SYNTHESIS OF 4’-ALLYLBENZO-3N-CROWN-N ETHERS AND THEIR MASS SPECTRA COMPARED WITH BENZO-3N-CROWN-N ETHERS

Chairil Anwar
Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Gadjah Mada Sekip Utara, Yogyakarta
E-mail : irilwar@yahoo.com

Abstract

Synthesis of 4’allylbenzo-3n-crown-n ethers was carried out by reacting demethylated eugenol with α,ω-dichloro-oligoethylene glycols in 1-butanol under basic condition. The mass spectra of 4’allylbenzo-3n-crown-n and benzo-3n-crown-n were investigated by mass spectrometry using electron impact under 70 eV of electron bombardment as ionisation method. The difference between the group of compounds is only the present of allyl moiety as a side chain at the other side of benzene ring. The first group consisting of four compounds (n= 4,5,6 and 7) are the products of synthesis from eugenol precursor while the reference consist of three compounds (n= 4,5, and 6). The mass spectra of the first group show m/z = 176 as the base peak except 4’allylbenzo-12-crown-4 base peak is the molecular ion with m/z= 264. Peak of m/z = 176 has the structure of stable 1,4-dioxane-like . The presence of allyl group at position 4 of the benzene ring show significant effect to mass spectra pattern especially to 4’allylbenzo-12-crown-4. While the three compounds of the second group gave m/z= 136 as the base peak. This ion has similar structure as 1,4-dioxane-like mentioned earlier. In general it can be said that the mass pattern of the studied compounds come from the cleavage of the polyether rings according to M-nx44, where mass of 44 is C_2H_4O (ethylene oxide-like). The allyl side chain is more stable than the polyether rings under the investigated ionisation. The same case happened to eugenol as well as to safrol where the base peak is the molecular ion.

Keywords: allyl-benzo-crown ethers, mass spectra, electron impact ionisation

1. INTRODUCTION

Since the report about unusual coordination numbers and arrangements to metal ions of crown ether compounds by Pedersen (1967), the crown ether compounds have attracted much attention. Pedersen proceeded to report systematic studies of the synthesis and binding properties of crown ethers in a numerous series of papers. The fields of organic synthesis, phase transfer catalysts, and other emerging disciplines benefited from the discovery of crown ethers. Pedersen particularly popularized the dibenzo crown ethers (Fig. 1). Pedersen shared the 1987 Nobel Prize in Chemistry for the discovery of the synthetic routes to, and binding properties of, crown ethers. Due to their novel coordination modes, crown ethers have been widely used in catalyst, solvent extraction, isotope separation, bionics, material chemistry, host-guest chemistry and supramolecular chemistry (Izatt and Christensen, 1978; Gokel, 1992; and Hua, *et al.*, 2007).

It is vital to study the synthesis of new crown ethers and their chemical properties. In recent years, there have been numerous reports about 4′-substituted benzo-crown ether, however, to the best of our knowledge, no report yet about 4′allyl-substituted benzo-crown ether derived from eugenol.

Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e., $-CH_2CH_2O-$. Important members of this series are the tetramer (n =4), the pentamer (n=5), and the hexamer (n=6). Some of structures of crown ethers are shown in Fig. 1, where DB18C6 stands for dibenzo-18-Crown-6 ether.

The term "crown" refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person's head. The first number in crown ether's name refers to the number of atoms in the cycle, and the second number refers to the number of those atoms that are oxygen. Crown ethers are much broader than the oligomers of ethylene oxide; an important group is derived from catechol. Most procedures to prepare benzo-crown ethers described in the literature consist of reacting catechol or a catechol-like compound with a dichloropolyethylene glycol under the influence of a base (Scheme 1). The base-solvent combinations most commonly used are an alkali hydroxide in ethanol or an alkali butoxide in n-butanol (Pedersen, 1967; Newcomb, *et al*., 1977; Poonia, 1981; An, *et al*., 1992). The method suffers from some serious fundamental drawbacks. Firstly chloride ion is not the best leaving group in the nucleophilic displacement reaction which has to take place. This makes rather drastic reaction conditions (high temperature; long reaction times) necessary. Secondly the base-solvent combinations mentioned above can give rise to extensive formation of side products by reaction of the base and/or the conjugated base of the solvent with the dichloropolyethylene glycol. The most important steps are nucleophilic substitutions and eliminations. Moreover it should be born in mind that in the case of demethylated-eugenol a base like butanolate in principle can bring about isomerization of the allylic moiety. From the preceeding considerations it will be clear that it is worthwhile to investigate whether a more sophisticated synthesis of 4’-allylbenzo-crown ethers can be developed. In this synthesis some principles are:

a. The carbonate ion is sufficiently basic to deprotonate catechol, but its nucleophilicity and/or basicity are presumably too low to perform nucleophilic displacement and/or elimination reactions on polyethylene glycol derivatives.
b. The nucleophilic character of anions is greatly enhanced by dipolar aprotic solvent like DMF, DMSO, HMPT and TMU.

In addition to these principles another consideration has to be taken into account:

c. It is probable that in crown ether synthesis, the cations present in the reaction mixture act as a template for the formation of the crown ether.

To illustrate what is meant by the last allegation, the reaction under basic conditions between catechol and a suitable

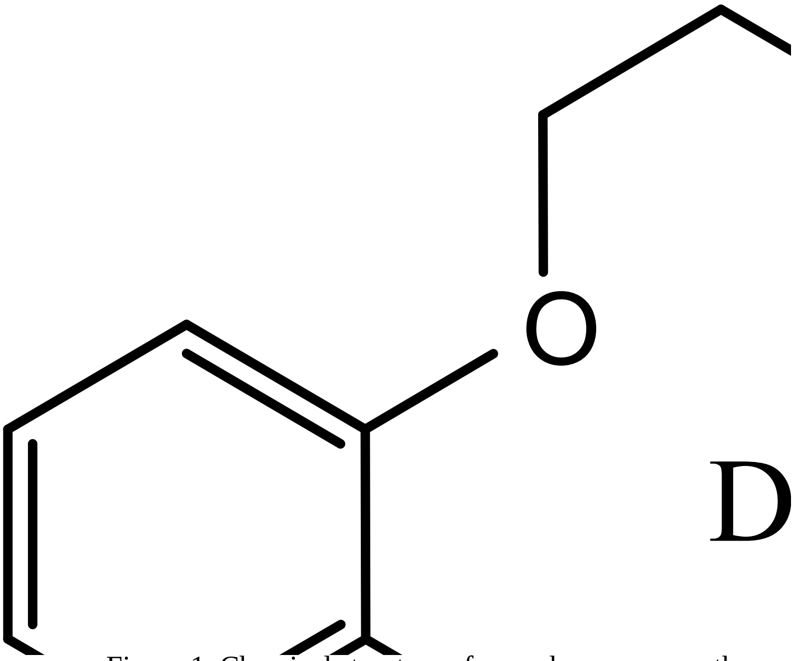


Figure 1. Chemical structure of some benzocrown ethers

derivative of tetraethylene glycol in order to prepare benzo-15-crown-5 is considered.

The first two steps of the reaction sequence (Scheme 2) leading to the desired product are a deprotonation of catechol, followed by a nucleophilic attack of the anion on the derivative of tetraethylene glycol. Subsequently, a second deprotonation occurs and in order to form benzo-15-crown-5 (**7**), the anion has now to perform a nucleophilic attack at the end of the chain already attached.

Scheme 1

It is clear that this nucleophilic attack can only occur when the carbon atom bearing the leaving group X is in the immediate vicinity of the anion. To this purpose the chain has to be folded in the proper way and in view of the complexing properties of crown ethers for cations it is reasonable to assume that this folding can be assisted by a cation having a radius corresponding to the diameter of the cavity of the crown ether **12** to be formed.

Benzocrown ethers can be prepared by a coupling reaction between the sodium salt of catechol and α,ω-dichloro oligoethylene glycols in 1-butanol. The method was introduced in 1967 by Pedersen. This versatile and simple procedure was applied to prepare 4'-allylbenzo-3n-crown-n ethers (4'AB3nCn stands for 4'allylbenzo-3n-crown-n, where n= 4,5,6 and 7). Benzocrown ethers with a vinyl group at the phenyl ring were synthesized for the first time by Smid and Sinta (1984) and his coworkers (Kopolow *et.al.*, 1973). In principle, the introduction of the vinyl group was performed at the end of a series of reactions.

On the other hand, our starting compound demethylated eugenol or 3-(3,4-dihydroxyphenyl)propene is already containing an allyl group. About eugenol and its green chem. point.

The crown formation was realized at the end of the reaction sequence. Nevertheless, using Pedersen's procedure four 4'-allylbenzocrown ethers with about 50% yield could be prepared. The present report is the first one in which the synthesis of crown ethers bearing an allyl group is described. The most recent reviews in the field of macrocyclic chemistry still mention Smid's report of this class of compounds.(Vogtle and Weber,1989; An *et. al.*,1992)

2. EXPERIMENTAL

2.1 Materials

Methyleugenol or 3-(3,4-dimethoxyphenyl) propene standard, aluminium triiodide (Aldrich), $SOCl_2$, α,ω-oligoethylene glycol, 1-butanol, Pyridine, toluene, aluminium oxide (70-290 mesh grade III), plate of TLC silica gel were used without further purification.

2.2 Instruments

Infrared spectra were recorded on Perkin-Elmer 283 spectrophotometers. ^{1}H NMR spectra were obtained on Varian EM 360(A) and Bruker WP 200 instruments. Chemical shifts are given downfield from internal standard tetramethyl silane (TMS). Mass spectra were recorded on a Kratos MS-80 mass spectrometer coupled to a Carlo Erba 4160 gas chromatograph with ionization energy 70 eV. The standard mass spectra of benzo-3n-crown-n, safrol and isosafrol were obtained from NIST data base.

2.3 Preparation of 4'-allylbenzo-3n-crown-n ethers from eugenol

2.3.1 Demethylation of methyleugenol with AlI_3

Bhatt and Kulkarni's (1983) procedure was adopted with small modification. The reaction was carried out in a nitrogen atmosphere in a 250 mL three necked round bottom flask. To a vigorously stirred solution of aluminium triiodide (22.9 g, 56.2 mole) in 60 mL CS_2 was added dropwise methyleugenol (58 g, 32.6 mmoles) in 20 mL CS_2 at room temperature. Subsequently the mixture was heated at 65°C for 4.5 h. The progress of the reaction was followed by TLC on silica gel using ether-hexane (2:1 v/v) as eluent.

After cooling to room temperature and removing of the solvent in vacuo, a deep brown sticky liquid residue was obtained. This was taken up in 200 mL ice water-ether (1:1 v/v) and the mixture was vigorously stirred. The water phase was separated and extracted several times with ether until the colour of ether layer was slightly yellow. The combined ether layers were washed with water until neutral and dried over Na_2SO_4. Evaporation of the solvent yielded 4.2 g (85%) of a dark brown viscous liquid. In the ^1H NMR spectra, no methoxy-signal at 3.7 ppm was detected. This demethylated eugenol was used directly without further purification to prepare 4-allylbenzo-3n-crown-n.

2.3.2 Preparation of α,ω-Dichloro-oligoethylene Glycols

A 500 mL three-necked flask was charged with 0.10 mol α,ω-oligoethylene glycol, pyridine (16 g, 0.20 mol), toluene (100 mL). The mixture was refluxed and $SOCl_2$ (24 g , 0.21 mol) was added dropwise (1 h), after which heating was continued for 22 h. The solution became turbid and finally was brown, and a dark precipitate was formed. After cooling to room temperature, 3 mL concentrated HCl and 20 mL water were added to the solution and the mixture was stirred vigorously. The toluene layer was separated, washed with water, and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure yielded 1,8-dichloro-3,6-Dioxaoctane (18.4 g, 98.5%) as a colourless liquid ; and 1,11-dichloro-3,6,9-trioxaundecane (22.8 g, 98.8 %), 1,15-dichloro-3,6,9,12-tetra-oxatetraadecane (25.1 g, 91.2%), 1,19-dichloro-3,6,9,12,15-pentaoxaheptadecane (31.2 g, 97.1%) as light yellow liquids, respectively. Infrared spectra of the products showed the absence of OH absorption at 3600-3100 cm^{-1}.

2.3.3 Crown Ether Formation from Demethylated Eugenol and α,ω-Dichloro-oligoethylene Glycols

Pedersens procedure was adopted (1967). Demethylated eugenol (1.9 g, 12.5 mmol) was dissolved in a mixture of 150 mL 1-butanol and a solution of 1.1 g NaOH in 10 mL water. To the mixture was added α,ω-dichloro-oligoethylene glycol (125 mol), and 10 mg MI (M= Li, Na, K, Cs depending on the size of crown to be synthesized, i.e. Li for m=12, Na for m=15, K for m=18, and Cs for m=2l; m being the number of atoms forming the crown ring). The mixture was heated at 70°C for 72 h , cooled to room temperature, decanted and the residue was extracted twice with 1-butanol (25 mL each). The solvent of the combined 1-butanol solutions was evaporated under diminished pressure affording the crude product. This was purified by column chromatography on aluminium oxide (150 g) using ethyl

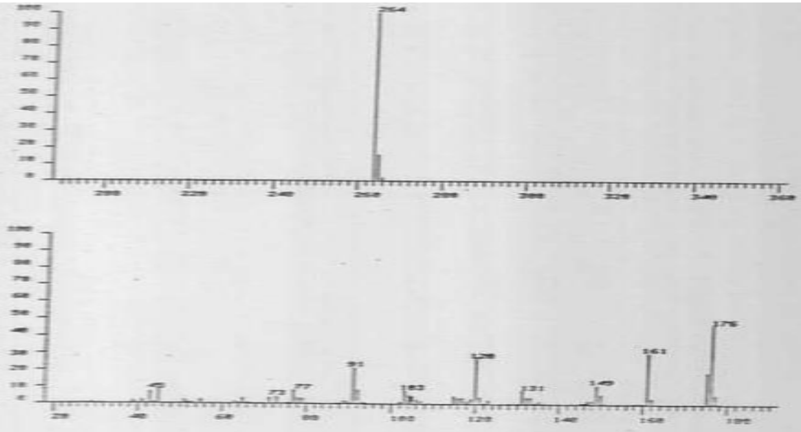


Figure 2. Mass Spectra of 4’Allylbenzo-12-Crown-4 ether

acetate—hexane (1:1 v/v) as eluent. This procedure yielded 4'allylbenzo-3n-crown-n and analysis was carried out by IR, ^{1}H NMR and MS spectrometers.

3. RESULTS AND DISCUSSION

The allylbenzo-3n-crown-n produced from the above reaction are 4'-allylbenzo-12-crown-4 (1.7 g, 60.1%), 4'-allylbenzo-15-crown-5 (2.1 g, 51.2 %) both as white solids and 4'-allylbenzo-18-crown-6 (2.2 g , 50 %) and 4'-allylbenzo-21-crown-7 (2.4 g, 51.1 %) as colourless oils, respectively. Using cations template related to the ring size of crown moiety gave satisfactory yields more than 50%. The allyl group does not change during the reaction, meaning that the base is not strong enough to isomerize the allyl to propenyl. The present method to introduce vinyl group to the benzene ring was done after the incorporation of crown ring (Chen, 1986; Daly, 1986, Varma *et al*.,1989; Takeda, 1984; and Kopolow *et al*., 1973). The intention to introduce of unsaturated side at the phenyl ring is to polymerize them to the corresponding crown ether polymers. These polymers can be used as catalyst, ionophore and adsorbent for heavy metals.

The spectroscopic properties of the 4'-allylbenzo-m-crown-n ethers are summarized in the Table 2. It shows that substitution of the methoxy group by a crown moiety does not change the absorption signals of the allyl group very much. The double bond clearly can be seen from an absorption at 1640 cm^{-1} in the IR spectrum. The same is the case with the ^{1}H-NMR spectra. The only difference with the parent compound (methyleugenol, shown in Table 3) was the appearance of signals belonging to the $–CH_2$-CH_2-O- moiety at 3.5-4.1 ppm. Depending on the crown ether, this signal integrates for 12H to 24H. The best data for comparison of the spectral properties of these compounds are those from Kopolow *et.al.* (1973). They showed that the vinyl group resonates at 5.4 ppm for $=CH_2$ and at 6.6 ppm for =CH. Moreover signals at 4.0 ppm for $–OCH_2$ and at 7.0 ppm for the aromatic protons are present.

Figure 2. shows the mass spectra of 4'allylbenzo-12-crown-4 ether. It is seen from that the base peak is m/z= 264 (100%), which is at the same time is also the molecular ion. The second largest peak is m/z= 176 (45%). The complete IR, NMR and MS spectra of these compounds can be found in the previous work (Anwar,1994).

Of the twelve principles of green chemistry, it is advisable to use renewable resources. Eugenol as a renewable resources can be converted into more i compound such as crown ethers.

The detail of mass spectra of the 4'-allylbenzo-3n-crown-n ethers and benzo-3n-crown-n ethers are summarized in Table 4 and 5, respectively.

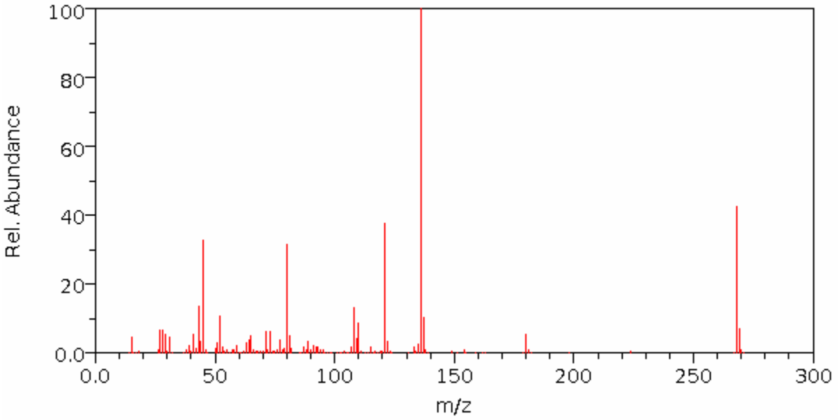


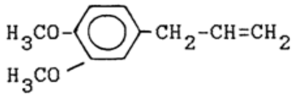
Figure 3. Mass spectra of benzo-15-crown-5 ether

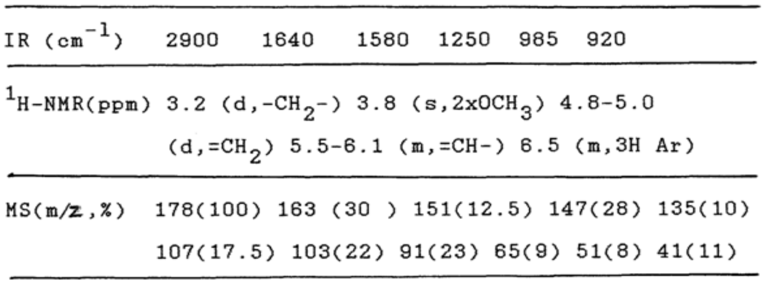
Table 2. Spectroscopic Characteristic of 4’AB-3n-C-n (4’AB3nCn stands for 4’allylbenzo-3n-crown-n, where n=4,5,6 and 7)

Compounds	IR (cm^{-1})	1H NMR (ppm)	MS (m/z, %)
4’AB12C4	1640 1260 1140	5.6-6.4 (m, 1H) 4.85-5.4 (d, 2H) 3.35 (d, 2H) 3.6-6.4 (m, 12H of –CH_2) 6.7-7.1 (m, 3H of Ar)	**264(M^+, 100)**, 220(10), 176(45), 161(32), 149(13), 120(28), 91(23), 45 (10).
4’AB15C5	1640 1250 1130	5.6-6.4 (m, 1H) 4.8-5.3 (d, 2H) 3.3 (d, 2H) 3.6-4.4 (m, 16H of –CH_2) 6.7-7.0 (m, 3H of Ar)	308(M^+, 93), 220(10), **176 (100)**, 161(34), 149(12), 131(10), 120(32), 91(18).
4’AB18C6	1640 1260 1130	5.6-6.3 (m, 1H) 4.8-5.3 (d, 2H) 3.3 (d, 2H) 3.5-4.3 (m, 20H of –CH_2) 6.6-6.9 (m, 3H of Ar)	352(M^+, 27), 308(2), 264(5), 220(5), **176(100)**, 161(28), 149(12), 120(32).
4’AB21C7	1650 1250	5.5-6.1 (m, 1H) 4.8-5.0 (d, 2H) 3.2 (d, 2H) 3.5-4.1 (m, 24H of –CH_2) 6.2-7.2 (m, 3H of Ar)	396(M^+, 27), 352(2), 308 (5), 264(5), 220(5), **176 (100)**, 161(25), 149(12), 120(32).

Table 3. Spectroscopic characteristic of methyleugenol

IR (cm^{-1})	1H NMR (ppm)	MS (m/z, %)
2900 1640 1580 1250 985 920	5.2 (d, -CH_2-) 3.8 (s, 2x -OCH_3) 4.8-5.0 (d, =CH_2) 5.5-6.1 (m, =CH-) 6.5 (m, 3H of Ar)	178(M^+, 100), 163(30), 151(12.5), 147(28), 135(10), 107(17.5), 103(22), 91(23), 65(9), 51(8), 41(11)





IR (cm^{-1})	2900 1640 1580 1250 985 920
^{1}H-NMR(ppm)	3.2 (d,-CH_2-) 3.8 (s,2xOCH_3) 4.8-5.0 (d,=CH_2) 5.5-6.1 (m,=CH-) 6.5 (m,3H Ar)
MS(m/z,%)	178(100) 163 (30) 151(12.5) 147(28) 135(10) 107(17.5) 103(22) 91(23) 65(9) 51(8) 41(11)

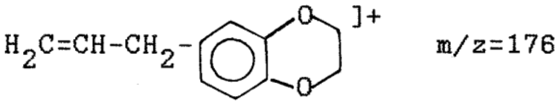
Table 4. Detail assignment of mass spectra of 4'-allylbenzo-3n-crown-n ethers

Compounds	m/z (%)
4'AB12C4	264 (M^+, 100); 220 (10); 176 (45); 161(32); 149 (13); 120 (28); 91 (23); 45 (10).
4'AB15C5	308 (M^+, 93); 220 (10); 176 (100); 161(34); 149 (12); 131 (10); 120 (32); 91 (18).
4'AB18C6	352 (M^+, 27); 308 (2); 264(5); 220 (5); 176 (100); 161(28); 149 (12); 120 (32).
4'AB21C7	396 (M^+, 27); 352 (2); 308 (5); 264(5); 220 (5); 176 (100); 161 (25); 149 (12); 120 (32).

Table 5. Detail assignment of mass spectra benzo-3n-crown-n ethers

Compounds	m/z (%)
B12C4	224 (M^+, 55); 180 (2,5); 136 (100);121 (75); 108 (22); 80 (70); 52 (27); 45 (37,5)
B15C5	268 (M^+, 52); 224 (2); 180 (6); 136 (100); 121 (52,5); 108 (14); 80 (35); 52 (30); 45 (54).
B18C6	312 (M^+, 17,5); 268 (7); 224 (7); 180 (12); 136 (100); 121 (35); 108 (15); 80 (27,5); 45 (37,5)

The mass spectra shown in the Table 4 of the three compounds (4'AB15C5, 4'AB18C6 and 4'AB21C7) indicate the same base peak at 176 except 4'AB12C4 showed the molecular ion, M^+ at 264). Ion 176 has an odd electron number which is indicative for a rearrangement process during its formation. The structure of this ion will be,



Scheme 3

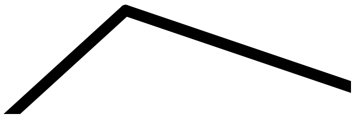


Figure 4. Structure of Alkylbenzo-15-crown- 5 ethers

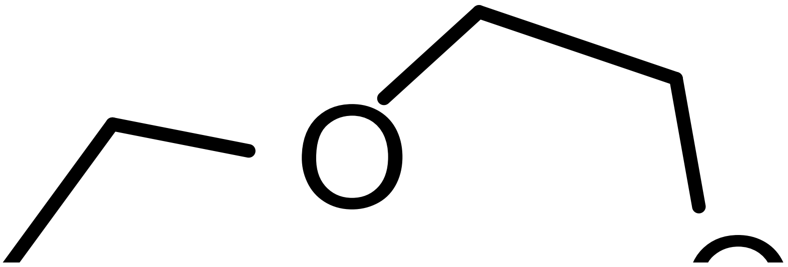
This ion is very similar to a well known stable compound, namely 1,4-dioxane. The formation of this ion from the molecular ion happens by releasing a stable molecule, C_2H_40 (m/z=44). The structure of the latter molecule is probably acetaldehyde, CH_3CHO or ethylene oxide. For instance, 4'-allylbenzo-15-crown-5 with molecular ion M^+=308 can be fragmented to ion 176 by releasing three times C_2H_40 (176 = 308-3x44). This kind of fragmentation is very common in benzocrown ether compounds (Zeliha *et al.*, 2004). For comparation the mass spectra of three benzocrown ethers are listed in Table 5.

The following mass spectra of benzo-15-crown-5 was taken from NIST data base. As shown in the Table 4 the molecular weight is

Scheme 4

Scheme 5

Scheme 5



M= 268 ($C_{14}H_{20}O_5$) while the base peak is m/z= 136 ($C_8H_8O_2$), the molecular ion was releasing 3xC_2H_4O or (M- 3x44).

To know more about the influence of allyl side chain to the mass spectra pattern, the following work of Shu (1991) can be used for comparation. The molecules studied by Shu are shown in Fig. 4, i.e: Alkylbenzo-15-crown-5 (RB15C5, **11**) and Alkyldibenzo-15-crown-5 (RDB15C5, **12**).

The above compounds are bearing alkyl group as side chain as well as bridge. Based on his studied, Shu found that the fragmentation starting whether on the polyether rings, the side chain or on the bridge chain is dependent upon the type of the chain. The detail fragmentation pattern of the compound RDB15C5 can be depicted in the Scheme 1.

The base peak of this compound is m/z= 149, $C_9H_9O_2$, this is an ion with even electrons contains 1,4-dioxane-like moiety just like in the case of 4'ABCE. Ion m/z=149 can be isomerized to tropilium-like ion, thus increasing the stability of the ion. When the alkyl is the side chain, the ion with m/z= 192 gave only 18% relative abundance and the base peak is m/z= 149. It means that the alkyl group was fragmented at the 2 position of benzene ring.

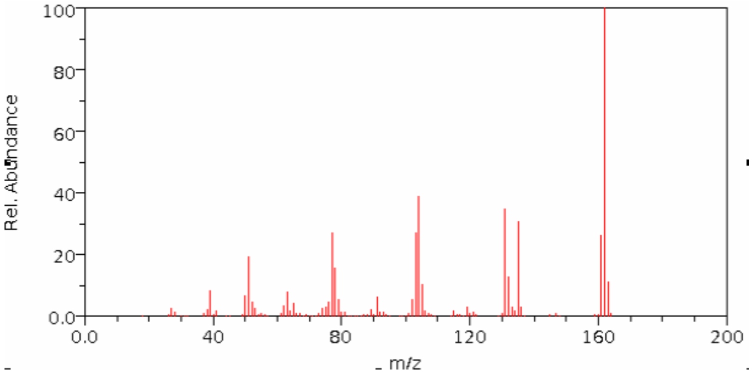


Figure 5. Mass spectrum of safrol

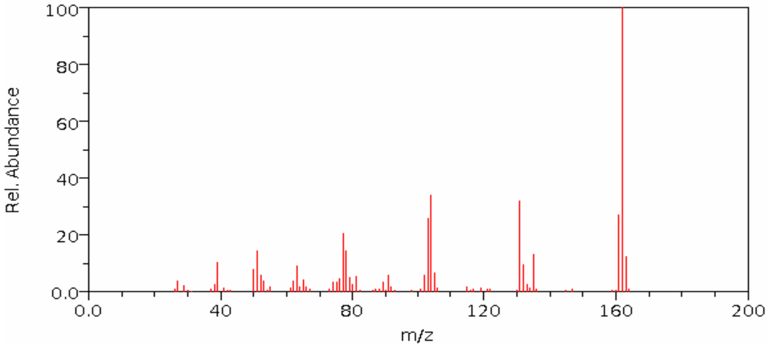


Figure 6. Mass spectrum of isosafrol

This is different from our compound where the base peak m/z= 176 is containing an odd electrons and still hold the allyl group. The strong attachment of allyl group to the phenyl ring can also be compared to safrol and isosafrol. These two compounds contain the smallest cyclic ether possible attached to phenyl ring as well as the allyl and or propenyl group. Herewith the following mass spectra of safrol (**13**) and isosafrol (**14**) (Fig. 5 and 6). Safrol with molecular formula $C_{10}H_{10}0_2$ has molecular weight, M= 162 and shows base peak at m/z=162.

Isosafrol is the isomer of safrol gave very similar mass spectra of safrol with the same base peak at m/z=162. The structure of 1,3-benzodioxole is comparable to 1,4-dioxane-like compound although the ring size is smaller. The recognizable peak is m/z= 135 (30%) more intense in safrol compare to isosafrol with only 10%. This probably due to the loss of C_2H_3, while mass of m/z= 131 lost of 30 from m/z= 161 or M-1. Based on this data it can be explained why in the case of 4'AB12C4 the base peak is the molecular ion itself. Even for 4'AB15C5 the molecular ion relatively stable with relative abundance 93%.

Another interesting analysis of Shu's report based on the scheme 5. When the side chain bridge is alcohol, one of the fragmented ion contained double bond like m/z= 321 and will cleave to m/z= 307 by releasing methylene, CH_2 to yield allylic cation moiety. This moiety is stable and the latter fragmentation took place at the polyether part until yielded the 1,4-dioxane-like ion with m/z= 175. The strange thing is, this ion is only 15% in relative abundance.

The last comment on the mass spectra pattern is, although the –OH group present like in the case of eugenol or isoeugenol (**15**), the base peak of these compounds is the same as the molecular ion which is m/z= 164. The fragmented ion of M-1(releasing H radical) is less abundant compare to M-15 (releasing CH_3 radical). Again it can be concluded that the allyl and or propenyl group attached more strongly to the phenyl ring compare to polyether moiety. Figure 7 shows isoeugenol mass spectrum.

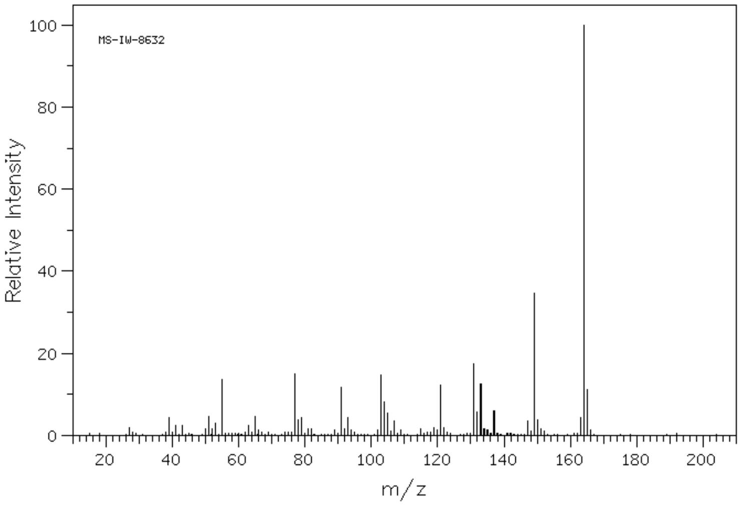


Figure 7. Mass spectrum of isoeugenol

4. CONCLUSION

4'-Allylbenzo-3n-crown-n ethers can be synthesized from methyleugenol via demethylation to yield cathecol-like compounds and reacting them with α,Ω-dichloro-oligoethylene glycol with more than 50% yield. These compounds are the first synthesized from the renewable material namely eugenol. The mass spectra pattern of 4'allylbenzo-3-n-crown-n ether showed very interesting fragmentation due to the presence of allyl side chain. The smaller of the polyether ring size, the more difficult to be cleaved as the case of 4'AB12C4 and safrol under 70 eV bombardment. The allyl and or propenyl group is more difficult to cleave even compare to more pronounce group to cleave such as OH.

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