[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF INDIANA UNIVERSITY]

CHEMICAL REACTIVITIES OF ARYLCYCLOALKENES. II. POLAROGRAPHIC REDUCTION AND DIELS-ALDER CONDENSATION OF NAPHTHYL-1-CYCLOPENTENES AND NAPHTHYL-1-CYCLOHEXENES[1, 2]

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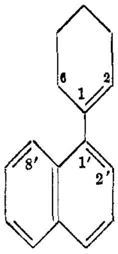
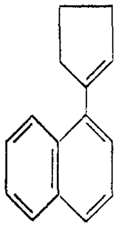
In the first paper of this series (1) we reported investigations on the reactivities of the four olefins, 1-(1′-naphthyl)-1-cyclohexene (I), 1-(1′-naphthyl)-1-cyclopentene (II), 1-(2′-naphthyl)-1-cyclopentene (III), and 1-(2′-naphthyl)-1-cyclohexene (IV), toward catalytic hydrogenation *via* Adams' platinum. The order of reactivity as based on rate of reaction, was found to be II = III = IV > I. Preliminary comparisons of these results with the reported Diels-Alder reactivities of I–IV were also made. The present paper is a report on polarographic reduction of these same four compounds and further comparisons of reactivities with the Diels-Alder reaction and catalytic hydrogenation.



I



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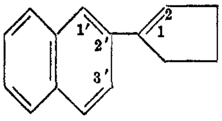

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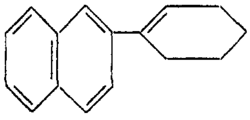

IV

Curves for the polarographic reductions are shown in Figure 1. It is immediately apparent from observation thereof that here again I is exceptional inasmuch as it exhibits a visually singular wave whereas each of the other olefins shows two distinct waves. Moreover, reduction of I is the least facile of the compounds for its wave falls at a potential more negative than for the first wave of any of the others.

Numerical data for these curves as well as for that of naphthalene (V) are presented in Table I. For all waves except that of I the corresponding half-wave potentials, $E_{1/2}'$ (first wave) and $E_{1/2}''$ (second wave) for II–IV or $E_{1/2}$ (single

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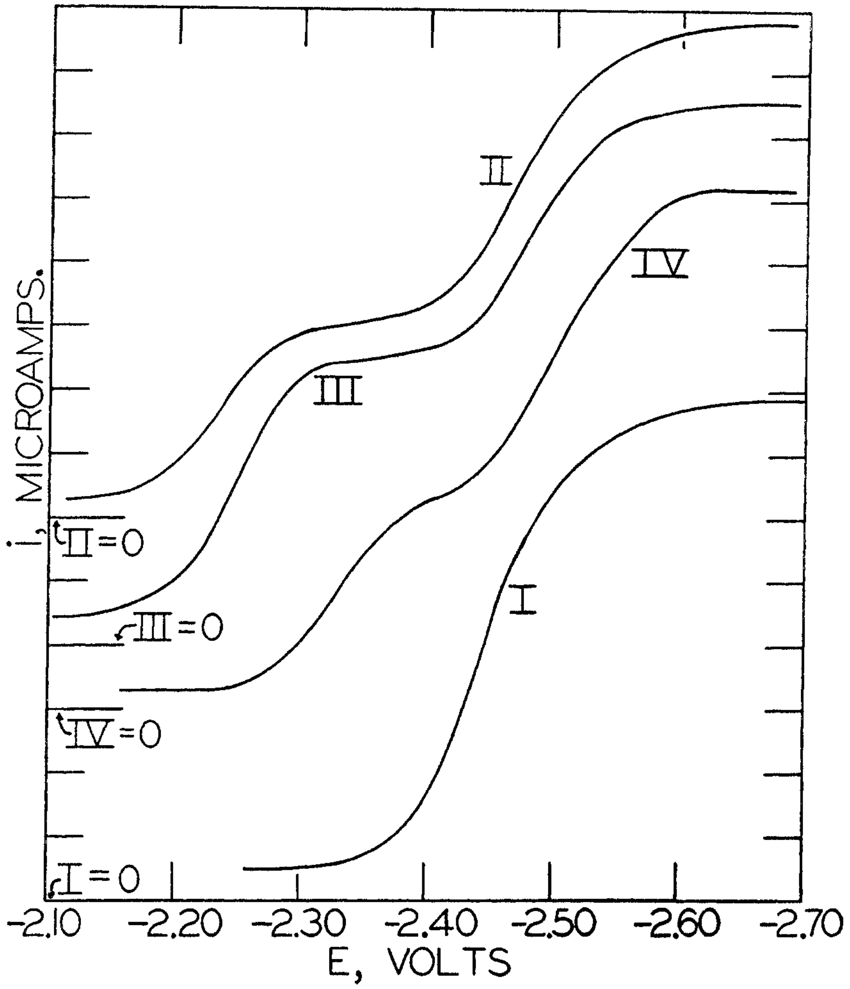

FIG. 1. POLAROGRAMS OF FOUR NAPHTHYLCYCLOALKENES. Solvent 75% aqueous dioxane containing 0.1 *M* tetra-*n*-butylammonium iodide. Conc'ns of olefins used: I, 1.13×10^{-3} *M*; II, 1.55×10^{-3} *M*; III, 1.25×10^{-3} *M*; IV, 7.5×10^{-4} *M*. Ordinate intervals represent 1 microamp. each for I, III, and IV and 2 microamps. each for II.

wave) for V, were read from the vertical intercepts of the linear plots (slope 0.059 ± 0.005) of $\log \frac{i_d - i}{i}$ *vs.* E. The first wave occurred at the same $E_{1/2}'$ (−2.25 v. *vs.* the standard calomel electrode) for II and III but at a more negative value (−2.33 v.) for IV, while the second wave was found at the same $E_{1/2}''$ (−2.49 ±0.01 v.) for all three compounds. Comparison of the heights of the waves (as evidenced by the diffusion current constants, $i_d/Cm^{2/3}t^{1/6}$) shows that the same number of electrons [two, according to information reported (2) for naphthalene] is probably involved in the over-all electrode process for either the first or second wave of II and III, the first wave of IV, and the single wave of V. The approximately double-heighted single wave of I indicates that twice as many

TABLE I

Half-Wave Potentials and Diffusion Current Constants of Naphthalene and Four Naphthylcycloalkenes[a]

COMPOUND	HALF-WAVE POTENTIAL[b]		i_d MICROAMP.		C^c MILLIMOLES-LITER^{-1}	$i_d/Cm^{2/3}t^{1/6}$ MICROAMP.-MILLIMOLE^{-1} LITER-MG.$^{-2/3}$-SEC.$^{1/2}$	
	1st Wave $E_{1/2}'$ v. *vs.* SCE	2nd Wave $E_{1/2}''$ v. *vs.* SCE	1st Wave	2nd Wave		1st Wave	2nd Wave
I[d]	−2.42	−2.47	28.95[e]		4.50	5.80[e]	
	−2.42	−2.49	6.68[e]		1.13	5.34[e]	
II	−2.25[f]		10.63		3.11[g]	2.82	
	−2.23	−2.47[h]	5.49	6.13	1.55[g]	3.03	3.60
	−2.25		2.63		0.78	2.87	
III	−2.25	−2.50	4.59	4.58	1.50[g]	2.64	2.80
	−2.25	−2.49	3.99	4.03	1.25	2.75	2.95
	−2.25	−2.49	2.35	2.17	0.75	2.70	2.65
IV	−2.32[f]		10.10		2.50	3.51	
	−2.33	−2.49	3.06	4.27	0.75	3.49	5.22
V[i]	—	−2.44[j]	—	6.39	2.00	—	2.93
	—	−2.43[j]	—	3.14	1.00	—	2.88
	—	−2.44[j]	—	1.16	0.50	—	2.13

[a] Solvent medium, 0.1 *M* tetra-*n*-butylammonium iodide in 75% aqueous dioxane. [b] Obtained from intercept of the log plot for all cases except I. [c] Most of the values listed for any one particular concentration represents averages of two or three runs. [d] Values of $E_{1/2'}$ and $E_{1/2''}$ for I are approximate only and were obtained by extrapolation of separate log plots. [e] For the singular wave observed. [f] The expanded scale used in these runs (mainly to check $E_{1/2'}$) allowed only the first wave to fall on the graph paper. [g] One run only. [h] This value may be 0.01–0.02 volts too low. [i] Only one wave found. [j] Values of −2.49 to −2.51 v. have been reported previously (2, 3) under somewhat different experimental conditions.

electrons are involved in the over-all process here. The relative number of electrons involved in the second wave of IV is somewhat questionable. Thus, although the diffusion current constant almost numerically equals that for I, this constant is, nonetheless, only about 1.5 times as large as that for the first wave of IV. Hence, it seems most likely that the second wave of IV is consistent with those of II and III also.

That two overlapping waves are actually present in the case of I was indicated by closer analysis. First a plot of $\Delta i/\Delta E$ *vs.* E showed two peaks instead of one in the region encompassing the singularly observed wave. Second, a single log plot for this entire region was not linear. However, when the assumption was made that two overlapping waves of equal height were involved and, correspondingly, two separate log plots were made (one from data for only the lower extremity of the observed wave and the other from data for only the upper extremity of the observed wave) there resulted two parallel linear segments, of the same slope as found for each separate wave of II-IV. Extrapolation of each plot to $\log\frac{i_d - i}{i}$ equals zero gave intercepts of −2.42 v. ($E_{1/2}'$) and −2.48 ± 0.01 v. ($E_{1/2}''$), respectively. Third, as mentioned previously, the height of the observed wave for I is essentially twice as great as that of the other observed waves. Hence, we shall subsequently speak of the first and second waves of I as if they were visually apparent.

The consistent value of *ca.* -2.49 v. for $E_{1/2}''$ for the olefins almost certainly indicates that the second waves involve reduction of the naphthyl moiety. This then must also mean that the first waves for the olefins correspond to reductions of the cycloalkenyl double bonds to give cycloalkylnaphthalenes, with the order of reactivity (as based on the $E_{1/2}'$ values) of II = III > IV > I. The normal inductive effects of the cycloalkyl groups might account for the shift of $E_{1/2}''$ to values somewhat more negative than the -2.44 v. found for the reduction half-wave potential of naphthalene itself.

It appears that in either electrolytic or catalytic reduction one is able to saturate the cycloalkenyl double bond of compounds II–IV without simultaneously appreciably attacking the naphthalene nucleus. Such is hardly the situation for I. A major difference between these two reduction processes appears, however, in the case of IV which is distinguishable from II and III as regards reduction half-wave potential but not as regards rate of catalytic hydrogenation. In an attempt to help clarify the position of IV we completed data [using the procedure of Bachmann and Kloetzel (4)] on the order of reactivity of these olefins towards Diels-Alder condensation with maleic anhydride for which the rates of reaction $II \leqq III \gg I$ (4, 5) and $IV \gg I$ (5, 6) had already been determined. The complete order was established as $II \leqq III > IV \gg I$, in qualitative conformance with the ease of electroreduction, though it would appear that a much greater difference in reactivities between IV and I prevails in the Diels-Alder case.

To explain these orders of reactivities we invoke two factors, namely (a) the previously postulated steric factor of coplanarity in the olefin (1), considered of importance in the formation of a transitional complex involving flatwise adsorption of the substrate (olefin) on the platinum in catalytic hydrogenation and planar parallelism of the diene-dienophile combination in the Diels-Alder condensation but presumably of no significance in the process of electroreduction, and (b) a conjugative factor in the olefin, considered of importance in the transitional complex for both the Diels-Alder reaction and electroreduction but presumably of no significance in the process of catalytic hydrogenation. The order observed for the Diels-Alder reaction may then be visualized as an approximate summation of the orders for catalytic hydrogenation and electroreduction.

Some evidence to support these proposals is already available in the literature. We note that an isolated carbon-carbon double bond is readily reducible *via* catalytic hydrogenation while such a bond is neither sufficient for Diels-Alder reactivity with a dienophile nor susceptible to electroreduction at currently obtainable potentials. Thus styrene has been reduced polarographically under conditions similar to those used in our studies while both benzene and ethylene have completely resisted such reduction (7, 8). Hence, facility of reaction in the Diels-Alder condensation or electroreduction would be expected to increase with the degree of conjugation between the cycloalkenyl double bond and the naphthalene nucleus. Contrariwise such conjugation would be expected to have little or no effect on the rate of catalytic hydrogenation, particularly if one adopts the suggestion of Smith, *et al.* (9) that resonance interaction is destroyed even in such molecules as benzene and biphenyl when these substrates are adsorbed on the platinum hydrogenation catalyst. The distinction between purely steric and purely conjugative factors, however, is indeed a subtle one for our olefins inasmuch as maximal conjugation should occur only if the cycloalkenyl double bond and the naphthyl moiety can become coplanar (10).

Adapting the suggestions of Laitinen and Wawzonek (2, 8) and of Stackelberg and Stracke (11) to our compounds, we tentatively propose that the first wave for electroreduction of I–IV involves 1,4-addition of two electrons to the same 1,3-dienic systems as are involved in the Diels-Alder reaction and that the numerical value of $E_{1/2}'$ is an indication of the facility of this electronic addition. It should then be noted that an electronic shift would be necessary during the subsequent addition of hydrions in order to produce the cycloalkylnaphthalene proposed as the product of the first reduction process.

Since such 1,4-addition involves the disappearance of a double bond from the cycloalkenyl ring (endocyclic) and the appearance of a new double bond in the pivotal position (exocyclic) between the cycloalkyl and naphthyl moieties the lower reactivity of IV, as compared to II and III, in both electroreduction and the Diels-Alder reaction may be yet another manifestation of the smaller tendency (conjugative effect) for the transformation cyclohexenyl → cyclohexylidene, as compared to the transformation cyclopentenyl → cyclopentylidene (12). For I in electroreduction we believe reactivity is further decreased from that of IV due indirectly to steric hindrance to coplanarity and its direct effect in decreasing conjugation. For I in the Diels-Alder reaction we believe that reactivity is decreased still further due to a double effect of steric hindrance to coplanarity which operates directly to counteract planar parallelism in the transitional complex and indirectly to decrease conjugation.

Additional studies on these and closely allied naphthylcycloalkenes are currently underway.

EXPERIMENTAL[5]

The *olefins* I–IV were prepared and purified *via* the picrates in exactly the same manner as reported previously (1). Except for some minor variations in melting points (IV, 59–60°; II picrate, 76.5–77.5°; III picrate, 104–105°; IV picrate, 82–83°) and one variation in boiling point (II, 116°/0.3 mm.) the physical constants were the same as before. Naphthalene was purified by the successive steps of sublimation *in vacuo*, repeated crystallization from methanol, conversion to the picrate and crystallization of this to constant melting point, 148–149° [reported (13a) 151°], dissociation of the picrate chromatographically and, finally, crystallization from ethanol to constant melting point, 80.5–81° [reported (13b) 80.1°, (3) 81°]. Tetra-*n*-butylammonium iodide, prepared according to the procedure of Laitinen and Wawzonek (8), was crystallized once from dilute ethanol and then three times from purified (14a) anhydrous ethyl acetate, m.p. 144–145° [reported (8) 141–142°, (15) 144°]. Dioxane was partially purified by refluxing with hydrochloric acid and drying with potassium hydroxide according to the procedure described by Fieser (14b). If desired the dioxane was then stored temporarily in an amber bottle over bright sodium wire and under nitrogen. Immediately before use the dioxane was refluxed with sodium metal for 10 hours in a dry atmosphere and distilled under nitrogen (in an apparatus previously rinsed once with a chloroform-acetic acid mixture and then several times with acetone to remove residual

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[5] Melting points are uncorrected.

peroxides) first into a preliminary vessel and then directly through a Vigreux column (1 × 12 in.) into a second receiver, b.p. 101–101.5°. Finally the distillate was forced through a column of activated alumina (16) (Alcoa F-20) by means of nitrogen.

For polarography sample solutions approximately 5, 2.5, 1.25, and 0.625 *millimolar* in hydrocarbon were prepared in a stock solution of 0.1 *M* tetra-*n*-butylammonium iodide in 75% (by volume) dioxane-conductivity water. The samples were thermostated (25.0 ± 0.1°) and maintained under purified nitrogen. No effort was made to adjust or control the *p*H of the samples since Laitinen and Wawzonek (2, 8) had found that $E_{1/2}$ for their analogous hydrocarbons was apparently *p*H-independent under similar conditions. Polarograms were obtained with a Sargent Recording Polarograph, Model XXI. Data for the approximate average current, i, were calculated as six-sevenths of the maximal values attained by the pen oscillations (undamped). Usual corrections were made to E, the applied potential, i and i_d, the diffusion current (8, 17). The corrected curves are given in Fig. 1.

SUMMARY

Polarography of 1-(1′-naphthyl)-1-cyclohexene (I) gave only one distinct reduction wave in contrast to the two separate waves obtained for 1-(1′-naphthyl)-1-cyclopentene (II), 1-(2′-naphthyl)-1-cyclopentene (III), and 1-(2′-naphthyl)-1-cyclohexene (IV). The single wave for I, however, was graphically resolvable into two superimposed waves analogous to those for II–IV. The first waves, assigned to reduction of the cycloalkenyl double bonds, showed the order of reactivity II = III > IV > I. The second waves, assigned to reduction of the naphthyl moieties, all occurred at the same half-wave potentials. Comparisons of reactivities of I–IV in electroreduction, catalytic hydrogenation, and Diels-Alder condensation are made and the data are interpreted in terms of postulated steric and conjugative factors.

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