Polarographic Reduction of Some Alkyl- and Polymethylanthracenes[1]

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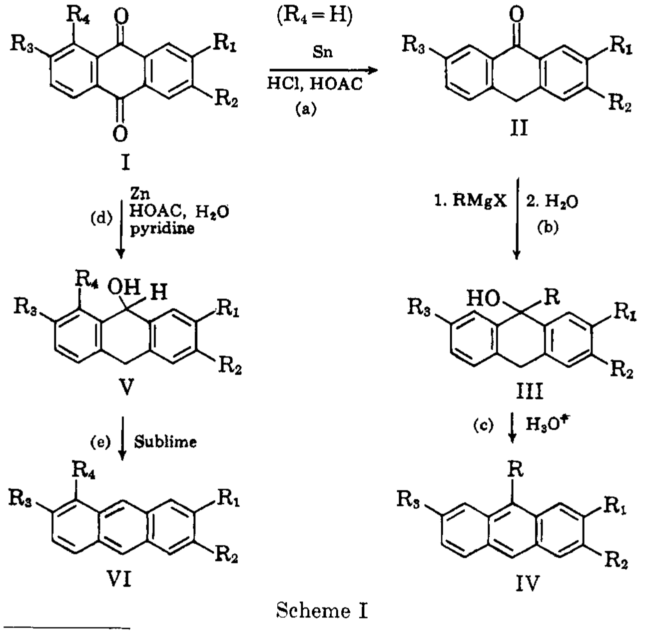
Received May 1, 1962

Polarography was conducted on anthracene, ten monoalkylanthracenes, and nine di- and polymethylanthracenes in 0.1 *M* tetra-*n*-butylammonium iodide in 75% dioxane–water. Using anthracene as a standard of comparison the change in the half-wave reduction potential, $-\Delta E_{1/2}$, for the single wave obtained for each of the other compounds is positive, consistent with a decrease in ease of electroreduction due to alkyl substitution. For isomeric monoalkyl derivatives, $-\Delta E_{1/2}$ is found to vary with the position of substitution in the manner 2- > 1- $\simeq$ 9-. Plots of $-\Delta E_{1/2}$ *vs.* σ^*, the polar substituent constant, for the 2- and for the 1- plus 9-series are linear. There is no indication of a steric effect due to the bulkiness of the alkyl group. For those compounds containing more than one methyl substituent (investigated for β- and/or *meso*- substituents only) a strict additivity relationship in $-\Delta E_{1/2}$ exists, except for the single change of 9-methylanthracene ⟶ 9,10-dimethylanthracene, for which an enhancement potential must be included in order to retain additivity. Comparison of data that $-E_{1/2}$ bears no simple relationship either to the frequency of the *p*-band (or other band) in the ultraviolet absorption spectrum or to the methyl affinity of the compound. In general, however, $-E_{1/2}$ bears an inverse relationship to the predicted value for the ionization potential. Syntheses of many of the compounds used are presented and discussed.

In a previous paper[4] it was noted that electroreducibility (as measured by $E_{1/2}$, the polarographic half-wave potential for the first or only reduction wave) of a structurally conjugated[5] biaryl or arylalkene increases with (a) increasing inherent conjugative powers, C_t, of the aryl and alkenyl moieties present and (b) decreasing angle of twist θ in the molecule. It was proposed that the pertinence of factor (b) might be ascribed to a variation (with varying θ) of electrical polarization of the molecule and/or to steric hindrance to adsorption of the substrate molecule on to the cathode surface. The effect on $E_{1/2}$ of varying θ was observed by Hoijtink[6] for various other compounds and by Klemm, Solomon, and Kohlik[7] for a series of 1-alkyl-1-(2-naphthyl)ethenes [where the alkyl group R = H (standard of comparison), Me, Et, *n*-Pr, *i*-Pr, and *t*-Bu]. For the naphthylethene series, it was also found that electroreducibility decreases with (c) increasing electron-donating properties (polar effect) of the alkyl group R or $RCHCH_3$.[8] A series of compounds susceptible to use in investigation of these various electrical, polar, and steric factors, but free of effects of varying θ, would seem to be the alkyl derivatives of a parent arene (for which uniplanarity of the electroreducible π-system would be expected to remain unaltered, at least prior to the electron-transfer process). Chopard-dit-Jean and Heilbronner[9] conducted polarographic studies on such a series derived from the nonalternant parent hydrocarbon azulene. It was found that methyl, ethyl, and isopropyl substituents decrease electroreducibility ($-\Delta E_{1/2} > 0$) as compared to azulene. For the 2-alkylazulenes $\Delta E_{1/2}$ did not vary with the alkyl group present. However, $\Delta E_{1/2}$ did vary with the position of substitution and showed a slight decrement from additivity upon di- and tri-substitution. Evidence to suggest the operation of a steric factor caused by the presence of the R groups was lacking. Miscellaneous observations[10,11] on other monoalkylsubstituted π-systems have likewise illustrated that alkyl groups, in general, decrease electroreducibility. Polarographic studies in our laboratory have now been made on two series of compounds derived from alternant arenes. The present paper presents the results obtained for a variety of monoalkyl- and polymethylanthracenes. A subsequent paper will be concerned with alkyl-, alkylene-, and polymethylnaphthalenes.

Used in these studies were the parent anthracene itself, ten monoalkylanthracenes (including the three possible methyl and three possible ethyl derivatives), and nine polymethylanthracenes containing two to six



Scheme I

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(1) This research was supported through sponsorship by the U. S. Air Force, contract no. AF 49(638)-473, monitored by the A.F. Office of Scientific Research of the Air Research and Development Command. Some of the syntheses reported were abstracted from the M.S. thesis of K. B. Desai, University of Oregon, June, 1962. Paper IV in the series on polarography of aromatic hydrocarbons. For paper III see ref. 7.

(2) Research Associate, 1959-1962.

(3) Research Assistant, 1960-1962.

(4) L. H. Klemm, C. D. Lind, and J. T. Spence, *J. Org. Chem.*, **25**, 611 (1960).

(5) For a definition of this term see footnote 11 in the paper by L. H. Klemm, B. T. Ho, C. D. Lind, B. I. MacGowan, and E. Y. K. Mak, *ibid.*, **24**, 949 (1959).

(6) G. J. Hoijtink, *Rec. trav. chim.*, **74**, 1525 (1955).

(7) L. H. Klemm, W. C. Solomon, and A. J. Kohlik, *J. Org. Chem.*, **27**, 2777 (1962).

(8) $RCHCH_3$ is presumed to result from initial reduction of the ethylenic double bond.

(9) L. H. Chopard-dit-Jean and E. Heilbronner, *Helv. Chim. Acta*, **36**, 144 (1953); E. Heilbronner, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, ed., Interscience Publishers, Inc., New York, N. Y., 1959, pp. 247-251.

(10) Compare 1-cyclopentylnaphthalene with naphthalene (see ref. 4).

(11) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," J. Wiley and Sons, Inc., New York, N. Y., 1961, pp. 182-183.

TABLE I

POLAROGRAPHIC AND OTHER DATA FOR SOME ALKYL-SUBSTITUTED ANTHRACENES

Substituent(s) on anthracene	Half-wave reduction potential, $-E_{1/2}$ (volts *vs.* S.C.E.)	$i_d/Cm^{2/3}t^{1/2}$ (μamp. mmole^{-1}–l. mg.$^{-2/3}$ sec.$^{1/2}$)	$\Delta E_{1/2}$[a] (mv.)		$\Delta\nu$[c] (cm.$^{-1}$)		Mean methyl affinity,[d] k_2/k_1
			Found	Calcd.[b]	Major β-band	Longest wave length *p*-band	
None	1.924	3.04	0		0	0	393
1-Methyl	1.937	2.90	13		200	270[e]	355
1-Ethyl	1.945	2.74	21		410	270	
2-Methyl	1.956	3.07	32	33	300	140[f]	355
2-Ethyl	1.960	2.81	36		370	100	
2-*t*-Butyl	1.966	2.65	42		360	−40	
9-Methyl	1.940	2.87	16	16	620	730[g]	190
9-Ethyl	1.948	2.79	24		620	720	
9-*n*-Propyl	1.948	2.58	24		620	730	
9-*n*-Butyl	1.947	2.57	23		670	1020[h]	
9-*n*-Decyl	1.945	2.18	21		670	770	
2,3-Dimethyl	1.991	2.87	67	66	600	230[f]	
2,6-Dimethyl	1.988	2.79	64	66	650	370	363
2,7-Dimethyl	1.991	2.69	67	66	670	120	
9,10-Dimethyl	1.976	2.71	52	52	1220	1510[g]	61.3
2,3,9-Trimethyl	2.007	2.61	83	82	1200	890[f]	
2,6,9-Trimethyl	2.003	2.71	79	82	1300	970	
2,3,6,7-Tetramethyl	2.054	...[i]	130	132	1200	280[f]	348
2,3,9,10-Tetramethyl	2.044	2.42	120	118	1780	1670[f]	
2,3,6,7,9,10-Hexamethyl	2.109	2.37	185	184	2350	1790[f]	

[a] Compared to $E_{1/2}$ for anthracene taken as a standard. [b] By means of equation 2 in text. [c] Shift from corresponding band for anthracene (measured in alkane or cyclohexane solvent) taken as a standard of comparison. [d] See ref. 31. [e] Solvent, isoöctane; W. L. Mosby, *J. Org. Chem.*, **18,** 964 (1953). [f] Solvent, cyclohexane; see ref. 48. [g] Solvent, *n*-heptane; R. N. Jones, *Chem. Rev.*, **41,** 353 (1947). [h] Solvent, isoöctane; American Petroleum Institute, "Catalog of Ultraviolet Spectral Data," no. 192. [i] The low solubility of this compound prevented accurate determination of *C*.

substituents (see Table I). Of the fourteen compounds synthesized especially for this investigation, eleven were obtained by modified procedures according to general Scheme I. Four anthraquinone derivatives (I-1-methyl, 2,3-dimethyl, 2,6-dimethyl, 2,7-dimethyl) were obtained by Diels–Alder condensations of the appropriate 1,3-butadienes and quinones followed by dehydrogenation of the resultant adducts. A novel approach to 1-methylanthraquinone involved the preliminary preparation of 1,3-pentadiene from crotonaldehyde by the Wittig procedure. In contrast to the facile, high-yielding oxidation (by means of ethanolic potassium hydroxide and air) of the tetrahydroanthraquinone adduct from naphthoquinone and 2,3-dimethyl-1,3-butadiene[12] is the difficult low-yielding oxidation (by the same method) of the octahydroanthraquinone adduct from *p*-benzoquinone and isoprene. This difference may be ascribed to a much greater ease of enolization in the conjugated tetrahydro derivative than in the unconjugated octahydro compound. 2-*t*-Butylanthraquinone was obtained (71% yield) by cyclization of 2-(4-*t*-butylbenzoyl)benzoic acid with polyphosphoric acid. This cyclization procedure has been reported[13] to give a quantitative yield of anthraquinone itself. However, attempts to extend the method to the syntheses of 2-methyl- and 2-*i*-propylanthraquinones yielded little, if any, of the desired products. Instead, impure colored products of melting points too high to be the desired compounds resulted. A test showed that 2-methylanthraquinone (from another source) was recovered unchanged on treatment with polyphosphoric acid under the same conditions. Step a, conducted with 2,3-dimethyl- and 2,6-dimethylanthraquinones, according to directions[14] published for reduction of anthraquinone itself, gave good yields (*ca.* 60%) of anthrones (II). Reactions of these dimethylanthrones with methylmagnesium iodide and subsequent treatment of the intermediates (presumably III) with concentrated hydrochloric acid gave 2,3,9- and 2,6,9-trimethylanthracenes (IV—40% and 94%, respectively). Using anthrone itself and steps b and c, there were also obtained *ca.* 40% yields of 9-*n*-propyl- and 9-*n*-butylanthracenes and a 5% yield of 9-*n*-decylanthracene.

Reduction by the Clar method[15] using zinc dust, aqueous acetic acid, and pyridine (step d) gave 23–40% yields of 1-methyl-, 2-methyl-, and 2-*t*-butylanthracenes as well as of 2,3-, 2,6-, and 2,7-dimethylanthracenes (VI). Clar and co-workers have reduced many complex polynuclear aromatic mono- and diquinones by this procedure but have not investigated its use for such simple molecules as employed here. The immediate product of this reaction, a water-insoluble material which leaves a residue on combustion, is presumed to be the zinc salt of V. Vacuum sublimation of this material, either directly or after preliminary treatment with hydrochloric acid, plus chromatography gives the pure anthracene VI. A single exploratory run showed that anthrone is convertible to anthracene under Clar reaction conditions. However, it is not clear at this time whether anthrones are actual intermediates in the Clar reaction or not.

Waldmann and Marmorstein[16] reported the preparation of 1- and 2-ethylanthracenes from the correspond-

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[12] C. F. H. Allen and A. Bell, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 310.

[13] H. R. Snyder and F. X. Werber, *J. Am. Chem. Soc.*, **72,** 2965 (1950).

[14] K. H. Meyer, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 60.

[15] E. Clar, *et al.*, *Ber.*, **81,** 68 (1948); **82,** 46 (1949); *J. Chem. Soc.*, 2013, 2440 (1949); 1833 (1956); 2681, 4163 (1957); 1577 (1958); *J. Am. Chem. Soc.*, **76,** 3502 (1954).

[16] H. Waldmann and E. Marmorstein, *Ber.*, **70,** 106 (1937).

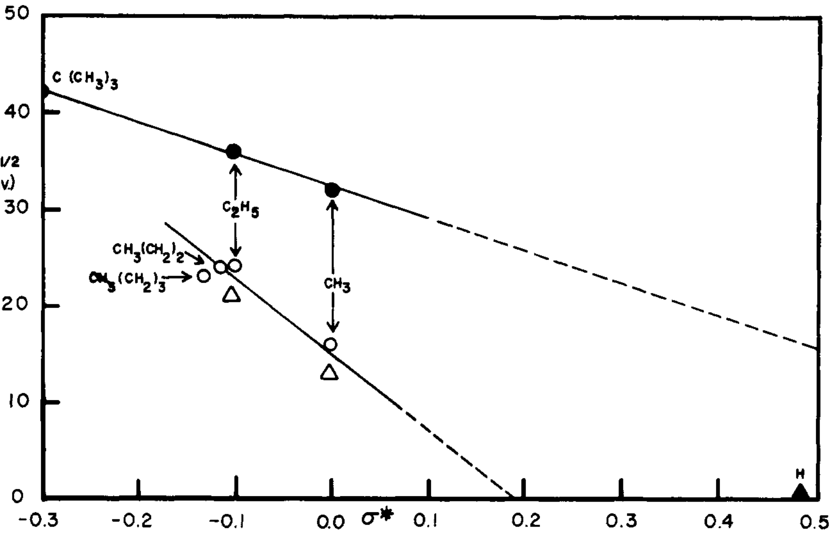

Fig. 1.—Plot of the difference between the polarographic half-wave reduction potential of an alkylanthracene and that of anthracene *vs.* Taft's polar substituent constant for the alkyl group. Solid circles are for 2-alkyl groups; open circles, 9-alkyl groups; open triangles, 1-alkyl groups.

ing acetylanthracenes by means of the regular Wolff–Kishner reaction conducted in a sealed tube. They found that 2-acetylanthracene could be reduced to 2-ethylanthracene directly, but that 1-acetylanthracene also gave 2-ethylanthracene under the same conditions. However, 1-ethylanthracene was obtainable by running the reduction on 1-acetylanthracene semicarbazone instead of on the ketone itself. Though we have not repeated their sealed tube reactions, we found that the Huang–Minlon procedure offered no such complications. Thus, 1-ethylanthracene was obtainable in good yield either from 1-acetylanthracene directly or *via* its semicarbazone. 2-Acetylanthracene could also be reduced to the 2-ethyl derivative.

Polarography was conducted using 0.1 *M* tetra-*n*-butylammonium iodide in 75% dioxane–25% water. Half-wave reduction potentials were reproducible to ±3 mv. Data concerning the average of runs at three different concentrations are presented in Table I. Observation of the table shows that all alkyl-substituted anthracenes studied were more difficultly electroreducible than anthracene itself, as would be consistent with electron donation by the alkyl group(s) to the aromatic ring and with a pertinent electrode process of electron transfer from the cathode to the π-system. As for the azulenes, $\Delta E_{1/2}$ is dependent upon the position of substitution. If conjugative power were the dominant factor in determining the size of $-\Delta E_{1/2}$, one would expect to find either the order (in $-\Delta E_{1/2}$) of 2- > 1- > 9- (as based on calculated free valences or autopolarizabilities of the positions[17] or as based on measured bathochromic shifts in the *p*-band of longest wave length, *cf.* Table I) or of 1- > 2- > 9- (as based on spectral shifts in the β-band) for isomeric alkylanthracenes. The observed order of 2- > 1- $\simeq$ 9- indicates a closer relationship between the effects of the 1- and 9-positions than would correspond to the operation of pure conjugative power.

In Fig. 1 are plotted values of $-\Delta E_{1/2}$ for the monoalkylanthracenes *vs.* Taft's polar substituent constants σ^* for the alkyl groups.[18,19] Excluding the point for anthracene itself (R = H), the data fit two straight lines within the accuracy of the experimental method. These lines may be represented by equation 1, where

$$\frac{n\mathfrak{F}}{2.303RT}\,\Delta E_{1/2} = \rho^*(\sigma^* - c) \qquad (1)$$

the factor $n\mathfrak{F}/2.303RT = 16.9$ when $\Delta E_{1/2}$ is expressed in volts and n is taken as 1,[7] ρ^* (obtained from the slope of the curve) equals +0.58 for the 2-alkyl series and +1.2 for the combined 1- and 9-alkyl series, and c is a constant which represents the intercept on the σ^* axis in each case. The closeness of polar effects for substituents in the 1- and 9- positions and the considerable difference between these effects and the coresponding ones for substituents in the 2-position are readily apparent. The fact that one does obtain linear σ^* plots for these monoalkyl derivatives may be taken as evidence that steric hindrance by the alkyl group to electroreduction (at least as measured by $E_{1/2}$) is negligibly small or completely missing. The change in R from 9-ethyl to 9-*n*-decyl without accompanying experimentally significant change in $-\Delta E_{1/2}$, as well as the very small effect on $-\Delta E_{1/2}$ (42 mv. < 1 kcal.) of even the bulky 2-*t*-Bu group, adds strong support to this proposal of a negligible steric effect.

Examination of data for the di- and polymethylanthracenes studied (Table I) shows that $-\Delta E_{1/2}$ is calculable within experimental error by means of equation 2, where n_β is the number of β-methyl substituents, n_m is the number of *meso*-methyl substituents, and $20\delta_m$ is an enhancement potential where δ_m equals one when a 9,10-dimethyl arrangement is present in the

$$-\Delta E_{1/2} = 33n_\beta + 16n_m + 20\delta_m \qquad (2)$$

molecule and equals zero in all other cases. Thus, good additivity prevails in $E_{1/2}$ as one introduces successive methyl groups into β- or *meso*-positions, except for the

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[17] B. Pullman and A. Pullman, "Progress in Organic Chemistry," Vol. 4, J. W. Cook, ed,, Butterworths, London, 1958, Chap. 2.

[18] No point for 9-decylanthracene is plotted, since the σ^* value for the 9-decyl group is unknown.

[19] R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13.

single step where one introduces the second *meso*-group, for which the change in $E_{1/2}$ is -36 mv. (as compared to -16 mv. when the first *meso*-group is introduced).

In searching for possible causes for this enhancement potential one can discard the possibilities of varying molecular symmetry, different sites of over-all reduction, irregularities in diffusion coefficients, and irregularities in mechanisms of reduction as likely factors. Thus, the 9,10-dimethyl, 2,3,6,7-tetramethyl, and 2,3,-6,7,9,10-hexamethyl derivatives all have the same symmetry (D_{2h} point group), but the second of these compounds does not exhibit enhancement in $-\Delta E_{1/2}$. From Table I one notes that all of the compounds have closely similar values for polarographic diffusion current constants, I_d. Thus, it is presumed that each compound gives one two-electron wave (just as anthracene itself does) and is thereby converted to a non-reducible 9,10-dihydroanthracene. In several cases, including anthracene and 9,10-dimethylanthracene, polarograms were checked as far as a cathode potential of -2.8 volts (where electrolysis of the solvent-electrolyte occurs) for the presence of a second wave. None was found. Except for 9-*n*-decylanthracene, a plot of I_d *vs.* molecular weight of the reducible molecule is nearly linear. Plots of

$$E \textit{ vs. } \log\left(\frac{i_d - i}{i}\right)$$

over the region of the reduction wave conform closely to straight lines of slope 0.0480 ± 0.0027 (average 0.0481).[20] Variations in $\Delta E_{1/2}$ do not follow variations in the slope of the log plot.

Aten, Büthker, and Hoijtink[21] have observed that addition of the first electron to anthracene in the aprotic solvent dimethylformamide occurs reversibly and is diffusion controlled. Katz, Reinmuth, and Smith,[22] using oscillopolarography, have likewise found a reversible one-electron first wave for anthracene in 95% dioxane-water. Aten and Hoijtink[23] and Katz, *et al.*[22] have commented on the difficulties of interpreting the single two-electron wave found in proton-active solvents (such as 75% dioxane–water used in our experiments). It is presumed, however, that the first step remains the same in all of these solvents and that it is followed by the irreversible addition of a second electron and two protons. It is not immediately apparent, therefore, whether the linear Taft relationships are to be ascribed to an equilibrium addition of the first electron, to a subsequent rate process, or to a combination of the two.

Matsen[24] has summarized a variety of correlations which have been predicted and/or discovered between $E_{1/2}$ of unsubstituted arenes and their physical and chemical properties. Thus, $E_{1/2}$ should bear a linear relationship to (a) the electron affinity of the molecule, (b) the ionization energy I_z of the molecule, (c) the frequency ν_p of the longest wave-length *p*-band in the ultraviolet absorption spectrum, and (d) the log methyl affinity of the molecule. The additivity and linear σ^* relationships observed in the present work imply that $E_{1/2}$ is, indeed, a linear function of electron affinity. Unfortunately, a direct comparison between $-\Delta E_{1/2}$ and $-\Delta I_z$, the change in the ionization potential, is not possible since data on I_z for alkylanthracenes seem not to be reported in the literature. The effect of single alkyl substituents and of increasing numbers of methyl substituents on the I_z of benzene as well as the effect of a methyl substituent on the I_z of naphthalene have been determined from photoionization[25] and/or charge-transfer spectral bands of molecular complexes.[26] In general, there exists an inverse relationship such that alkyl groups lower I_z, but raise $-E_{1/2}$.

For relationship (c) to hold one should find a direct proportionality between $-\Delta E_{1/2}$ and $-\Delta\nu_p$. Brief examination of the data in Table I shows that such a correlation does not exist, perhaps because substitution in the anthracene molecule affects the energy levels of both the ground state and the excited state in a somewhat irregular manner. A particularly striking example of this situation is exhibited by 2-*t*-butylanthracene where the alkyl group shows a small, though definite, hypsochromic effect on the *p*-band but a normal bathochromic effect on the β-band. For purposes of comparison, in Table I there are also included data on $-\Delta\nu_\beta$. Here a high degree of consistency and excellent additivity is apparent. Thus, the magnitude of $-\Delta\nu_\beta$ is relatively independent of the size of the R group, at least in the 2-alkyl (300–370 cm.$^{-1}$) and the 9-alkyl (620–670 cm.$^{-1}$) cases. For di- and polymethylanthracenes the bathochromic shift observed (in alkane solvent) is predictable to within 100 cm.$^{-1}$ by equation 7,

$$-\Delta\nu_\beta = 300n_\beta + 600n_m \qquad (7)$$

where n^β is the number of β-methyl groups and n_m is the number of *meso*-methyl groups.

Also in Table I are shown the mean methyl affinities of anthracene and those of our methylated anthracenes for which data have been reported by Binks, Gresser, and Szwarc.[27] It is clear that values of $-\Delta E_1/_2$ do not correlate directly with methyl affinities. Two important differences between the two processes of electron addition and methyl addition may be noted. First, the electrically neutral methyl radical should lead to a negligible polarization of the aromatic molecule, in contrast to the situation believed to prevail in the vicinity of the cathode.[7,28] Second, occupation of a *meso*-position by methyl is considered to block completely (or nearly so) the addition of a methyl radical to that position but not to block electroreduction of the central ring.

Experimental[29]

9-Alkylanthracenes.—9-*n*-Propyl-,[30] 9-*n*-butyl-,[30] and 9-*n* decylanthracenes[31] were prepared in the same manner as used for

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[20] L. Meites and Y. Israel, *J. Am. Chem. Soc.*, **83**, 4903 (1961).

[21] A. C. Aten, C. Büthker, and G. J. Hoijtink, *Trans. Faraday Soc.*, **55**, 324 (1959).

[22] T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962).

[23] A. C. Aten and G. J. Hoijtink, *Zeit. Phys. Chem.*, **21**, 192 (1959).

[24] F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956); "Proceedings of the Third Conference on Carbon," Pergamon Press, Inc., New York, N. Y., 1959, pp. 21-26.

[25] W. C. Price, R. Bralsford, P. V. Harris, and R. G. Ridley, *Spectrochim. Acta*, **14**, 45 (1959).

[26] G. Briegleb and J. Czekalla, *Zeit. Elektrochem.*, **63**, 6 (1959).

[27] J. H. Binks and M. Szwarc, *J. Chem. Phys.*, **30**, 1494 (1959); J. H. Binks, J. Gresser, and M. Szwarc, *J. Chem. Soc.*, 3944 (1960).

[28] P. J. Elving and B. Pullman, "Advances in Chemical Physics," Vol. 3, I. Prigogine, ed., Interscience Publishers Inc., New York, N. Y., 1961, pp. 1-31.

[29] Melting points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

[30] Prepared by Miss Huei-ying Sun.

[31] Prepared by Miss Sajida Kareem.

9-ethylanthracene[32] except that refluxing was conducted for 18–24 hr., the residue from evaporation of the dried organic layer was recrystallized from ethanol (instead of being distilled), and Celite-Alcoa F-20 alumina (1:1 v./v.) was used for chromatography. Further recrystallization from ethanol gave fluorescent needles in yields of 36% (m.p. 64–65°), 40% (m.p. 48–49°), and *ca.* 5% (m.p. 42.5–43.5°), respectively. The *n*-decyl derivative was purified further (for analysis and polarography) by rechromatography on alumina only and then two recrystallizations from methanol, m.p. 42.5–43°.

Anal. Calcd. for $C_{24}H_{30}$: C, 90.50; H, 9.50. Found: C, 90.50; H, 9.58.

2-*t*-Butylanthraquinone.—A mixture of 14.1 g. of crude 2-(4-*t*-butylbenzoyl)benzoic acid[33] (m.p. 123–132°) and 58 g. of polyphosphoric acid was stirred for 50 min. at 150°.[13] The hard black mass which formed on addition of ice was air-dried and sublimed at 150–160° (1 mm.) to give 9.3 g. (71%) of yellow needles of product, m.p. 103–104° after one recrystallization from ethanol.

2-*t*-Butylanthracene.—To a refluxing mixture of 6.9 g. of the preceding quinone, 100 ml. of pyridine, and 30 g. of zinc dust was added dropwise 40 ml. of 80% acetic acid over a period of 4 hr. The green color, which formed immediately, gradually disappeared as reaction proceeded. After 9 hr. the liquid was decanted into 3.5 l. of water and the yellow precipitate (7.0 g.) which formed was collected, dried in air, and sublimed at 180° (1 mm.). The yellow sublimate (1.4 g., 23%) was recrystallized from ethanol to give white leaves, m.p. 145.5–146.5°, showing strong purple fluorescence in ultraviolet light.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.83.

2-Methylanthracene.—A mixture of 2.23 g. of 2-methylanthraquinone (Distillation Products Industries, yellow label), 20 ml. of pyridine, and 7.8 g. of zinc dust was refluxed and stirred over a period of 2 hr., while 20 ml. of 80% acetic acid was added dropwise, and for 8 hr. longer. The filtered mixture was evaporated *in vacuo* and the brown residue was treated with 50 ml. of water, collected by filtration, washed with water, boiled with 40 ml. of concd. hydrochloric acid for 5 min., washed with water, and dried. Sublimation at 190° (0.3 mm.) gave 1.0 g. of yellow product. A solution of this product in 500 ml. of petroleum ether (30–60°) was passed through a column (22 × 2.1 cm.) of Alcoa F-20 activated alumina and the adsorbate was eluted with an additional l. of solvent. The residue from evaporation of the effluent was recrystallized from ethanol, yield 0.75 g. (39%) of white flakes, m.p. 200–202°.

The same yield was obtained if the intermediate was boiled with 25 ml. of 5% sodium hydroxide instead of with hydrochloric acid. A yield of 21% was obtained if the amounts of all reactants other than 2-methylanthraquinone were halved.

1-Methylanthracene.—To an ethereal solution of triphenylphosphine methylide,[34] prepared from 58.9 g. (0.16 mole) of triphenylmethylphosphonium bromide (Aldrich Chemical Co.) and excess phenyllithium[7] was slowly added 10.7 g. (0.15 mole) of freshly distilled crotonaldehyde. The mixture was agitated in a pressure bottle at 65° for 5 hr. and then cooled to 3° in a cold room where it was filtered through a layer of Celite and the filtrate was washed with aqueous sodium bisulfite solution and then water. The moist organic layer (850 ml., ether–benzene) resulting from combination of the filtrate and washings was refluxed with 8.0 g. (0.05 mole) of purified 1,4-naphthoquinone for 50 hr. The black, tarry residue from evaporation of the solution was extracted with boiling methanol. Concentration and cooling of the extract deposited 1.9 g. of brown crystals, m.p. 162–165°. Vacuum sublimation and two recrystallizations from methanol gave faintly pink leaflets of 1-methylanthraquinone, m.p. 170.5–171.5° (reported[35] m.p. 171–172°).

Reduction of 1.61 g. of the purified 1-methylanthraquinone by a method similar to that used for the 2-isomer, except that sublimation was conducted at 80° (1 mm.) and chromatography was omitted, gave 0.34 g. (25%) of white hydrocarbon, m.p. 84–85°, after one recrystallization from 30–60° petroleum ether.

Clar Reduction of Anthrone. Clar reduction of anthrone (under conditions which gave a 21% yield of 2-methylanthraquinone, *vide supra*) gave a 14% yield of anthracene, m.p. 212–213°, undepressed on admixture with an authentic sample.

1-Ethylanthracene. A mixture of 1- and 2-acetylanthracenes[36] was separated by fractional crystallization from benzene. A mixture of 2.2 g. of the 1-isomer (m.p. 101–108°), 10 ml. of diethylene glycol, 1.5 ml. of hydrazine hydrate, and 1.5 g. of potassium hydroxide was heated and processed essentially as per previously published directions[37] for the Huang–Minlon reaction. The crude product was chromatographed using benzene and alumina. Evaporation of the effluent left 2.03 g. of hydrocarbon, converted to 1-ethylanthracene picrate, m.p. 124.5–126° after recrystallization from ethanol, yield 2.85 g. (66%); reported[16] 1-ethylanthracene picrate, m.p. 126–127°; 2-ethylanthracene picrate, m.p. 92°. The picrate was dissociated chromatographically and the recovered hydrocarbon was distilled *in vacuo* and recrystallized from pentane (by cooling the solution in a Dry Ice bath) to give fine faintly yellow crystals, m.p. 32.0–32.6° (reported[16] 33–34°).

Repetition of the Huang–Minlon reaction using 2 g. of 1-acetylanthracene semicarbazone[16] gave 1.75 g. of brown, crude liquid hydrocarbon, converted to a picrate, m.p. 121–123°, undepressed on admixture with the preceding picrate.

2-Ethylanthracene.[39]—Huang–Minlon reaction[38] on 12 g. of 2-acetylanthracene (m.p. 185–186°, *vide supra*), 18 ml. of hydrazine hydrate, 7.9 g. of sodium hydroxide, and 125 ml. of triethylene glycol gave 8.4 g. of crude yellow product. On recrystallization (twice, using charcoal) from ethanol there resulted pale yellow leaves of hydrocarbon, m.p. 148–150°; reported[16] yellow crystals, m.p. 150–151°, from regular Wolff–Kishner reduction.

Dimethylanthracenes.—2,3-Dimethylanthraquinone was prepared by the method of Allen and Bell.[12] In an adaptation of this procedure, a solution of 54 g. (0.5 mole) of *p*-benzoquinone and 136 g. (2 moles) of isoprene in 300 ml. of ethanol was stirred in an autoclave at 75°. A solution of the entire adduct, 102 g. of tan prisms, in 1200 ml. of 5% ethanolic potassium hydroxide was aerated for 96 hr. Filtration of the dark red-brown solution gave a brown precipitate which was recrystallized from acetic acid (yield 25 g.) and then sublimed at 160–200° (0.1 mm.) to give 13 g. of yellow mixed dimethylanthraquinones, m.p. 170–220°. Fractional crystallization of 10 g. of this mixture from a total of 5 l. of ethanol gave 7.3 g. of 2,6-dimethylanthraquinone, m.p. 235–236° (reported m.p. 236–237°,[39] 242°[40]) and 2.4 g. of 2,7-dimethylanthraquinone, m.p. 162–164° (reported m.p. 162°,[39] 170°[40]). Clar reduction of 2,3-dimethylanthraquinone, as well as the 2,6- and 2,7-isomers, was conducted in the manner used with 2-methylanthraquinone, to give 33–39% yields of white crystals of the respective dimethylanthracenes; m.p.'s 248–252°, 230–235°, and 222–225° (without recrystallization).

9,10-Dimethylanthracene was prepared by methylation of disodio-[41] or dilithionaphthalene[42] with methyl iodide and subsequent dehydrogenation of the intermediate first with sulfur and then with copper powder, m.p. 180–181° after repeated recrystallizations from benzene.

Trimethylanthracenes.—Following published directions[14] for conversion of anthraquinone to anthrone, but using 0.01–0.05*M* quantities of starting 2,3- and 2,6-dimethylanthraquinones instead, there were obtained 54–62% yields of yellow 2,3- and 2,6-dimethylanthrones, m.p.'s 157–158° and 149–150°, respectively, after recrystallization from glacial acetic acid. These dimethylanthrones were treated with methylmagnesium iodide and processed in the manner used for preparation of 9-ethylanthracene from anthrone, except that the residues from evaporation of the organic layers were dissolved in 60–90° petroleum ether, these solutions were passed through short columns of Alcoa F-20 alumina, and the effluents plus column washings (with same solvent) were evaporated to dryness; yields of yellow products, 40% for 2,3,9-trimethylanthracene, m.p. 117–120°, and 94% for 2,6,9-

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[32] L. H. Klemm, D. Reed, L. A. Miller, and B. T. Ho, *J. Org. Chem.*, **24**, 1468 (1959).

[33] G. F. Lewenz and K. T. Serijan, *J. Am. Chem. Soc.*, **75**, 4087 (1953).

[34] G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

[35] "Elsevier's Encyclopaedia of Organic Chemistry," Vol. 13, E. Josephy and F. Radt, ed., Elsevier Publishing Co., Inc., New York, N. Y., 1946, p. 400.

[36] French Patent, 633,071 (April 22, 1927), to I. G. Farbenindustrie, A. G. [*Chem. Zentr.*, **I**, 2209 (1928)].

[37] L. J. Durham, D. J. McLeod, and J. Cason, *Org. Syntheses*, **38**, 34 (1958).

[38] Huang–Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

[39] F. Mayer and H. Günther, *Ber.*, **63B**, 1455 (1930).

[40] G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2203 (1929).

[41] G. M. Badger, F. Goulden, and F. L. Warren, *J. Chem. Soc.*, 18 (1941).

[42] B. M. Mikhailov, *Akad. Nauk SSSR, Inst. Organ. Khim. Sintezy Organ. Soedin. Sb.*, I, 54 (1950) [*Chem. Abstr.*, **47**, 8005a (1953)].

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA FOR SOME ALKYL-SUBSTITUTED ANTHRACENES[a]

Substituent(s) on anthracene	λ_{max}[b] mμ	Log ε	λ_{max} mμ	Log ε	λ_{max}[b] mμ	Log ε	λ_{max} mμ	Log ε	λ_{max} mμ	Log ε	λ_{max} mμ	Log ε	λ_{max} mμ	Log ε	λ_{max} mμ	Log ε
1-Ethyl	(251	5.15)	254	5.23	311	3.12	326	3.48	341	3.77	358	3.93			376	3.89
2-Ethyl	246	5.00	254	5.37	(310	3.10)	323	3.41	339	3.65	356	3.80			374	3.75
2-*t*-Butyl	246	5.03	254	5.39	(308	3.11)	322	3.42	337	3.67	354	3.82			372	3.77
9-Ethyl	248	4.98	256	5.33	316	3.07	331	3.48	347	3.81	364	4.03	378	3.74	383	4.03
9-*n*-Propyl	248	4.98	256	5.32	316	3.06	331	3.47	347	3.82	364	4.03	378	3.74	383	4.03
9-*n*-Decyl	248	4.93	256	5.27	316	3.07	331	3.45	347	3.79	365	4.01	379	3.72	383	4.01
2,6-Dimethyl	248	5.00	256	5.38			333	3.54	350	3.61	358	3.65			378	3.66
2,7-Dimethyl	248	4.98	256	5.35			329	3.42	340	3.62	356	3.74			374	3.62
2,6,9-Trimethyl	251	4.98	260	5.41			338	3.51	352	3.68	368	3.72			386	3.76

[a] Solvent, isoöctane. [b] Data in parentheses are for shoulders, not true maxima.

trimethylanthracene, m.p. 77–78°. The latter compound was recrystallized thrice from ethanol to give pale yellow, strongly fluorescent (purple) leaflets, m.p. 86.5–87.5°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.43; H, 7.55.

Tetra- and Hexamethylanthracenes.—Samples of these compounds[43] were kindly supplied by Dr. Enno Wolthuis for use in these studies.

Polarography.—Only analytically pure hydrocarbons were used in polarographic studies. Such samples were prepared by first recrystallization of the available compounds to narrow melting range (1–2°), then (in many cases) chromatography, and finally at least two recrystallizations from an appropriate solvent within 2 weeks of running the polarogram. Melting ranges on the compounds used were no greater than 1°. The polarographic apparatus and procedure were the same as previously described.[7] Each compound was run at three different concentrations (*ca.* 3.5, 6.3, and 8.3 × 10^{-4} *M*) in succession. Several compounds were run from time to time over a period of more than one year and with occasional repurification. For each compound the various values of $E_{1/2}$ found were within ± 3 mv. of the average value. All polarograms were regular in shape. Calculations were made by taking the instantaneous current as the maxima of the pen oscillations. The diffusion current i_d was determined for the most dilute solution of the hydrocarbon and was calculated as $^6/_7$ of the vertical distance between the residual current (a straight line extended) and the limiting current (represented by a line parallel to the one for the residual current). Polarographic data are given in Table I.

Ultraviolet Spectra.—Ultraviolet absorption spectra of those hydrocarbons for which such data were not readily available were determined in spectral grade isoöctane using a Cary Model 11 spectrophotometer. Data on the absorption maxima are presented in Table II.

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[43] E. Wolthuis, *J. Org. Chem.*, **26**, 2215 (1961).

Halogenation with Copper(II). I. Saturated Ketones and Phenol

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Received September 17, 1962

A procedure for halogenation of enolizable compounds using copper(II) chloride or bromide in dimethylformamide is described. Methyl ethyl ketone yields 55–70% 3-chlorobutanone, methyl cyclopropyl ketone yields both chloromethyl and dichloromethyl cyclopropyl ketones, propiophenone gives an excellent yield of α-chloropropiophenone, and phenol leads to *o*- and *p*-chlorophenols, in a ratio (1:6) substantially different from that of other chlorination methods, along with some 2,4-dichlorophenol. A convenient test for relative reactivities of enols and enolizable compounds is also included.

Copper(II) reactions are of great interest because of such organic reactions as the oxidative dimerization of acetylenes and such biochemical reactions as the oxidation of tyrosine by the copper-containing enzyme, tyrosinase. Copper(II) halogenation was selected as a possible model for these oxidations. An examination of the reaction with a variety of substrates is reported in this paper and the succeeding one.[3–5]

In 1897, Ley[6] reported that the conductivity of copper(II) chloride solutions in acetone increased with time. Kohlschütter[7] noted the formation of copper(I) chloride from these solutions, interpreted this as resulting from the disappearance of chlorine derived from reversible dissociation of copper(II) chloride into copper(I) chloride and chlorine, and suggested that the solution might be useful as a chlorinating agent. Others[8,9] have come across the same phenomenon. Although the formation of chloroacetone was an important facet of the Meerwein reaction of aryldiazonium ions with alkenes, it was ignored as a side reaction.[10] In one case, for example, a 65% yield of chloroacetone was obtained from the reaction of 2,4-dichlorobenzene diazonium

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[2] Taken in part from the (a) M.S. thesis of W. J. Cole, June, 1959; (b) Ph.D. thesis of G.-S. Wu, January, 1962; (c) B.S. thesis of G. Meisters, June, 1958.

[3] E. M. Kosower and G.-S. Wu, *J. Org. Chem.*, **28**, 633 (1963).

[4] Grateful acknowledgment is made for support from the Air Force Office of Scientific Research through contract AF 49 (638)-282 and to the National Institutes of Health under grant E-1608.

[5] (a) Presented in part at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960, Abstracts 138, 7-P; (b) The oxidation of phenols by copper–amine complexes and oxygen has been reported by W. Brackman and E. Havinga, *Rec. trav. chim.*, **74**, 937, 1021, 1070, 1100, 1107 (1955).

[6] H. Ley, *Z. physik. Chem.*, **22**, 83 (1897).

[7] V. Kohlschütter, *Ber.*, **37**, 1169 (1904).

[8] H. Jones and W. Veazey, *Z. physik. Chem.*, **61**, 641 (1908).

[9] P. Schulz "Verhalten von Salzen in Aceton," Dissertation, Giessen, 1901; cited by A. Nauman, *Ber.*, **37**, 4328 (1904).

[10] H. Meerwein, E. Buchner, and K. van Emster, *J. prakt. Chem.*, **260**, 248 (1939).