methanol and dried at 100° for 2 hr. over P_2O_5 at 1.0 mm., m.p. 189–190°.

Anal. Calcd. for $C_{16}H_{12}O_4S_2$: C, 57.81; H, 3.64; S, 19.30. Found: C, 58.1; H, 3.81; S, 19.45.

1,4-Anthraquinonedisulfenyl Morpholide (VIII).—Either VI or VII when boiled for a short time in a small volume of morpholine dissolves, and on cooling, red-brown needles of the dimorpholide are deposited. After collecting and washing with hot ethanol and benzene the product was found to sinter at 271° and not to melt below 300°, though decomposition was complete. For analysis the compound was recrystallized from pyridine (charcoal) several times (melting characteristic unchanged) and dried at 100° for 12 hr. over P_2O_5 at 1.0 mm.

Anal. Calcd. for $C_{22}H_{22}O_4S_2N_2$: C, 59.9; H, 5.01; N, 6.34; S, 14.49. Found: C, 59.91; H, 5.21; N, 6.33; S, 14.14.

1,4-Anthraquinonedisulfenic Acid (II).—The disulfenate ester VII (0.5 g., 0.0015 mole) was suspended in 20 ml. of absolute ethanol which was brought to a boil and 1.0 ml. of 33% aqueous potassium hydroxide (0.006 mole) added. Boiling was continued for 4 min. when 100 ml. of hot distilled water was added. The resultant clear blue solution was then quickly chilled, filtered and the filtrate made weakly acid with acetic acid. The purple coagulant was collected and washed with a large quantity of cold water. The moist precipitate was then taken up in cold acetone, the deep magenta solution filtered, and to the filtrate there was added water until the solution became just slightly cloudy. The solution was then refrigerated and water added very gradually until precipitation was completed. In this manner the acid II was obtained as purple microscopic needles (0.1 to 0.12 g., 22–26%). When heated above 100° II turned from purple to yellow.

Additional recrystallizations from acetone always resulted in the formation of small amounts of alkali-insoluble material. No other solvent was found that was better for recrystallization than acetone and an analytical sample could not be prepared.

The Stability of II and the Conversion of II to VII.—Anhydrous chloroform (100 ml.) previously saturated with dry hydrogen chloride at 0° was added to 118 mg. (0.00039 mole) of dry II and the reaction mixture allowed to set at 0° for 12 hr. All the solvent was then aspirated off, and to the dry residue there was added 100 ml. of anhydrous methanol and 1 ml. of dry pyridine. The flask was then warmed to a boil and set aside for 12 hr. The methanolic supernatant solution was decanted and the residue taken up in 50 ml. of hot, anhydrous benzene. The benzene and methanolic solutions were then combined and allowed to cool. After a few hr. the precipitation of a high melting amorphous material (*ca.* 40 mg.) was complete. This substance was removed and the filtrate concentrated to 100 ml. and set aside. The characteristic crystals of the diester soon appeared. These were collected and the filtrate concentrated in turn to 50 and 25 ml., respectively, the crystalline ester being removed each time. In this fashion there was obtained a total of 60–70 mg. of VII, m.p. 176–179° (47–55% yield from II). The melting point was identical to that of VII as obtained from the reaction of VI and methanol, and on recrystallization several times from benzene and methanol the melting points were found to be between 185–188° which is very close to that of the analytical sample of VII (no mixed melting point depression with an authentic sample of VII).

This procedure was carried out on samples of the sulfenic acid prepared a month in advance with no appreciable difference in yield of VII if II were kept in a desiccator under refrigeration.

1,4-Anthraquinonedisulfonic Acid (IX) and 1,4-Dichloroanthraquinone (X).—The disulfonic acid IX was obtained in good yield when either V, VI, VII or II was suspended in 200 volumes of 90% aqueous acetic acid which was then saturated, in the cold, with chlorine gas. The reaction mixture was filtered and allowed to set for 10 hr. when the white to yellow needles were collected. The crude acid is best recrystallized from 90% acetic acid, m.p. 269–269.5° (lit.[21] 264–265°). The crude yield from 0.4 g. (0.0015 mole) of V was 0.41 g. or 75% of theory (m.p. 263–264°).

Anal. Calcd. for $C_{14}H_8O_8S_2 \cdot H_2O$: C, 43.52; H, 2.61; S, 16.60. Found: C, 43.61; H, 2.85; S, 17.47.

The disulfonic acid could be converted to 1,4-dichloroanthraquinone by the usual procedure,[20] m.p. 190° (lit.[21] 186.5°). When the dihalide, so obtained (0.531 g., 0.0019 mole), was treated in the same manner as in the preparation of V from IV, the polymeric disulfide was obtained (0.52 g., 100% yield), m.p. > 360°.

Absorption Spectra.—These were determined with a Model DU Beckman spectrophotometer. Extinction coefficients were calculated from spectral measurements made with $\sim 10^{-4}$ molar solutions; the maximum absorbances were all between 0.5 and 0.8. The solvents employed are as noted in Table II.

Acknowledgments.—This work was supported by grants from the Rockefeller Foundation and the Institute of Arthritis and Metabolic Diseases, National Institutes of Health.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA, AND THE RESEARCH COUNCIL OF ALBERTA]

Observations on Some Alkyl Substituted Anthracenes and Anthraquinones

BY ROBERT J. CRAWFORD, SIDNEY LEVINE, RICHARD M. ELOFSON AND REUBEN B. SANDIN

RECEIVED JANUARY 9, 1957

1,2-Dimethylanthraquinone and some related alkyl substituted anthraquinones have been examined from the standpoint of polarographic and chemical reduction and controlled potential electrolysis. The effectiveness of alkyl substitution in lowering the negative potential is: $\alpha > \beta$, dimethyl > monomethyl, six-membered ring > five-membered ring and 1,2-dimethyl > six-membered ring. The α-substituted anthraquinones show evidence of oxanthrol isomerization. It is suggested that 1,2,9,10-tetramethylanthracene behaves as a crowded molecule from the standpoint of preparation and properties.

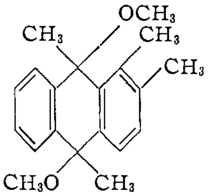
It is known that 9,10-dihydro derivatives of 1,2-dimethylanthracene are very resistant to aromatization. For example, compound II resists demethoxylation and does not yield 1,2,9,10-tetramethylanthracene (I) even after shaking for six days with sodium powder in ether.[1] On the other hand, 9,10-dimethylanthracene is obtained in good yield from the corresponding dimethoxy compound. Again, compound III does not undergo dehydrogenation to yield I, whereas 9,10-dihydroanthracene is smoothly transformed into 9,10-dimethylanthracene with sulfur at 230°.[2]

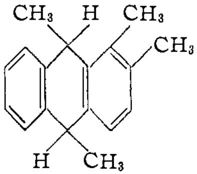
In contrast to this behavior it is known that compound I tends to lose aromaticity and to revert to the 9,10-dihydro state. For example, I has been

(1) G. M. Badger, J. W. Cook and F. Goulden, *J. Chem. Soc.*, 16 (1940).

(2) G. M. Badger, F. Goulden and F. L. Warren, *ibid.*, 18 (1941).

found to undergo peroxidation after brief periods of storage in the solid state.[3]


II


III

The marked stability of the 9,10-dihydro derivatives of 1,2-dimethylanthracene appeared to us to justify a polarographic study of 1,2-dimethylanthraquinone and some related compounds. Therefore in this paper are reported some observations which have been made on the polarographic reduction and also the chemical reduction and the controlled potential electrolysis of 1,2-dimethylanthraquinone and some related quinones. A difference has also been noted in the stability of some 1,2-disubstituted hydrocarbons.

Experimental

Anthraquinones.—The quinones were for the most part well known and all of them have been described previously. Anthraquinone (Eastman Kodak Co.) melted at 286–288°. 2-Methylanthraquinone (Eastman Kodak Co.) was crystallized from alcohol and melted at 175°. 1,2-Dimethylanthraquinone,[3] m.p. 156–157°, 1,4-dimethylanthraquinone,[4] m.p. 140.5–141.5°, 1-methylanthraquinone,[5] m.p. 172–173°, and 1′,2′,3′,4′-tetrahydro-1,2-benzanthraquinone,[6] m.p. 153–154°, were made by the ring closures of the substituted *o*-benzoylbenzoic acids. 1,2-Cyclopenteno-9,10-anthraquinone[7] melted at 126.5–127.5°.

9,10-Dimethyl-1′,2′,3′,4′-tetrahydrobenzanthracene (IV).—To a solution of the Grignard reagent from 0.5 g. of magnesium and methyl iodide (2.0 ml.) in anhydrous ether (15 ml.) was added 0.5 g. of 1′,2′,3′,4′-tetrahydro-1,2-benzanthraquinone. The flask was stoppered and after standing at 0° for four days, the fluorescent solution was poured dropwise and with constant stirring into a cold solution of 50% hydriodic acid (5.7 ml.), hydrobromic acid (d. 1.4, 4 ml.) and methanol (15 ml.). Glacial acetic acid (15 ml.) was added and the iodo compound (0.6 g.) separated as an orange solid. A solution of the iodo compound (1.2 g.) in dioxane (45 ml.) was added to a solution of stannous chloride (7.5 g.) in dioxane (40 ml.) and concentrated hydrochloric acid (12 ml.). The solution was brought to its boiling point, diluted with water (250 ml.) and extracted with benzene. The highly fluorescent benzene extract was washed with water and dried by filtering through ordinary filter paper. The benzene was evaporated under diminished pressure, which afforded a brown sirupy material which was extracted with alcohol. The alcohol extract was saturated with picric acid and yielded a black crystalline picrate. It was crystallized from alcohol; weight 0.6 g., m.p. 153–154°.

Anal. Calcd. for $C_{26}H_{23}N_3O_7$: C, 63.81; H, 4.74. Found: C, 64.09; H, 4.93.

The picrate was dissolved in benzene (30 ml.), and the solution was passed through a column consisting of an equal part mixture of activated alumina and Super-cel. The benzene was evaporated under reduced pressure and afforded 9,10-dimethyl-1′,2′,3′,4′-tetrahydrobenzanthracene as a yellow solid, m.p. 89–90°.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.23; H, 7.73. Found: C, 91.98; H, 7.65.

Reduction at the Dropping Mercury Electrode.—A Leeds and Northrup Electro-chemograph, type E, was used to record the polarograms. A minimum of damping (position 1) was used to prevent distortion of the waves. Half-wave potentials were measured with both increasing and decreasing cathodic voltage and the average was computed. The capillary used was made from marine barometer tubing obtained from the Corning Glass Works. The value of the capillary constant $M^{2/3} t^{1/6}$ was 2.27 at *h* equal to 35.6 cm. The drop time was measured with the current flowing in the region of the half-wave potential. The electrolysis cells were of the usual type. A saturated calomel electrode was used as the anode and was connected by means of a flexible saturated potassium chloride agar bridge to the electrolysis cell. The quinones were dissolved in a 50:50 mixture of reagent grade isopropyl alcohol and 0.1 *M* acetate buffer, *p*H 5.6, or in 0.1 *M* hydrochloric acid in 50% isopropyl alcohol, *p*H 1.5, to give a final concentration of 5×10^{-4} *M*. The *p*H measurements were recorded with a Beckman model G *p*H meter. All of the solutions were kept out of direct sunlight and preferably in the dark to prevent any possible reaction between the alcohol and the quinone. Also determinations were carried out as soon as possible after the solutions had been made, and all determinations were carried out under the same conditions. The nitrogen used was purified grade supplied by Canadian Liquid Air. The temperature during the experiments was thermostated at 25°. A summary of observed half-wave potentials is given in Table I. In the acetate buffer the waves did not show semiquinone formation. Instead, perfectly smooth waves were obtained, corresponding to a reversible two-electron reduction. In strongly acid solutions the waves were not quite so well formed, but the potentials correspond quite closely with those measured in the acetate buffer and indicate quite clearly the reliability of the measurements to the nearest 0.01 V.

TABLE I

$E_{1/2}$ *vs.* THE SATURATED CALOMEL ELECTRODE FOR ANTHRAQUINONES IN VARIOUS BUFFERS AND 50% ISOPROPYL ALCOHOL. ALL $E_{1/2}$ VALUES ARE NEGATIVE

Quinone	0.1 *M* Acetate buffer, *p*H 5.6	0.1 *M* HCl, *p*H 1.5
Anthraquinone	0.43[a]	0.18
2-Methylanthraquinone	.44[a]	.19
1-Methylanthraquinone	.48	.23
1,2-Dimethylanthraquinone	.51	.25
1,3-Dimethylanthraquinone	.50	..
1,2-Cyclopenteno-9,10-anthraquinone	.47	..
1′,2′,3′,4′-Tetrahydro-1,2-benzanthraquinone	.49	..
1,4-Dimethylanthraquinone	.53	0.29

[a] These values correspond to E_0 values of +0.15 and +0.14 v. for anthraquinone and 2-methylanthraquinone, respectively. This is in good agreement with the values of +0.155 and +0.150 v. obtained by J. B. Conant and L. F. Fieser, *ibid.*, **46**, 1858 (1924). See also (a) H. Adkins and F. W. Cox, *ibid.*, **60**, 1151 (1938); (b) S. Wawzonek, H. A. Laitinen and S. J. Kwiatkowski, *ibid.*, **66**, 827 (1944); (c) N. H. Furman and K. G. Stone, ref. 8.

Polarograms which were run in 0.1 *M* tetramethylammonium hydroxide, *p*H 13.7, and which are not reported in this paper, indicated semiquinone formation by the fact that two-step waves, each involving one electron, were noticed. The separation of the two waves varied considerably from one compound to another but was greatest with anthraquinone and a minimum with 1,4-dimethylanthraquinone. Furman and Stone[8] in their careful work have attributed this phenomenon to complex formation with the buffer. However, in the present work the waves were too indistinct to permit quantitative measurements of the differences.

In order to establish whether the systems studied were strictly reversible or not, the quinones were reduced to the hydroquinones and then the oxidation waves of the hydroquinones were determined. Reduction was carried out by chemical means and also by controlled potential electrolysis as described by Lingane.[9]

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[3] R. B. Sandin, R. Kitchen and L. F. Fieser, THIS JOURNAL, **65**, 2018 (1943).

[4] G. Heller, *Ber.*, **43**, 2890 (1910).

[5] L. F. Fieser and H. Heymann, THIS JOURNAL, **64**, 376 (1942).

[6] L. F. Fieser and E. B. Hershberg, *ibid.*, **59**, 2331 (1937).

[7] H. J. Backer and J. R. van der Bij, *Rev. trav. chim.*, **62**, 561 (1943).

[8] N. H. Furman and K. G. Stone, THIS JOURNAL, **70**, 3055 (1948).

[9] J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953. Chapter XII.

Chemical Reduction.—Titanous chloride in the acetate buffer reduced all compounds smoothly and produced anodic waves, the potentials of which were in exact agreement with the cathodic waves of the hydroquinones. In hydrochloric acid solution the expected anodic waves were likewise obtained for all compounds except 1,4-dimethylanthraquinone, which was not reduced under these conditions. When sodium hydrosulfite reduction of the quinone in 0.1 *M* tetramethylammonium hydroxide was carried out, anodic waves were obtained and the potential agreed within experimental error with the cathodic waves of the quinone. In the case of anthraquinone and 2-methylanthraquinone, the anodic waves were of the same height as the original cathodic waves. However, with the 1-substituted anthraquinones, the hydroquinone waves were greatly reduced in height. Apparently the hydroquinone primarily formed was changing rapidly to some other form such as the oxanthrol. No reduction wave could be found for the postulated oxanthrol.

Electrochemical Reduction.—In order to check the results of chemical reduction, 1,2-dimethylanthraquinone was reduced by controlled potential electrolysis. In these experiments 0.5×10^{-4} *M* solutions in 50% isopropyl alcohol were electrolyzed under purified nitrogen using a large mercury pool stirred magnetically as cathode and a saturated calomel electrode as anode. The cathode potential was controlled manually.

In 0.1 *M* tetramethylammonium hydroxide the reduction of 1,2-dimethylanthraquinone proceeded smoothly, but the height of the anodic wave decreased rapidly to a small fraction of the original height of the cathodic wave. The half-wave potential of this wave was the same as that of the quinone. Bubbling oxygen through the solution followed by nitrogen produced the original cathodic wave corresponding to the original concentration. This indicated that the isomerization that was taking place was completely reversible. Anthraquinone under these conditions showed no decrease in height of the anodic wave over a 12-hr. period.

Electrolysis of 1,2-dimethylanthraquinone in the acetate buffer produced an anodic wave, with unchanged half-wave potential. The height of this wave decreased to about 60% of its original value after 4 hr. and 30% of its former value after 8 hr. In addition, a reduction wave developed at −1.1 v. which probably corresponds to the oxanthrol. The over-all height of the two waves equalled that of the original quinone. When the solution was oxidized with oxygen, the cathodic wave of the quinone was produced, but its height was only slightly higher than that of the hydroquinone. This indicated that the isomerization between the hydroquinone and oxanthrol was much slower at the lower *p*H.

In 0.1 *M* HCl, 1,2-dimethylanthraquinone was reduced smoothly to the hydroquinone which did not indicate any appreciable isomerization to the oxanthrol. In 0.1 *M* HCl, 1,4-dimethylanthraquinone, which was not reduced by titanous chloride, was reduced smoothly to the hydroquinone with no evidence of isomerization. In both cases the potentials of the hydroquinone were the same as that of the original quinones.

Air Oxidation of 1,2,9,10-Tetramethylanthracene (I) and 9,10-Dimethyl-1′,2′,3′,4′-tetrahydrobenzanthracene (IV) in the Solid State.—Freshly prepared hydrocarbon I, m.p. 52–54°,[3] and hydrocarbon IV, m.p. 89–90°, were exposed to air in the solid state. Compound I, after 7 days exposure, had a m.p. 50–73° and gave off bubbles of gas at 109°. Freshly prepared I gave no reaction with starch–potassium iodide solution, whereas the exposed material gave a definite test. In contrast to this behavior, IV after 7 days of exposure had a m.p. 89.5–91° and gave no evidence of having undergone oxidation. Moreover, IV after one month of exposure showed no appreciable change in chemical composition as indicated by analysis.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.23; H, 7.73. Found: C, 91.56; H, 7.86.

Discussion

The influence of alkyl substitution upon the ease of polarographic reduction is indicated in Table I. α-Substitution yields a more negative potential than β-substitution. Potentials become more negative with disubstitution and a six-membered ring is more effective in lowering the potential than a five-membered ring.[10] Our observed value for 2-methylanthraquinone probably gives a rough estimate of the conjugative and inductive effects of the methyl group.[11] However, our recorded potential difference between anthraquinone and the 2-methylanthraquinone may not be too significant.

The lower negative value for α-methylanthraquinone brings in an added steric effect.[12,13]

Leonard, Laitinen and Mottus[14] have given a very clear picture of the type of polarization which is believed to occur at the electrode in the case of the polarography of certain 1,2-diketones. They have also suggested that the lowering of the potential is due in part to a steric hindrance to coplanarity of the dicarbonyl system. In the present work it is quite possible that the steric requirements of the carbonyl group and the α-substituent are involved. Gill and Stonehill[12a] suggest a steric hindrance which pushes both the =O and large α-substituent out of the ring plane. This would inhibit any resonance of the carbonyl group and also of the α-substituent with the ring. The enhanced effect of 1,2-dimethyl substitution over an additive effect may be due to a buttressing action where the α-methyl group is buttressed by the adjacent methyl group.[15] That the six-membered ring is more effective in lowering the potential than the five-membered ring may be due to the greater amount of crowding associated with the conformation of the six-membered ring. However, a six-membered ring is not as important from the standpoint of crowding as 1,2-dimethyl substitution. This is particularly noticeable when the stabilities of the two hydrocarbons I and IV are compared. The chemical and electrochemical reduction of α-substituted anthraquinones indicates isomerization to an oxanthrol. Gill and Stonehill[16] have shown that certain anthrahydroquinones give polarographic oxidation waves which decrease in height with time. This decrease is attributed to a reversible change to oxanthrols. The latter are polarographically reducible only at highly negative potentials. There are two possible structures for

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[10] This is consistent with the interesting work of Arnold and coworkers who have shown that the relative steric influence of methylene groups decreases in the order CH_2 (in CH_3) > CH_2 (in a six-membered ring) > CH_2 (in a five-membered ring). For leading references see S. W. Fenton, A. E. DeWald and R. T. Arnold, THIS JOURNAL, **77**, 979 (1955); R. T. Arnold, V. J. Webers and R. M. Dodson, *ibid.*, **74**, 368 (1952).

[11] The classic work of Fieser and collaborators has shown that electron-donating substituents lower the potential. For a bibliography and reviews of the work of Fieser, *et al.*, see (a) M. G. Evans and J. De Heer, *Quart. Revs.*, **4**, 94 (1950); (b) G. K. Branch and M. Calvin in "The Theory of Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1946, p. 315; (c) L. F. Fieser and M. Fieser in "Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1956, p. 710.

[12] (a) R. Gill and H. I. Stonehill, *J. Chem. Soc.*, 1845 (1952); (b) R. H. Peters and H. H. Sumner, *ibid.*, 2101 (1953).

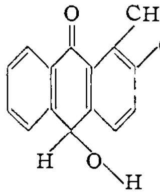
[13] Prelog, *et al.* (V. Prelog, O. Häfliger and K. Wiesner, *Helv. Chim. Acta*, **31**, 878 (1948); V. Prelog, K. Wiesner, W. Ingold and O. Häfliger, *ibid.*, **31**, 1325 (1948); V. Prelog, *J. Chem. Soc.*, 420 (1950)) have concluded that hydrogen-bridge formation between methylene groups and the oxygen atoms of certain *p*-benzoquinone derivatives is also responsible for the lowered potential.

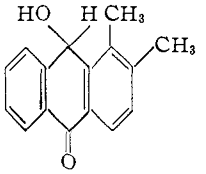
[14] N. J. Leonard, H. A. Laitinen and E. H. Mottus, THIS JOURNAL, **75**, 3300 (1953).

[15] See F. H. Westheimer in the excellent treatise "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 552. See also L. L. Ingraham in the same treatise, p. 486.

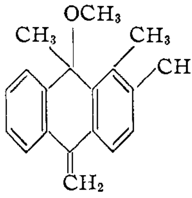
[16] R. Gill and H. I. Stonehill, *J. Chem. Soc.*, 1857 (1952).

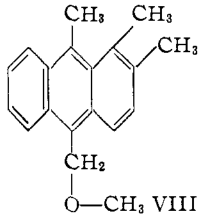
the oxanthrol from 1,2-dimethylanthraquinone, *viz.*, V and VI.


V

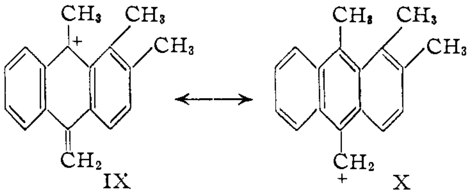

VI

The preferred structure is believed to be VI, *i.e.*, the carbon atom which is the more crowded is believed to be the one which becomes tetrahedral. Moreover there is a precedent for this type of structure in the 1,2-benzanthracene series.[17] It is also interesting that a mixture of the compounds VII and VIII has been isolated.[3] It is quite possible that the isomerization may be due to the resistance offered to the formation of a planar crowded molecule, which in this case is the hydroquinone.


VII


VIII

From our study we conclude that compounds such as 1,2,9,10-tetramethylanthracene and the corresponding hydroquinones behave as crowded molecules. Superficially, from the standpoint of structure, I resembles the crowded molecule of octamethylnaphthalene.[18] The successful preparation of hydrocarbon I evidently requires, besides the driving force of aromatization, the added effect of a carbonium ion stabilized by the resonance forms IX and X.[3]


IX X

The unsuccessful demethoxylation[1] and dehydrogenation[2] attempts to prepare I, compared with the successful reactions where there is no 1,2-disubstitution, may involve an unfavorable reaction mechanism. Again it is possible that a hindered or unfavorable conformation of the starting material is involved, where a preferrred conformation for 9,10-elimination is necessary. Some recent interesting work has been carried out[19] which indicates that 9,10-dihydroanthracenes may be considered as cyclo-1,4-hexadienes and therefore may have bond orientations at the 9- and 10-positions which are not equivalent. For example, *cis*-9,10-dihydro-9,10-dimethylanthracene[19c] is stable to aluminum chloride in benzene, whereas the *trans* isomer[19c] is dehydrogenated under the same conditions.[20] Evidently in the former compound both hydrogen atoms are in equatorial positions, and in the latter compound one hydrogen is in an axial position. It should be mentioned, however, that the first compound, in spite of its stability to aluminum chloride in benzene, is dehydrogenated with sulfur without any difficulty.

Acknowledgment.—We take pleasure in expressing our appreciation to Dr. Richard T. Arnold of the Sloan Foundation for very stimulating discussions and suggestions, to Dr. Walter Harris for his help in connection with polarographic technique, and to Dr. Robert Christiansen for his help in the preparation and analysis of some of the compounds.

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[17] R. B. Sandin and L. F. Fieser, THIS JOURNAL, **62**, 3098 (1940).

[18] (a) D. M. Donaldson and J. M. Robertson, *J. Chem. Soc.*, 17 (1953); (b) M. S. Newman and R. M. Wise, THIS JOURNAL, **78**, 450 (1956).

[19] (a) S. J. Cristol, W. Barasch and C. H. Tieman, *ibid.*, **77**, 583 (1955); (b) A. H. Beckett and B. A. Mulley, *Chemistry & Industry*, 146 (1955); (c) A. H. Beckett and B. A. Mulley, *J. Chem. Soc.*, 4159 (1955); (d) W. G. Ferrier and J. Iball, *Chemistry & Industry*, 1296 (1954).

[20] G. M. Badger, M. L. Jones and R. S. Pearce, *J. Chem. Soc.*, 1700 (1950).

EDMONTON, ALBERTA, CANADA

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The *para* Claisen Rearrangement: Rearrangement of 6-Allyl-2,6-dimethyl-2,4-cyclohexadienone[1]

BY DAVID Y. CURTIN AND ROBERT J. CRAWFORD

RECEIVED JANUARY 10, 1957

The synthesis of 6-allyl-2,6-dimethyl-2,4-cyclohexadienone from sodium 2,6-dimethylphenoxide and allyl bromide is here reported. The dienone rearranges to a mixture of 4-allyl-2,6-dimethylphenol and allyl 2,6-dimethylphenyl ether in a ratio of 2.7/1 when heated to 70°. On standing at room temperature it yields a dimer. The rates of the rearrangements have been measured at three temperatures. The results are compared with data of previous workers. The steady state concentration of dienone in the *para* Claisen rearrangement is shown by examination of the reaction mixture to be of the order of 0.1%.

Studies[2] of the mechanism of the *para* Claisen rearrangement have indicated that allyl-cyclohexadienones are intermediates in this reaction. It was the purpose of the present investigation to prepare such a compound and examine its behavior under the conditions of the Claisen rearrangement. The compound chosen for study was 6-allyl-2,6-di-

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[1] Taken from a Ph.D. thesis submitted by Robert J. Crawford to the University of Illinois, August, 1956.

[2] See D. Y. Curtin and H. W. Johnson, Jr., THIS JOURNAL, **76**, 2611 (1956), for references.