FORMATION OF ANIONIC INTERMEDIATES
IN THE REDUCTION AND ALKYLATION OF ANTHRACENE AND
ITS DERIVATIVES BY SODIUM BIS(2-METHOXYETHOXY)ALUMINUM
HYDRIDE*

J.MÁLEK, M.ČERNÝ and R.ŘEŘICHA

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

Anthracene is reduced by sodium bis(2-methoxyethoxy)aluminum hydride in solutions of benzenoid hydrocarbons under the formation of radical-anion, dianion, and monoanion of 9-hydroanthracene. The existence of these species was confirmed by their electronic spectra. The main product of thermally induced alkylation reaction of the 9-hydroanthracene monoanion by the hydride at 140—160°C was 9,9,10,10-tetramethyl-9,10-dihydroanthracene, accompanied by spiro[cyclopropane-1,9'-9',10'-dihydroanthracene] and spiro[cyclopropane-1,9'-10'methyl-9',10'-dihydroanthracene]. These products were also formed by the alkylation of 9,10-dihydroanthracene and by the hydrogenolytic alkylation of anthraquinone with the hydride.

A general method of reduction of anthracene is the interaction of the hydrocarbon with alkali metal solutions in liquid ammonia[1]. Anionic intermediate products formed in the course of the reaction give by protonation 9,10-dihydroanthracene or by alkylation[2-5], which proceeds exclusively in the *meso*-position, mono-, di-, tri-[6,7], or tetraalkyl-substituted 9,10-dihydroanthracenes[8]. 9,10-Dihydroanthracene can also be obtained[9] (32%) by reduction of anthracene with lithium aluminum hydride at 220—230°C. In solutions of this hydride in tetrahydrofuran-methyltetrahydrofuran or in solutions of sodium borohydride in hexamethylphosphoric triamide anthracene and other condensed aromatic hydrocarbons undergo photoreduction to corresponding radical-anions, as confirmed by their electronic absorption and EPR spectra[10]. Anthracene anions are also formed by pulse radiolysis of solutions of anthracene and lithium aluminum hydride in tetrahydrofuran[11]. The reaction of anthraquinone with complex metal hydrides produces a variety of products, depending on the hydride used. While the reduction with sodium borohydride[12] or with diphenylsilane[13,14] leads to anthracene, the product of the reaction of anthraquinone with the complex of sodium borohydride with boron trifluoride, aluminum trichloride, or titanium tetrachloride, is a mixture of anthracene, 9,10-dihydroanthracene, and 10,10'-bianthronyl[12]; in the presence of peroxides anthraquinone reacts with sodium borohydride to give anthracene and 9,10-anthradiol[15]. This diol is also formed by the action of sodium trimethoxyborohydride[15] or of lithium aluminum hydride[16]. However, under different conditions anthraquinone is reduced by lithium aluminum hydride to 9,10-dihydroanthracene-9,10-diol[17,18], which was isolated as *cis*- and *trans*-conformers[18], or to a mixture of this diol and 9,10-anthra-

diol[19,20]; a mixture of both diols arises also in the reaction of anthraquinone with lithium trimethoxyaluminum hydride[19]. On the other hand, the reaction with aluminum hydride[19] or with lithium tri-tert-butoxyaluminum hydride[19,21] gives 9,10-dihydroanthracene-9,10-diol as a sole product.

In previous papers of this Series we reported on reactions of aromatic alkyl ketones and diaryl ketones with sodium bis(2-methoxyethoxy)aluminum hydride, which in dependence on the ketone structure led at a temperature above 100°C to arylalkanes[22,23], diarylalkanes[23], or to diarylalkylalkanes and cyclopropyl derivatives[22,24]. The aim of the present communication was to clarify which of the abovementioned reactions proceeds preferentially in anthracene series and to summarise results obtained in the study of reduction-alkylation reactions of anthracene, 9,10--dihydroanthracene, and anthraquinone with sodium bis(2-methoxyethoxy)aluminum hydride at elevated temperatures.

EXPERIMENTAL

Compounds used. Sodium bis(2-methoxyethoxy)aluminum hydride paste was prepared by evaporating 70% benzene solution of the hydride (supplied by the Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences, Prague - Řež) at 10—15 Torr (a 50—70°C bath temperature). Solutions of the hydride in higher boiling hydrocarbons were obtained by dissolving hot paste--like distillation residue in the appropriate amount of n-propylbenzene or o-xylene. o-Xylene (purum, Lachema, Brno) and n-propylbenzene (puriss., Fluka, Basel) were distilled in the presence of a small amount of the hydride prior use. Anthracene (analytically pure, Research Institute of Organic Syntheses, Pardubice - Rybitví) was recrystallised from absolute ethanol to give product melting at 215·0—216·5°C (ref.[25] m.p. 216·2—216·4°C); 9,10-dihydroanthracene was prepared by reduction of anthracene[26] and melted at 106—107°C (ref.[26] m.p. 108—109°C); anthraquinone (analytically pure, Research Institute of Organic Syntheses, Pardubice - Rybitví) was used without further purification (m.p. 285—286°C (subl.); ref.[27] m.p. 286°C (subl.)).

Analysis. Running and final compositions of reaction mixtures from hydrogenolytic alkylation of anthraquinone and from alkylation of 9,10-dihydroanthracene were determined (after decomposition of the mixture) on a Chrom III chromatograph equipped with flame-ionization detector (a column 4 m × 3 mm filled with AK 30 000, column temperature 145°C, nitrogen as a carrier gas). Reaction mixture from the reductive alkylation of anthracene was analysed on a 2 m × 3 mm column filled with 3% SE 30 silicone elastomer + 3% Apiezon L (10 : 4) on Chromaton N-AW-HMDS at 190°C (250°C in the evaporator). Preparative gas chromatography was performed on an instrument produced by Vývojové dílny, Czechoslovak Academy of Science, Prague, which was equipped with thermal-conductivity detector (a column 6 m × 8 mm filled with AK 30 000 as a stationary phase, column temperature 190°C, hydrogen as a carrier gas). The products of reductive alkylation of anthracene, alkylation of 9,10-dihydroanthracene, and of hydrogenolytic alkylation of anthraquinone were analysed on Pye 104 chromatograph equipped with flame-ionisation detector [a column 4 m × 3 mm filled with 3% SE 30 silicone elastomer on Diatomite Gas-Chrom Q (100—120 mesh), column temperature 115°C programmed with a temperature increase of 2°C/min, helium as a carrier gas] and combined with an AEI, model MS 902, mass spectrometer. The ^{1}H NMR spectrum of 9,9,10,10-tetramethyl-9,10-dihydroanthracene (*I*) was taken on a Varian A-100 spectrometer, and that of 9-ethyl-9,10-dimethyl--9,10-dihydroanthracene (*VII*) on a Tesla BS 477 instrument (modified model — 60 MHz).

IR spectra of isolated products were recorded with Zeiss (Jena) spectrometer, model UR-20, and mass spectra with MCH-1 303 instrument. Electronic absorption spectra (250—1 000 nm) were recorded with a double-beam prism Beckman spectrophotometer, model DK-2A. Wave length scale of the instrument was calibrated against holmium oxide or didym glass standards. Positions of absorption maxima were read with the accuracy of ± 2 nm. The spectra of undiluted solutions of anthracene containing the hydride were measured in Quartz-Suprasil cells 1 or 2 mm thick (with Teflon stopper) with respect to the pure solvent (absorption edge of benzene 285 nm and of o-xylene 300 nm). The cells were filled with samples in a dry box flushed with dry nitrogen; permanent damage of the cells on exposure to 70% benzene solution of the hydride was not observed (an eventual white coating of internal walls of the cells, formed during washing, was easily removed by dilute hydrochloric acid). Spectral measurements were made of 70% benzene solution of the hydride, 30% solution of the hydride in o-xylene, the blue solution prepared by mixing 30% hydride solution in o-xylene with anthracene (initial concentration 1—5 . . 10^{-4}M) and by stirring this solution for 1 h at ambient temperature, the green solution obtained by heating shortly the blue solution to about 80°C and diluting it with cold o-xylene (1 : 1 vol. ratio), the orange solution prepared by allowing hot (80°C) blue solution to stand overnight or by heating the blue solution at 80°C for several hours, followed in both cases by dilution of the solutions with o-xylene (1 : 1 vol. ratio), and of the orange solution obtained by dissolving 9,10-dihydroanthracene in 30% solution of the hydride in o-xylene (initial 9,10-dihydroanthracene concentration 1—5 . 10^{-4}M), followed by standing the solution at ambient temperature for about 20 h. The presence of anthracene in the mentioned solutions observed even with the above-mentioned excess of the hydride, along with the absorption edge of anthracene at about 380 nm, caused that the region below 380 nm was not accessible to measurements. Melting points were determined with a Kofler hot stage microscope and are uncorrected.

Alkylation of 9,10-dihydroanthracene. A solution of 3·6 g (0·02 mol) of 9,10-dihydroanthracene in 39 g of n-propylbenzene was added under nitrogen to 21·0 g (0·104 mol) of sodium bis(2-methoxyethoxy)aluminum hydride and the mixture was brought to boiling under a reflux condenser. Before reaction temperature had raised to 162°C, strongly exothermic reaction occurred, accompanied by evolution of great amount of hydrogen, and the solution turned red. After heating the solution at 162°C for 6 h, the concentration of 9,10-dihydroanthracene decreased to 2%. Gas chromatographic analysis of the reaction mixture revealed that it contains, besides 61% of the main product identified by means of an authentic sample as 9,9,10,10-tetramethyl-9,10-dihydroanthracene (*I*), 17% of product *A* and 11% of product *B*. On decomposition of cooled reaction mixture with 20% sulphuric acid, 570 ml of hydrogen evolved, *i.e.* 11 per cent based on the initial amount of the hydride. The propylbenzene layer was combined with ether extracts of the aqueous layer, washed successively with aqueous sodium hydrogen carbonate solution and water, and dried over sodium sulphate. After solvent removal the distillation residue (4·7 g) solidified, and its crystallisation from ethanol gave 1·3 g of crude product; this was recrystallised from ethanol to give 1·2 g (26%) of white crystals of substance *I*, m.p. 168—169°C (ref.[6] m.p. 167—168·5°C, corrected; ref.[28] m.p. 168°C). Mixed melting point with authentic sample was 168—169°C. Mass spectrum: M^+ 236, base peak at m/e 221 and peaks at m/e 206, 191, 178, 165, 103, and 89; NMR spectrum [in CDCl$_3$, with respect to (CH$_3$)$_4$Si: τ 2·75, multiplet, 4 H, β-aryl; τ 2·50, multiplet, 4 H, α-aryl; τ 8·33, singlet, 12 H, methyl (ref.[6] NMR spectrum: τ 8·32, 2·75, and 2·50)]. For C$_{18}$H$_{20}$ (236·3) calcld.: 91·47% C, 8·53% H; found: 91·54% C, 8·49% H. Mother liquor from crystallisation of tetramethyl derivative *I* was freed of the solvent and the residue (3·1 g) was distilled to give 2·1 g of a fraction of b.p. 105—106°C/0·1—0·5 Torr which solidified on cooling. Crystallisation from ethanol yielded 0·1 g of white crystals of substance *I* (over-all yield 28%). Mother liquor was freed of ethanol and the residue was distilled to give a fraction boiling at 88—89°C/0·2 Torr which was separated by preparative gas chromato-

graphy; the lower boiling fraction obtained was identical with product A and the higher boiling one with product B; products A and B were injected separately to the gas chromatograph combined with mass spectrometer. Product A contained 3 substances in the weight ratio $6:3:1$, which on the basis of their mass spectra were assigned the structures of spiro[cyclopropane-1,9′−9′,10′-dihydronathracene] (II) (10%) (M^+ 206, base peak at m/e 178 and peaks at m/e 152, 89, 76), spiro[cyclopropane-1,9′-10′-methyl-9′,10′-dihydroanthracene] (III) (5%) (M^+ 220, base peak at m/e 192 and peaks at m/e 205, 204, 203, 202, 178, 165, 97, 96, 95, and 94), and of 9-ethyl-9-methyl-9,10-dihydroanthracene or 9-ethyl-10-methyl-9,10-dihydroanthracene (2%) (M^+ 222, base peak at m/e 207 and peaks at m/e 192, 178, 152, 89, 76). Product B consisted of single compound having m.p. $81−82°C$ (white crystals); this compound was found by mass spectrometry (M^+ 236, base peak at m/e 192 and peaks at m/e 221, 220, 206, 191, 189, 178, and 165), NMR spectroscopy [in CCl_4 with respect to $(CH_3)_6Si_2O$: τ $2·82−3·18$, multiplet, 8 H, aryl protons; τ $5·86$, multiplet, 1 H, benzylic proton; τ $8·15$ singlet, 6 H, methyl protons; τ $8·44$, unsymmetrical multiplet, 5 H, ethyl protons], and by IR spectroscopy (CCl_4: single band at $1\ 379\ cm^{-1}$ which indicates that the two methyl groups are not geminal[29]) to be 9-ethyl-9,10-dimethyl-9,10-dihydroanthracene (VII). Gas chromatographic analysis of the reaction mixture from alkylation of 9,10-dihydroanthracene revealed that the mixture contains also sec-butylbenzene[22] whose peak appears on the chromatogram after 30 min of the reaction.

Hydrogenolytic alkylation of anthraquinone. A solution of $4·08$ g ($0·02$ mol) of anthraquinone in 69 g of n-propylbenzene was added to 37 g ($0·183$ mol) of sodium bis(2-methoxyethoxy)-aluminium hydride, and the mixture was refluxed under nitrogen. During heating the reaction mixture to $162°C$ an exothermic reaction occurred which was accompanied with evolution of hydrogen and the mixture turned first dark green and then brown-red. According to gas chromatographic analysis the reaction mixture contained already after 30 min 67% of 9,10-dihydroanthracene and its concentration decreased after 7 h-heating at $162°C$ to 5 per cent. At this time the reaction was stopped; the main product, formed in 64% yield, was identified as tetramethyl derivative I (by g.l.c. and by comparing retention times with an authentic sample). On decomposition of the reaction mixture with 20% sulphuric acid, $2\ 335$ ml of hydrogen evolved, which corresponded to 26 percent of the initial amount of the hydride. The reaction mixture was worked-up similarly as in alkylation of 9,10-dihydroanthracene and the solid distillation residue, obtained by evaporating the solvent, was crystallised from absolute ethanol; repeated crystallisation of the crude product ($1·45$ g) from the same solvent gave $1·25$ g (27%) of white crystals of I, m.p. $168−169°C$, which did not show mixed melting point depression with an authentic sample of this compound. The mass and NMR spectra of the product were identical with the spectra of the tetramethyl derivative I prepared by alkylation of 9,10-dihydroanthracene. Evaporation of the mother liquor from crystallisation of tetramethyl derivative I at $0·1$ Torr (bath temperature $200°C$) gave $2·6$ g of a fraction which solidified on standing; its crystallisation from absolute ethanol yielded an additional amount of I. According to mass spectra (see alkylation of 9,10-dihydroanthracene) the condensed ethanolic mother liquor contained hydrocarbons II, III and VII, and a substance which can be assigned the structure of either 9-ethyl-9-methyl-9,10-dihydroanthracene, or 9-ethyl-10-methyl-9,10-dihydroanthracene; according to gas chromatographic analysis, all products were present in amounts practically equal to those obtained in alkylation of 9,10-dihydroanthracene. By gas chromatographic analysis of the reaction mixture after 90 min of the reaction it was found that the mixture contains about 1% of sec-butylbenzene, whose concentration at the end of the reaction increased to 3%.

Reductive alkylation of anthracene. A solution of $56·7$ g ($0·28$ mol) of sodium bis(2-methoxy-ethoxy)aluminium hydride in 72 g of o-xylene was mixed under nitrogen with $7·13$ g ($0·04$ mol)

of anthracene, while stirring. The intense blue reaction mixture turned gradually green, and already before the boiling point had been reached, an exothermic reaction with evolution of hydrogen occurred and the solution so obtained turned red. After 16 h-heating at 140°C, the concentration of anthracene decreased to 3%. After 22 h-heating, the reaction mixture did not contain anthracene, and the content of 9,10-dihydroanthracene decreased to 3·5%. After 31 h-heating, when the reaction mixture contained 0·3% of this intermediate product, the reaction was stopped and the sample of the reaction mixture was analysed by gas chromatography combined with mass spectrometry. According to mass spectra, individual products, given in the order of their increasing retention times, were identified as 9,10-dihydroanthracene (0·3%) (the identity verified by injection of an authentic sample), compound *II* (14%) (M^+ 206, base peak at m/e 178), compound *I* (58%) (the identity verified by injection of an authentic sample) (M^+ 236, base peak at m/e 221 and another ion at m/e 206), 9-ethyl-9,10,10-trimethyl-9,10-dihydroanthracene (*V*) (2%) (M^+ 250, base peak at m/e 221 and other ions at m/e 206 and 235), compound *III* (12%) (M^+ 220, base peak at m/e 192, and another ion at m/e 205), spiro[cyclopropane-1,9′-10′,10′-dimethyl-9′,10′-dihydroanthracene] (*IV*) (9%) (M^+ 234, base peak at m/e 206 and other ions at m/e 192 and 216), and spiro[cyclopropane-1,9′-10′-ethyl-10′-methyl-9′,10′-dihydroanthracene] (*VI*) (1%) (M^+ 248, base peak at m/e 220 and another ion at m/e 205). The above yields are the average of three experiments. The reaction was accompanied by formation of fine aluminum powder; the aluminum was separated by filtration of hot reaction mixture under nitrogen, and the tetramethyl derivative *I* was isolated by the above described procedure in 30% yield.

RESULTS AND DISCUSSION

Hydrogenolytic alkylation of anthraquinone, alkylation of 9,10-dihydroanthracene, as well as reductive alkylation of anthracene by sodium bis(2-methoxyethoxy)aluminum hydride proceeded at 140−160°C in solutions of aromatic hydrocarbons in a homogeneous phase, and in the presence of the hydride in excess with practically quantitative conversion of starting compounds to derivatives of 9,10-dihydroanthracene alkylated exclusively in *meso*-position. All reactions produced 9,9,10,10-tetramethyl-9,10-dihydroanthracene (*I*) (58−64%) as the main product, which was

Scheme 1

I   *II*   *III*
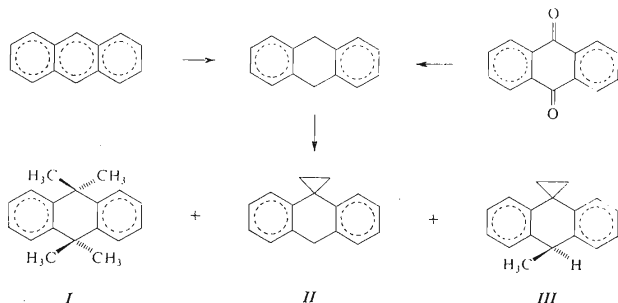
identical with that obtained by Harvey and coworkers on reductive methylation of dilithio-adduct of 9,10-dimethylanthracene in liquid ammonia by methyl bromide[6]; by the one-step reaction of anthraquinone, anthracene, or its 9,10-dihydroderivative with the hydride and by simple isolation of this compound even from a complex reaction mixture, a new alternative route for preparing the hydrocarbon (*I*) is thus offered to the Harvey's procedure and analogous multistep syntheses[8,30]. Tetramethyl derivative *I* was in reduction-alkylation reactions with the hydride always accompanied by spiro[cyclopropane-1,9'-9',10'-dihydroanthracene] (*II*) (10–14%) and spiro[cyclopropane-1,9'-10'-methyl-9',10'-dihydroanthracene] (*III*) (5–12%) as side products (Scheme 1). Yields of hydrocarbons *II* and *III* were always higher at a lower temperature (140°C). The structure of other minor products mentioned below depended on the reaction temperature. Another product of the reaction at 140°C was spiro[cyclopropane-1,9'-10',10'-dimethyl-9'-,10'-dihydroanthracene] (*IV*) (9%), 9-ethyl-9,10,10-trimethyl-9,10-dihydroanthracene (*V*) (2%), and spiro[cyclopropane-1,9'-10'-ethyl-10'-methyl-9',10'-dihydroanthracene] (*VI*) (1%). From the reaction mixture obtained by reductive alkylation at 160°C 9-ethyl-9,10-dimethyl-9,10-dihydroanthracene (*VII*) (11%) of unknown configuration was isolated; in this case the formation of hydrocarbons *IV*, *V*, and *VI* was not confirmed. In none of reduction-alkylation reactions di-spirocyclopropyl derivatives of 9,10-dihydroanthracene were detected. The over-all yield of monospirocyclopropane hydrocarbons (36%) *II*, *III*, *IV*, and *VI* is, however, three times as high as the yield of diarylcyclopropanes obtained in a similar reaction of diphenylmethane derivatives[22,24] and it increases with decreasing reaction temperature; the competitive formation of ethyl-substituted hydrocarbons (3%), presumably from a common organometallic intermediate[22], is under these conditions unimportant. The above reactions with the hydride in anthracene series differ in this respect from similar reactions of fluorene derivatives[22] which are characterised by the absence of the corresponding spirocyclopropyl derivatives. The fact that anthracene and 9,10-dihydroanthracene undergo reductive alkylation, or alkylation, with sodium bis(2-methoxyethoxy)aluminum hydride to give exclusively *meso*-substituted 9,10-dihydroanthracenes is in harmony with Streitwieser prediction of the positions of the highest electron density in these systems, based on MO calculations[31].

Anthracene is the first aromatic hydrocarbon, which by the reaction with the metal hydride, $NaAlH_2(OCH_2CH_2OCH_3)_2$, gave directly alkylated products. A characte-

IV   *V*   *VI*   *VII*
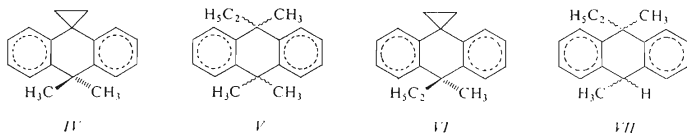
ristic feature of the reaction is the colour change of solutions of anthracene and the hydride in benzenoid hydrocarbons, which from blue turn gradually to green, orange, and in concentrated solutions to intense red, in dependence on temperature and the age of the mixture. These facts led us to a more detailed investigation of the reaction. In analogy with reductions of aromatic hydrocarbons by alkaline metals in tetrahydrofuran–ammonia systems, for which similar colour changes are typical[7], it could be expected that anionic intermediate products are also formed in the reaction of anthracene with sodium bis(2-methoxyethoxy)aluminum hydride. The existence and electronic spectra of anionic intermediates from aromatic hydrocarbons were already investigated in detail[32]. A solution of the hydride in o-xylene $(20-80°C)$ does not show absorption bands in the $250-1\,000$ nm region. The spectrum of an anthracene solution in these solvents shows under identical conditions only known absorption bands[33]. We have found that blue reaction mixtures are characterised by the absorption band with several more or less resolved shoulders and with maximum at 736 nm (Fig. 1). The shape of this band is identical with
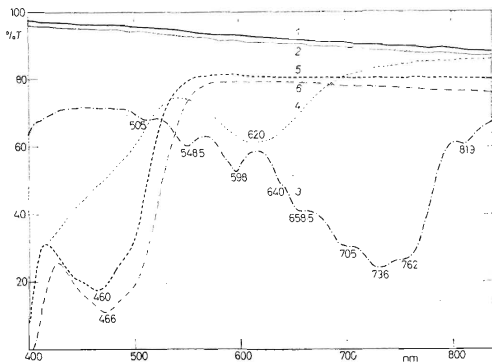

Fig. 1

Visible Spectra of Anionic Intermediates of the Reactions of Anthracene and 9,10-Dihydroanthracene with Sodium Bis(2-methoxyethoxy)aluminum Hydride in o-Xylene (0·1 cm cell)

1 100% transmission line of o-xylene, *2* 100% transmission line of 30% hydride solution in o-xylene, *3* blue solution of the anthracene radical-anion, *4* green solution of the anthracene dianion, *5* orange solution of the 9-hydroanthracene monoanion, *6* orange solution of the anion generated by the reaction of 9,10-dihydroanthracene with the hydride.

that of the reported spectrum of radical-anion of anthracene (*VIII*), prepared by interaction of sodium film with anthracene vapours in a high vacuum[34,35] (Table I). We have further found that unstable green reaction mixtures can be divided into two groups, in dependence on the pattern of the spectra. The first, uninteresting group comprises solutions in which both the blue radical-anion of anthracene with maximum at 736 nm, and the orange monoanion of 9-hydroanthracene with maximum at 430—470 nm are present; the green colouration observed is then the result of superposition of blue and orange colour. The second group involves the green solutions which exhibit single, symmetrical and broad band with maximum at 620 nm (Fig. 1). This band was by some authors[35,36] assigned to the dianion of anthracene (*IX*) (for sodium at 613·5 nm (ref.[35]); for potassium at 617 nm (ref.[36]). A similar band was observed by us in the spectrum of the green solutions prepared by diluting the blue, hot (80°) solution with cold *o*-xylene. The position of the band excludes the possibility that we deal here with an anion of the solvent, the band of which should have maximum at 675 nm (ref.[32]). Although the reason why anthracene dianion is formed on diluting blue solutions of the radical-anion is not yet clear, the presence of the dianion in the green solutions can be considered as confirmed. The spectra of the bright orange solutions prepared by heating the blue solutions at 80°C for several hours or by allowing hot (80°C) blue solutions to stand overnight, and diluting them with *o*-xylene, showed only single band at 460 nm with two unresolved shoulders (Fig. 1). The position of this bands was dependent on the solvent, the concentration of anthracene, the temperature and age of the solution (12 h up to several months), and probably also on different formation of ionic associates between aromatic anion and alkaline metal cation[36], and shifted within the 430 to 470 nm range. Brandes and Gerdes observed a broad band at 435—445 nm, which was assigned to monoanion *X*, formed by aging the dianion generated by interaction of potassium film with anthracene vapours in a high vacuum[36]. A similar change

TABLE I

Electronic Absorption Bands of Anthracene Radical-Anion Generated by Sodium Bis(2-methoxyethoxy)aluminum Hydride and by Metallic Sodium[35,38] and Potassium[39]

Reduction system[a]	Wavenumber, $10^3 \times cm^{-1}$									
NaAlH$_2$(OCH$_2$.CH$_2$OCH$_3$)$_2$ + A	19·8	18·2	16·8	15·6 (sh)	15·2	14·2	13·6[b]	13·1 (sh)	12·2	10·7[c]
Na + A[35]	—	18·2	16·7	—	15·1	—	14·0	12·6	11·2	—
Na + A[38]	19·5	18·3	16·8	—	15·1	—	13·9	—	—	—
K + A[39]	—	18·3	16·8	15·7	15·3	14·4	13·8	—	—	—

[a] A anthracene; [b] absorption band maximum; [c] very weak band, approximate value.

of the green to a yellow-orange colour on standing for 1 day was observed for the naphthalene monoanion which was generated by metallic sodium; however, the details and assignment of the band in the spectrum have bot been reported[35]. In order to define more accurately the anionic intermediate present in the above-mentioned orange solutions, we have prepared solutions of the authentic 9,10-dihydro-anthracene and the hydride in benzene and in o-xylene; the initial colourless solution turned orange by standing overnight or by heating it to 86°C. The spectrum was similar to that of the orange solutions prepared from anthracene and the hydride and showed a band at 430 nm in benzene or at 466 nm in o-xylene (Fig. 1). We consider these findings as evidence for the presence of the monoanion of 9-hydroanthracene[36] (X) in the orange solutions formed by reaction of anthracene with the hydride in o-xylene; the identical spectrum of the orange solution obtained by reaction of 9,10-dihydroanthracene with the hydride demonstrates that the anion present is identical with the anion intermediate X. From these results, reported data on electronic spectra of anionic intermediates[32−39], and in analogy to conclusions about the mechanism of reductions of aromatic hydrocarbons by alkaline metals in an ammonia–tetrahydrofuran system arrived at by Harvey[7], we believe that the reduction of anthracene with sodium bis(2-methoxyethoxy)aluminium hydride and the interaction of the hydride with 9,10-dihydroanthracene can be described by Scheme 2.

The monoanion X formed then undergoes on the action of the hydride the above alkylation, followed by formation of the monoanion of the corresponding alkyl derivative, analogously to Scheme 2; the whole process is then repeated until final reaction products are formed.

It is remarkable that in the spectrum of the orange solution prepared by interaction of 9,10-dihydroanthracene with the hydride in o-xylene, which originally showed only single band at 466 nm, a band at 736 nm appeared after the solution had been allowed to stand for 12 h. This partial conversion of anion X to radical-anion VIII, for which an unambiguous explanation cannot at present be offered,
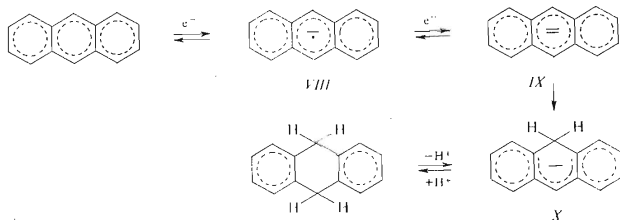
SCHEME 2

speaks for the reversibility of the whole system $VIII - X$. Regardless of this circumstance monoanion X, when compared to dianion IX and to corresponding radical-anion $VIII$ (or their ionic associates), exhibits highest stability. The formation of the common anion X in the reaction of the hydride with both anthracene and 9,10-di-hydroanthracene is also in accordance with formation of identical products $I - III$ on the action of the hydride at elevated temperatures *via* alkylation and cycloalkylation reactions. The mechanism of these reactions will be discussed in a subsequent paper.

REFERENCES

1. Harvey R. G., Arzadon L., Grant J., Urberg K.: J. Am. Chem. Soc. *91*, 4535 (1969).
2. Southern P. F., Waters W. A.: J. Chem. Soc. *1960*, 4340.
3. Harvey R. G.: J. Org. Chem. *32*, 238 (1967).
4. Harvey R. G., Urberg K.: J. Org. Chem. *33*, 2206 (1968).
5. Harvey R. G., Urberg K.: J. Org. Chem. *33*, 2570 (1968).
6. Harvey R. G., Arzadon L.: Tetrahedron *25*, 4887 (1969).
7. Lindow D. F., Cortez C. N., Harvey R. G.: J. Am. Chem. Soc. *94*, 5406 (1972).
8. Michajlov B. M., Blochina A. N.: Izv. Akad. Nauk SSSR, Ser. Chim. *1949*, 164.
9. Goodman I.: J. Chem. Soc. *1951*, 846.
10. Paskovich D. H., Reddoch A. H., Williams A. H.: J. Chem. Soc. Chem. Commun. *1972*, 1195.
11. Baxendale J. H., Beaumond D., Rodgers M. A. J.: Trans. Faraday Soc. *66*, 1996 (1970).
12. Sanchorawala C. J., Subba Rao B. C., Unni M. K., Venkataraman K.: Indian J. Chem. *1*, 19 (1963).
13. Gilman H., Diehl J.: J. Org. Chem. *26*, 4817 (1961).
14. Diehl J. W., Gilman H.: Chem. Ind. (London) *1959*, 1095.
15. Panson G. S., Weill C. E.: J. Org. Chem. *22*, 120 (1957).
16. Nystrom R. F., Brown W. G.: J. Am. Chem. Soc. *70*, 3738 (1948).
17. Boyland E., Manson D.: J. Chem. Soc. *1951*, 1837.
18. Dufraisse Ch., Rio G., Lepage Y.: Compt. Rend. *247*, 1928 (1958).
19. Brown H. C., Yoon N. M.: J. Am. Chem. Soc. *88*, 1464 (1966).
20. Brown H. C., Weissman P. M., Yoon N. M.: J. Am. Chem. Soc. *88*, 1458 (1966).
21. Brown H. C., Weissman P. M.: Israel J. Chem. *1*, 430 (1963).
22. Černý M., Málek J.: This Journal, *39*, 842 (1974).
23. Málek J., Černý M.: Synthesis *1973*, 53.
24. Černý M., Málek J.: Tetrahedron Letters *1972*, 691.
25. *Handbook of Chemistry and Physics* (D. Hodgman, Ed.), p. C 121. Chemical Rubber Publishing Co., Cleveland 1968.
26. Bass K. C.: *Organic Syntheses* 42, p. 48. Wiley, New York 1962.
27. Ref. 25, p. C 123.
28. Ipatieff V. N., Appell H. R., Pines H.: J. Am. Chem. Soc. *73*, 5507 (1951).

29. Nakanishi K.: *Practical Infrared Absorption Spectroscopy*, p. 20. Holden-Day, San Francisco 1962.
30. Michajlov B. M., Kozminskaja T. K.: Dokl. Akad. Nauk SSSR, *58*, 811 (1947).
31. Streitwieser A. jr: *Molecular Orbital Theory for Organic Chemists*, p. 425. Wiley, New York 1961.
32. Rao C. N. R., Kalyanaraman V., George M. V.: Appl. Spectry. Rev. *3*, 153 (1970).
33. *Documentation of Molecular Spectroscopy*: UV *Atlas of Organic Compounds*, Spectrum E2/1. Butherworths, London 1966.
34. Paul D. E., Lipkin D., Weissman S. I.: J. Am. Chem. Soc. *78*, 116 (1956).
35. Balk P., Hoijtink G. J., Schreurs J. W. H.: Rec. Trav. Chim. *76*, 813 (1957).
36. Brandes K. K., Gerdes R. J.: J. Phys. Chem. *71*, 508 (1967).
37. Buschow K. H. J., Dieleman J., Hoijting G. J.: J. Chem. Phys. *42*, 1993 (1965).
38. Evans A. G., Tabner B. J.: J. Chem. Soc. *1963*, 5560.
39. de Boer E., Weissman S. I.: Rec. Trav. Chim. *76*, 824 (1957).

Translated by J. Hetflejš.