Coplanarity Effects on the Spectral, Gas Chromatographic, Polarographic, and Diels–Alder Characteristics of 1-Alkyl-1-(2-naphthyl)ethenes[1]

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Syntheses of a series of 1-alkyl-1-(2-naphthyl)ethenes (where the alkyl group R = Me, Et, *n*-Pr, *i*-Pr, and *t*-Bu) from alkyl 2-naphthyl ketones by Grignard and Wittig methods are described. Comparison of ultraviolet absorption spectra of the alkenes shows a shift, $\Delta\nu$, to higher frequency of the major absorption maximum in the order *t*-Bu $\gg$ *i*-Pr > *n*-Pr = Et = Me > H (taken as standard). From general appearances of the spectra and examination of molecular models it is presumed that the average inherent angles of twist in these molecules follow the order *t*-Bu $\gg$ *i*-Pr > *n*-Pr $\simeq$ Et > Me > H (virtually coplanar). Polarographic reduction of the alkenes gives two waves at potentials of $E_{1/2}'$ (first wave, reduction of alkenyl double bond) and $E_{1/2}''$ (second wave, reduction of naphthalene nucleus). A plot of $\Delta\nu$ vs. $-\Delta E_{1/2}'$ (where the standard for comparison is also R = H) is linear, as would correspond to a linear relationship between the changes in energy of activation (from that of R = H) for the processes of ultraviolet absorption and electroreduction. A plot of $-\Delta E_{1/2}''$ vs. Taft's σ^* — values for the substituents R—CHCH₃ is linear, while that of $-\Delta E_{1/2}'$ vs. σ^* (for R) is linear only for R = H, Me, Et, and *n*-Pr. It is proposed that only the polar effect is a determining factor of $-\Delta E_{1/2}''$ for all of these alkenes as well as of $-\Delta E_{1/2}'$ for the cases R = Me, Et, and *n*-Pr (all three effectively coplanar during the process of transfer of the first electron), while both polar and resonance factors contribute to the determination of $-\Delta E_{1/2}'$ for R = *i*-Pr and *t*-Bu (both twisted during this electron-transfer process). Gas chromatographic retention times (using Apiezon M as the stationary liquid phase) of the alkenes fall in the order *n*-Pr > Et — *t*-Bu — *i*-Pr > Me > H. This order is ascribed to two opposing factors present in the alkene and serving to alter retentivity by the column, namely (a) increasing molecular weight and (b) accompanying increasing angle of twist. The same phenomena may account for the order of retention times observed for the alkyl 2-naphthyl ketones on Carbowax 20M, namely (for R) *n*-Pr > Et > *i*-Pr > *t*-Bu > Me. All of the alkenes react with tetracyanoethylene to give 1:1-adducts which are assigned structures of 1-alkyl-3,3,4,4-tetracyano-2,3,4,4a-tetrahydrophenanthrenes.

This paper is a continuation of studies[4] on the effects on physical and chemical properties of twisting conjugated arylalkenes out of coplanarity. In the present investigations the hydrocarbons used were 1-(2-naphthyl)-1-alkylethenes, I–VI, wherein twisting of the vinyl group out of coplanarity with the naphthyl ring could be ascribed
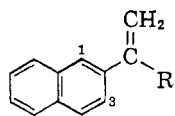
I. R = H	IV. R = *n*-C₃H₇
II. R = CH₃	V. R = *i*-C₃H₇
III. R = C₂H₅	VI. R = *t*-C₄H₉

to steric hindrance between the aromatic hydrogen atoms on positions 1 and/or 3 of the naphthalene ring and the R-group.

Compound I was prepared in 41% yield by bromination of 2-ethylnaphthalene with N-bromosuccinimide and subsequent dehydrobromination of the intermediate with potassium *t*-butoxide. Compound II was obtained in 91% yield from dehydration of dimethyl-2-naphthylcarbinol over alumina at 370°. VI was prepared both by the alumina dehydration method on the corresponding carbinol

(10% over-all yield from 2-acetylnaphthalene) and by the Wittig procedure using *t*-butyl 2-naphthyl ketone (87%). The Wittig method was likewise used for the syntheses of III, IV, and V. Use of acetic anhydride[5] in place of alumina for effecting dehydration in the syntheses of II and VI gave poor results in our hands. Infrared spectra of the alkenes showed the presence of the vinylene group (ν = 890–900 cm.⁻¹ in I–V; doublet at 900 and 910 cm.⁻¹ in VI) and, in II–VI only, of the 1,1-disubstituted vinyl grouping (ν = 1425–1430 cm.⁻¹). These alkenes reacted with tetracyanoethylene to give crystalline 1:1 adducts (*vide infra*).[6]

All purified alkenes except VI exhibited single peaks in gas chromatography on an Apiezon M column under identical conditions. Despite the fact that identical products of narrow melting range had been obtained for VI by both the dehydration and Wittig methods, and that the latter method is believed to be free of rearrangement,[7] there were found (for product from either source) two chromatographic peaks (the second corresponding to *ca.* 15% impurity) with closely similar retention times. That VI was actually present in the isolated product was indicated by the formation of a small amount of *t*-butyl 2-naphthyl ketone, identical with an authentic synthetic specimen, on permanganate oxidation thereof. That at least the major com-

(2) Research Assistant, 1959–1962.
(3) Research Associate, 1959–1962.
(4) For leading references see footnotes 11, 17, 20, 37, 41, as well as L. H. Klemm and J. W. Sprague, *J. Org. Chem.*, **19**, 1464 (1954).

(5) F. Bergmann and A. Weizmann, *ibid.*, **9**, 352 (1944).
(6) Further studies on the Diels–Alder reactions of I–VI with tetracyanoethylene are under way in our laboratory.
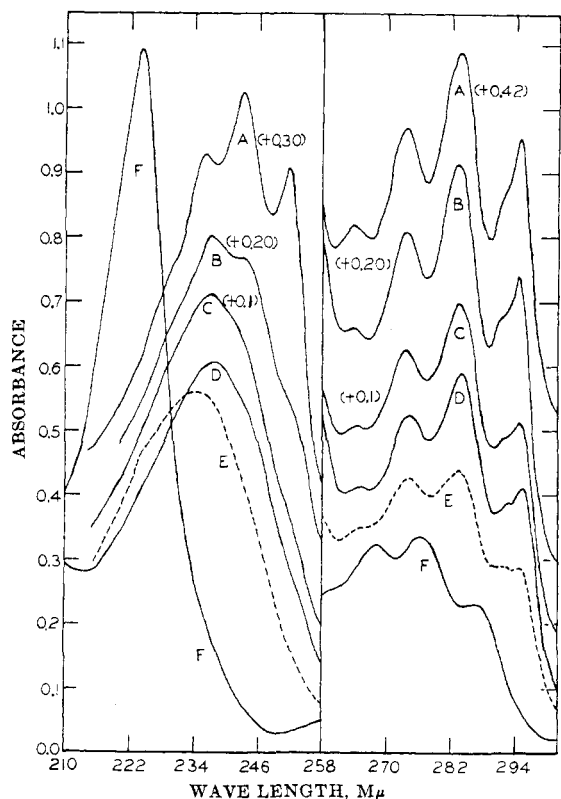(7) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

Fig. 1.—Ultraviolet absorption spectra of 1-alkyl-1-(2-naphthyl)ethenes in absolute ethanol. Lettering of curves corresponds to the alkyl group (R) as follows—A: R = H; B: R = Me; C: R = Et; D: R = n-Pr; E: R = i-Pr; F: R = t-Bu. Concentrations of solutions used in the region 210–258 mμ, 1.30 × 10⁻⁵ M, for A–F; in the region 258–302 mμ, 5.19 × 10⁻⁵ M for A, 6.49 × 10⁻⁵ M for B–F. Numbers in parentheses represent vertical displacements of the curves.

ponent was a structurally conjugated naphthylalkene was shown by means of polarography, whereby two waves of essentially equal heights and of diffusion current constants consistent with those of the other naphthylalkenes were obtained. Further clarification of the situation resulted from dissociation in boiling benzene of the analytically pure Diels-Alder adduct. Crystalline VI, identical in m.p., infrared spectrum, and gas chromatographic characteristics with the previous material, was obtained. It is thus apparent[8] that partial rearrangement of VI, perhaps to a structurally nonconjugated isomer[9] occurs during the gas chromatographic process.

Ultraviolet absorption spectra for alkenes I–VI are shown in Fig. 1 and data concerning the observed maxima and shoulders are presented in Table I. Observation of Fig. 1 shows that major changes in the spectra occur in the region 210–258 mμ on progressing through the series from I to VI (R = H to R = t-Bu). Thus, one finds a change from three sharp bands in I, to one rather sharp

band plus a shoulder in II, to a single broad band each in III, IV, and V, and finally to one very sharp band in VI. Moreover, in terms of the wave length of the most intense band, the effect of the R-group in causing a hypsochromic shift of the principal maximum is H (taken as standard of comparison) < Me = Et = n-Pr< i-Pr<<t-Bu. In the region 258–302 mμ the spectra change less markedly though there is a general weakening in contrast amongst the peaks as one goes from R = H to R = i-Pr with little concomitant shifting of positions of the corresponding maxima. The maxima for R = t-Bu are, however, shifted hypsochromically. Notable in this region is the gradual decrease in intensity of absorption in going through the series.

Ultraviolet absorption spectra of naphthalene and phenanthrene show three main groups of bands, which (in order of increasing wave length and decreasing intensity) have been designated by Clar[10a] as β-, p-, and α-bands,[10b] respectively. Since it has been noted previously[11] that I (and, hence, also II–VI) lies in the same vari-conjugate sequence as naphthalene and phenanthrene one would expect corresponding groups of bands for I–VI. By analogy then one may designate the bands in the region of 210–258 mμ as β-bands and those in the region of 258–302 mμ as p-bands. At the solution concentrations used to measure the p-bands, only I showed definite, though weak, absorption bands (presumably α-type) beyond 302 mμ (at 308, 323.5, and 339 mμ, respectively). Clar[10a,12] has noted a close correlation between the positions of the α- and β-bands for many aromatic hydrocarbons such that $\frac{\lambda_\alpha}{\lambda_\beta} = \frac{\nu_\beta}{\nu_\alpha} \simeq 1.4$ (1.42 for naphthalene, 1.35 for phenanthrene) where λ_β and ν_β refer to the wave length and frequency, respectively, of the most intense β-band and λ_α and ν_α refer to the same quantities for the α-band of longest wave length. The fact that this ratio (339/242.5) is 1.40 for I lends credence to the assignment of the bands for this compound. Despite interest in the α-bands of compounds II–VI (vide infra) lack of appropriate apparatus for ultraviolet spectral studies at low temperatures[13] prevented further investigation of them at the present time. McClure[14] has ascertained that the α-band for naphthalene involves longitudinal polarization of the molecule, while the p-band involves transverse polarization.[15] The β-band,

(8) Final proof of such rearrangement would await actual isolation and structural investigation of the minor component.

(9) G. H. Beaven, A. T. James, and E. A. Johnson, Nature, 179, 490 (1957).

(10) (a) E. Clar, "Aromatische Kohlenwasserstoffe," Springer Verlag, Berlin, 1952, pp. 27–30, 36–37, 134, 142; (b) These bands have been designated as ¹Bb, ¹La, and ¹Lb, respectively, by J. R. Platt [J. Chem. Phys., 17, 484 (1949)].

(11) L. H. Klemm, H. Ziffer, J. W. Sprague, and W. Hodes, J. Org. Chem., 20, 190 (1955).

(12) S. F. Mason, Quart. Rev. (London), 15, 287 (1961).

(13) E. Clar, Spectrochim. Acta, 4, 116 (1950).

(14) D. S. McClure, J. Chem. Phys., 22, 1256, 1668 (1954); 24, 1 (1956); Solid State Phys., 8, 1 (1959).

(15) H. Zimmermann and N. Joop, Z. Elektrochem., 64, 1215 (1960); 65, 61 (1961).

TABLE I
ULTRAVIOLET ABSORPTION MAXIMA FOR SOME 1-ALKYL-1-(2-NAPHTHYL)ETHENES[a]

Alkyl substituent	Corresponding Absorption Maxima[b] — λ_{max} in mμ,[c] log ϵ							
H	236, 4.68	242.5, 4.75	251.5, 4.68	264, 3.89	274, 4.03	284, 4.11	(292.5, 3.95)	295, 4.02
Me		237.5, 4.66	(243, 4.64)	264, 3.85	273.5, 3.97	283.5, 4.05	(291.5, 3.87)	295, 3.93
Et		237.5, 4.68		265, 3.80	274, 3.91	284, 3.97	(292, 3.80)	295, 3.82
n-Pr		237.5, 4.67		264, 3.81	274.5, 3.92	284.5, 3.97	(293, 3.79)	296, 3.81
i-Pr		234, 4.63		(265, 3.74)	274, 3.83	284.5, 3.84	(292, 3.67)	295, 3.66
t-Bu[d]		224, 4.92			268, 3.71	276, 3.73		287, 3.57

[a] Solvent: absolute ethanol, prepared by treatment of 95% ethanol with calcium oxide. [b] Values in parentheses represent shoulders, not true maxima. [c] Estimated to closest 0.5 mμ. [d] Compare with spectra of 2-methylnaphthalene [224, 4.94; (267, 3.65); 276, 3.68; (286, 3.51)] and naphthalene [corresponding bands at 221, 4.98; 267, 3.62; 276, 3.76; 287, 3.60; α-band of longest wave length at 312 mμ] measured in 95% ethanol [R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1951].

through its characteristics closely similar to those of the α-band[12] and through the effects observed in the spectrum on going from naphthalene to 1- and 2-naphthylamines[16] (cf. spectra for 1- and 2-vinylnaphthalenes),[11] has also been associated with longitudinal polarization, though efforts to determine this direction of polarization directly from spectral measurements on naphthalene have not been completely successful.[16]

Interpretations concerning the relative inherent angles (θ) of interplanar twisting (between the planes of the naphthyl and alkenyl moieties) in I–VI (in solvent ethanol) may be made using qualitative aspects of the spectra in the manner of Klemm, et al.,[11,17] or semiquantitative aspects in the manner of Braude, et al.[18] Thus, general observations on the fine structural characteristics of the spectra indicate θ-distributions varying in the order R = H (much fine structure, effectively coplanar) < Me (some retention of fine structure but major alteration toward diffuse bands) < Et = n-Pr (diffuse bands) < i-Pr (bands somewhat more diffuse) << t-Bu (electronically nonconjugated alkylnaphthalene-like [see footnote d, Table I], effectively perpendicular). Observations of Fisher-Hirschfelder-Taylor molecular models are consistent with these general proposals of varying degrees of twist.

The combined hypsochromic shifts in wave length and hypochromic shifts in intensity of the β-bands in going through the series from I to V may be ascribed to the effects of large increases in average θ or of strong steric hindrance to the attainment of coplanarity in the order R = H < Me = Et =

n-Pr < i-Pr. The t-Bu member (VI) is not included in this series for it shows hyperchromic rather than hypochromic effects when compared to I. The β-bands in II–V are presumed to arise from transitions involving noncoplanar ground states (GS$_\beta$) and noncoplanar excited states (ES$_\beta$) with polarization over the entire vinylnaphthalene π-system in the longitudinal direction of the molecule. It is assumed that GS$_\beta$ is relatively independent of θ, but that ES$_\beta$ will fall at the lowest (most stable) level for $\theta = 0°$ and rise as θ increases to 90°. The variation of ES$_\beta$ with θ rests on the propositions that the pivotal bond between the naphthyl and alkenyl moieties assumes considerable double bond character in this activated state and increased twisting should therefore make the state more strained. The much lessened double bond character of the corresponding bond in the ground state makes GS$_\beta$ less subject to such variation. For I itself the β-bands will correspond to $\theta \simeq 0°$; while for VI they will involve transitions in the naphthalene π-system only, without interaction with the alkenyl π-system. It is noteworthy that in each of four 1-(2-naphthyl)-1-cycloalkenes (where the cycloalkenyl group varies from C_5 to C_8) the principal β-band is shifted bathochromically from that of I.[11] This has been ascribed to the action of the polymethylene chain in the cycloalkenyl ring in the manner of dialkyl substitution on the π-system. Such bathochromic alkyl shift would be expected only for molecules which are not twisted too far out of coplanarity, i.e. for molecules having θ less than that in II. At the other end of the scale, where θ approaches 90° as in VI, the β-band is also shifted bathochromically from that of the effective parent molecule naphthalene (see footnote d, Table I).

The p-bands for compounds II–V show only hypochromic shifts in intensity (from I) without concomitant change in wave length. This effect has been considered to result from relatively weak steric hindrance to the attainment of coplanarity. The p-bands in II–V are presumed to arise from transitions involving noncoplanar ground states (GS$_p$), either identical with GS$_\beta$ or else closely similar in molecular structural characteris-

(16) R. N. Jones, J. Am. Chem. Soc., 67, 2127 (1945); Y. Hirshberg and R. N. Jones, Can. J. Res., 27B, 437 (1949). W. West, "Physical Methods of Organic Chemistry," 3rd ed., Vol. I, Part 3, A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp. 1950–1952.

(17) L. H. Klemm, B. T. Ho, C. D. Lind, B. I. MacGowan, and E. Y. K. Mak, J. Org. Chem., 24, 949 (1959).

(18) E. A. Braude, F. Sondheimer, and W. F. Forbes, Nature, 173, 117 (1954); E. A. Braude and E. S. Waight, Progress in Stereochemistry, Vol. I, W. Klyne, ed., Butterworths, London, 1954, Chap. 4. See also L. L. Ingraham, "Steric Effects in Organic Chemistry," M. S. Newman, ed., J. Wiley and Sons, Inc., New York, N. Y., 1956, pp. 481–489.

TABLE II

GAS CHROMATOGRAPHIC AND POLAROGRAPHIC DATA FOR SOME ALKYL 2-NAPHTHYL KETONES AND 1-ALKYL-1-(2-NAPHTHYL)-
ETHENES[a]

Alkyl group	Relative gas chromatographic retention times, t_R For ketones[b]	For naphthyl-ethenes[c]	Polarographic half-wave reduction potentials of naphthylethenes First wave $-E_{1/2}'$ (v. vs. S.C.E.)	$-\Delta E_{1/2}'^d$ (mv.)	Second wave $-E_{1/2}''$ (v. vs. S.C.E.)	$-\Delta E''^e$ (mv.)
H	...	0.78	2.110	0	2.477	0
Me	1.00[f,g]	1.00[h,i]	2.164	54	2.482	5
Et	1.16	1.26	2.178	68	2.486	9
n-Pr	1.44	1.57	2.174	64	2.489	12
i-Pr	1.11	1.22	2.204	94	2.492	15
t-Bu	1.04	1.24[j]	2.346	236	2.495[k]	18

[a] See Experimental for details of runs. [b] Compared to $t_R = 1.00$ for 2-acetylnaphthalene. [c] Compared to $t_R = 1.00$ for 1-methyl-1-(2-naphthyl)ethene. [d] Difference in $E_{1/2}'$ from that of 2-vinylnaphthalene. [e] Difference in $E_{1/2}''$ from that of 2-vinylnaphthalene. [f] Retention time = 13.8 min. [g] $t_R = 0.88$ for 1-acetylnaphthalene. [h] Retention time = 30.6 min. [i] $t_R = 0.99$ for 1,3,7-trimethylnaphthalene. [j] A minor peak also occurs at 1.34 (cf. Discussion and Experimental). [k] Compare with $-E_{1/2} = 2.438$ for the single wave of naphthalene.

tics to it, but planar excited states (ES$_p$) and with polarization restricted to the transverse direction of the naphthalene molecule. It follows that ES$_p$ is essentially independent of θ. Correspondingly, in VI there is no bathochromic effect, as compared to naphthalene (see footnote d, Table I), for the p-bands.

Data on the relative retention times, t_R, in vapor phase chromatography of alkenes I–IV and the alkyl 2-naphthyl ketones used as intermediates in their syntheses are presented in Table II. For the alkenes the stationary phase Apiezon M was selected since it had been noted that with this material t_R increased with molecular weight and decreased with approach to coplanarity in alkyl-substituted biphenyls[9] and selected naphthylcycloalkenes.[19] The present series confirms such relationships. Thus, there is a regular increase in t_R with molecular weight for R = H to R = n-Pr. An inversion in the trend occurs at the i-Pr member which, along with the t-Bu compound, is retained less tenaciously than either the n-Pr or the Et compound. A similar inversion in the series at the i-Pr member occurs in t_R for the alkyl 2-naphthyl ketones chromatographed on Carbowax-20M, a high-molecular-weight polyethylene glycol.

Also shown in Table II are the polarographic half-wave reduction potentials of I–VI measured in 75% dioxane–water containing 0.1 M tetra-n-butylammonium iodide as supporting electrolyte. As noted previously for structurally conjugated naphthylalkenes[30] there are observed two polarographic waves, the first of which (at $E_{1/2}'$) corresponds to reduction of the alkenyl double bond and the second of which (at $E_{1/2}''$) corresponds to reduction of the naphthalene ring. A check on this latter assignment was made using 2-ethylnaphthalene which exhibited only one reduction wave at -2.467 ± 0.003 v. (vs. S.C.E.) as compared to

$E_{1/2}''$ of -2.477 ± 0.003 v. for 2-vinylnaphthalene.[21] From Table II one observes that $-E_{1/2}''$ increases very slightly as one proceeds through the series from I to VI. The difference of only 18 mv. (ca. 400 cal./mole) between I and VI seems much too small to be the result of the change in bulkiness of the R-group, a factor which would be expected to alter $-E_{1/2}''$ significantly if steric hindrance by R were pertinent to the process which serves to determine half-wave reduction potential. In fact, although experimental errors in $-\Delta E_{1/2}''$ are large (± 3 mv. in $E_{1/2}''$) in comparison with observed values, a plot of $-\Delta E_{1/2}''$ vs. Taft's polar substituent constant[22a] $\sigma_{RCHCH_3}^*$ (for the alkyl group RCH(CH$_3$) present in the 2-alkylnaphthalene formed in the first reduction step) fits a straight line reasonably well[22b] (Fig. 2 inset). Modifying the simple Taft relationship[22a] to fit this case one obtains

$$\log \left(\frac{k''}{k_1''}\right) = \frac{n\mathfrak{F}}{2.303\,RT}\,\Delta E_{1/2}'' = \rho^*_{RCHCH_3}(\sigma^*_{RCHCH_3} + 0.100) \quad (1)$$

equation 1, where k'' refers either to the rate constant or to the equilibrium constant (whichever serves to determine the measured value of $E_{1/2}''$)[23] for the second reduction process of one of the compounds II–VI, k_1'' is the corresponding constant for the standard of comparison (compound I), $n = 1$, the factor $\dfrac{n\mathfrak{F}}{2.303\,RT} = 16.9$ when $\Delta E_{1/2}''$ is

(19) Unpublished work of G. H. Beaven, E. A. Johnson, and L. H. Klemm from the Medical Research Council Laboratories, Holly Hill, Hampstead, London, England.

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

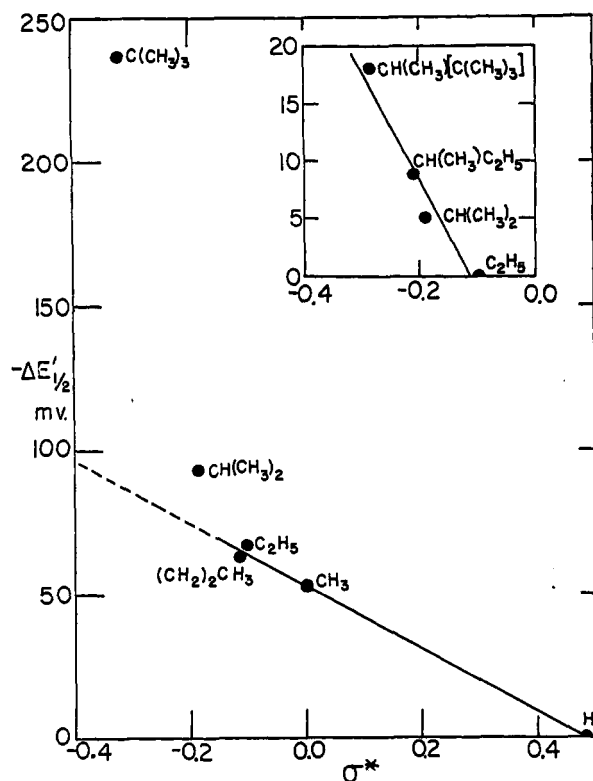(21) The reason for the small discrepancy between these two values which lies just outside of the limits of experimental error in each potential is not clear. A similar check on the structural assignment for the second wave of 1-(1-naphthyl)cyclopentene has been reported.[20]

(22) (a) R. W. Taft, J. Am. Chem. Soc., 75, 4231 (1953). R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, ed., J. Wiley and Sons, Inc., New York, N. Y., 1956, chap. 13; (b) Data for only four of the desired alkyl groups are given in Taft's tables.

(23) The use of alternating current polarography to investigate this problem has been made for aromatic hydrocarbons and 1,ω-diphenylpolyenes by A. C. Aten, C. Büthker, and C. J. Hoijtink, Trans. Faraday Soc., 55, 324 (1959); Z. Physik. Chem. (Frankfurt), 21, 192 (1959). Lacking data which could help to decide this question for our compounds, we refer here only to the process of transfer of the first electron from the cathode to the substrate without commitment as to whether $E_{1/2}$ is determined by an equilibrium process, by a rate process, or by some combination of these processes.

Fig. 2.—Plots of the change in the polarographic half-wave reduction potential (from the standard of comparison 2-vinylnaphthalene) vs. Taft's σ^* values. Large graph, for the first wave of 1-alkyl-1-(2-naphthyl)ethenes where σ^* values refer to the alkyl group R. Inset graph, for the second wave of 1-alkyl-1-(2-naphthyl)ethenes where σ^* values refer to the group $RCH(CH_3)$— resulting after initial reduction of the R—CH=CH_2 group.

expressed in volts, ρ_{RCHCH_3}* is the reaction constant for the second reduction process, and the value 0.100 is added to σ_{RCHCH_3}* in order to transform Taft's σ^*-values (based on methyl as the standard substituent of comparison) to the present standard of comparison $RCHCH_3 = C_2H_5$. The numerical value of ρ_{RCHCH_3}* obtained from the slope of the curve is $+1.6$. A similar plot (Fig. 2) of $-\Delta E_{1/2}'$ (for the first wave) vs. σ_R* for the R-group present on 2-vinylnaphthalene is linear (ρ_R* $= +1.84$) for I–IV only. Using this plot (extrapolated) as a standard of comparison it is found that the i-Pr (V) and the t-Bu (VI) members are more difficult to reduce (by 18 and 148 mv., respectively) than would correspond to operation of the polar effect alone.

As noted previously the ultraviolet absorption spectra indicate that only I is effectively coplanar in solution and that II–VI are twisted out of coplanarity by various amounts. Because of operation of the Franck-Condon principle in ultraviolet spectroscopy each of these molecules must retain its inherent angle of twist during the spectral transition. A similar principle would not be expected to apply in the case of polarography where the relatively slow movement of the electroreducible molecules into the polarizing atmosphere sur-

rounding the cathode should serve to cause rotation of the noncoplanar alkenes II–VI toward more polarizable, $i.e.$, more nearly coplanar, conformations $prior$ to electron transfer from the cathode.[23a] It is proposed that compounds II–IV are thereby brought into effective coplanarity before transfer of the first electron, and that the linear $-\Delta E_{1/2}'$ vs. σ_R* plot for I–IV reflects the resultant unperturbed polar effects of the groups H, Me, Et, and n-Pr on the ease of electroreduction. The discrepancies between the $-\Delta E_{1/2}'$-values for V and VI and the values predicted from the extrapolated plot then represent differences in energy between the actual twisted polarized states of these two molecules during transfer of the first electron and the hypothetical coplanar polarized states which they fail to attain. The relationship is expressed mathematically by equation 2, where the last term is a resonance energy function

$$\log \left(\frac{k'}{k_I'}\right) = \frac{n\mathfrak{F}}{2.303\,RT}\,\Delta E_{1/2}' =$$
$$\rho_R^*\,(\sigma_R^* - 0.490) + \frac{0.367\,n\mathfrak{F}}{2.303\,RT}\,f(\theta_p) \quad (2)$$

which expresses the contribution to $\Delta E_{1/2}'$ due to the existence of an average angle of twist θ_p in the molecule during transfer of the first electron, 0.490 serves to transform Taft's σ^*-values to the present standard of comparison $R = H$, and the other symbols are the same as, or analogous to, those used in equation 1. The function $f(\theta_p)$ is subject to the boundary conditions that $f = 0$ for $\theta_p = 0°$ and $f = 1$ for $\theta_p = 90°$. The latter condition is derived from the observation that $-(E_{1/2}'' - E_{1/2}') = 0.367$ v. (from whence comes the numerical coefficient introduced into the last term of equation 2) for I and the hypothesis that if I could be constrained to maintain a twist of 90° during the polarographic process it should give only one wave at $ca.$ $-E_{1/2}''$, in the manner of 2-ethylnaphthalene. In general, that portion of $\Delta E_{1/2}'$ which can be ascribed to the polar effect of the R-group will be given by the expression, $\Delta E_{1/2}' - 0.367\,f(\theta_p)$.

Based on the data for I as standard there are plotted in Fig. 3 data for the change in frequency $\Delta\nu$ of the principle absorption maximum in the wave length region of 210–258 mμ vs. $-\Delta E_{1/2}'$ for compounds II–VI. It is readily apparent that a direct proportionality exists between these two quantities, and, therefore, also between the change in the energy of the spectroscopic transition $\Delta\Delta E_s$ and the change in the energy of polarographic activation $\Delta\Delta F_p$. The broken line in the same diagram is the theoretical curve for the case $\Delta\Delta E_s = \Delta\Delta F_p$, when both variables are expressed

(23a) This proposal, previously made by Klemm, Lind, and Spence[20] for arylalkenes and biaryls, is a special case of a more general relationship suggested by R. A. Marcus, "Transactions of the Symposium on Electrode Processes," E. Yeager, ed., J. Wiley and Sons, Inc., New York, N. Y., 1961, Chap. 13. On the other hand, Marcus proposes that the Franck-Condon principle should apply to the electron-transfer process itself.
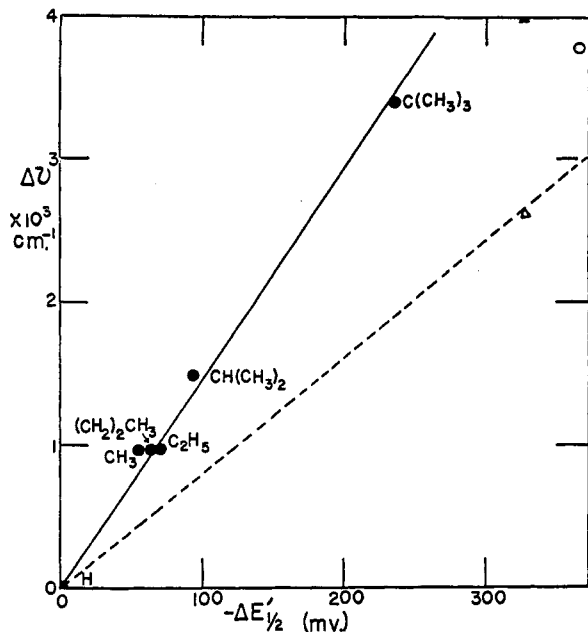
Fig. 3.—Plot of the change in frequency $\Delta \nu_\beta$ of the principal absorption maximum in the wave length region 210–258 mμ vs. the change in the polarographic half-wave reduction potential of the first wave for 1-alkyl-1-(2-naphthyl)ethenes as compared to 2-vinylnaphthalene as a standard. ● indicates the alkyl group in the substituted ethene. O corresponds to an average 2-alkylnaphthalene; ▲, to naphthalene. -------- is the theoretical curve for the case where the changes in transition energy in ultraviolet absorption and energy of activation in polarographic reduction would be equal. The Δ represents $\Delta \nu_\alpha$ vs. $-\Delta E_{1/2}$ for naphthalene.

in the same energy units. Comparison of the slope of the theoretical curve with that of the experimental one shows that actually $\Delta \Delta E_s = 1.83 \Delta \Delta F_p$. Using the Clar notation for the assignment of absorption bands, one then obtains equation 3 and (by extension through the presumed relationship

$$\Delta \Delta E_\beta = -1.83 \Delta E_{1/2}' \quad (3)$$

$$\Delta \Delta E_\alpha = -1.31 \Delta E_{1/2}' \quad (4)$$

$\nu_\beta / \nu_\alpha = 1.40$) equation 4, where $\Delta \Delta E$ and $\Delta E_{1/2}'$ are expressed in the same energy units such as electron-volts. It is interesting that the decimal part of the proportionality constant of equation 4 is, within experimental error, accountable for by action of the aforementioned polarographic polarization of the reducing molecule. This polarization factor can be estimated by resorting once again to the hypothesis that spectroscopically and polarographically a 2-alkylnaphthalene is essentially indistinguishable from a 1-alkyl-1-(2-naphthyl)ethene rigidly constrained to the perpendicular conformation. The open circle plotted in Fig. 3 represents experimental data for an average 2-alkylnaphthalene.[24] If one had a series of 2-vinylnaphthal-

(24) Only minor variations occur in λ_{max} and $E_{1/2}$ as one varies the nature of the alkyl group. $E_{1/2}$ for the open circle is the average of values for 2-ethyl- and 2-t-butylnaphthalenes as measured in this laboratory by Dr. A. J. Kohlik.

enes rigidly constrained to remain at various specified angles of twist somewhat greater than 0° and somewhat less than 90°, data for these conformers should fall approximately on a straight line (slope $\simeq$ 1.28 times that of the broken line) joining the open circle to the origin (Fig. 3).[25] This new line may then be considered a new hypothetical curve (replacing the broken line) which includes corrections for the discrepancy between the average spectroscopic angle of twist and θ_p in molecules II–VI. This relationship may be expressed by equation 5, where P_c is the energy of polarization (in e.v.) due to the conformational orientation of the molecule. Assuming P_c is proportional to

$$\Delta \Delta E_\alpha + \Delta P_c = -\Delta E_{1/2}' \quad (5)$$

the nth power of the applied electrical field at the cathode surface (where n is a positive number), then one may replace ΔP_c by the quantity $k \Delta E_{1/2}'$ (where k is a constant)[26] to give equation 6, of the same form as equation 4.

$$\Delta \Delta E_\alpha = -(1 + k) \Delta E_{1/2}' \quad (6)$$

It would appear that the quantitative energy relationships expressed in equations 4 to 6 indicate an intimate relationship between the α-transition process and a polarographic activation process. Thus, $E_{1/2}'$ is a linear function of ν_β and (presumably) of ν_α, in contrast to the observations of Bergman[27] who found a linear relationship between the first polarographic half-wave reduction potential ($E_{1/2}'$) and ν_p (the frequency of the p-band of longest wave length), but not between $E_{1/2}'$ and ν_α, for several series of aromatic hydrocarbons. A check of Bergman's graph, however, shows that ν_α for naphthalene fits the linear relationship nearly as well as ν_p since the frequencies of these two bands are relatively close together. It is to be expected that longitudinal polarization, both in the α-band and in polarographic activation would occur in compounds I–VI, as well as in naphthalene. Comparison of data for naphthalene with that of 2-vinylnaphthalene (where $\theta = \theta_p$) shows $-\Delta E_{1/2}' = 328$ m.e.v. (using the single wave for naphthalene; see footnote k, Table II). A direct comparison with $\Delta \nu_\alpha$ (2600 cm.$^{-1}$, see footnote d, Table I) and $\Delta \Delta E_\alpha$ (322 m.e.v.) is possible for these two compounds. In this case where $\Delta P_c = 0$, k also is zero and close agreement with equations 5 and 6 is found. For comparative purposes there are plotted in Fig. 3 data for

(25) A direct proportionality merely expresses the apparent fact that both ν and $E_{1/2}$ vary directly with the resonance energy of the twisted vinylnaphthalene.

(26) See C. J. F. Böttcher, "Theory of Electric Polarisation," Elsevier Publishing Co., New York, N. Y., 1952, pp. 126–127. Let

$P_c = k'(a + \Delta E_{1/2}')^n = k'a^n + nk'a^{n-1}(\Delta E_{1/2}') + \dfrac{n(n-1)}{2} k'a^{n-2}$

$(\Delta E_{1/2}')^2 + \ldots$, where a is the polarographic half-wave reduction potential of 2-vinylnaphthalene (expressed in units of absolute voltage). Then $\Delta P_c \simeq nk'a^{n-1}\Delta E_{1/2}' = k\Delta E_{1/2}'$ where smaller terms are neglected.

(27) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954); **52**, 690 (1956).

$\Delta\nu_\alpha$ vs. $-\Delta E_{1/_2}$ (open triangle) and $\Delta\nu\beta$ vs. $-\Delta E_{1/_2}$ (solid triangle) for naphthalene. The former point falls on the broken line for the ideal case $\Delta\Delta E_\alpha = -\Delta E_{1/_2}$, while the latter point falls between the solid line for the corresponding 1-alkyl-1-(2-naphthyl)ethenes and the hypothetical line joining the origin to the open circle. It is instructive to compare the relative positions of the solid triangle and the open circle in Fig 3. Thus, the introduction of a 2-alkyl group into naphthalene decreases $\nu\beta$ (bathochromic effect) and increases $-E_{1/_2}$ (polar effect). It is apparent, therefore, that for the hypothetical case of I (or II–VI) constrained to $\theta = \theta_p \simeq 90°$ (as compared to I at $\theta = \theta_p = 0°$ or to naphthalene) k in equation 6 will no longer remain constant but will become a function of θ and will assume a negative value. A similar variation of k with θ would be expected for the hypothetical case of II (or III–VI) constrained to $\theta = \theta_p \simeq 0°$ (as compared to I at $\theta = \theta_p = 0°$) where the bathochromic effect of the R-group should make $\Delta\nu\beta < 0$ and give a plotted point in Fig. 3 (extended) in the fourth quadrant. One can now see that the linear relationship between $\Delta\nu\beta$ and $-\Delta E_{1/_2}$, found in Fig. 3 is the fortuitous result of the combination of circumstances that all of the molecules II–VI are sufficiently twisted (θ appreciably $> 0°$) so as to lack noticeable bathochromic effects (as compared to I) of the R-groups and that VI is sufficiently susceptible to untwisting under polarographic conditions (θ_p appreciably $<$ 90°) as to lack noticeable polar effect (as compared to naphthalene) of the t-Bu group. It follows that despite the linear relationships between $-\Delta E_{1/_2}$, and both $\Delta\nu\beta$ and σ^* for the compounds I–IV the differences in angle of twist in II–IV under spectral and polarographic conditions negate any mathematically apparent linear relationship between $\Delta\nu\beta$ and σ^*. Further comparisons of the bathochromic and polar effects of alkyl substituents on naphthalene and anthracene rings will be presented in subsequent papers.

Despite the widely variable inherent angles of twist present in the alkenes I–VI, 1-(2-naphthyl)-cyclopentene, and 1-(2-naphthyl)cyclohexene, all of them form crystalline 1:1 adducts with tetracyanoethylene.[6] Structural formulas VII–XV are assigned to these adducts on the basis of chemical tests and infrared spectra. Thus, the adduct (VII) from 2-vinylnaphthalene reacts rapidly with permanganate in acetone. Treatment of VII with sodamide in benzene gives a new crystalline product (XV) which reacts more slowly with permanganate in acetone. All of the alkenes used showed aromatic C–H out-of-plane deformation bands (characteristic of 2-substituted naphthalenes) at 750–755, 820–830, and 855–865 cm.$^{-1}$, corresponding to the groups of hydrogens on C-5,6,7,8, C-3,4, and C-1, respectively.[28,29] The Diels-Alder adducts VII–XIV, on the other hand, lack the latter two of
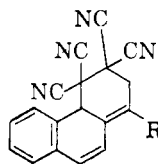
VII. R = H
VIII. R = CH₃
IX. R = C₂H₅
X. R = n-C₃H₇
XI. R = i-C₃H₇
XII. R = t-C₄H₉

XIII. n = 3
XIV. n = 4

XV
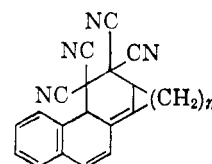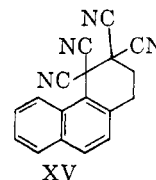
these bands, retain the first band essentially unaltered, and exhibit an additional band at 690–695 cm.$^{-1}$ (presumably due to C—H out-of-plane deformation in the cis vinylene group).[28] Compound XV, moreover, shows absorption bands at 750 and 825 cm.$^{-1}$ but lacks bands in the 690 and 860 regions.

Experimental[30]

Alkyl 2-Naphthyl Ketones.—2-Acetylnaphthalene (Distillation Products Industries, m.p. 53–54°) was used without further purification. 2-Propionylnaphthalene, m.p. 59.5–60.5°, and 2-butyrylnaphthalene, m.p., 53–54.5°, were prepared by Friedel-Crafts acylation of naphthalene essentially according to the procedure of Buu-Hoï and Cagniant.[31] Similar acylation using isobutyryl chloride gave a 49% yield of crude ketone, b.p. 129–131° (1.4 mm.). Treatment of an ethanolic solution of this ketone with an equimolar quantity of picric acid and repetitive fractional recrystallization from methanol of the precipitated picrate gave yellow needles, m.p. 76–77°. Chromatographic dissociation of the picrate using Alcoa F-20 alumina as adsorbent and 1:1 (by vol.) acetone–chloroform as eluent gave an effluent which yielded a white residue upon evaporation. Two recrystallizations of the residue from methanol gave prisms of 2-isobutyrylnaphthalene, m.p. 29.5–31° (17% from naphthalene).[32] 2-Pivalylnaphthalene, formed by methylation of 2-acetylnaphthalene,[33] was fractionally distilled. The fraction of b.p. 118–127° (0.6 mm.) was converted to a picrate, obtained as yellow needles, m.p. 98–100°,[33] after repeated recrystallization from methanol. Chromatographic dissociation of the picrate in the preceding manner gave 19 g. (38%) of solid, m.p. 54.5–57°, after one recrystallization from ethanol. Further recrystallizations from meth-

(28) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, N. Y., 1959.

(29) L. H. Klemm and J. T. Spence, unpublished data from this laboratory for six 2-cycloalkenylnaphthalenes.

(30) Melting points are corrected. Microanalyses were performed by Micro-Tech Labs., Skokie, Illinois.

(31) N. P. Buu-Hoï and P. Cagniant, Bull. soc. chim. [5], 12, 307 (1945). In this article the melting point of 2-butyrylnaphthalene is given as 34° in the experimental part and as 55° in a graph.

(32) A. Barbot, Bull. soc. chim. [4], 47, 1314 (1930), reported the formation of a liquid, b.p. 180–181° (18 mm.), by a different procedure.

(33) M. V. Volmar, Compt. rend., 150, 1174 (1910). His report of a melting point of 74–75° for 2-pivalylnaphthalene picrate may have resulted from confusion with 2-acetylnaphthalene picrate.

anol gave an analytical sample obtained as needles, m.p. 59–60°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.82; H, 7.51.

2-Vinylnaphthalene (I).—A mixture of 23.6 g. (0.15 mole) of 2-ethylnaphthalene (obtained by Clemmensen reduction of 2-acetylnaphthalene),[34] 26.6 g. (0.15 mole) of N-bromosuccinimide, 0.24 g. of α,α'-azodiisobutyronitrile, and 130 ml. of dry carbon tetrachloride was refluxed with vigorous agitation for 12 hr. and processed in a manner similar to that used by Buu-Hoï and Lecocq[35] for transformation of 1-ethylnaphthalene into 1-vinylnaphthalene. The product, presumably 1-bromo-1-(2-naphthyl)ethane, which did not undergo spontaneous dehydrobromination as reported for the 1-isomer, was recrystallized from petroleum ether (b.p. 30–60°) as white granules, m.p. 48–52°, yield 31.5 g. (89%). A solution of 81 g. (0.34 mole) of this crude bromide (m.p. 48–49.5°) in the mixture resulting from dissolving 19.5 g. (0.5 mole) of potassium in 500 ml. of anhydrous *t*-butyl alcohol was refluxed for 9 hr. The solvent was removed by distillation and the residue was washed with water and dissolved in petroleum ether. The organic layer was combined with petroleum ether extracts of the water wash, dried (calcium chloride), and evaporated. Batchwise sublimation of the residue at 140° and 0.5 mm. yielded 58 g. of product, comprised of *ca.* 70% 2-vinylnaphthalene and 30% carbinol as estimated by infrared analysis. The sublimate was dissolved in methanol, treated with Norit, passed through a short column of Florisil, and allowed to crystallize from the effluent. Recrystallization from the same solvent gave white flakes, m.p. 64.5–66°, yield 32 g. One half of this material was chromatographed on a 500 × 60-mm. column of Alcoa F-20 alumina using petroleum ether as eluent. One additional recrystallization from methanol, followed by vacuum-drying, gave 12 g. of alkene (46% yield from bromide), m.p. 66–67°. The product was stored in a freezer and re-purified by some of these same steps just prior to use.

1-Methyl-1-(2-naphthyl)ethene (II).—The mixture from interaction of 2-acetylnaphthalene and methylmagnesium iodide[36] was hydrolyzed by means of a mixture of ice, water, and ammonium chloride. The resultant carbinol (collected by ether extraction) was recrystallized from petroleum ether, m.p. 58.5–61°; 73% yield. For dehydration, the molten carbinol (80 g.) was added dropwise to the distillation flask, bearing 5 ml. of Hyvac oil maintained at 200°, of a simple vacuum (1.5 mm.) distillation apparatus. The distilling vapors passed through a 200-mm. Allihn condenser packed with ¹/₈- to ¹/₄-inch particles of Alcoa F-1 alumina, maintained at 360–380° by means of a heating jacket. The solid product (II) was collected from the receiver and recrystallized from methanol; yield 65 g. (91%), m.p. 54–55°.

1-Isopropyl-1-(2-naphthyl)ethene (V).—In an atmosphere of highly purified nitrogen contained in a closed, vertical system consisting of two pressure-equilibrating dropping funnels separated by a reflux condenser there was added, at such a rate as to maintain spontaneous refluxing, a solution of 28.2 g. (0.18 mole) of bromobenzene in anhydrous ether to 2.5 g. (0.36 g.-atom) of lithium wire under 180 ml. of ether. The solution of phenyllithium so obtained was filtered through a plug of glass wool (retained in the bottom of the lower funnel) directly into a three-necked round-bottomed flask containing 48.2 g. (0.135 mole) of dried methyltriphenylphosphonium bromide (Aldrich Chemical Co.) suspended in 160 ml. of ether in a nitrogen atmosphere. The mixture was stirred at room temperature for 4 days and then siphoned directly into an evacuated pressure bottle containing 23 g. (0.116 mole) of powdered 2-isobutyrylnaphthalene where it was heated at 70° for 3 hr. The cooled

mixture was washed with water, dried with anhydrous calcium chloride, and evaporated. A solution of the brown residue in petroleum ether was chromatographed on Alcoa F-20 alumina. Evaporation of the effluent gave 17 g. of colorless liquid which was distilled through a 550 × 10-mm. column bearing a wire spiral; yield 12 g. (53%), b.p. 157–160° (9 mm.). It was re-chromatographed using pentane and a 45 × 5-cm. column of alumina. The first 130 ml. of effluent was discarded. Evaporation of the next 190 ml. of effluent gave 10.5 g. of liquid residue which was dissolved in methanol and treated with an equimolar quantity of trinitrobenzene. The resultant adduct was recrystallized twice from methanol (yellow needles, m.p. 71–72°), dissolved in benzene, and dissociated by means of an alumina column using pentane as eluent. Distillation of the effluent gave analytically pure V, b.p. 82–83° (0.1 mm.).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.79; H, 8.34.

1-Ethyl-1-(2-naphthyl)ethene (III).—Using the same general procedure as for the synthesis of V, from 25 g. of propionylnaphthalene there was obtained 12.4 g. (50%) of III upon evaporation of the effluent from the first chromatographic column. This product was converted directly to the trinitrobenzene adduct which was recrystallized three times (yellow needles, m.p. 65–66°) and dissociated chromatographically. Distillation of the effluent gave a colorless liquid, b.p. 112–114° (0.8 mm.).

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.26; H, 7.71.

1-*n*-Propyl-1-(2-naphthyl)ethene (IV).—Following the procedure used in the synthesis of III, the corresponding yield of IV (from 30 g. of 2-butyrylnaphthalene) was 16 g. (54%). This product failed to give a crystalline picrate from methanol or chloroform but did yield a trinitrobenzene adduct (yellow needles, melting point mainly at 53° but ranging to 70°, after two recrystallizations). Dissociation of the adduct gave purified IV as a liquid, b.p. 109–110° (0.9 mm.).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.75; H, 8.02.

1-*t*-Butyl-1-(2-naphthyl)ethene (VI). (a). Grignard Method.—To the Grignard reagent from 54.4 g. (0.59 mole) of purified *t*-butyl chloride, 14.3 g. (0.59 g.-atom) of magnesium and 135 ml. of anhydrous ether was added a solution of 50 g. (0.29 mole) of 2-acetylnaphthalene in 100 ml. of ether. The mixture was refluxed for 2 hr. and processed as usual. The residue from evaporation of the ethereal extract was a yellow viscous liquid which showed the presence of both carbinol and ketonic groupings by infrared analysis. Dehydration by means of alumina, as for II, gave 20 g. of red-yellow liquid distillate. Chromatography of 40 g. of this distillate using a 500 × 50-mm. column of Alcoa F-20 alumina and petroleum ether (as eluent) gave two fractions—first, 13.4 g. of nearly pure VI and, second, 5.2 g. of nearly pure I[37] (identified by infrared). Recrystallization of the first fraction from methanol gave 12.4 g. (10%) of VI, obtained as white needles, m.p. 33.5–35°. An analytical sample resulted from two more recrystallizations from the same solvent followed by vacuum sublimation, m.p. 37–38.5°.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.27; H, 8.57.

Gas chromatography of the analytically pure material using a 4-ft. silicone rubber column and temperature programming gave only one peak, in contrast to two peaks shown by an analogous alkenic product obtained from dehydration of the carbinol with acetic anhydride. Efforts to prepare a crystalline derivative with picric acid, trinitrobenzene, and trinitrofluorene were unsuccessful.

(34) W. E. Bachmann and L. H. Klemm, *J. Am. Chem. Soc.,* **72**, 4911 (1950).

(35) N. P. Buu-Hoï and J. Lecocq, *J. Chem. Soc.,* 830 (1946).

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

(37) The weaker adsorption of VI, as compared to I, is consistent with proposed rules of adsorbability. See L. H. Klemm, D. Reed, L. A. Miller, and B. T. Ho, *ibid.,* **24**, 1468 (1959).

To a refluxing acetone solution of 2.5 g. of the alkene was added 5 g. of potassium permanganate over a period of 1 hr. Refluxing was continued for 1.5 hr. and then the mixture was kept at room temperature until decoloration occurred. Evaporation of the solvent, extraction of the residue with petroleum ether, and re-evaporation gave a crystalline product which was chromatographed using alumina as adsorbent and petroleum ether as eluent. From the effluent was obtained 1.5 g. of recovered alkene. Elution of the column with ethanol gave 0.2 g. of ketone, m.p. 58.5–60° after one recrystallization from methanol, identified as 2-pivalylnaphthalene by mixture melting point (undepressed) and infrared spectrum (identical) with a synthetic sample.

(b). **Wittig Method.**—Following the procedure used in the synthesis of III, the corresponding yield of VI (from 7 g. of 2-pivalylnaphthalene) was 6.0 g. (87%) of colorless liquid. Two recrystallizations from methanol gave crystalline VI, m.p. 37.5–38.5°, identical with product from (a) as based on mixed melting point, infrared and gas chromatography.

Purification of Tetracyanoethylene.—A suspension of 11 g. of tetracyanoethylene[38] sublimed two times in 800 ml. of purified 1,2-dichloroethane was stirred at room temperature until solution was effected. The solution was filtered, protected from atmospheric moisture, and cooled slowly to −35° with slow stirring. The white crystals (8 g.) which formed were collected by filtration and dried *in vacuo*, m.p. 199–200° (sealed tube).

3,3,4,4-Tetracyano-2,3,4,4a-tetrahydrophenanthrene (VII).—A mixture of 3 g. of 2-vinylnaphthalene (I) and 2.50 g. of tetracyanoethylene (equimolar amounts) in 270 ml. of chloroform was allowed to stand at room temperature for 2.5 hr., whereupon the initial azure color had disappeared. Concentration of the solution deposited 5.1 g. (93%) of adduct. Three recrystallizations from chloroform gave prisms, m.p. 170.5–171.5°.

Anal. Calcd. for $C_{18}H_{10}N_4$: C, 76.59; H, 3.57; N, 19.85. Found: C, 76.32; H, 3.54; N, 19.85.

3,3,4,4-Tetracyano-1,2,3,4-tetrahydrophenanthrene (XV).—A mixture of 2 g. of VII, 300 ml. of anhydrous benzene, and sodamide (freshly prepared from 0.5 g. of sodium)[39] was stirred at room temperature for 3 hr. The benzene layer was separated by decantation, washed with dilute hydrochloric acid and then water, dried with anhydrous calcium chloride, and concentrated, yield 1.4 g. (70%) of crude XV. Two recrystallizations from benzene gave rhombs, m.p. 201–202°.

Anal. Calcd. for $C_{18}H_{10}N_4$: C, 76.59; H, 3.57; N, 19.85. Found: C, 76.31; H, 3.86; N, 19.94.

1-Methyl-3,3,4,4-tetracyano-2,3,4,4a-tetrahydrophenanthrene (VIII).—Using the method for preparation of VII but with II instead of I, the blue color disappeared in only 4 min. Concentration of the solution gave an 83% yield of adduct, m.p. 146–147°, after three recrystallizations from chloroform.

Anal. Calcd. for $C_{19}H_{12}N_4$: C, 77.01; H, 4.08; N, 18.91. Found: C, 76.83; H, 4.20; N, 18.91.

1-Ethyl-3,3,4,4-tetracyano-2,3,4,4a-tetrahydrophenanthrene (IX).—The method for the preparation of VII was followed except the concentrated chloroform solution was cooled in ice before the crystals were collected, 93% yield. Two recrystallizations gave prisms, m.p. 148.5–150°, which decolorized permanganate readily.

Anal. Calcd. for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.06. Found: C, 77.34; H, 4.50; N, 18.28.

1-n-Propyl-3,3,4,4-tetracyano-2,3,4,4a-tetrahydrophenanthrene (X).—The procedure was the same as for preparation of IX, 91% yield. The product was recrystallized once from ethyl acetate and twice from ethyl acetate–chloro-

form (4:1 v./v.) in the absence of direct light and dried in the dark *in vacuo* to give prisms, m.p. 132–133°.

Anal. Calcd. for $C_{21}H_{16}N_4$: C, 77.75; H, 4.97; N, 17.27. Found: C, 77.45; H, 5.12; N, 17.11.

1-Isopropyl-3,3,4,4-tetracyano-2,3,4,4a-tetrahydrophenanthrene (XI).—A nearly saturated solution of V and a 10–20% excess of tetracyanoethylene in anhydrous ethyl acetate was allowed to stand in a refrigerator for 48 hr. The large rhombs (97% yield, m.p. 170–173°) which formed were recrystallized twice from ethyl acetate, m.p. 172.5–173.5°.

Anal. Calcd. for $C_{21}H_{16}N_4$: C, 77.75; H, 4.97; N, 17.27. Found: C, 77.87; H, 4.99; N, 17.22.

1-t-Butyl-3,3,4,4-tetracyano-2,3,4,4a-tetrahydrophenanthrene (XII).—XII was prepared in the manner used for XI but with standing at −10° for 10 days. The adduct was filtered from the cold, blue solution (39% yield) and recrystallized once from chloroform to give prisms, m.p. 130–131°, light sensitive.

Anal. Calcd. for $C_{22}H_{18}N_4$: C, 78.08; H, 5.36; N, 16.56. Found: C, 77.94; H, 5.32; N, 16.71.

11,11,12,12-Tetracyano-1,2,3,4,10b,11,12,12a-octahydrochrysene[40] (XIV).—XIV was prepared from 1-(2-naphthyl)cyclohexene[41] in the manner used for XII but with standing for 2 weeks, yield 78%. Recrystallization first from ethyl acetate (at −10°) and then from chloroform gave prisms, m.p. 106.5–107.5° dec., light sensitive.

Anal. Calcd. for $C_{22}H_{16}N_4$: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.40; H, 4.86; N, 16.51.

11,11,12,12-Tetracyano-9,11,12,13,15,16-hexahydro-17-H-cyclopenta[a]phenanthrene[40] (XIII).—A mixture of 2.14 g. of 1-(2-naphthyl)cyclopentene,[41] 1.42 g. of tetracyanoethylene, and 20 ml. of ether was refluxed for 28 hr. The original blue color of the mixture faded gradually. Concentration of the solution yielded 3.35 g. (94%) of XIII, m.p. 139–142°. Recrystallization three times from chloroform gave prisms, m.p. 140.5–141.5° (sealed tube).

Anal. Calcd. for $C_{21}H_{14}N_4$: C, 78.24; H, 4.38; N, 17.38. Found: C, 78.20; H, 4.60; N, 17.19.

Spectral Investigations.—Ultraviolet spectra of the alkenes I–VI were obtained in absolute ethanol (prepared by treatment of 95% ethanol with calcium oxide) as solvent using a Cary Model 11 spectrophotometer. Spectra are shown in Fig. 1 and pertinent data thereon are presented in Table I. Infrared spectra for these alkenes, the ketones from which they were derived, and the Diels-Alder adducts were obtained by means of a Perkin-Elmer Model 137 spectrophotometer using pure liquids, Nujol mulls, or potassium bromide pellets. Each ketone showed carbonyl absorption in the region 1660–1675 cm.⁻¹ and the three characteristic 2-naphthyl aromatic C–H out-of-plane deformation bands at 755–760, 810–830, and 840–870 cm.⁻¹, respectively. Despite the presence of four cyano groups in the Diels-Alder adducts the spectra exhibited little absorption near 2240 cm.⁻¹, a frequency corresponding to stretching of the C≡N bond.[28]

Gas Chromatography.—Gas-liquid chromatographic investigations were made on 1-acetylnaphthalene and the aforementioned alkyl 2-naphthyl ketones as well as on the alkenes I–VI by means of an F and M Model 202 linear programmed gas chromatograph using helium as a carrier gas. Benzene solutions of the ketones were injected into a 6-ft. column containing Carbowax 20M as stationary phase and held at constant temperature 225°. The carrier gas flow rate was 46 ml./min. The alkenes in chloroform solution were injected into a 6-ft. column containing Apiezon M as stationary phase at 200° and with carrier gas flow rate of 40 ml./min. In the latter case only, linear temperature programming at an increase of 4.3°/min. up to a maxi-

(38) T. L. Cairns, *et al.*, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(39) C. R. Hauser, J. T. Adams, and R. Levine, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p. 291.

(40) Numbering according to A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," American Chemical Society, Washington, 1960.

(41) L. H. Klemm and W. Hodes, *J. Am. Chem. Soc.*, **73**, 5181 (1951).

mum of 285° was used. All compounds except the *t*-butyl-naphthylalkene VI gave only one observable peak (*vide supra*). Data on relative retention times are presented in Table II.

Polarography.—The solvent-electrolyte mixture, 0.1 M tetra-*n*-butylammonium iodide in 75% (by volume) dioxane in water, was pre-electrolyzed in an H-type cell for 80–110 min. at 3.0 v. in an atmosphere of pre-purified (>99.99%) nitrogen. Polarography proper was conducted using a Sargent Model XXI polarograph; an attached potentiometer for measuring E, the applied potential, to an accuracy of ±0.2 mv.; Sargent S-29417 capillary tubing (m, 0.67 mg. per sec.; t, 9.9 sec. at $E = 0$), and a thermostated (25.0 ± 0.1°) H-cell with a fine sintered glass disk separating anode compartment (containing a saturated aqueous solution of tetra-*n*-butylammonium iodide in water) from cathode compartment. Two saturated potassium chloride salt bridges (containing filter paper plugs in the ends toward the H-cell and joined in series *via* a test tube containing the same solution) connected the anode compartment with a saturated calomel electrode (S.C.E.). Solutions *ca.* 3.5, 6.3, and 8.3 × 10^{-4} M in hydrocarbon were run for each alkene. The current i was obtained from the maxima of the pen oscillations. Values of $E_{1/2}$ were corrected for iR drop (R≃8000 ohms, measured during each run and at maximum drop size by means of a General Radio Co. impedance bridge Type 650-A using a 1000 c.p.s. current and an attached oscilloscope) across the cell and were within ±3 mv. of the average value for the various runs on naphthalene and on each of the compounds I–VI. Polarographic data are presented in Table II.

The Partial Reduction of Thujic Acid

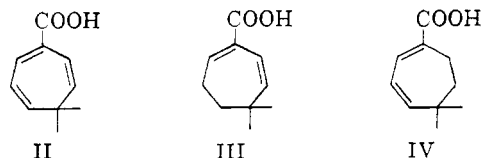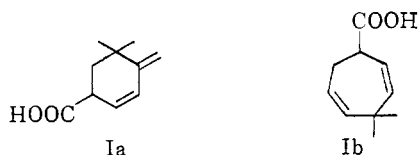D. J. PASTO

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The partial reduction of thujic acid has been shown to give 4,4-dimethyl-2,6-cycloheptadienecarboxylic acid (V). The isomerization of V was studied and the structures of the isomerization products determined using spectral, chemical, and photochemical evidence. The possible identity of the isomerization products of V with naturally occurring acids isolated from *Libocedrus formosana* is indicated.

The essential oil of *Libocedrus formosana*, found throughout the region surrounding the Pacific Ocean, has been investigated by Ichikawa[1] and was found to contain three crystalline $C_{10}H_{14}O_2$ acids with melting points of 40–41°, 78–81°, and 103°. Of these acids, only the lower melting acid, termed shonanic acid, was studied in any detail and structure Ia was proposed.[2] In reviewing the earlier work, Erdtman[3] suggested that structure Ib is more reasonable for shonanic acid based on its reported chemistry. Lo and Lin[4] reinvestigated the

Ia   Ib

acidic residue from *Libocedrus formosana* and isolated two acids, one melting at 40–41° ($C_{10}H_{14}O_2$, no absorption between 220 and 340 mμ in the ultraviolet) apparently identical with Ichikawa's shonanic acid and the second acid melting at 89–90° and identified as thujic acid (II). Shonanic acid could be hydrogenated to tetrahydroshonanic acid, which was identical with hexahydrothujic acid. Ichikawa[2] reported that shonanic acid could be converted to isoshonanic acid (m.p. 44–46°) on treatment with base. Lo and Lin[4] confirmed this isomerization but reported a melting point of 87–87.5° with absorption in the ultraviolet at 278 mμ (log ϵ 4.56).

Lin, Lo, and Lin[5] reported that the reduction of thujic acid with sodium amalgam in a boric acid buffer followed by distillation gave isoshonanic acid. These authors proposed that isoshonanic acid could be represented by either of the formulas III or IV with the former seemingly more probable.

II   III   IV

It seemed unlikely to the present author that sodium amalgam reduction of thujic acid should give either III or IV, since both III and IV are still α,β-unsaturated acids and should undergo further competitive reduction. This would result in a complex mixture of mono-, di-, and triunsaturated acids. It was felt that shonanic acid, represented as Ib, or the previously unmentioned acid V, was the prime reduction product which underwent isomerization during distillation. (Reduction of thujic

(1) N. Ichikawa, *J. Chem. Soc. Japan*, **53**, 353 (1932); *Bull. Chem. Soc. Japan*, **11**, 759 (1936).

(2) N. Ichikawa, *J. Chem. Soc. Japan*, **55**, 85, 95, 105, 111, 1074, 1124 (1934); *Bull. Chem. Soc. Japan*, **12**, 233, 243, 253, 258, 267 (1937).

(3) H. Erdtman, "Progress in Organic Chemistry," Vol. 1, J. W. Cook, ed., Academic Press Inc., New York, N. Y., 1952, p. 51.

(4) T. B. Lo and Y. T. Lin, *J. Chinese Chem. Soc.*, **3**, #3, 30 (1956).

(5) Y. T. Lin, T. B. Lo, and T. H. Lin, *ibid.*, **3**, #3, 36 (1956).