

Naphthalene Chemistry: I: Studies on the Metallation of Naphthalene and the β -Ethyl-Naphthalene by Potassium in THF and its Application as a Di-functional Anionic Initiator for Ethylene Oxide.

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Introduction

It has been well established that naphthalene can be reduced by alkali metals in ether solvent (i.e. Tetrahydrofuran) to the anion radical (A.R.) or dianion (D.A.) state (1-13). The use of the (D.A.) as an anionic initiator for styrene has been briefly reported by Pillot (12), however, a detailed analytical study of the naphthalene group, which would establish whether the mechanism involved electron transfer or addition was not provided.

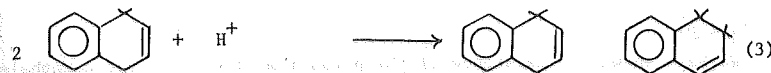
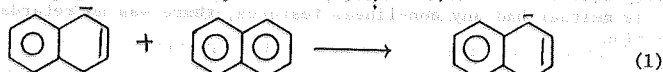
Previous literature has not reported the existence of the dianion K of naphthalene, with the exception of the use of a cryptate compound (14).

The purpose of this paper is to report the metallation of naphthalene by potassium in the range of the concentration varying from $4.5 \cdot 10^{-3}$ to $1.1 \cdot 10^{-1}$ mol ℓ^{-1} . We have also studied the metallation of the β -substituted naphthalene: β -Ethyl-naphthalene (BEN) in the range of concentration $1.5 \cdot 10^{-1}$ to $1.6 \cdot 10^{-1}$ mol ℓ^{-1} . Finally we will show that the last anionic species is an effective initiator for ethylene oxide (EO) in THF at room temperature.

Results and Discussion

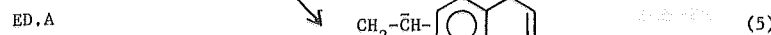
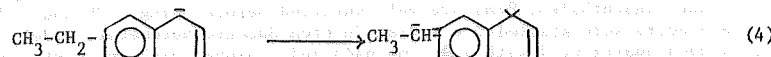
When one metalates naphthalene with potassium (K/Napht 4), depending on time and concentration, one can obtain R=2 (R: ratio of the number of carbanions per naphthalene (Table I)).

Since the UV spectrum of the AR and DA are different, one can follow the kinetics of the metallation. The spectra are shown in Fig. 1. UV1 is the metallation of naphthalene by the Na and is identical to the AR spectrum. (1,8-11,15) - UV2 is for K after six hours, UV3 after thirty-three hours (id as 100 hrs.) with $\lambda_{max} = 440-442$ nm and a shoulder at $\lambda = 600-650$ nm. At this moment, if one adds some neutral naphthalene to the solution, the UV spectrum (UV4) is identical to the (AR). Based on the hydrolysis properties, the solution after 100 hrs. of metallation is quenched in water and subjected to NMR analysis yields 100% of dihydronaphthalene. This method (titration, UV, hydrolysis) has been used by Smid (2), Pillot (12), Hsieh (6), and Richards (3) for studying the dianion of naphthalene lithium. The following reactions are postulated (eqs. 1-3).



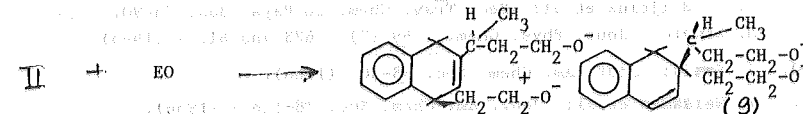
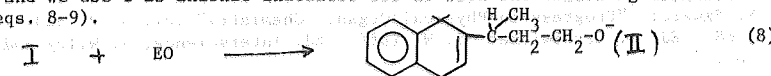
Our results are consistent with the above reactions, hence we propose that the species consists of two carbanions per naphthalene and UV3 is the hitherto unknown dianion potassium of naphthalene.

The β -ethylnaphthalene (BEN) reacts similarly as the naphthalene (Table II), but it has been shown (16) that the dianion isomerized by the following mechanism (eqs. 4-7), which is supported by titration, UV spectra (Fig. 2), and NMR hydrolysis results.



In Fig. 2, one can see the formation of AR (UV5: after 10 minutes of metallation); UV6, after 10 hrs., shows λ_{max} at 438 nm and a shoulder at $\lambda = 600-650$ nm (dianion). But after 49 hrs. (UV7), the shoulder disappears and no longer transfers the second electron, if neutral naphthalene is added. The UV8 is with $\lambda_{max} = 432$ nm is obtained after hydrolysis of the isomerized dianion (eqs.: 4-7) and re-metallated.

As the isomerized dianion shows always one anion in the cycle and the other on the side chain, for clarification we represent by structure I and we use I as anionic initiator for EO with the following mechanism: (eqs. 8-9).



The mass molecular weight can be predicted by the following equation: (10).

$$M = \frac{(\text{EO}) \times 44}{(\text{C})} \quad (10)$$

where (EO) and (C) is the concentration of EO, and EN respectively. Table III shows the three results of polymerization where the conversion is quantitative and good correlation between experimental and theoretical value of M. The GPC of these samples are shown in Fig. 3 where M_w/M_n is less than 1.1.

Conclusion:

We have shown the existence of the potassium dianion of the naphthalene hitherto unknown. Furthermore its stability is very high compared to equivalent lithium. The model compound EN reacts similarly, but the final dianion isomerized to another (I), which is still able to quantitatively polymerized ethyleneoxide - the mechanism is shown to be living and produces two poly-ether chains per naphthalene unit with very low polydispersity.

Experimental

All manipulations were done under high vacuum. The solvents as well as reactants (naphthalene, EN) are well purified before using. UV and Visible Spectra were studied on a Varian Tectron Spectrophotometer, model 535, using a quartz cell with a 0.1 mm path and equipped with an inlet tube.

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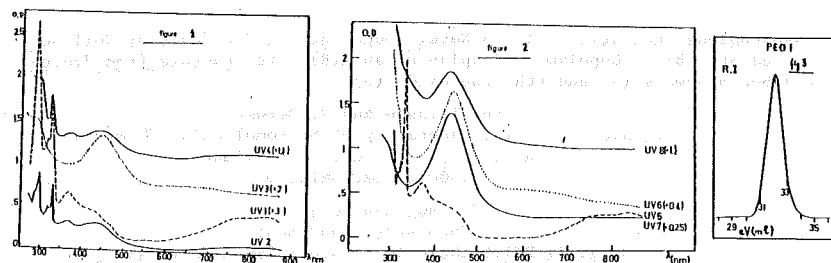


Table I

[Naphth.] mol l ⁻¹	Time of metalation (hours)	[Carbanions] [C] mol l ⁻¹	[C] [Naphth.]
4,5.10 ⁻³	100 h	8,9.10 ⁻³	1,98
9,3.10 ⁻³	120 h	18,41.10 ⁻³	1,98
3.10 ⁻²	72 h	5,9.10 ⁻²	1,96
2,26.10 ⁻²	168 h	4,52.10 ⁻²	2
7.10 ⁻²	200 h	11,2.10 ⁻²	1,6
11.10 ⁻²	24 h	9,5.10 ⁻²	0,86
11.10 ⁻²	240 h	11.10 ⁻²	1

Table II

[Ethyl Naphth.] mol l ⁻¹	[C] by titration mol l ⁻¹	[C] [ethyl naphth.]	Time (hours)
0,159	0,318	2	120 h
0,124	0,236	1,9	96 h
0,015	0,029	1,9	33 h

Table III

Experiment No.	[EO] Mol l ⁻¹	[EN] Mol l ⁻¹	[EO] [EN]	Conversion (%)	(Theory)	(Experiment)
1	10 ⁻¹	16,32.10 ⁻⁴	61	100	2640	2700
2	10 ⁻¹	8,16.10 ⁻⁴	122	93	5000	5200
3	10 ⁻¹	5,44.10 ⁻⁴	183	95	7700	7500