

## REDUCTION OF METHYLATED ANTHRAQUINONES TO METHYLATED ANTHRACENES WITH ALUMINIUM TRI(CYCLOHEXYL OXIDE)

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The effect of reaction conditions has been examined in the aluminium tri(cyclohexyloxyde) reductions of 1,3- and 2,3-dimethyl-9,10-anthraquinone to 1,3- and 2,3-dimethylantracene. With the use of the same reagent, the following compounds have been also prepared; 1- and 2-methyl-, 1,2-, 1,4-, 2,6-, and 2,7-dimethyl-, 2,3,6-trimethyl-, and 2,3,6,7-tetramethylantracene. A mechanism of the aluminium tri(cyclohexyl oxide) reduction of anthraquinones has been proposed. The IR spectra of solid samples of 1-methyl-, 1,2-, 1,3-, and 1,4-dimethylantracenes have been measured and some absorption bands of characteristic vibrations have been interpreted.

In spite of the existence of numerous methods<sup>1</sup> for the reduction of quinones to the corresponding aromatic hydrocarbons, still further procedures would be desirable that would make possible to reduce quinones under less severe reaction conditions. Numerous quinones have been successfully reduced with aluminium tri(cyclohexyl oxide), *e.g.*, 9,10-anthraquinone<sup>2</sup>, 6,11-naphthacenedione and 1,2,3,4-tetrahydro-6,11-naphthacenedione<sup>3</sup>, 6,13-pentacenedione<sup>4-6</sup>, 5,8,13,14-pentaphenetrone<sup>7,8</sup>, and benzo[*rst*]pentaphene-5,8-dione<sup>8</sup>.

In the present paper, the effect of reaction conditions on the yield of the aluminium tri(cyclohexyl oxide) reduction of selected anthraquinones to the corresponding hydrocarbons has been examined with the aim to find optimum conditions of this reduction and to verify these conditions in reductions of some further methylated 9,10-anthraquinones. The IR spectra of those anthracenes that have not been mentioned in the earlier paper<sup>9</sup> have been measured.

The effect of the reaction time, the catalytic concentration of tetrachloromethane, and the amount of 1,3- or 2,3-dimethyl-9,10-anthraquinone to be reduced on the yield of the corresponding anthracenes may be seen from Table I. In analogous investigations on conditions of the reduction of 6,13-pentacenedione to pentacene performed by Bruckner and coworkers<sup>6</sup>, the yield was highly influenced by the reaction time and the amount of tetrachloromethane added. In contrast to these results the influence of the reaction time on the reduction of 9,10-anthraquinones is less

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pronounced, but an optimum may be observed after elapse of two hours. The presence of tetrachloromethane in the reduction mixture leads to the formation of compounds of the  $\text{ClAl(OR)}_2$  type which are in the Meerwein type reductions more active<sup>10</sup> than the alkoxides. In our case, however, the amount of tetrachloromethane is almost without any influence on the yield; nevertheless, the yield is somewhat lowered in the absence of tetrachloromethane, particularly when the concentration of mercuric chloride is decreased at the same time.

Higher concentrations of the anthraquinones lead to higher yields of the anthracenes up to the optimum molar ratio aluminium/quinone 7.5; a further increase of the anthraquinone concentration results in a lower yield and contamination with the unreacted quinone. At the molar ratio aluminium/quinone 2.5 (corresponding to the highest quinone concentration given in Table I), only a partial reduction is observed. For comparison, the following optimum molar ratios aluminium/quinone for reductions of some other quinones were calculated from the literature data: 12.5 (5,8,13,14-pentaphenetetrone<sup>7</sup>); 11.5 (6,13-pentacenedione<sup>6</sup>); and 4.0 (9,10-anthraquinone<sup>2</sup>). The present reduction obviously represents an equilibrium-controlled reaction in which the equilibrium is shifted in favour of the product by an excess of the reducing agent.

The course of the reduction is also considerably influenced by the temperature. Thus, in the aluminium tri(cyclohexyl oxide) reduction of 6,13-pentacenedione no pentacene was formed at 100°C/24 h while at the boiling point of cyclohexanol, pentacene was obtained without any difficulty<sup>6</sup>. In the aluminium triisopropoxide reduction of the unsubstituted 9,10-anthraquinone, 9,10-dihydro-9,10-dihydroxyanthracene<sup>2</sup> was obtained at the boiling point of isopropyl alcohol at ordinary pressure while anthracene resulted in a high yield at 250°C and elevated pressure<sup>11</sup>. The effect of temperature has not been examined in the present work and all reductions have been performed at the boiling point of cyclohexanol.

The various effects observed in reductions of 1,3- and 2,3-dimethyl-9,10-anthraquinone (Table I) were used to select the optimum conditions for reductions of some other methylated 9,10-anthraquinones. The results are shown in Table II. When compared with other methods, the present route does not afford higher yields. Somewhat lower yields of monomethylanthracenes and dimethylanthracenes substituted at position 1 might be ascribed to a higher solubility of these anthracene derivatives in methanol which is used in the purification process. Owing to the loss of material during the crystallization, an about fourfold amount of the starting quinones was used in the preparation of 1-substituted anthracenes than stated in Table II (the proportion of other reactants and reaction conditions remained without any change). The success of the purification process was also somewhat dependent on the purity of the starting anthraquinones. The present method appears somewhat more advantageous than the earlier reduction methods but still it can not be regarded as general because of its failure in the attempted preparation of chloroanthracenes substituted at position 1 or of nitroanthracenes<sup>2</sup>.

In the mechanism of the present reduction which is of the Meerwein-Ponndorf-Verley type, the principal role is probably played by the cyclohexyl oxide anion. From this anion, the hydride ion is intermolecularly transferred<sup>19</sup> to the positively charged oxygen of the quinone structure, activated by the formation of a bond between the second quinone oxygen and the alkoxide aluminium atom (Scheme 1). The complex aluminium alkoxide anion *A* can be stabilized by removal of the cyclohexyl oxide anion under the formation of the half-alkoxide *B*. This idea seems to be supported by the aluminium tri(cyclohexyl oxide) reduction of 9,10-dihydroxyanthracene<sup>2</sup> to anthracene. In the first stage of this reduction there is formed the symmetrical alkoxide<sup>2</sup> *C* which may also result from the alkoxide *B*. In the next stage, although we cannot exclude an intermolecular transfer of hydride ions from cyclohexyl oxide anions present in the alkaline medium of the reaction mixture to C<sub>(9)</sub> and C<sub>(10)</sub> carbon atoms of the alkoxide *C*, it is more probable that an intramolecular transfer of hydride ions takes place in this alkoxide by a cyclic mechanism as proposed by Hoffsommer and coworkers<sup>11</sup> (Scheme 2).

TABLE I

Influence of Conditions in Reductions of 1,3- and 2,3-Dimethyl-9,10-anthraquinones on the Yield<sup>a</sup> of 1,3- and 2,3-Dimethylanthracenes (in each reduction, there was used 500 mg of Al, 12.5 mg of HgCl<sub>2</sub>, and 10 ml of cyclohexanol)

Time effect; 0.25 ml of CCl <sub>4</sub> , 570 mg of the quinone							
Time (hours)		1/2	1	2	4	8	16
1,3-Dimethylanthracene	%,	73.5	74.5	75.5	63.0	61.5	—
2,3-Dimethylanthracene	%,	74.5	77.5	79.5	78.5	78.5	75.5
CCl <sub>4</sub> concentration effect; 2 hours, 570 mg of the quinone							
CCl <sub>4</sub> (ml)		0	0.125	0.25	0.375	0.50	
1,3-Dimethylanthracene	%,	—	69.5	75.5	—	74.5	
2,3-Dimethylanthracene	%,	66.0 <sup>b</sup>	74.0	79.5	77.0	77.5	
Quinone concentration effect; 2 hours, 0.25 ml of CCl <sub>4</sub>							
Quinone (mg)		380	570	1 135		1 700	
Molar ratio Al/quinone		11.5	7.5	3.9		2.5	
1,3-Dimethylanthracene	%,	—	75.5	67.0		65.0 <sup>c</sup>	
2,3-Dimethylanthracene	%,	78.5	79.5	73.5		74.0 <sup>c</sup>	

<sup>a</sup> The yields refer to dry noncrystallized 1,3- and 2,3-dimethylanthracenes; <sup>b</sup> with the use of 4 mg of HgCl<sub>2</sub>, the yield was 64%; <sup>c</sup> as indicated by IR spectra and the yellow colour, the product contained some unreacted quinone.

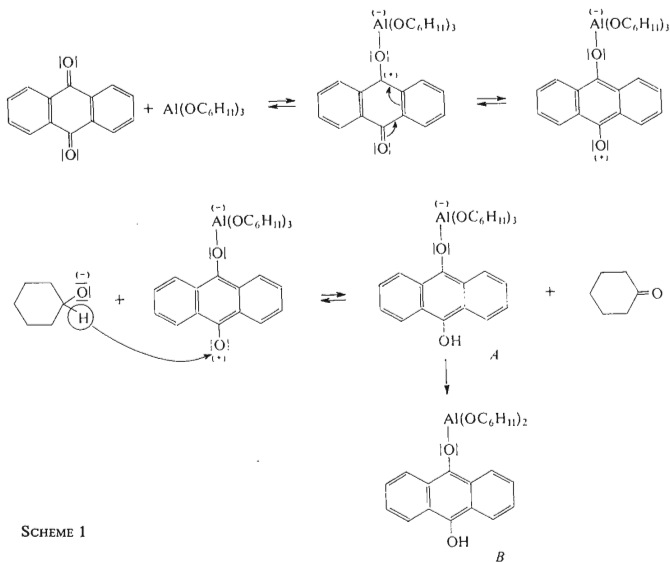


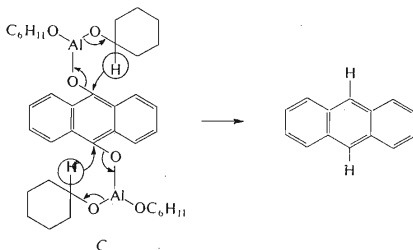
TABLE II

Reduction of Methylated 9,10-Anthraquinones to Anthracenes

Conditions: 500 mg of Al, 12.5 mg of  $\text{HgCl}_2$ , 10 ml of cyclohexanol, 0.25 ml of  $\text{CCl}_4$ , 2.75 mmol of the quinone, 2 h.

Positions of methyl groups	Yield	M.p., °C/solvent	M.p. °C (ref.)
1-	42.0	86/ $\text{CH}_3\text{COOH}$	86 (12)
2-	54.0	207/ $\text{C}_2\text{H}_5\text{OH}$	207 (13)
1,2-	42.5	86/ $\text{CH}_3\text{COOH}$	86 (14)
1,3-	53.0	82/ $\text{CH}_3\text{COOH}$	83 (12)
1,4-	51.5	75/ $\text{CH}_3\text{OH}$	74 (12)
2,3-	67.0	253/ $\text{C}_6\text{H}_6$	252 (15)
2,6-	70.0	248/ $\text{C}_6\text{H}_6$	250 (16)
2,7-	68.5	241/ $\text{C}_6\text{H}_6$	241 (16)
2,3,6-	75.0	253/ $\text{C}_6\text{H}_6$	255 (17)
2,3,6,7-	74.0	301/ $\text{C}_6\text{H}_6$	301 (18)

The wavenumbers of absorption bands in IR spectra of 1-methyl-, 1,2-, 1,3-, and 1,4-dimethylantracenes in the  $4000-250\text{ cm}^{-1}$  region are shown in Table III along with probable vibrational assignments. The spectral data are arranged analogously to those of some other anthracene methyl derivatives studied previously<sup>9</sup>. The CH stretching vibration region at  $3100-2800\text{ cm}^{-1}$  as well as the CH in-plane bending vibration region at  $1280-980\text{ cm}^{-1}$  contain numerous bands of a medium or weak intensity. Noteworthy is the region of out-of-plane CH bending vibrations; the



SCHEME 2

absorption band frequencies corresponding to these vibrations depend on the substitution type of the aromatic ring<sup>20</sup>. Determination of the substitution type in the anthracene ring system is almost unequivocal when a single lateral ring (ending the molecule) is substituted; the situation is more difficult when both the lateral rings carry substituents. In addition to bands common to all the four methyl anthracenes studied (bands at  $878-875\text{ cm}^{-1}$  attributed to out-of-plane bending vibrations of "isolated" H atoms at positions 9 and 10 of the anthracene ring system and a band at  $739-731\text{ cm}^{-1}$  ascribed to out-of-plane bending vibrations of the four vicinal H atoms on the unsubstituted lateral ring, *i.e.* at positions 5 to 8 of the anthracene ring system), probably also bands ascribed to the out-of-plane bending vibrations of H atoms on the lateral substituted ring occur in this region, namely, at  $784\text{ cm}^{-1}$  in the case of 1-methylantracene (three vicinal H atoms), at  $802\text{ cm}^{-1}$  and  $714\text{ cm}^{-1}$  in the case of 1,2-dimethylantracene, at  $821\text{ cm}^{-1}$  and  $712\text{ cm}^{-1}$  in the case of 1,4-dimethylantracene (both the latter derivatives carry two vicinal H atoms on the lateral substituted ring and exhibit therefore similar frequencies in this region of vibrations), and at  $886\text{ cm}^{-1}$  in the case of 1,3-dimethylantracene ("isolated" H atoms at positions 2 and 4 of the lateral substituted ring). The latter band is superimposed on the above mentioned band of "isolated" H atoms at  $878\text{ cm}^{-1}$  similarly to some other

TABLE III  
Vibrational Assignment of 1-Methyl-, 1,2-, 1,3-, and 1,4-Dimethylantracenes

Vibrational assignment	Position of methyl groups			
	1-	1,2-	1,3-	1,4-
CH stretch. arom.	3 054 s	3 047 s	3 051 s	3 056 s
CH stretch. arom.	3 025 m	3 012 m	3 013 sh	3 024 m
	3 008 sh	—	3 008 m	3 002 w
	—	—	—	2 981 sh
CH stretch. antisym. CH <sub>3</sub>	2 969 m	2 964 sh	2 971 m	2 967 m
	2 953 sh	—	2 951 w	2 946 w
	2 926 sh	—	2 944 sh	—
CH stretch.	2 922 s	2 918 s	2 915 m	2 923 m
	2 898 m	—	—	2 891 m
CH stretch. CH <sub>3</sub> sym.	2 852 m	2 862 m	2 861 w	2 858 w
	2 733 w	2 735 w	2 734 w	2 733 w
	1 937 w	1 938 w	1 938 w	1 938 w
	1 919 sh	—	1 914 w	1 918 w
	1 904 vw	1 912 w	1 903 s	1 901 vw
	1 865 vw	—	—	—
	1 852 vw	1 847 vw	—	1 851 sh
	1 830 vw	—	—	1 835 sh
Region of overtone and combination tone bands	1 805 sh	1 806 vw	—	1 829 w
	1 799 w	—	1 798 w	1 800 w
	1 786 sh	1 782 vw	—	1 785 vw
	1 776 w	—	—	—
	1 758 sh	—	1 767 w	1 757 sh
	1 750 w	1 751 vw	1 745 w	1 750 w
	1 713 w	1 708 sh	1 714 w	1 709 sh
	1 697 sh	—	—	—
	1 685 vw	1 689 vw	1 689 sh	1 689 w
	1 665 w	1 655 sh	1 660 sh	1 655 sh
	1 626 sh	1 636 sh	—	1 636 sh
	—	—	—	1 627 sh
Ring stretch.	1 621 s	1 621 s	1 629 s	1 617 s
	—	1 600 sh	1 623 sh	—
Ring stretch.	1 580 vw	1 579 vw	1 582 w	1 578 sh
	1 571 sh	—	—	1 574 w
Ring stretch.	1 557 w	1 554 vw	1 562 w	1 563 sh
Ring stretch.	1 542 w	1 537 w	1 542 w	1 546 m
Ring stretch.	1 492 sh	1 480 sh	1 479 sh	1 488 sh
	1 473 sh	1 470 sh	1 471 sh	1 475 sh
CH deform. asym. CH <sub>3</sub>	1 454 s	1 458 s	1 461 s	1 458 s
	—	—	—	1 456 sh
	—	—	—	1 447 w

TABLE III  
 (Continued)

Vibrational assignment	Position of methyl groups			
	1-	1,2-	1,3-	1,4-
	1 433 s	1 442 sh	1 441 s	1 435 s
	1 424 sh	1 423 sh	—	—
Ring stretch.	1 401 w	1 402 w	1 407 w	1 398 w
	—	—	1 395 sh	—
CH deform. sym. CH <sub>3</sub>	1 379 w	1 381 m	1 381 w	1 384 m
	—	1 375 sh	1 373 sh	—
Ring stretch.	1 344 w	1 340 w	1 342 w	1 340 w
	1 323 sh	—	1 330 vw	—
Ring stretch.	1 314 s	1 315 m	1 316 w	1 316 m
	1 293 vw	1 297 vw	1 305 w	—
	1 276 w	1 276 w	1 280 w	1 282 w
	1 258 w	1 264 sh	1 255 w	1 265 w
	—	1 229 w	1 234 vw	1 235 vw
	—	—	1 213 sh	1 207 vw
	1 197 m	1 193 w	1 198 w	1 185 sh
	—	1 178 w	1 171 w	1 178 w
Region of CH in-plane bending bands	1 162 m	1 168 m	1 168 sh	1 156 w
	—	1 154 w	1 145 w	1 145 sh
	—	1 137 sh	—	1 136 w
	1 132 w	1 132 w	1 129 w	1 126 w
	—	1 095 vw	—	1 070 w
	1 065 w	1 041 sh	1 055 w	1 040 sh
	1 037 w	1 035 w	1 035 m	1 034 m
	—	1 011 sh	—	—
	1 006 w	1 004 w	1 002 w	1 008 w
	—	982 w	—	992 vw
	968 w	973 sh	—	971 vw
CH out-of-plane bending	953 m	956 m	952 m	952 m
	—	953 sh	951 sh	919 sh
	912 vw	—	909 sh	915 vw
CH out-of-plane bending	903 s	894 s	902 s	886 sh
	883 sh	—	—	—
CH out-of-plane bending	—	—	886 vs	—
CH out-of-plane bending	876 vs	877 vs	878 s	875 vs
	854 w	838 w	856 vw	—
	841 w	—	846 vw	841 vw
	—	828 vw	—	824 sh
	—	819 w	—	—
CH out-of-plane bending	784 s	802 m	—	821 s
	—	—	—	817 sh

TABLE III  
(Continued)

Vibrational assignment	Position of methyl groups			
	1-	1,2-	1,3-	1,4-
	—	798 sh	—	797 sh
	—	770 sh	765 sh	770 sh
	764 w	760 sh	758 sh	762 vw
Skelet. deform.	745 s	747 m	744 m	742 sh
	—	739 sh	—	—
CH out-of-plane bending	731 vs	734 vs	738 vs	739 vs
	716 sh	714 w	715 vw	712 w
	—	682 vw	679 vw	—
	665 vw	663 vw	—	664 vw
	646 w	637 w	—	636 w
	—	625 w	624 w	—
	—	622 w	—	617 w
	613 w	608 w	612 w	—
	—	597 w	597 w	—
	—	—	593 w	—
	577 w	—	—	579 w
	—	—	546 sh	—
Region of skelet. deform.	—	—	543 w	547 vw
	535 vw	532 w	534 vw	536 w
	515 w	517 vw	518 vw	—
	—	507 vw	503 vw	—
	—	—	479 sh	475 sh
	—	475 s	471 s	—
	466 s	467 s	466 sh	467 s
	444 sh	—	—	—
	—	403 w	412 vw	411 vw
	391 m	—	—	397 m
	—	331 m	—	—

methylanthracenes containing "isolated" H atoms of this type<sup>9</sup>. Vibrations of the anthracene skeleton manifest themselves by absorption bands at 1630–1615 cm<sup>-1</sup> and near 1540 cm<sup>-1</sup>, and bands of ring deformation modes in the region below 700 cm<sup>-1</sup>. As expected, the methyl groups manifest themselves by an antisymmetric vibration at 2970–2960 cm<sup>-1</sup> and a symmetric vibration at 2860–2850 cm<sup>-1</sup>. The deformation vibrations of methyl groups occur near 1460 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> similarly as in the IR spectra of the earlier investigated methylanthracenes<sup>9</sup>.



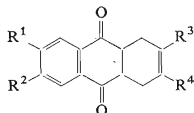
## EXPERIMENTAL

Melting points were taken on a heated microscopic stage (Kofler block) or in a capillary (in the case of some higher-melting anthracenes) and are uncorrected.

**Materials.** Cyclohexanol (4 volumes) was shaken for 1 h with 15% aqueous potassium hydroxide (1 volume), washed with three portions of distilled water (in 10-min intervals), dried by azeotropic distillation with benzene, and rectified on a column (about 15 TP). The fraction of the b.p. 161°C solidified on cooling down to room temperature. Aluminium in shavings; purity, 99-97%. Mercuric chloride, pure. Tetrachloromethane (Analytical Grade) was rectified on a column (about 10 TP).

The 9,10-anthraquinones methylated at positions 1 to 4 were prepared by cyclization of the corresponding methyl derivatives of *o*-benzoylbenzoic acid on heating in conc. sulfuric acid or benzoyl chloride. The *o*-benzoylbenzoic acids were prepared according to ref.<sup>21</sup>.

The tetrahydroanthraquinones *I*–*V* are assumed to exhibit the *cis* junction of partially unsaturated rings (*I*) by analogy with the structure of 1,4,4a,5,8,8a,9a,10a-octahydro-9,10-anthraquinone prepared by the addition of 1,3-butadiene to *p*-benzoquinone<sup>22</sup> and (2) on the basis of the observation that open-chain conjugated dienes add to a dienophile in the *cisoid* conformation<sup>23</sup>.



- I*; R<sup>1</sup> = R<sup>4</sup> = H, R<sup>2</sup> = R<sup>3</sup> = CH<sub>3</sub>  
*II*; R<sup>1</sup> = R<sup>3</sup> = CH<sub>3</sub>, R<sup>2</sup> = R<sup>4</sup> = H  
*III*; R<sup>1</sup> = H, R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = CH<sub>3</sub>  
*IV*; R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = CH<sub>3</sub>, R<sup>4</sup> = H  
*V*; R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = CH<sub>3</sub>

2,6-Dimethyl- (*I*) and 2,7-Dimethyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone (*II*)

A solution of 6-methyl-1,4-naphthoquinone<sup>24</sup> (20.7 g; 0.12 mol) and isoprene (16.3 g; 0.24 mol) in ethanol (170 ml) was refluxed for 5 h, filtered with active charcoal, and the filtrate diluted with water. The precipitate was collected with suction, washed with water, and dried at 40°C. Yield of the crude material, 22.5 g (72%); m.p. 78–80°C. The material was crystallized twice from methanol, eight times from 4 : 1 (v/v) methanol-water, and several times from methanol to afford 0.99 g of compound *I*, m.p. 92–93°C. For C<sub>16</sub>H<sub>16</sub>O<sub>2</sub> (240.3) calculated: 79.97% C, 6.71% H; found: 80.30% C, 6.73% H. The position of methyl groups was established by dehydrogenation to 2,6-dimethyl-9,10-anthraquinone, m.p. 242°C (reported<sup>16</sup>, m.p. 242°C). The first two mother liquors after the crystallisation from methanol were combined and concentrated to about half of the original volume; the concentrate was kept at room temperature for several days to deposit crystals which were recrystallized six to eight times from hexane until the melting point value was constant. Yield, 0.82 g of compound *II*, m.p. 104°C. For C<sub>16</sub>H<sub>16</sub>O<sub>2</sub> (240.3) calculated: 79.97% C, 6.71% H; found: 80.21% C, 6.85% H. Dehydrogenation of compound *II* afforded 2,7-dimethyl-9,10-anthraquinone, m.p. 169°C (reported<sup>16</sup>, m.p. 170°C).

2,3,6-Trimethyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone (*III*)

6-Methyl-1,4-naphthoquinone<sup>24</sup> (0.01 mol) and 2,3-dimethyl-1,3-butadiene (0.02 mol) were refluxed in ethanol (6.5 ml) for 5 h. Yield, 74.5% of compound *III*, m.p. 119–120°C (ethanol);

reported<sup>24</sup>, 119–120°C. Dehydrogenation of compound *III* afforded 2,3,6-trimethyl-9,10-anthraquinone, m.p. 239°C; reported<sup>17</sup>, 240°C.

#### 2,6,7-Trimethyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone (*IV*)

6,7-Dimethyl-1,4-naphthoquinone<sup>24</sup> (0.005 mol) and isoprene (0.01 mol) were refluxed in ethanol (20 ml) for 6 h. Yield, 72% of compound *IV*, m.p. 143–144°C (methanol). For C<sub>17</sub>H<sub>18</sub>O<sub>2</sub> (254.3) calculated: 80.28% C, 7.13% H; found: 80.23% C, 7.16% H. Dehydrogenation of compound *IV* afforded 2,3,6-trimethyl-9,10-anthraquinone, identical with the specimen obtained by dehydrogenation of compound *III*.

#### 2,3,6,7-Tetramethyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone (*V*)

6,7-Dimethyl-1,4-naphthoquinone<sup>24</sup> (0.005 mol) and 2,3-dimethyl-1,3-butadiene (0.01 mol) were refluxed in ethanol (10 ml) for 5 h. Yield, 73% of compound *V*, m.p. 201–202°C (ethanol). For C<sub>18</sub>H<sub>20</sub>O<sub>2</sub> (268.3) calculated: 80.56% C, 7.51% H; found: 80.78% C, 7.49% H. Dehydrogenation of compound *V* afforded 2,3,6,7-tetramethyl-9,10-anthraquinone, m.p. 331°C; reported<sup>18</sup>, m.p. 330°C.

#### Dehydrogenation of 1,4,4a,9a-tetrahydro-9,10-anthraquinones (*cf.*<sup>25</sup>)

A gentle stream of oxygen was introduced into a hot mixture obtained by mixing a solution of the corresponding tetrahydroanthraquinone (500 mg) in ethanol (75 ml) with a solution of potassium hydroxide (5 g) in ethanol (25 ml). The reaction proceeded without external heating. The colour of the solution rapidly changed from deep red or brown to green and finally to yellow accompanied by the deposition of yellow crystals of the corresponding anthraquinone. After 2.0–2.5 h at room temperature, the crystals were collected with suction, washed with water and methanol, and air-dried to afford almost theoretical yields of anthraquinones. The recrystallization was performed from acetic acid or ethanol.

#### Reduction of Anthraquinones

Cyclohexanol (10 ml) and a catalytical amount of tetrachloromethane were added to aluminium shavings (500 mg) and mercuric chloride (12.5 mg), and the mixture was cautiously warmed. When the vigorous reaction was over, the mixture was refluxed until the metal dissolved (about 3 h). The reaction mixture was then cooled, the corresponding solid anthraquinone was added (for the amounts see Table I and II), the mixture refluxed (for the periods of time see the tables), cooled, and poured into a mixture of 37% hydrochloric acid (4 ml) and water (20 ml). The organic phase was repeatedly extracted with equal volumes of toluene, the extracts were combined, and steam-distilled. The distillation residue usually deposited crystals which were collected with suction, washed with methanol, dried under diminished pressure at a moderately elevated temperature, and recrystallized from benzene, acetic acid, methanol or ethanol (Table II). When the distillation residue did not solidify (1-methyl-, 1,2- and 1,4-dimethylanthracenes), the oily product was extracted with a small amount of toluene and distilled under diminished pressure. The fore-run contained cyclohexanone and its condensation products. The principal fractions solidified on cooling and were purified by crystallisation. For the thus-obtained anthracenes see Table II.

## Measurements of IR Spectra

The IR spectra were taken on a double-beam grating Perkin Elmer 621 spectrophotometer in the range of 4000 — 250  $\text{cm}^{-1}$ . For the sake of comparison with spectra of other methylanthracenes<sup>9</sup>, the present samples were measured in potassium bromide pellets (concentrations: 3 mg of the sample per 300 mg of KBr and 1 mg of the sample per 300 mg KBr).

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