 24.2 min

Fig. 3. SEC chromatogram of run 1.

product (19.4 g, 0.082 mol, 95%), recrystallization from cyclohexane–chloroform (45/55) gave yellow needles (m.p. 156–158°C) of pure product (6.9 g, 0.03 mol, 34%; see Fig. 7).

H NMR: (solvent: $CDCl_3$); 6.9_0 (s, 2H, H_1); 7.8_2 (d, 2H, H_4); 7.9_2 (d, 2H, H_5); 7.5_5 (d, 2H, H_9); 7.5_0 (t, 2H, H_{10}); 7.6_1 (t, 1H, H_{11}); $J_{H4H5} = 8.4$ Hz, $J_{H9H10} = 8.3$ Hz, $J_{H10H11} = 7.3$ Hz.

C^{-13}-NMR: (solvent: $CDCl_3$); $125.1_1(C_4)$; $128_9(C_{10})$; $130.0_5(C_9)$; $130.9_7(C_5)$; $132.6_3(C_{11})$; $134.4_2(C_1)$; $134.8_9(C_3)$; $136.4_6(C_6)$; $137.2_0(C_8)$; $169.0_8(C_2)$; $195.6_0(C_7)$.

2.3. Condensation of the run 1 product with N-(4-benzoyl)-phenylmaleimide

To a solution of the run 1 product (0.30 g, 1.82 mmol of the supposed benzylcyclopentadiene) in 2 ml of THF, a solution of N-(4-benzoyl)phenylmaleimide (0.55 g, 2.0 mmol), in 7 ml of THF is added under stirring and nitrogen atmosphere. The mixture is left at 60°C for 22 h and
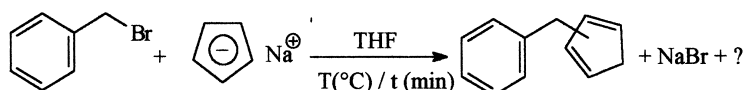

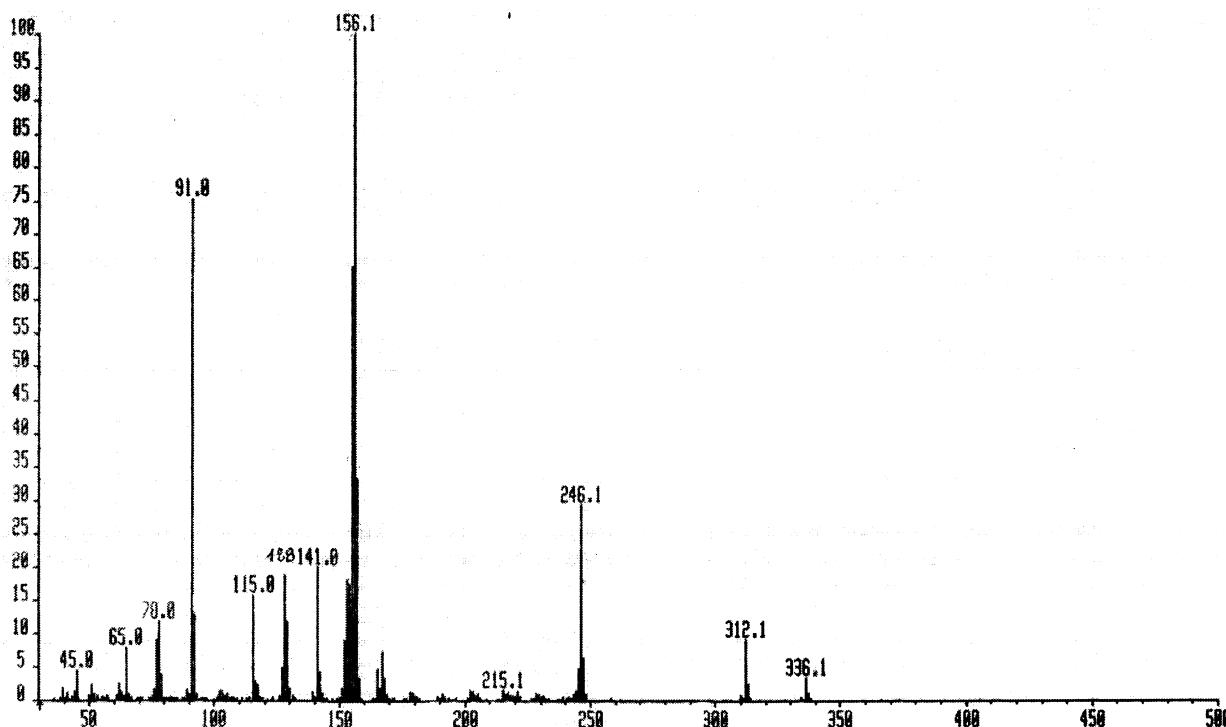Fig. 1. Synthesis scheme of benzylcyclopentadiene (runs 1–3).

Fig. 4. MS–EI spectrum of run 1.

then poured into excess of petroleum ether. The product is filtered off, washed with petroleum ether and dried in a vacuum dessicator.

2.4. Steric exclusion chromatography

A Waters SEC apparatus, fitted with UV and refractive index detectors is used (only the latter is used for this work). This is equipped with a series of three columns (μStyragel HR 0.5 + μStyragelHT3 + μStyragel10^3 a) able to separate masses in the range of 10–10,000. The operating solvent is THF (1 ml/min).

A sample of 0.1 ml, removed from product (I), is diluted in 1 ml of THF, and 20 μl from this solution is injected through a Millipore filter.

2.5. HPLC–MS analyses

Analyses were conducted with a Hewlett Packard 1100 equipped with MS and UV ($\lambda = 260 \pm 10$ nm) detectors.

The mobile phase A (water + trifluoroacetic acid pH = 2.45), B acetonitrile was used with an elution gradient A/B from 30/70 at 0/100 in 30 min and a flow rate of 0.5 ml/min

The columns were Chrompack Inertsil ODS- μm–(150 × 3) mm and precolumn

The MS conditions used for the identification of the peaks detected by UV are:

- *Ionization:* atmospheric pressure chemical ionization (positive mode).

- *Gas:* dry nitrogen (350°C, 4 l/min).
- *Nebulizer pressure:* 60 psig.
- *Capillary voltage:* 2000 V.
- *Vaporizer temperature:* 400°C.
- *Corona current:* 8 μA.

2.6. Mass spectrometry analyses

All the mass spectrometric experiments were carried out with a Micromass ZAB 2-SEQ using an electron ionization (EI) source. The ion source was operated with an accelerating voltage of 8 kV, ionizing electron energy of 70 eV and ion source temperature of 200°C.

3. Discussion

3.1. Attempt to synthesize benzylcyclopentadiene

The condensation of the sodium cyclopentadienide with the benzylbromide (Fig. 1) in THF was carried out at different temperatures (Table 1).

Sodium bromide precipitation took place immediately, and the final weight showed a transformation with about 100% yield.

Working with methylcyclopentadiene, Fritz et al. [12] pointed out the presence of three isomers (Fig. 2).

Unfortunately with the benzyl group, the complex mixture obtained did not allow a correct NMR ^{1}H attribution.

Current Chromatogram(s)

a : HPLC chromatogram
b : total ion current (TIC)
c : traces of ion 157 : $(156+H)^+$ in the TIC

d : traces of ion 247 : $(246+H)^+$ in the TIC
e : traces of ion 313 : $(312+H)^+$ in the TIC
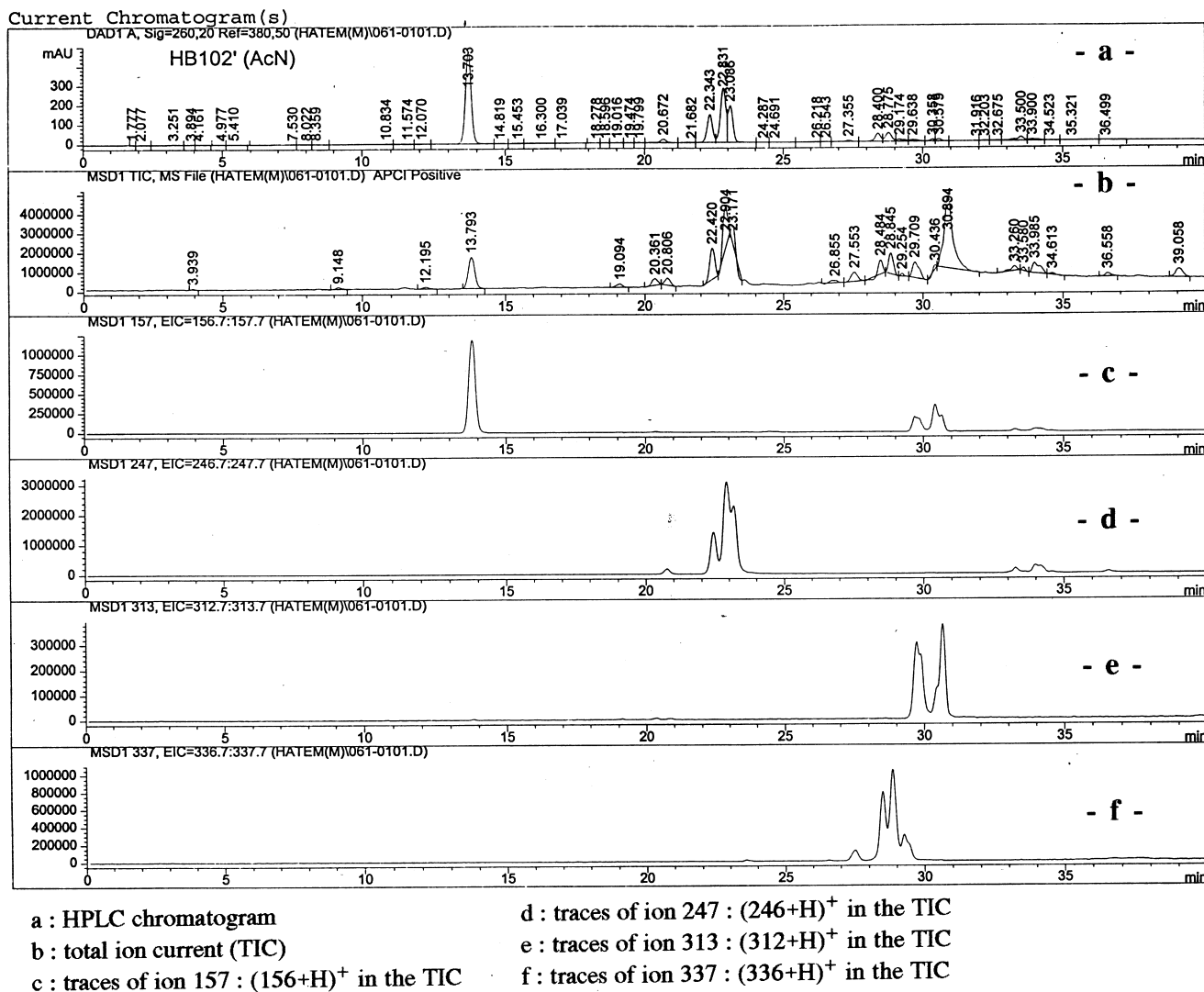f : traces of ion 337 : $(336+H)^+$ in the TIC

Fig. 5. HPLC spectrum of run 1.

3.2. Size exclusion chromatography analysis

The detection was performed by refractometry, and the traces were identical for runs 1, 2 and 3. Fig. 3 shows the chromatogram obtained with run 1.

The signal located at 28.5 min can be unequivocally attributed to the cyclopentadiene dimer (CPD) and the formation of products (a)–(d) was observed.

3.3. Mass spectroscopy characterization

The products obtained in run 1 were identified by MS–EI (electron impact ionization; Fig. 4).

The expected benzylcyclopentadiene was identified by the peak, $M/Z = 156$, and the presence of three other products observed by SEC was confirmed by three peaks $M/Z = 246, 312, 336$.

HPLC/MS coupling (using atmospheric pressure chemical ionization, positive mode) allowed a more precise identification of each product after separation. Fig. 5 shows the HPLC trace of the run 1 mixture.

HPLC shows the presence of several peaks which can be assigned to several isomers for each compound $M/Z = 156$, 246, 312, 336.

From these data the general formula (including isomers) of the four products obtained by condensation of sodium cyclopentadienide with benzylbromide are given in Fig. 6.

3.4. Condensation of the run 1 product with N-(4-benzoyl)-phenylmaleimide (Fig. 7)

The reaction was performed at 60°C in THF, and after work up, the product was analyzed by MS–EI; the spectrum is shown in Fig. 8. Three expected adducts I_1 from (1), I_2 from (2) and I_4 from (4) are observed $M/Z = 433, 513, 613$ (Table 2).

Compound (3) $M/Z = 312$ cannot react as a diene, but at 60°C an equilibrium between (1) and (3) probably took
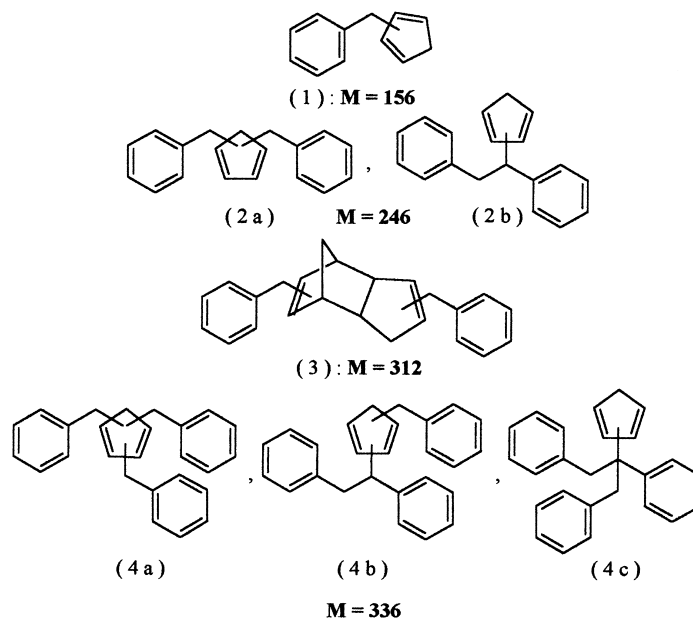
(1): M = 156

(2a)   M = 246   (2b)

(3): M = 312

(4a)   (4b)   (4c)

M = 336

Fig. 6. Probable structures of products present in run 1.

Table 2
Structures of examples of adducts formed by condensation of run 1 with N-(4-bnezoyl)-phenylmaleimide

Ion	Observed mass	Calculated mass	Proposed structure
I$_1$	433	156 + 277 = 433	
			(1)
I$_2$	523	246 + 277 = 523	
			[a]
			(1)
I$_3$	613	336 + 277 = 613	
			[a]

[a] This structure corresponds to isomer (2a) and (4b), but other isomers are probably formed.
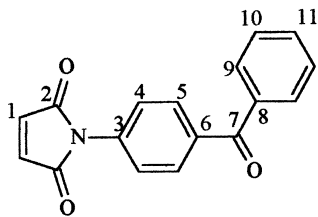
Fig. 7. *N*-(4-benzoyl)-phenylmaleimide.

place and this equilibrium was displaced by the reaction of (1) with the maleimide.

During MS analysis, the reverse Diels–Alder reaction of the three nadimides occurred, and the peaks corresponding to maleimide $M/Z = 277$ and to the three dienes were observed.

These results confirm the structures suggested (Fig. 6) which are in agreement with all the analytical data. A mechanism for the reaction of the benzylbromide with sodium cyclopentadienide is presented in Fig. 9.

The expected formation of benzylcyclopentadiene (probably a mixture of isomers according to Fig. 9) resulted from the nucleophilic substitution of the benzylbromide (Fig. 9(a-1)). However, the acidic hydrogen belonging to the benzylcyclopentadiene should allow a proton transfer

to cyclopentadienide with an equilibrium (Fig. 9(a-2)). The new carbanions were able to react with the benzylbromide with the formation of the isomer mixture (2). A similar reaction with (2) would give the mixture (4).

Higher molecular weight products coming from (4) were not detected, one reason would be either steric hindrance or higher conjugation decreasing the reactivity of the corresponding carbanion.

The formation of dimer (3) is easily explained by Diels–Alder dimerization of benzylcyclopentadiene (Fig. 9(b)).

4. Conclusion

The formation of benzylcyclopentadiene by reaction of the benzylbromide with sodium cyclopentadienide is not a one way reaction.

Two side reactions take place: the first is due to the formation of benzylcyclopentadiene carbanion by proton transfer with sodium cyclopentadienide. The second is a classical Diels–Alder dimerization of the expected product. For each species, liquid chromatography shows the presence of different isomers. All the dienic products in the medium can react with a maleimide giving a nadic adduct.
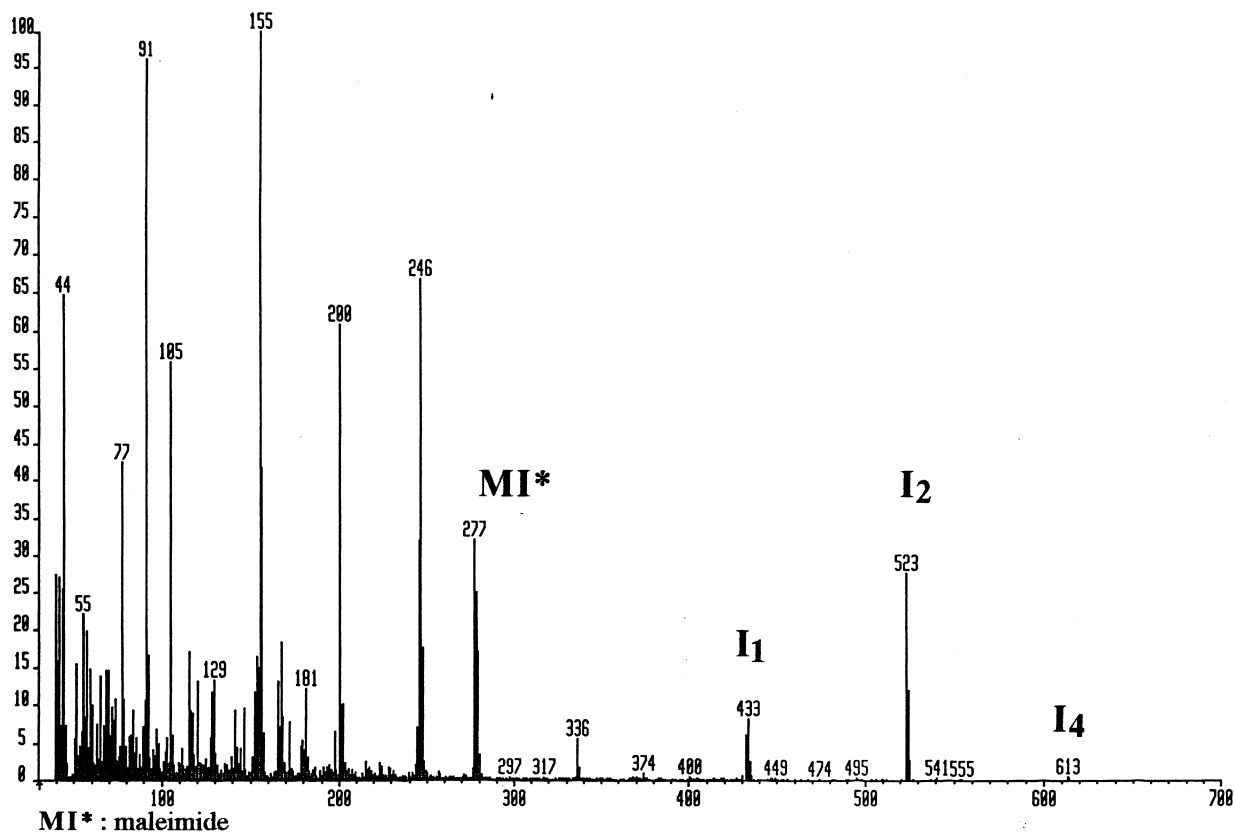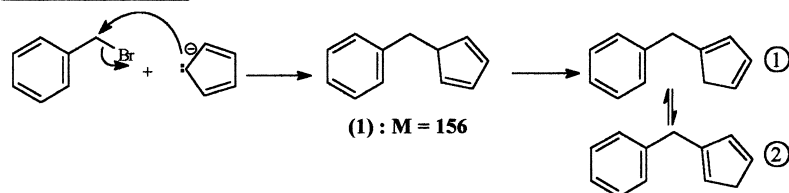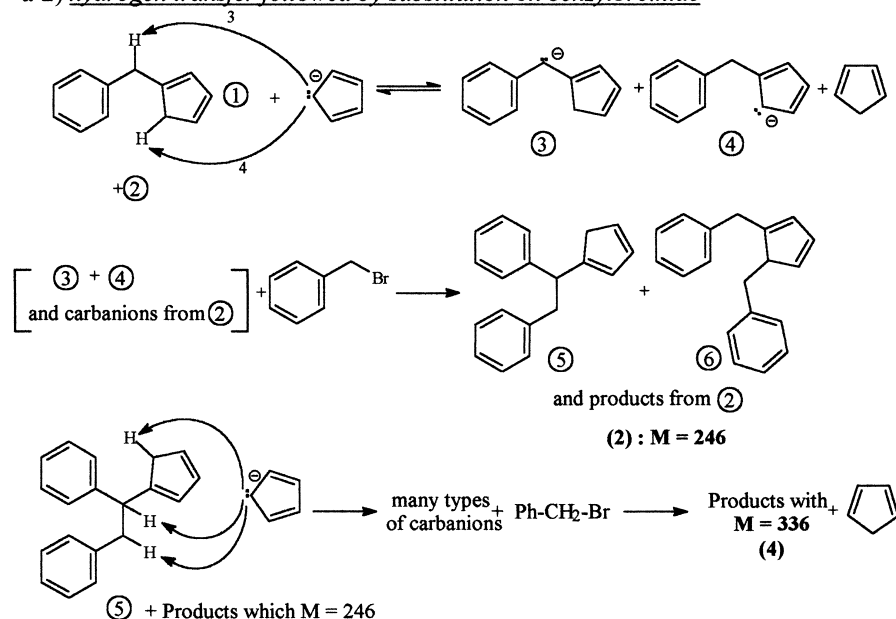

Fig. 8. MS–EI spectrum of condensation product of run 1 with *N*-(4-benzoyl)-phenylmaleimide.

a) nucleophilic substitution :

a-1) direct substitution

(1) : M = 156

a-2) hydrogen transfer followed by substitution on benzylbromide

and products from ②

(2) : M = 246

b) Diels-Alder cycloaddition
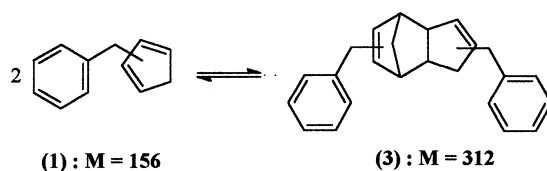

(1) : M = 156   **(3) : M = 312**

Fig. 9. Proposition for reaction mechanism of benzylbromide with sodium cyclopentadienide.

References

[1] Stenzenberger HD. In: Abadie MJM, Silion B, editors. Polyimides and other high-temperature polymers, New York: Elsevier, 1991. p. 215.

[2] March J. Advanced organic chemistry reactions, mechanisms and structures, 3, 1984. p. 749.

[3] Hawthorne DG, Hodkin JH, Jakson MB, Mortoncisro TC. High Perf Polym 1994;6:249.

[4] Watson KA, Bass RG. Polym Prepr (Am Chem Soc, Div Polym Chem) 1979;38(2):237.

[5] Turpin F, Mison P, Sillion B. In: Feger C, Khojastech MM, Molis SE, Hopewell Jct, editors. Polyimides: trends in materials and applications, New York: Soc Plast Engng Mid Hudson Sect, 1996. p. 169.

[6] Harris FW, Norris SO. J Polym Sci Chem Ed 1973;11:2143.

[7] Kottner N, Klemm E. Angew Makromol Chem 1998;254:39.

[8] Mison P, Sillion B. In: Kicheldorf HR, editor. Thermosetting oligomers containing maleimides and nadimides end groups in; advances in polymer science, Berlin: Springer, 1999. p. 137.

[9] Stille JK, Plummer. J Org Chem 1961;26:4026.

[10] Kiselev VD, Sakhabutdinov AG, Sharikov IM, Zverv VV, Konovalov AI. Org Chem USSR 1991;27:1437.

[11] Kiselev VD, Sakhabutdinov AG, Sharikov IM, Zverv VV, Konovalov AI. Org Chem USSR 1992;28:1806.

[12] Fritz HP, Kreitner CG. J Organometallic Chem 1965;4:313.