Tritan, tritanol, benzophenone, and biphenyl were caught in the ice trap, but isobutylene was found in all containers including the liquid nitrogen trap. After rinsing the column with dry benzene, the solution of pyrolysate in the ice trap was made up to a total volume of 500 ml. The solid products caught in the ice trap were chromatographed on alumina as described previously, and were analyzed by gas chromatography with columns cited earlier. The remaining cold traps were warmed and purged with helium through a gas scrubber to dissolve residual isobutylene in benzene. All solutions were combined and made up to a volume of 500 ml. with benzene. Isobutylene proved more difficult to determine, but with meticulous effort a modification of the Fritz and Hammond method[43] was developed which gave reproducible results. Bromine was generated in an evacuated system by introducing 5 ml. of 6 *N* sulfuric acid into the bromination flask containing a known quantity of standardized potassium bromate solution (*ca.* 15% excess). After 3 min. a sample (20-ml. aliquot) from the ice trap solution was introduced into the dark bromination flask. Enough benzene was added to bring the volume to 40 ml. and an additional 20 ml. of acetic acid was introduced. The mixture was stirred and shaken vigorously for 9 min. and 15 ml. of 20% potassium iodide solution was added. After another minute, vacuum was alleviated in the system, and the excess free iodine was titrated at once with standard sodium thiosulfate solution to a starch end point. Triplicate runs were performed on aliquots from both the ice traps and the combined contents of the other cold traps. In several determinations an average yield of 86% was obtained for isobutylene. Duplicate blanks were also run in benzene to check the fading end point and to establish the small correction factor for the end point observed in titration of the aliquot from the ice trap solution. Moreover, to ascertain the reliability of the method a sample of 1-heptene (98% pure by gas chromatography) served as a test substrate. An average recovery of 97% was realized. To complete the determination, a sample of the pyrolysate was treated with bromine and 1,2-dibromo-2-methylpropane was actually isolated from the mixture. Comparison of the dihalide with the bromination product from pure isobutylene showed them to be identical.

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[43] J. L. Fritz and G. S. Hammond, "Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 275.

Polarographic Reduction of Some Alkyl-, Alkylene-, and Polymethylnaphthalenes[1]

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Polarography was conducted on naphthalene and twenty-seven substituted naphthalenes (bearing monoalkyl, dimethyl, trimethyl, allyl, and alkylene substituents) in 0.1 *M* tetra-*n*-butylammonium iodide in 75% dioxane–water. Using naphthalene 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 derivatives is positive, consistent with a decrease in ease of electroreduction due to the substituent(s). For the monoalkyl derivatives plots of $-\Delta E_{1/2}$ *vs.* σ^*, the polar substituent constant, for the 1- and for the 2-series are linear. There is no indication of a steric effect due to the bulkiness of the alkyl group. For dimethylnaphthalenes approximate additivity in $-\Delta E_{1/2}$ exists, except for the cases of the 1,8- and 2,3-isomers, where an enhancement potential must be included in order to retain additivity. For trimethylnaphthalenes, acenaphthene, and hexahydropyrene, $-\Delta E_{1/2}$ is an additive function of the effects of the individual substituents and the over-all geometric pattern of substitution.

In a previous paper[3] data were reported on the polarographic reduction of some alkyl- and polymethylanthracenes in 0.1 *M* tetra-*n*-butylammonium iodide in 75% dioxane–25% water as solvent–electrolyte. The present paper concerns an extension of this study to polarographic reduction of alkyl-, allyl-, alkylene-, and polymethylnaphthalenes.

Used in these studies were the parent naphthalene itself, as well as nine monoalkyl, the two allyl, all of the ten possible dimethyl, four trimethyl, and two alkylene derivatives. Six of these compounds were synthesized by new or modified procedures. Thus, the allylnaphthalenes were obtained by coupling the naphthylmagnesium bromides with allyl bromide (62% crude yield for 1-isomer). Catalytic hydrogenation of the allyl substituents occurred readily using glacial acetic acid and platinum to form the *n*-propylnaphthalenes. 1-*t*-Butylnaphthalene resulted in 13% yield from dehydration (with alumina at 380°) and subsequent dehydrogenation of the carbinol obtained by interaction of α-tetralone and *t*-butylmagnesium bromide. Chloromethylation of 1,8-dimethylnaphthalene produced 1-chloromethyl-4,5-dimethylnaphthalene, hydrogenolyzable to 1,4,5-trimethylnaphthalene in good yield.

Polarography was conducted in the same manner as employed for the anthracenes. Polarograms, obtained for three different concentrations of each hydrocarbon, showed the presence of only one wave out to a cathode potential of *ca.* −2.8 v. (*vs.* the saturated calomel electrode), where the solvent–electrolyte undergoes reduction. In contrast to the regular waves found for the anthracenes the upper portions of the sigmoid-shaped waves for the naphthalenes increased linearly with increasing E, the applied cathode potential, instead of levelling off or paralleling the slightly rising line for the residual current. Onset of electrolysis of the solvent–electrolyte prevented checking this upper linear portion over a sufficiently extensive range in E so as to allow determination of the true asymptotic diffusion current, i_d. Under these circumstances an approximate diffusion current, i_d' (where $i_d' < i_d$), was measured (*cf.* Experimental) and used in calculations. Polarographic diffusion current constants, I_d', average values (reproducible to ±3 mv.) of $-E_{1/2}$, and values of $-\Delta E_{1/2}$ (the difference between $-E_{1/2}$ for a substituted naphthalene and that for naphthalene itself as a standard of comparison) are presented in Table I. On the basis of the fact that values of I_d' do not vary markedly from one compound to another it is presumed that all of the waves correspond to the uptake of two electrons (as found by coulometry for naphthalene)[4] to produce 1,4-dihydronaphthalenes, compounds which should not be

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[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under contract AF 49(638)-473. It is paper V in the series on polarography of aromatic hydrocarbons. For paper IV see ref. 3.

[2] Research Associate, 1959–1962.

[3] L. H. Klemm, A. J. Kohlik, and K. B. Desai, *J. Org. Chem.*, **28**, 625 (1963).

[4] L. H. Klemm, C. D. Lind, and J. T. Spence, *ibid.*, **25**, 611 (1960).

TABLE I

POLAROGRAPHIC AND OTHER DATA FOR SOME ALKYL-, ALLYL-, AND ALKYLENE-SUBSTITUTED NAPHTHALENES

Substituent(s) on naphthalene	Half-wave reduction potential, $-E_{1/2}$ (v. *vs.* S.C.E.)	$\frac{i_d'}{Cm^{2/3}t^{1/6}}$ (μamp. mmole^{-1}-l. mg.$^{-2/3}$ sec.$^{1/2}$)	$\Delta E_{1/2}$[a] (mv.)		$\Delta\nu$[c] (cm.$^{-1}$)		Mean methyl affinity,[f] k_2/k_1	Picrate stability constant[g] (l. mole^{-1})
			Found	Calcd.[b]	Most intense central band[d]	Longest wave length α-band[e]		
None	2.437	3.71	0	0	0	0[l]	9.4	1.13
1-Methyl	2.458	3.87	21	19	900	300[l]	8.1	1.47
1-Ethyl	2.470	3.24	33	(33)[j]	900	300[l]	8.0	1.41
1-*n*-Propyl	2.471	3.24	34	(34)[k]	1000	300[l]		
1-*t*-Butyl	2.493	3.10	56		800	200		
1-Allyl	2.447	3.46	10		900	300		
2-Methyl	2.460	3.06	23	21	200	800[l]	13.0	1.76
2-Ethyl	2.468	3.05	31		200	700[m]	8.9	1.45
2-*n*-Propyl	2.471	3.03	34		200	800		
2-*i*-Propyl	2.476	2.97	39		−100	800		1.35
2-*t*-Butyl	2.482	2.67	45		−100	600		1.16
2-Allyl	2.444	3.13	7		0	800		
1,2-Dimethyl	2.479	3.01	42	40	1500	1100[l]		
1,3-Dimethyl	2.483	3.19	46	40	1100	1100[l]		
1,4-Dimethyl	2.471	3.28	34	38	1800	1000[l]		
1,5-Dimethyl	2.475	3.99	38	38	1400	1000[l]	5.8	
1,6-Dimethyl	2.476	3.03	39	40	900	1100[l]		
1,7-Dimethyl	2.469	2.86	32	40	800	1100[l]		
1,8-Dimethyl	2.521	3.69	84	38	1400	1100[l]		
2,3-Dimethyl	2.501	2.87	64	42	600	700[l]	10.5	
2,6-Dimethyl	2.476	3.22	39	42	−100	1300[l]	13.9	
2,7-Dimethyl	2.485	3.09	48	42	100	1000[l]		
1,3,7-Trimethyl	2.496	3.03	59	56	800	1600[n]		
1,4,5-Trimethyl	2.529	3.23	92	99	2200	1600[n]		
2,3,5-Trimethyl	2.515	2.67	78	74	1100	700		
2,3,6-Trimethyl	2.523	2.81	86	88	600	1300		
1,8-Dimethylene[h]	2.549	3.57	112	(112)[j]	1800	1000[l]	4.7	
1,8;4,5-Bis(trimethylene)[i]	2.66	. . .	220	(220)[k]	2700	1800		

[a] Compared to $E_{1/2}$ for naphthalene taken as a standard. [b] By means of equations 2 and 3 in text, where δ_j is taken as zero for mono- and disubstituted naphthalenes only. [c] Shift from corresponding band for naphthalene (measured in alkane or cyclohexane solvent) taken as a standard of comparison. [d] In naphthalene this band falls at 274.5 mμ (36,500 cm.$^{-1}$). It is designated as an α'-band (E. Clar, "Aromatische Kohlenwasserstoffe," Springer Verlag, Berlin, 1952, p. 134) and as a ^1L_a-band [J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949)]. [e] In naphthalene this band falls at 311 mμ (32,200 cm.$^{-1}$). It has been designated as a ^1L_b-band by Platt (footnote *d*). [f] See ref. 12. [g] See ref. 15. [h] Common name, acenaphthene. [i] Common name, 1,2,3,6,7,8-hexahydropyrene. [j] The value calculated for acenaphthene is based on the assumption that acenaphthene ≃ 1,8-diethylnaphthalene. [k] The value calculated for hexahydropyrene is based on the assumption that hexahydropyrene ≃ 1,4,5,8-tetra-*n*-propylnaphthalene. [l] Solvent, isooctane; American Petroleum Institute, "Catalog of Ultraviolet Spectral Data." [m] Solvent, cyclohexane; Ramart-Lucas and M. J. Hoch, *Bull. soc. chim.* (France), [5] **19**, 422 (1952). [n] Solvent, petroleum ether; E. Heilbronner, U. Fröhlicher, and P. A. Plattner, *Helv. Chim. Acta*, **32**, 2479 (1949).

further electroreducible under the experimental conditions used. If the electroreducible and thermodynamically more stable 1,2-dihydronaphthalenes had been formed as intermediates the reduction wave should have involved uptake of four electrons.[5] In Fig. 1, I_d' is plotted *vs.* the total number of carbon atoms in the side chain(s) on the naphthalene ring. It is apparent that compounds containing α-substituents only have higher values of I_d' than do those of the same molecular weight bearing one or more β-substituents. From the polarogram for the most dilute solution of each hydrocarbon, a plot (over the region of the reduction wave) was made of E *vs.* $\log\left[\frac{(i_d' - i)}{i}\right]$. All plots conformed closely to straight lines of slope 0.0519 ± 0.0078 (average 0.0514).[6]

Observation of Table I shows that all of the substituted naphthalenes studied were more difficultly electroreducible than naphthalene itself. For the monoalkyl- and allylnaphthalenes (except the *t*-butylnaphthalenes) there is no experimentally significant difference between $-\Delta E_{1/2}$ for corresponding 1- and 2-isomers. Again, as in the case of alkylanthracenes, relative conjugative power of the aryl group would thus seem to be of little or no pertinence in determining electroreducibility (as measured by $E_{1/2}$) of an alkyl-substituted alternant arene. Comparison of data for methyl or ethyl derivatives in both arene series shows the order 2-alkylanthracene > 2-alkylnaphthalene ≃ 1-alkylnaphthalene > 9-alkylanthracene ≃ 1-alkylanthracene in $-\Delta E_{1/2}$ from the corresponding parent arene.

In Fig. 2 are plotted values of $-\Delta E_{1/2}$ for the monoalkylnaphthalenes *vs.* Taft's polar substituent constants σ^* for the alkyl groups.[7] Excluding the point for naphthalene itself (R = H), the data fit two straight lines within the accuracy of the experimental method. As with the alkylanthracenes these lines fit equation 1,[3]

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(5) It is possible that i increases following the reduction wave due to partial conversion of 1,4-dihydronaphthalenes to 1,2-dihydronaphthalenes at the high negative potentials involved.

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

(7) R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13.

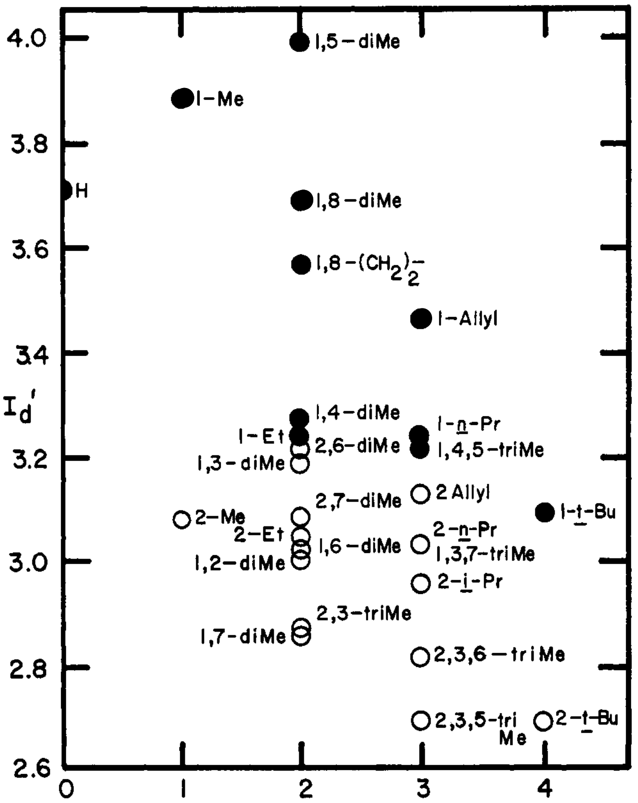

Fig. 1.—Plot of apparent polarographic diffusion current constant, I_d', *vs.* the total number of carbon atoms in the side chain(s) of alkyl- and alkylene-substituted naphthalenes.

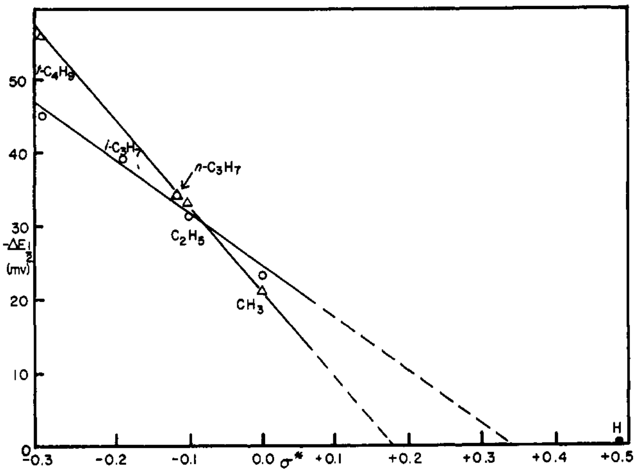

Fig. 2.—Plot of the difference between the polarographic half-wave reduction potential of an alkylnaphthalene and that of naphthalene *vs.* Taft's polar substituent constant for the alkyl group. Circles are for 2-alkyl groups; triangles for 1-alkyl groups.

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

where (if n is taken as 1) ρ^* equals +1.2 for the 1-alkylnaphthalene series (the same as for the combined 1- and 9-alkylanthracene series) and equals +1.9 for the 2-alkylnaphthalene series [as compared to +1.6 for the second wave of 1-alkyl-1-(2-naphthyl)ethenes[8] and to +0.58 for the 2-alkylanthracene series], and c is a constant which represents the intercept on the σ^* axis in each case. The considerable difference between the 2-alkylanthracene series ($c \simeq +1.0$, *i.e.*, $c > \sigma^*$ for H), on the one hand, and the four other series (c varies fron +0.18 to +0.34, *i.e.*, $c < \sigma^*$ for H), on the other, i readily apparent. The fact that ρ^* has a positive valu in every case is consistent with the action of alky groups in increasing electronic charge in the π-systen and, hence, in making more difficult the addition of a electron during the polarographic process.[9]

From Table I one notes that the allyl substituen shows a much smaller $-\Delta E_{1/2}$ than does the corresponding n-propyl (or even the methyl) group. It i clear that the low value in $-\Delta E_{1/2}$ cannot result fron the transformation, allyl (unconjugated) → propeny (conjugated), for then the product should exhibit tw waves (in contrast to only one found) with the firs wave at $-E_{1/2} < 2.2$ v.[10] and I_d' should be nearly twic as large as found (corresponding to the uptake of fou electrons rather than of two). A σ^* value for the ally group is not available from Taft's tables.[7] If the ally group were to fit the Taft relationship of Fig. 2 it shoul have $\sigma^* = +0.18 \pm 0.1$, a value consistent with that o +0.13 reported for the 1-(2-butenyl) group.

In two cases, those of 2-ethyl- and 2-isopropyl naphthalenes, $E_{1/2}$ can be compared with $E_{1/2}''$ for th second reduction wave of the corresponding conjugate 2-alkenylnaphthalene, previously investigated unde the same experimental conditions.[8] The first wave fo a conjugated 2-alkenylnaphthalene is believed to relat to transformation a, 2-alkenylnaphthalene → 2 alkylnaphthalene; and the second wave to concer transformation b, 2-alkenylnaphthalene → 2-alkyl dihydronaphthalene. Transformation b is commonl visualized as occurring in two discrete steps at $E_{1/2}''$ *viz.* a followed by c, 2-alkylnaphthalene → 2-alkyl dihydronaphthalene. If this concept is strictly correct then $E_{1/2}''$ should be determined by the energeticall less facile conversion c and one should find $E_{1/2} = E_{1/2}''$. Comparison shows that such relationship i approximately, but not exactly, true. In both case $-E_{1/2}''$ is 6–8 mv. greater than $-E_{1/2}$. This discrepancy is slightly larger than the experimental erro of ±3 mv. in the measurements. Although the exac reason for this discrepancy is not clear at this time, on possible explanation is that the addition of a third electron to the 2-alkenylnaphthalene may, on the average start to occur slightly before addition of the secon proton has been completed.

For various methylated naphthalenes one can represent $-\Delta E_{1/2}$ by equation 2, where n_α is the number o

$$-\Delta E_{1/2} = 19n_\alpha + 21n_\beta + \delta_j \qquad (2$$

α-substituents, n_β is the number of β-substituents, δ is a potential associated with the geometric arrangemen of substituents (*e.g.*, j = 137 for 1,3,7-trisubstitution) and all values are expressed in units of millivolts. Although δ_1 and δ_2 (for the monomethyl derivatives) ar presumed to be zero, coefficients of 19 and 21 (rathe than the measured values of 21 and 23, respectively are used in equation 2 in order to give the best fit of a data. Values of δ_j may be considered as discrepancie from additivity in $-\Delta E_{1/2}$ (as based solely on the tota

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

(9) It is not clear at this time whether the linear Taft relationships are t be ascribed to an equilibrium addition of the first electron, to a subsequer rate process, or to a combination of the two.

(10) Predicted from the observation that $-E_{1/2}$ = 2.164 v. for 1-methyl- (2-naphthyl)ethene (see ref. 8).

mbers of α- and β-substituents). In order to as-
rtain the magnitudes of δ_j for dimethylnaphthalenes,
e calculated values shown for these compounds in
ble I are based on the approximation that $\delta_j = 0$.
omparison of found and calculated values for $-\Delta E_{1/2}$
en shows that the 1,2-, 1,4-, 1,5-, 1,6-, 2,6- and 2,7-
omers appear to be normal ($\delta_j = 0 \pm 6$), while the 1,7-
omer shows a slight repression potential ($\delta_{17} = -8$)
d the 2,3- and 1,8-isomers show large enhancement
tentials ($\delta_{23} = +22$; $\delta_{18} = +46$). The same en-
ncement potential for the 1,8-disubstitution pattern
observed for acenaphthene where the value of $-\Delta E_{1/2}$
ay be rationalized in terms of the relationship 1,8-
methylene ≈ 1,8-diethyl or $-\Delta E_{1/2} = 2 \times 33 + 46 =$
2. For the trimethylnaphthalenes and hexahydro-
rene, the calculated values of $-\Delta E_{1/2}$ are not based
the assumption that $\delta_j = 0$, but rather on the as-
med relationship shown in equation 3, where the
bscript *kl* represents all possible combinations of two

$$\delta_j = \sum_j \delta_{kl} \qquad (3)$$

git numbers contained in the subscript *j*, and *kl*
expressed in the lowest possible numbering for the
rresponding pattern of disubstitution. Thus, for
ample, $\delta_{137} = \delta_{13} + \delta_{17} + \delta_{26}$; where $\delta_{26} \equiv \delta_{37}$. For a
trasubstituted naphthalene δ_j will be given by the
mmation of six δ_{kl} terms. The calculated value of
$\Delta E_{1/2}$ for hexahydropyrene is based on the relation-
ip hexahydropyrene ≈ 1,4,5,8-tetra-*n*-propylnaph-
alene. Use of equations 2 and 3 gives good agree-
ent between found and calculated values in all cases
cept 1,4,5-trimethylnaphthalene, where there is a
fference of only seven millivolts.

Amongst the dimethylanthracenes studied an en-
ncement potential was associated with methyl groups
uated in the two *meso*-positions and not with any
mbination of β-positions. In contrast, amongst di-
ethylnaphthalenes enhancement potentials are as-
ciated with the *peri*- and the vicinal β-positions. It
clear that the general effects on $-\Delta E_{1/2}$ of substitu-
on patterns in the anthracene and naphthalene series
e different, but more di- and polymethylanthracenes
ust be investigated before relationships can be clari-
d further.

In Table I are recorded values for the change in
equency, $-\Delta\nu$ (with respect to naphthalene taken as a
andard), for the most intense central absorption
aximum, and for the longest wave-length α-band in
e ultraviolet spectrum (measured in alkane or cyclo-
xane as solvent) for each of the substituted naphtha-
es studied here. Consistent with assignments (for
ese bands) of directions of polarization in the mole-
le[11] is the fact that the bathochromic effect of a 1-
kyl group is larger in the former band, whereas that
a 2-alkyl group is larger in the latter band. In fact,
the case of the former band the groups 2-allyl, 2-*i*-
opyl, and 2-*t*-butyl give either no shift or else a hypso-
romic one. The dimethylnaphthalenes bearing at
st one α-substituent show a consistent bathochromic
ect ($-\Delta\nu$ 1000–1100 cm.$^{-1}$) in the α-band. All other
ifts appear irregular insofar as correlation with
olecular structure is concerned.

As in the alkylanthracenes[3] there is no apparent correlation between $-\Delta E_{1/2}$ and $-\Delta\nu$ (for either band) or between $-\Delta E_{1/2}$ values and methyl affinities as measured by Gresser, Binks, and Szwarc.[12] There is, however, qualitatively the same general inverse relationship[3] between the ionization potential, I_z, and $-E_{1/2}$ in that alkyl groups lower the former, but raise the latter. Values of I_z have been ascertained for naphthalene and the monomethylnaphthalenes by means of the charge-transfer spectra of the trinitrobenzene complexes (for naphthalene and 1-methylnaphthalene only)[13] and by means of photoionization.[14] Although precision in measurement of $E_{1/2}$ is at least an order of magnitude greater than in that of I_z, the 1- and 2-methylnaphthalenes give experimentally indistinguishable results by both methods.

Gardner, *et al.*,[15] have measured the stability constants of the picrates of naphthalene and monoalkylnaphthalenes in chloroform solution (see Table I). These molecular complexes (presumably present preferentially in parallel planar structures) exhibit the counteracting effects of electron donation and steric hindrance by the alkyl group to specific adsorption (on a molecular basis) of the electron-donating naphthyl moiety onto the electron-accepting picric acid surface. Similar effects of alkyl groups on adsorbability (presumably preferentially flatwise) of 2-alkylnaphthalenes and 9-alkylanthracenes onto an electron-accepting alumina surface have been noted by Klemm, *et al.*[16] In polarography the cathode surface differs from that of alumina or of a polynitroaromatic complexing agent in that it is an electron donor, rather than an electron acceptor. If specific adsorption (especially in a flatwise manner) of the alkylarene onto the cathode surface were pertinent to the polarographic process, polar and steric effects by the alkyl groups should reinforce one another with the excepted result that values of $-\Delta\Delta E_{1/2}$ should increase in progressing through the series in the order H, Me, Et, *i*-Pr, *t*-Bu. As observed in Table I $-\Delta\Delta E_{1/2}$ decreases in this progression, instead. Combined with the observed linear σ^* relationship for monoalkylnaphthalenes and anthracenes as well as the general additivity of substituent and geometric factors,[17] these data indicate that steric hindrance between the electroreducible molecule and the mercury cathode surface is of little or no pertinence to the electron-transfer process (at least as measured by $E_{1/2}$) and that specific adsorption of the hydrocarbon does not occur. Breiter, Kleinerman, and Delahay[18] have considered electrode processes which occur with and without specific adsorption of the electroreducible entity onto the electrode and, in the latter case, have suggested that the reacting species would approach the cathode no closer than the outer boundary of the Helmholtz

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11) H. Zimmermann and N. Joop, *Z. Elektrochem.*, **64**, 1215 (1960);
61 (1961).

(12) J. Gresser, J. H. Binks, and M. Szwarc, *J. Am. Chem. Soc.*, **81**, 5004 (1959).

(13) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).

(14) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957); ASTIA report no. AD 152 934 [A. Streitweiser, *J. Phys. Chem.*, **66**, 368 (1962)].

(15) P. D. Gardner, R. L. Brandon, N. J. Nix, and I. Y. Chang, *J. Am. Chem. Soc.*, **81**, 3413 (1959).

(16) L. H. Klemm, D. Reed, L. A. Miller, and B. T. Ho, *J. Org. Chem.*, **24**, 1468 (1959). The general preference for flatwise adsorption of aromatic hydrocarbons on alumina has been corroborated by the studies of L. R. Snyder, *J. Chromatog.*, **6**, 22 (1961); *J. Phys. Chem.*, **67**, 234 (1963).

(17) As shown by equations 2 and 3 in this paper and by equation 2 in ref. 3.

(18) M. Breiter, M. Kleinerman, and P. Delahay, *J. Am. Chem. Soc.*, **80**, 5111 (1958).

double layer; *i.e.*, presumably the molecule would remain largely within the diffuse double layer during the electron-transfer process.

Experimental[19]

Source and Purification of Hydrocarbons.—Except as otherwise noted, all hydrocarbons were purchased from Aldrich Chemical Company and purified by the same general procedure. 1-Methylnaphthalene (purum grade) was obtained from Fluka, A. G. Hydrocarbons of m.p. <75° were purified by conversion to the picrate (or sometimes the 1,3,5-trinitrobenzene) derivatives, which were recrystallized to constant melting point from ethanol and dissociated chromatographically by adding a solution of the complex in the minimum amount of benzene to a column of Alcoa F-20 alumina and eluting with petroleum ether (30–60°). The effluent was evaporated in an atmosphere of nitrogen and the residue was fractionally distilled *in vacuo.* Those products which were solid were also recrystallized to constant melting point. Generally for solids of m.p. >75° only direct recrystallization was used. Naphthalene (Distillation Products Industries, reagent grade) was purified by a combination of direct recrystallization, sublimation, and the picrate procedure. Although 1,6-dimethylnaphthalene was purified through its picrate this complex was rather unstable. Purified hydrocarbons were stored at 0–10° until use.

Where information to the contrary is not given, melting points, boiling points, and refractive indices of our products agreed closely with those reported in the literature. One exception was found for 1,3,7-trimethylnaphthalene, n^{20}_{D} 1.6010 (reported[20] n^{20}_{D} 1.5759). This compound did, however, show data for melting point, boiling point, and melting point of picrate consistent with those reported. Moreover, it gave the expected elemental analysis. Although 2,3-dimethylnaphthalene gave consistent data on melting points of the hydrocarbon and its picrate, its identity was checked further by microanalysis and mass spectra[21] (mol. wt. found: 156).

Hydrocarbons listed in subsequent paragraphs were synthesized in this laboratory and purified as noted in each case.

1-Allylnaphthalene.—To the cold (−30°) stirred Grignard reagent prepared from 2.75 g. of magnesium turnings, 23.3 g. (0.112 mole) of 1-bromonaphthalene, and 100 ml. of ether was added dropwise a solution of 13.6 g. (0.111 mole) of freshly distilled allyl bromide in 50 ml. of ether, maintained at −25°. The mixture was processed in the manner used for 3-(1-naphthyl)-cyclopentene[22]; crude yield 11.7 g. (63%), b.p. 140–141° (15 mm.). For use in polarography the hydrocarbon was converted to a 1,3,5-trinitrobenzene complex, m.p. 79–80°, after two recrystallizations from ethanol. The hydrocarbon was recovered by chromatographic dissociation of the complex using benzene and Alcoa F-20 alumina and fractional distillation of the effluent, b.p. 126.5–127° (10 mm.); n^{25}_{D} 1.6081, reported[23] n^{25}_{D} 1.6089.

1-*n*-Propylnaphthalene.—A solution of 6.0 g. of 1-allylnaphthalene in 150 ml. of glacial acetic acid was shaken with 0.1 g. of platinum oxide for 7 min. under hydrogen at 3-atm. pressure. The filtered solution was evaporated and the residue was converted to its 1,3,5-trinitrobenzene complex, obtained as yellow needles, m.p. 86–87°, after four recrystallizations from ethanol.

Anal. Calcd. for $C_{19}H_{17}N_3O_6$: N, 10.96. Found: N, 11.13.

The hydrocarbon, recovered from the complex, distilled at 126–127° (10 mm.); n^{20}_{D} 1.5920, reported[24] n^{20}_{D} 1.5928.

1-*t*-Butylnaphthalene.—To the cold (0°) stirred Grignard reagent prepared from 15.8 g. of magnesium turnings, 79.2 g. (0.58 mole) of *t*-butyl bromide, and 65 ml. of ether was added dropwise a solution of 84.5 g. (0.58 mole) of α-tetralone in 80 ml. of ether. The mixture was refluxed for 2 hr. and processed further as for 1-allylnaphthalene; yield 80 g. of distillate, b.p. 133–165° (15 mm.). This crude carbinol was dehydrated by distillation *in vacuo* (0.3 mm.) through a column of Alcoa F-1 alumina[8] maintained at 370–385° over a period of 2.5 hr. An infrared spectrum of the red, viscous distillate showed the presence of both hydroxyl and carbonyl bands. Chromatography of this red liquid using a column (4.2 × 71 cm.) packed with Alcoa F-20 alumina and 2 l. of reagent grade petroleum ether (30–60°) as eluent gave three main fractions. Fraction no. 1 (1.2 l.) yielded a colorless liquid residue on evaporation; no. 2 (90 ml.), liquid plus some crystals; and no. 3 (240 ml.), white crystals (presumably naphthalene).[25] Infrared spectra of these residues showed neither hydroxyl nor carbonyl bands. A mixture of 15.8 g. of combined residues from fractions no. 1 and 2 (total 35.8 g.) and 1.6 g. of 30% palladium on charcoal was heated at 250° for 5 hr. in a stream of nitrogen. Tests of the effluent gases showed the presence of considerable permanganate-oxidizable product (isobutene?). Rechromatography partially separated 1-*t*-butylnaphthalene (liquid residue) from the more strongly adsorbed naphthalene.[25] Distillation of the liquid residue gave 5.8 g. (12%) of 1-*t*-butylnaphthalene, b.p. 148–149° (15 mm.), purified further by means of the picrate, m.p. 100.5–102°, after two recrystallizations from ethanol, chromatography, and distillation, b.p. 135–135.5° (12 mm.); n^{20}_{D} 1.5914, reported[26] n^{20}_{D} 1.5726.

2-Allylnaphthalene.—This compound, prepared from 2-bromonaphthalene by the procedure used for the 1-allyl isomer,[27] was purified by chromatography on Alcoa F-20 alumina, distillation, b.p. 95–96° (2 mm.), conversion to its picrate (m.p. 72–73° after two recrystallizations from ethanol), chromatographic dissociation of the picrate, and redistillation, b.p. 128° (14 mm.); n^{25}_{D} 1.6027.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.80; H, 7.05.

2-*n*-Propylnaphthalene.—This compound was prepared by catalytic hydrogenation of 2-allylnaphthalene in the same manner as employed for the 1-isomer and was purified in the manner used for 2-allylnaphthalene, b.p. 135–136° (15 mm.); n^{25}_{D}1.5852.

2-Isopropylnaphthalene.—2-Isopropenylnaphthalene[8] was hydrogenated as described by Bergmann and Weizmann.[28] The hydrogenated product was purified in the manner used for 2-allylnaphthalene, b.p. 125–126° (12 mm.); n^{20}_{D} 1.5864, reported[26] n^{20}_{D} 1.577.

2-*t*-Butylnaphthalene.—This compound was prepared[29] by the Friedel-Crafts method of Bromby, Peters, and Rowe[30] using *t*-butyl chloride and naphthalene. It was purified through the picrate.

1,4-Dimethylnaphthalene.—The Grignard reagent from 2.4 g. of magnesium, 60 ml. of ether, and 22.1 g. of 1-methyl-4-bromonaphthalene[31] (purified by recrystallization of its picrate, chromatography, and distillation) was refluxed with 20 ml. of methyl iodide for 2 hr. Treatment of the reaction mixture with ice and hydrochloric acid and evaporation of the ethereal layer gave a yellow liquid which was chromatographed on alumina and converted to a trinitrobenzene complex. The hydrocarbon was then processed in the usual manner, b.p. 125–126.5° (12 mm.); m.p. 8–9°; $n^{16.4}_{\mathrm{D}}$ 1.6154, reported[32] $n^{16.4}_{\mathrm{D}}$ 1.6157.

1,8-Dimethylnaphthalene.—Naphthalic anhydride (Aldrich Chemical Co., recrystallized from acetone, m.p. 265–268°) was reduced to 1,8-dihydroxymethylnaphthalene by the lithium aluminum hydride method of Boekelheide and Vick.[33] The diol was hydrogenolyzed to 1,8-dimethylnaphthalene as described by Beyler and Sarett.[34] The hydrocarbon was purified first *via* the picrate (m.p. 154–156°) and then by recrystallization thrice from

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[19] Melting points are uncorrected. Unless otherwise noted microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were determined by means of a Perkin-Elmer Model 137 spectrophotometer.

[20] O. Kruber, *Ber.*, **72**, 1972 (1939).

[21] We are indebted to Klaus Biemann of the Massachusetts Institute of Technology for this measurement.

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[24] R. Y. Levina, L. E. Karelova, and I. A. El'yashberg, *J. Gen. Chem. USSR*, **10**, 913 (1940); *Chem. Abstr.*, **35**, 2479 (1941).

[25] From the adsorbability rules previously proposed,[16] 1,2-dihydronaphthalene, 1-*t*-butyl-3,4-dihydronaphthalene, and 1-*t*-butylnaphthalene should all be less strongly adsorbed than naphthalene.

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[27] Prepared by S. K. Airee.

[28] F. Bergmann and A. Weizmann, *J. Org. Chem.*, **9**, 352 (1944).

[29] Prepared by J. T. Spence.

[30] N. G. Bromby, A. T. Peters, and F. M. Rowe, *J. Chem. Soc.*, 144 (1943).

[31] L. F. Fieser and D. M. Bowen, *J. Am. Chem. Soc.*, **62**, 2103 (1940).

[32] "Elsevier's Encyclopaedia of Organic Chemistry," Vol. 12B, F. Radt, Ed., Elsevier Publishing Co., Inc., New York, N. Y., 1948, p. 135.

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TABLE II

ULTRAVIOLET ABSORPTION MAXIMA FOR SOME ALKYL- AND ALKYLENE-SUBSTITUTED NAPHTHALENES[a]

Substituent(s) on naphthalene	$\lambda_{\max}$ mμ	log ε	$\lambda_{\max}$ mμ	log ε	$\lambda_{\max}$ mμ	log ε	$\lambda_{\max}$ mμ	log ε	$\lambda_{\max}$ mμ	log ε	$\lambda_{\max}$ mμ	log ε	$\lambda_{\max}$ mμ	log ε	$\lambda_{\max}$ mμ	log ε
1-*t*-Butyl	225	4.98	(262	3.59)	270	3.78	280	3.87	288	3.70	291	3.70			313	2.53
1-Allyl	225	4.95	(262	3.59)	271	3.78	281	3.87	289	3.69	292	3.69			313	2.57
2-*n*-Propyl	225	5.10	(266	3.67)	275	3.71			(286	3.53)			305	2.64	318	2.64
2-*i*-Propyl	224	5.09	(265	3.67)	274	3.71			(285	3.54)			304	2.64	318	2.60
2-*t*-Butyl	224	5.09	264	3.67	274	3.72			(282	3.56)			303	2.56	317	2.43
2-Allyl	225	5.09	266	3.69	275	3.72			(286	3.55)			304	2.64	318	2.56
2,3,5-Trimethyl	229	4.94	(265	3.58)	274	3.74	283	3.79			295	3.61			318	2.44
2,3,6-Trimethyl	229	5.08	268	3.66	278	3.66							309	2.81	323	2.87
1,8;4,5-Bis(trimethylene[b]	(228	4.70)	234	4.83	285	3.84	296	3.96	(301	3.88)	308	3.82	315	3.67	329	3.48

[a] Solvent, isooctane. Data in parentheses are for shoulders, not true maxima. [b] Common name, 1,2,3,6,7,8-hexahydropyrene. Other maxima at $\lambda_{\max}$ 214 mμ, ε 4.33; 306, 3.80; and 323, 3.19.

75% ethanol, m.p. 62.5–64°; intense infrared bands (Nujol) in the region 670–850 cm.$^{-1}$ at *ca.* 774 and 817.

1-Chloromethyl-4,5-dimethylnaphthalene.—Into a mixture of 3.13 g. of 1,8-dimethylnaphthalene, 3.3 g. of paraformaldehyde, and 36 ml. of hydrogen chloride-saturated dioxane–water (6:1, v./v.), maintained at 85°, was passed a stream of hydrogen chloride gas for 2 hr. The resultant solution was refluxed for 9 hr., whereupon two liquid phases were present. Evaporation of the upper layer yielded 4.0 g. of liquid which crystallized on cooling, m.p. 57–65°. Three recrystallizations from petroleum ether (b.p. 30–60°) gave prisms, m.p. 71–72°; intense infrared bands (Nujol) in the region 670–850 cm.$^{-1}$ at 692, 759, 765, and 810 and medium bands at 749 and 835.

Anal. Calcd. for $C_{13}H_{13}Cl$: C, 76.26; H, 6.40; Cl, 17.3. Found[35]: C, 76.25; H, 6.52; Cl, 16.6.

1,4,5-Trimethylnaphthalene.—A solution of 7.53 g. of the preceding chloromethyl compound in 400 ml. of methanol was shaken for 1 hr. with 1.2 g. of 5% palladium on charcoal in the presence of hydrogen gas at 3-atm. pressure. Evaporation of the filtered solution and chromatography of a petroleum ether (b.p. 30–60°) solution of the residue on Alcoa F-20 alumina gave 5.34 g. (86%) of crystalline product. It was recrystallized thrice from methanol, m.p. 61.5–62° (reported[36] m.p. 63°) and purified further through the picrate, m.p. 144–145.5° (reported[36] m.p. 144–145°). The hydrocarbon showed intense infrared bands (Nujol) in the region 670–850 cm.$^{-1}$ at *ca.* 762 and 825 and relatively weak bands, at *ca.* 793 and 807.

Polarography.—Only analytically pure hydrocarbons were used in the polarographic studies. The polarographic apparatus, the procedure, and the general reproducibility (±3 mv.) in $E_{1/2}$ were the same as previously described.[3,8] Only in the case of hexahydropyrene did $E_{1/2}$ fall at such a negative value as to cause serious overlapping of the reduction wave for the solvent–electrolyte with the limiting current portion of the polarogram. For this reason $-E_{1/2}$ is reported to only the closest 0.01 v. for this one substrate. Otherwise, all polarograms showed only one reduction wave and were regular in shape except for the fact that the slope of the straight line representing the limiting current was greater than that of the straight line representing the residual current, where such lines were drawn through the maxima of the pen oscillations. $E_{1/2}$ was ascertained graphically by construction of a rectangle on the polarogram (as described in the "point method" of Willard, *et al.*)[37] and determination of the center of gravity (at $E_{1/2}$) of this rectangle by bisection of its diagonal. The diffusion current i_d' was determined for the most dilute solution of the hydrocarbon and was calculated as six-sevenths of the vertical height of the rectangle. 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 isooctane using a Cary Model 11 spectrophotometer. Data on the absorption maxima are presented in Table II.

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[35] Analysis for chlorine was performed by A. J. Kohlik using a method described for benzyl chloride by G. S. Tsypin and A. I. Chekalina, *Org. Chem. Ind. (USSR)*, **6**, 504 (1939); *Chem. Abstr.*, **34**, 2288 (1940).

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