

NEW OBSERVATIONS ON THE METALATION OF NAPHTHALENE AND β -ETHYLNAPHTHALENE BY POTASSIUM

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Summary

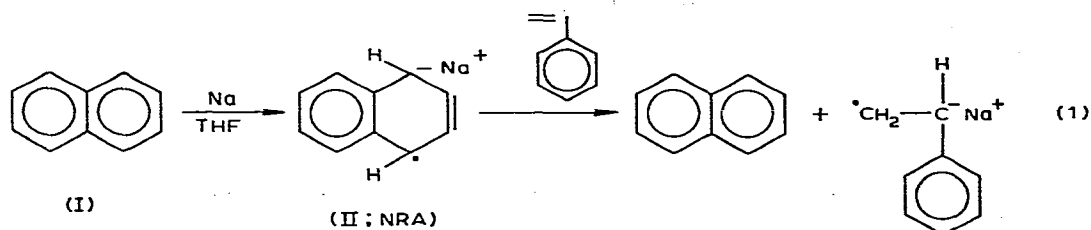
A stable dinegative ion can be formed when naphthalene is metalated by an excess of potassium in tetrahydrofuran at 25°C; this previously unreported species is obtained only at naphthalene concentrations lower than $3 \times 10^{-2} \text{ m l}^{-1}$. In the case of β -ethylnaphthalene, the initial dianion is isomerized into a dihydronaphthalene monoanion carrying an extra-cyclic anion as a result of an intramolecular hydrogen transfer; this dianionic species can be formed at concentrations higher than $3 \times 10^{-2} \text{ m l}^{-1}$.

Introduction

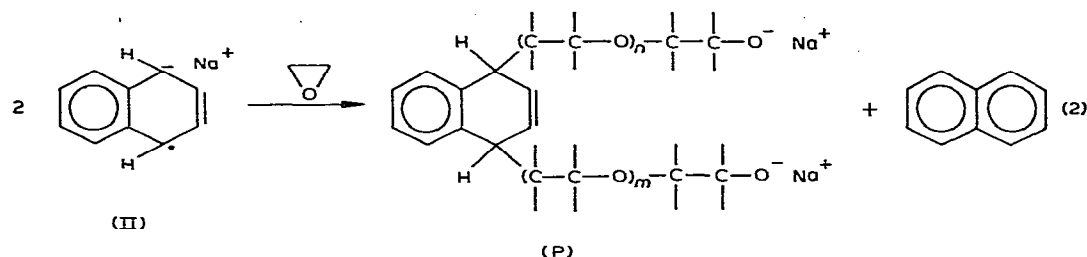
Naphthalene is readily metalated by alkali metals in polar solvents such as tetrahydrofuran (THF). Either an anion-radical or a dianion can be formed, depending on the counter-ion, reagent concentration, time and temperature [1—4]. At room temperature or lower temperature, only a stable deep green radical-anion is formed in the presence of sodium [4]. Lithium is known to produce a radical-anion at -80°C , but in a second step and at naphthalene concentration lower than 0.5 m l^{-1} a stable dianion is observed, which slowly decomposes at room temperature [2,5—7]. In the presence of potassium at -80°C the exclusive formation of the radical-anion has been claimed [8]. Although we do not know of any experimental evidence for a dianion of naphthalene potassium or sodium in THF at room temperature, their transient participation in the Birch reduction in liquid ammonia has been invoked by some authors [9—11] but rejected by Smid [5].

Control of the naphthalene metalation is very important because the naphthalene radical-anion (NRA) and dianion are potential initiators of anionic polymerizations. The anion-radical is widely used in vinyl polymerization, the initiation taking place by transfer of the unpaired electron of the NRA to the

unsaturated monomer [1,4,12] (eq. 1).



However, in the case of cyclic monomers such as cyclic ethers and siloxanes, the initiation proceeds differently and leads to a covalent bonding of the naphthalene to the growing chain [1,12–14] (eq. 2).



This mechanism has attracted attention as a potential way to prepare graft copolymers. For instance, ethylene oxide (EO) has been grafted onto polyvinyl naphthalene, and the initiation of two polyether chains per aromatic nucleus has been reported; however, the yield is limited with respect to the naphthalene units (eq. 2) and the metalation is complicated by a competing cleavage reaction [15,16].

The only known naphthalene dianion (Li) has never been described as an initiator, but it is an excellent reagent for the synthesis of β -hydroxyacids [17]. If the existence and the stability of a potassium or sodium naphthalene dianion could be established, the polymer (P) would be obtained without releasing half the naphthalene initiator as observed with the NRA (eq. 2). Furthermore, the attachment of a potassium or sodium naphthalene dianion to the end of a chain (i.e. PA) would open a very attractive pathway to prepare PEO based block copolymers with an original PA(PEO)₂ star-shaped structure*. The lithium naphthalene dianion cannot be used for this purpose, as the organolithium compounds are unable to polymerize EO [18].

The aim of this work is to report a new aspect of the metalation of naphthalene and β -ethylnaphthalene by potassium in THF at RT, and especially the formation of a stable potassium dianion.

Experimental

THF (pure grade) was dried by refluxing over the benzophenone-sodium complex, and distilled under argon.

Anhydrous naphthalene and small clean pieces of potassium were placed into

* A series of four papers is to be published on this subject.

an argon-purged and flamed glass apparatus. After 3 cycles of evacuation and repressurization with argon, dried THF was introduced by distillation from a solution of oligomeric polystyryl potassium connected to the reaction vessel through a breakseal. The system was magnetically stirred during the metalation.

UV and visible spectra were recorded on a Varian Techtron spectrophotometer, model 635, using a 0.1 mm path quartz cell equipped with an inlet tube. The cell was argon-purged and flamed before being filled with the solution and before the final sealing. ^1H NMR spectra were obtained from a Varian T 60 apparatus.

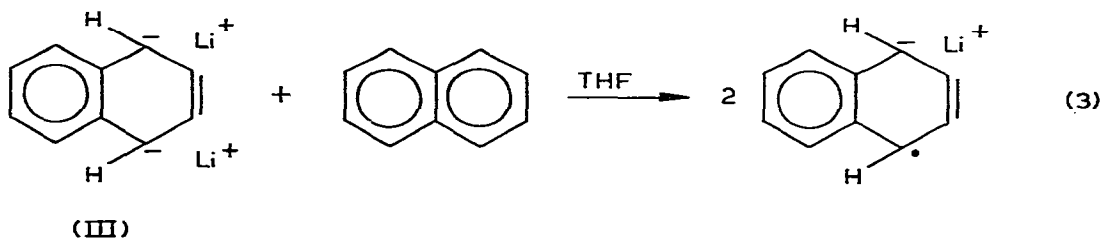
Titration. The carbanions were titrated potentiometrically by the Gilman's procedure (double titration) [19]. The content of hydroxyl end-groups was determined by back-titration with NaOH standard solution (0.1 M) of the excess of phthalic anhydride ($3 \times 10^{-2} \text{ m l}^{-1}$ in pyridine) added to the dried polymer solution in THF. Accurately known amounts of polymer and phthalic anhydride were mixed and heated at 100°C for 4 hours before titration.

Results and discussion

Metalation of naphthalene by potassium in THF at room temperature

In the presence of potassium in THF at room temperature, naphthalene is first reduced to an anion-radical (deep green), but in a second step, new species are formed and a stable red-brown color is finally observed.

Titration at the end of the metalation (Table 1) shows the presence of two anions per naphthalene unit provided the naphthalene concentration is lower than $3 \times 10^{-2} \text{ m l}^{-1}$; beyond this limit the metalation falls to one carbanion per naphthalene. It is to be noted that the formation of the naphthalene dianion with lithium is similarly dependent on naphthalene concentration [2]. On the other hand, these anionic species are able to transfer one of their electrons to neutral naphthalene and the characteristic deep green color of the NRA is again observed. Similar behavior has been reported for the dianion of the naphthalene lithium (eq. 3) [5].



The following reaction scheme is accordingly proposed for the metalation of naphthalene by potassium in THF at room temperature (eq. 4).

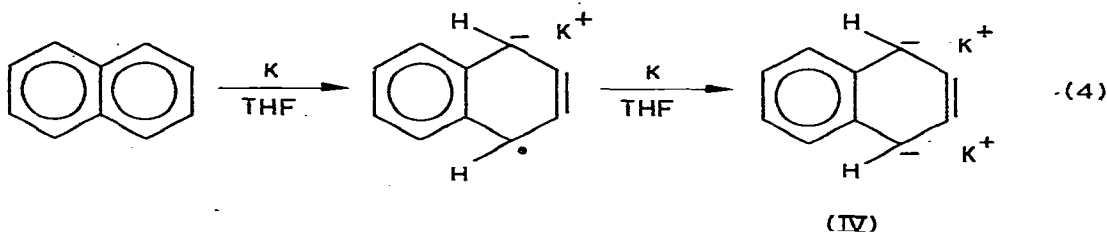


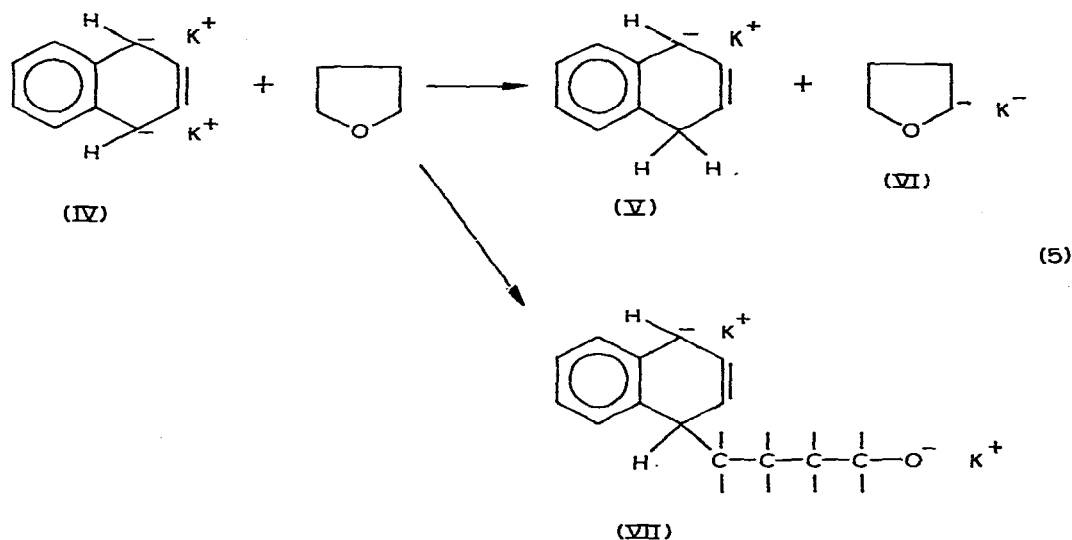
TABLE 1

NAPHTHALENE METALATION BY POTASSIUM IN THF AT ROOM TEMPERATURE

Naphthalene Concentration [N] (ml ⁻¹)	Carbanions Concentration ^a [C ⁻] (ml ⁻¹)	$\frac{[C^-]}{[N]}$
4.5×10^{-3}	0.9×10^{-2}	2.0
9.5×10^{-3}	1.9×10^{-2}	2.0
2.0×10^{-2}	4.0×10^{-2}	2.0
3.0×10^{-2}	5.9×10^{-2}	1.97
7.0×10^{-2}	1.1×10^{-1}	1.57
1.1×10^{-1}	1.1×10^{-1}	1.00

^a Final constant values.

The metalation of naphthalene by potassium can also be studied by visible and ultra-violet spectrophotometry. After 6 h the absorption curve characteristic of the NRA [8] is observed (Fig. 1, A), whereas after 33 h the absorption is much modified and can be ascribed to the dianion of the naphthalene potassium derivative (Fig. 1, B). The assumed dianion is still stable at room temperature after 100 h; however in the presence of an excess of neutral naphthalene, the absorption of the NRA is again observed. (Fig. 1, C). Once generated, the K dianion (IV) could react with the solvent and give rise to the three anionic species V, VI and VII (eq. 5).



However, it is well established that naphthalene monoanion (V, VII) is unable to transfer one electron to a neutral naphthalene molecule [5], while VI is quickly rearranged into ethylene and potassium-vinylalkoxide [20]. The two carbanions observed by titration per naphthalene molecule must accordingly be attributed to the dianion IV itself.

The hydrolysis of the naphthalene dianion must give rise to dihydronaphthalene, as described by eqs. 6 and 7, whereas it is well-known that equal

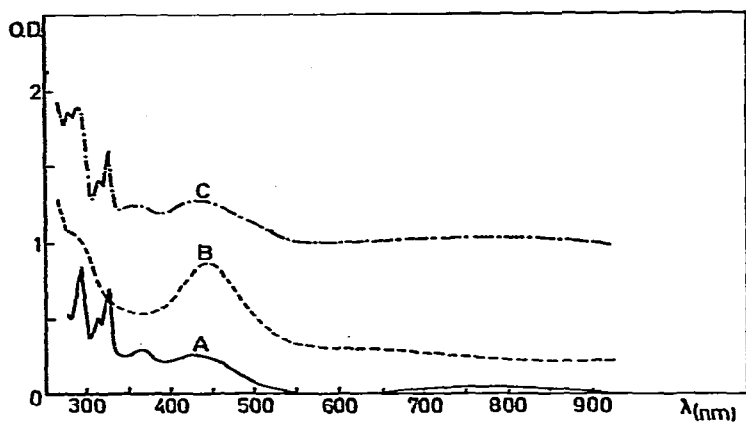
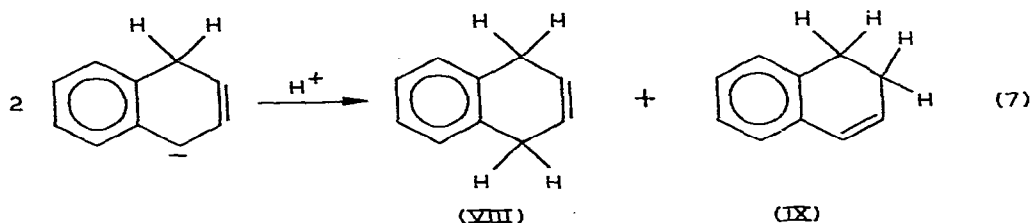
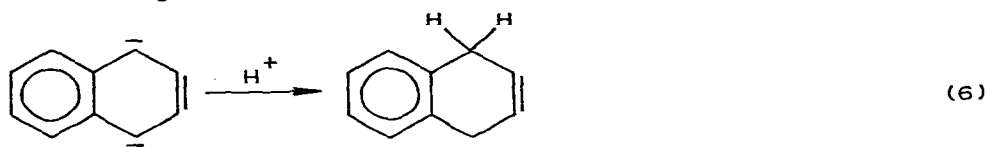
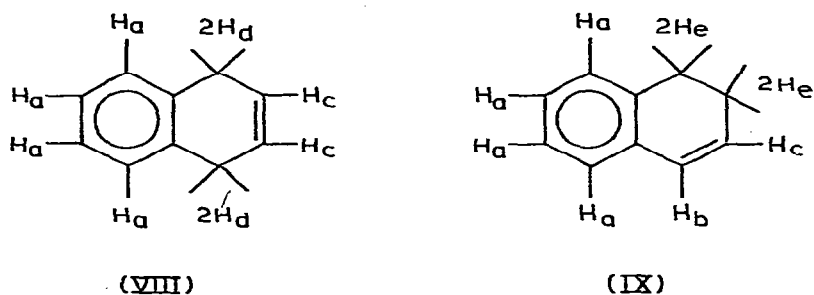


Fig. 1. Visible and UV spectra of: A, naphthalene metalated by K for 6 h (THF, 25°C); B, *ibid.* for 33 and 100 h (O.D. values shifted upwards by 0.2 units); C, naphthalene metalated by K for 100 h, with further addition of neutral naphthalene (O.D. values shifted upwards by 1 unit).

amounts of naphthalene and dihydronaphthalene are obtained by the hydroly-



sis of NRA [2,3,8,13]. The hydrolysis products obtained from the assumed potassium naphthalene dianion have been studied by ^1H NMR spectroscopy; all the signals observed can be attributed to dihydronaphthalene protons (Table 2), and their assignment is in accordance with the results published by



Zilkha [21] and Richards [2]. From the integration of the signals correspond-

TABLE 2

¹H NMR ANALYSIS OF THE HYDROLYSIS PRODUCTS FROM THE POTASSIUM NAPHTHALENE DIANION

Protons	Chemical shift (ppm) ^a	Multiplicity ^b
H _a	7.15	s
H _b	6.3	d
H _c	5.9	m
H _d	3,3	s
H _e	2.5	m

^a In ppm from tetramethylsilane as internal reference. ^b s, d and m for singlet, doublet and multiplet, respectively.

ing to H_d and H_e protons, the ratio between the forms VIII and IX was evaluated as being close to 3.

In conclusion, complexes are formed in THF at RT between naphthalene and excess of alkali metals; the anion-radical only is formed with sodium, whereas dianions are observed with potassium and lithium. The potassium dianion is stable, in contrast to the lithium dinegative ion which has a half-life of about 11 h [22]. From a comparison of the standard potential $\epsilon(M^+, M)$ of the alkali metals, it is evident that the reducing power decreases from lithium ($\epsilon -3.02$ V) to potassium (-2.92 V) and again to sodium (-2.71 V). As the first reduction potential of naphthalene in THF is larger than the second, but just lower ($\Delta\epsilon 0.01$ V) than the standard potential of sodium [23], it is not surprising that a naphthalene dinegative ion cannot be formed by this metal. The instability of the organolithium compounds in ether solvents is often mentioned in the literature [24], whereas the organopotassium derivatives are generally more stable [25]. This different behavior is probably related to the high solvation energy of the Li⁺ ion, which is greater than that of the K⁺ ion [5,26]; in THF, the C-Li link is accordingly more ionic, and the attack on the ether solvent by the carbanion is favoured.

Metalation of β -ethylnaphthalene by potassium in THF at room temperature

To assess the influence of substitution on the metalation of naphthalene, β -ethylnaphthalene (EN) was studied as a model compound. Upon metalation under the same conditions, both naphthalene and β -ethylnaphthalene form a dianion as determined by titration, but two differences are to be noted. In contrast to the potassium naphthalene dianion, the dianionic species derived from EN can be formed at concentrations higher than 3×10^{-2} m l⁻¹ (Table 3), and it is unable to transfer one electron to another naphthalene molecule. These differences are to be attributed to the participation of the β -ethyl group in the metalation process.

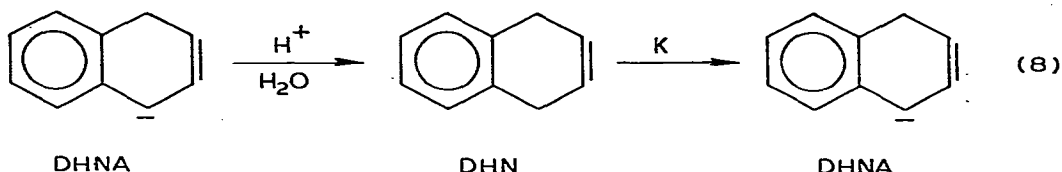
The EN metalation has been analyzed by UV spectrophotometry (Fig. 2). The spectrum A obtained after 10 minutes presents the absorption characteristic of the naphthalene radical-anion (NRA) [8]. After 10 h, a spectrum B corresponding to the potassium naphthalene dianion (see Fig. 1, B) is observed, but changes gradually until the absorption at 600–650 nm disappears and a shoul-

TABLE 3

METALATION OF β -ETHYLNAPHTHALENE (EN) BY K IN THF AT ROOM TEMPERATURE.

EN (ml ⁻¹)	Time of metalation (hours)	[Carbanions] (ml ⁻¹)	No. of carbanions per EN
0.160	120	0.32	2.0
0.125	96	0.24	1.9
0.015	33	0.03	2.0

der at 280–290 nm is formed (spectrum C: 50 h of metalation). Spectrum C is not changed at all by the addition of pure naphthalene. It is noteworthy that the absorption at 435 nm (spectrum C) corresponds to the value reported for the dihydronaphthalene monoanion (DHNA) 433–435 nm [27].



Upon hydrolysis of DHNA, dihydronaphthalene (DHN) is formed, but this can be metalated again to give DHNA (eq. 8). Similarly, the anionic species derived from EN (Fig. 2, C) was hydrolyzed and the product after purification was metalated again by potassium under the same conditions; spectrum D (Fig. 2) so obtained is very similar to spectrum C except for a slight modification

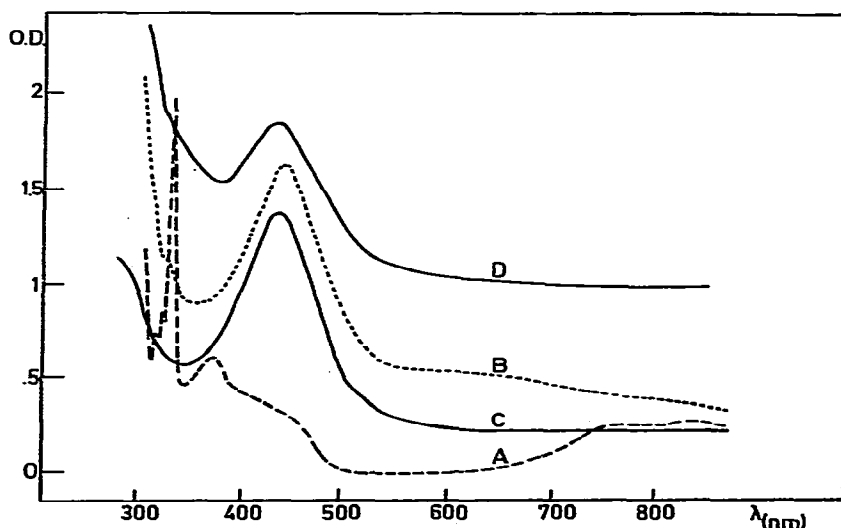
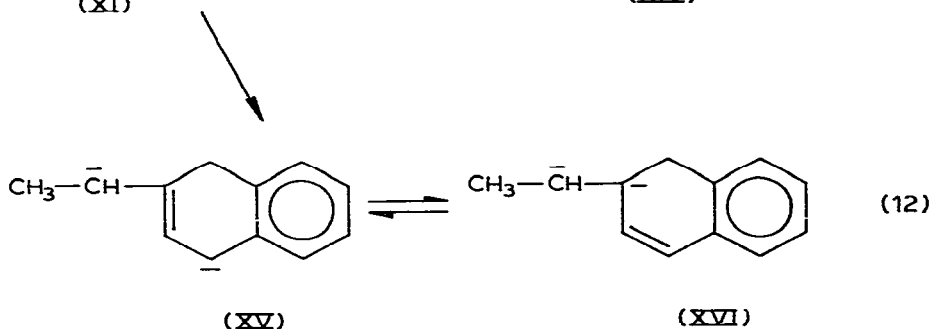
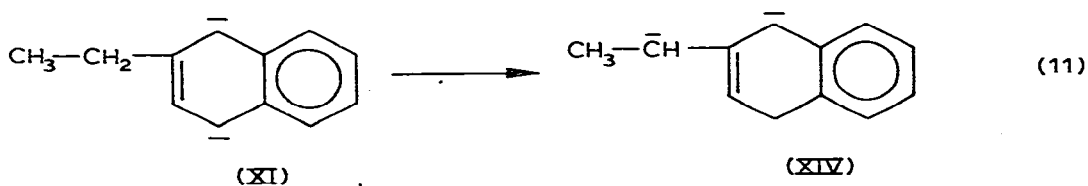
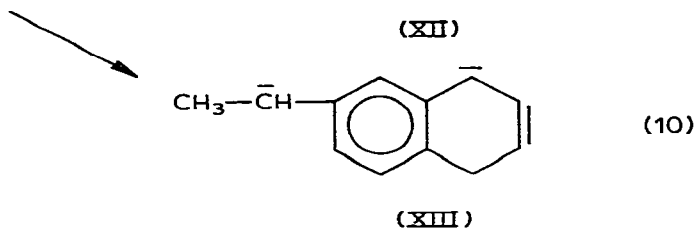
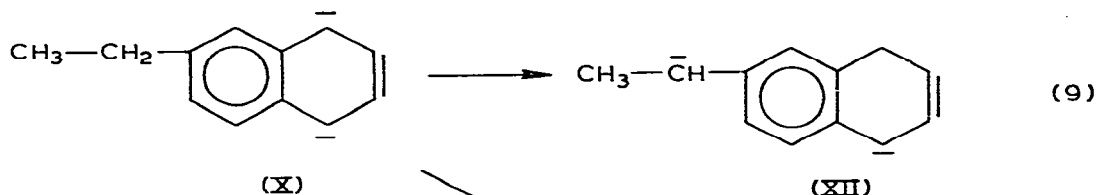


Fig. 2. β -ethylnaphthalene metalation by K in THF at room temperature. Visible and UV spectra after: A, 10 minutes — NRA spectrum; B, 10 hours — naphthalene dianion spectrum (O.D. shifted upwards by 0.4 unit); C, 50 hours — (O.D. shifted upwards by 0.25 unit); D, Compound corresponding to spectrum C, water deactivated, purified and again metalated by K (O.D. shifted upwards by 1 unit).

around 350 nm. These observations suggest that the EN dinegative species includes a DHNA anion as well as a second, probably extra-cyclic, carbanion which can slightly modify the UV absorption of the former. To explain this participation of the ethyl group to the EN dianionic species, an intramolecular hydrogen transfer can be invoked (eqs. 9–12).



The naphthalene-type dianion which is first formed during the metalation of EN (Fig. 2, B) can be represented by the forms X and XI depending on the presence of the ethyl group on the aromatic (X) or the dihydronaphthalene (XI) ring. The isomerized EN dianions (XII–XVI and Fig. 2, C) were hydrolyzed and the resulting products studied by ^1H NMR. The resonances of the methyl and the alicyclic methylene groups are observed at 0.8 (triplet) and 2.2 ppm (quadruplet), respectively, which proves the existence of the form XI and favors species XV and XVI. This conclusion is in accord with the observations of Watanabe [6] and Rembaum [15]: the alkylation of the radical-anion or the anion derived from monosubstituted naphthalene takes exclusively place on the dihydronaphthalene nucleus. From the results of titration, UV and NMR measurements, the following mechanism can be proposed for EN metalation (eq. 13).

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