authentic samples, and the relative intensities were measured from integrated spectra.

Isomer assignments were confirmed by infrared comparison of the spectrum of each fraction with authentic spectra of *m*- and *p*-tolyl trifluoromethyl sulfides: *para*, 812 (s), 755 (w), and 705 cm.$^{-1}$; *meta*, 782 (s), 690 (m), and 685 cm.$^{-1}$. In particular, a comparison was made of the CH out-of-plane deformation bands. In the spectrum of each fraction, the strong band at 815 cm.$^{-1}$ was assigned to *para* and was noted to increase in relative intensity in going from fraction 2–5. In accord with the other analysis, a strong band at 760 cm.$^{-1}$ was assigned to the *ortho* isomer and decreased in relative intensity from fraction 2–5. Weak absorption at 685 and 785 cm.$^{-1}$ was assigned to the *meta* isomer. A weak absorption at 715 cm.$^{-1}$ may be associated with the *para* isomer but was not definitely assigned.

On the basis of the above analyses, the approximate isomer composition of the product was *ortho*, 52%; *para*, 47%; and *meta*, 1–2%.

F. Halobenzenes.—Twenty-seven grams of CF_3SCl was treated with 40 g. of chlorobenzene in the presence of 10 g. of anhydrous hydrogen fluoride in a 240-ml. "Hastelloy" bomb heated at 100° for 2 hr., 150° for 2 hr., 175° for 2 hr., and 200° for 2 hr. A total of 10.5 g. of product, b.p. 171–177°, n^{23}_{D} 1.509–1.497, was obtained. From gas phase chromatographic analyses, confirmed with infrared and proton n.m.r. studies as described for the tolyl derivative, the product was shown to contain relative isomer ratios of *ortho*, 24%; *meta*, 2–3%; and *para*, 74%. In this case, the *ortho* isomer concentrated in the higher boiling fraction and was eluted at longer times in gas chromatographic analysis on the same column as above. Identification of product was made on an eluted sample by mass spectrometric, infrared, and n.m.r. analyses. Dichlorobenzenes also are believed to be present as impurities in reaction mixtures.

The above reaction was repeated using 50 g. of bromobenzene instead of chlorobenzene. A total of 20.3 g. of product, b.p. 105–118° (50 mm.), was collected. This material partially crystallized; the crystals were removed by filtration and were found not to contain fluorine. The liquid fraction, 13.1 g., was analyzed by gas chromatography as described above. It was shown to contain the *ortho*, *meta*, and *para* isomers in approximately the same relative amounts as from chlorobenzene but with approximately 30% impurity of a mixture of dibromo- and bromochlorobenzenes, tentatively characterized by mass spectrometric analysis of fractions eluted by gas chromatography. The crystallized fraction also was characterized tentatively by spectral analysis as a mixture of dihalobenzenes.

Catalytic Hydrogenation of Some Naphthyl Alkenes[1-3]

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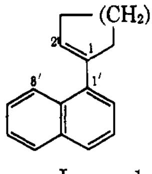
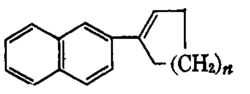
Received September 18, 1963

Rates of catalytic hydrogenation of twelve naphthyl alkenes and two cycloalkyl naphthalenes have been studied using acetic and propionic acids as solvents, Adams' platinum as catalyst, both constant volume and constant temperature (5–40°), and 1-2-atm. pressure. For most of the naphthyl alkenes, first-order rate plots (with respect to the pressure of hydrogen) showed two linear portions corresponding to (1) more rapid reduction of the alkenyl double bond (accompanied by some reduction of the naphthalene ring) and to (2) slower reduction of the resultant alkyl naphthalene, respectively. In general, rate constants for hydrogenation increased with increasing temperature, with change from acetic acid to propionic acid, and (for process 1) with decrease in number of substituents on the carbon atoms of the alkenyl double bond. There was no evidence of preliminary double bond migration.

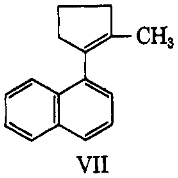
In an earlier publication Klemm and Hodes[4] found that 1-(1-naphthyl)cyclohexene (III) hydrogenated at a slower rate (for reduction of the alkenyl double bond) than that found for its analogs, 1-(1-naphthyl)cyclopentene (I), 1-(2-naphthyl)cyclopentene (II), and 1-(2-naphthyl)cyclohexene (IV), which hydrogenated at essentially identical rates. These results, obtained at 25° with Adams' platinum catalyst in glacial acetic acid, were interpreted in terms of steric hindrance to the attainment of coplanarity in III (but not in the others) during the complex-forming phase of the reaction owing to the fact that collision between hydrogen atoms on C-2 and -8′ would occur. The present investigation is an extension of the previous work. Compounds studied were I–X, 1-vinylnaphthalene (XI), 2-vinylnaphthalene (XII), 1-cyclopentylnaphthalene (XIII), and 1-cyclohexylnaphthalene (XIV).



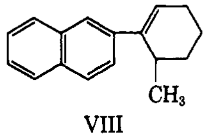
I, $n = 1$
III, $n = 2$
V, $n = 3$



II, $n = 1$
IV, $n = 2$
VI, $n = 3$



VII



VIII

Experimental

Compounds I–XIII were available or prepared in the purified forms previously described[4-9] and were stored as the narrow-melting polynitro aromatic molecular compounds indicated. Immediately before use each complex was dissociated by adding

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(1) Abstracted (in part) from the Ph.D. thesis of R. Mann, University of Oregon, June, 1959. A detailed description of the construction and manipulation of the apparatus used in this research as well as plots of many kinetic runs may be found in this thesis.

(2) Part XIII, in the series on Chemical Reactivities of Arylcycloalkenes. For part XII, see L. H. Klemm, W. C. Solomon, and A. J. Kohlik, *J. Org. Chem.*, **27**, 2777 (1962).

(3) This research was supported (in part) through sponsorship by the Office of Ordnance Research, U. S. Army, Contract No. DA-04-200-ORD-176; by the U. S. Air Force under Contract No. AF 49(638)-473, monitored by the Air Force Office of Scientific Research of the Air Research and Development Command; and (in part) by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to these donors.

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

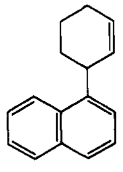
(5) L. H. Klemm and H. Ziffer, *J. Org. Chem.*, **20**, 182 (1955).

(6) For the revised structure of VII, see footnote 7 in ref. 25 and the discussion in the present paper.

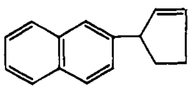
(7) L. H. Klemm, J. W. Sprague, and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

(8) L. H. Klemm, B. T. Ho, C. D. Lind, B. I. MacGowan, and E. Y. K. Mak, *ibid.*, **24**, 949 (1959).

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



IX



X

a concentrated benzene solution of it to a column of alumina-Celite (1:1 by vol.) and eluting with reagent grade petroleum ether (30–60°). The residue from evaporation of the effluent was distilled under nitrogen *in vacuo*. In the case of a liquid product, a center fraction of 1–2° boiling range was selected for use. For a solid product, the distillate was recrystallized to constant melting point from absolute ethanol or methanol. Perbenzoic acid titration[5] showed the presence of 98.8 mole % unsaturation in the sample of VII used.

For preparation of XIV, a solution of 223 g. (0.88 mole) of cyclohexyl *p*-toluenesulfonate[10] (prepared in 88% yield, m.p. 42–44°, from purified[11] *p*-toluenesulfonyl chloride) in 500 ml. of anhydrous ether was added dropwise to the Grignard reagent prepared from 21.1 g. (0.87 g.-atom) of magnesium turnings, 180 g. (0.87 mole) of 1-bromonaphthalene, and 250 ml. of ether. The mixture was stirred for 2 days at room temperature, treated with ice-cold aqueous ammonium chloride, and extracted with ether. Fractional distillation of the dried ethereal layer produced 14.8 g. (8%) of pale yellow XIV, b.p. 118–123° (0.4 mm.). It was purified further by three recrystallizations of its monopicrate (m.p. 125–126°)[12] from absolute ethanol, chromatographic dissociation of the picrate, and distillation of the effluent, obtained as a colorless liquid, b.p. 121–123° (0.7 mm.).

Except for one run, the catalyst, Adams' platinum oxide American Platinum Works), was taken from the same thoroughly premixed batch in every case. Hydrogen (electrolytic grade) was used from one tank only. Mass spectral analysis[13] of this gas indicated the probable presence of 0.7% nitrogen and 0.1% oxygen therein. In a few runs, the hydrogen was deoxygenated before use but this procedure was discontinued since it showed no significant effect on the values of the rate constants obtained. Solvent A_1 was Baker and Adamson glacial acetic acid (99.7%), used directly from the bottle. Batch A_2 acetic acid (anhydrous, b.p. 116°) was prepared by treating the foregoing solvent with chromium trioxide according to the directions of Eichelberger and LaMer[14] and then distilling it through a 2 × 120 cm. column packed with glass helices. Batch P_1 propionic acid (b.p. 138–139°) was prepared from practical grade (Distillation Products Industries) material by refluxing with potassium permanganate, distilling therefrom, and then carefully fractionating by means of the aforementioned column. It gave negative tests with bromine in carbon tetrachloride and aqueous permanganate. Batch P_2 propionic acid resulted from the same practical grade material, but was purified according to the method of Vogel.[15]

Rate studies were made in an all-glass (except for one ground-glass joint lubricated with Dow Corning silicone high vacuum grease and the contact with the column of mercury in the attached manometer) system completely bathed in water thermostated to ±0.1°. Stirring (150 cycles/min.) was accomplished by means of a stomping device (similar to one described by Castille)[16] consisting of a Teflon disk attached to a long glass rod containing a soft iron core, activated by means of water-cooled solenoids surrounding the narrow upper portion of the water-jacketed reaction vessel. During a run, the volume of the system (V) was maintained constant (0.256 l.) to within a fraction of a milliliter, and the decreasing pressure was measured to ±0.3 cm. in the manner described previously.[4] In a typical experiment, the reaction vessel (a flat-bottomed cylindrical cell) was charged with 50 ml. of solvent, 5.00 mmoles of hydrocarbon) and 75.0 mg. of catalyst. The initial pressure of hydrogen was 2 atm. and the final pressure (after 40 min. when measurements were terminated) was 1 atm. or more. Observed manometric pressures were corrected for barometric reading and vapor pressure of the solvent. The logarithm of the ratio of the initial pressure, p_0, to the instantaneous pressure, p, was plotted against reaction time, t, in minutes (see Fig. 1 and 2) and (except in a few cases such as curve E in Fig. 1 and curve D in Fig. 2 where one considers that a *bona fide* first linearity is missing) the slopes (k_1' and k_2') of the first and second linear portions of the resulting curve were determined graphically. The corresponding specific reaction rates, k_1 and k_2, were calculated from the relationships[17a] $k_1 = 2.303\ k_1'V/RTW$ and $k_2 = 2.303\ k_2'V/RTW$, where R is the molar gas constant, T is the reaction temperature in °K.,[17b] and W is weight of catalyst used in grams. The second linear portion of the curve was extrapolated to $t = 0$ in order to obtain the intercept on the $\log(p_0/p)$ axis. Values (for single trials or averages for duplicate or multiple trials made under identical conditions of temperature, solvent, and substrate) for the rate constants and the intercepts are given in Table I. With only a few exceptions, variation of results from individual trials was $< \pm 5\%$ of the average value for k_1 and $< \pm 10\%$, for k_2. Periodic checks on the activity of the catalyst were made using I, 29.9°, and A_1 solvent (run 27). Variations in values of k_1 and k_2 from duplicate trials made over the period of 18 months which elapsed during collection of the kinetic data in Table I were no greater than those from consecutive duplicate trials.

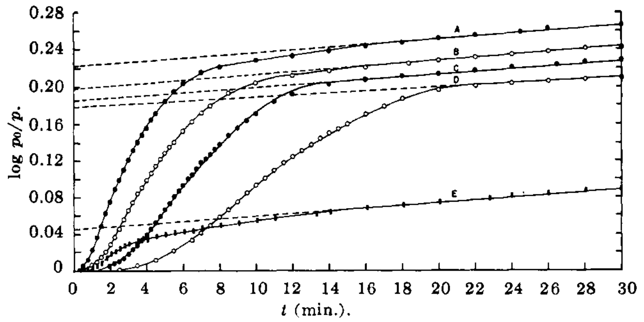


Fig. 1.—Hydrogenation kinetic runs in P_2 propionic acid. Curves A–D for 1-(2-naphthyl)cyclohexene (IV) at temperatures of 39.9, 29.9, 19.9, and 9.9°, respectively, curve E for 2-methyl-1-(1-naphthyl)cyclopentene (VII) at 29.9°.

Discussion

Examination of Table I shows that, in general in the same solvent, k_1 and k_2 increase with increasing temperature over the range of temperatures studied (5–40° in propionic acid, 20–40° in acetic acid). This phenomenon readily is observable for k_1' in curves A–D in Fig. 1, where the increase in induction period with decreasing temperature is apparent also. Since reduction of the platinum oxide catalyst was conducted *in situ* and no special precautions were taken to protect the solvent from absorption of moisture from the air while it was being transferred to the reaction chamber, all solvents used contained at least small amounts of water. Comparison of runs 3 and 5 shows that the deliberate addition of water to the solvent served to decrease k_1 somewhat but scarcely affected k_2 beyond experimental error. The gross change of solvent from acetic acid to propionic acid, on the other hand, brought about a consistent increase (up to 46% at 29.9°) in k_1, but gave variable effects on k_2 (*cf.* runs 27, 3; 30, 4; 35, 9; 36, 10; 40, 13).[18]

Comparison of data for intercepts on the log axis shows that in only three cases (compounds VII, XIII,

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[10] W. J. Hickinbottom and N. W. Rogers, *J. Chem. Soc.*, 4131 (1957).

[11] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 380.

[12] Reported m.p. 126.7–127.4°, M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **69**, 505 (1947).

[13] We are indebted to Dr. Thomas A. Whatley and Dr. D. F. Swinehart for this analysis.

[14] W. C. Eichelberger and V. K. LaMer, *J. Am. Chem. Soc.*, **55**, 3633 (1933).

[15] A. I. Vogel, *J. Chem. Soc.*, 1814 (1948).

[16] A. Castille, *Bull. soc. chim. Belges*, **46**, 5 (1937).

[17] (a) R. D. Schuetz, L. R. Caswell, and J. C. Sternberg, *J. Org. Chem.*, **24**, 1080 (1959); (b) temperature was converted from °C.

[18] The effect of varying solvent on the kinetics of hydrogenation of nitro compounds has been investigated by H. C. Yao and P. H. Emmett, *J. Am. Chem. Soc.*, **81**, 4125 (1959); **83**, 796, 799 (1961).

TABLE I

RATES OF HYDROGENATION OF SOME NAPHTHYL ALKENES[a]

In propionic acid[b]							In acetic acid[c]						
Run no.[d]	Compound	t, °C.	No. of trials[e]	k_1, mmoles min.$^{-1}$ atm.$^{-1}$ g.$^{-1}$	k_2 mmoles min.$^{-1}$ atm.$^{-1}$ g.$^{-1}$	Intercept on log p_0/p axis	Run no.[d]	Compound	t, °C.	No. of trials[e]	k_1 mmoles min.$^{-1}$ atm.$^{-1}$ g.$^{-1}$	k_2 mmoles min.$^{-1}$ atm.$^{-1}$ g.$^{-1}$	Intercept on log p_0/p axis
1	I	4.9	2	3.71	0.27	0.15	25	I	19.7	2	5.64	0.31	0.15
2	I	14.9	2	5.9	0.42	0.15	26	I	24.9	2	6.39	0.48	0.16
3	I	29.9	3	10.4	0.71	0.18	27	I	29.9	6[f]	7.11	0.53	0.17
							28[g]	I	32.5	2	8.90	0.75	0.18
							29[g]	I	35.0	3	8.86	0.72	0.17
4	I	39.9	1	16.5	0.96	0.16	30	I	39.7	3	9.54	0.75	0.17
5[h]	I	30.1	1	9.1	0.81	0.17	31*	I	29.9	2	9.98	0.85	0.18
6	II	5.0	1	3.98	0.37	0.14	32*	II	29.9	2	9.01	1.15	0.17
7	II	6.9	1	4.54	0.36	0.15	33[i]	II	29.9	1	10.3	0.75	0.18
8	II	17.9	1	6.99	0.73	0.16	34	II	19.9	2	6.3	0.50	0.15
9	II	29.9	2	11.5	0.80	0.17	35	II	29.9	2	9.07	0.75	0.16
10	II	39.9	2	15.9	1.2	0.19	36	II	39.9	2	10.4	0.95	0.17
11*	IV	9.9	1	4.61	0.23	0.19							
12*	IV	19.9	1	6.59	0.36[j]	0.19	37	III	19.9	1	3.47	0.39	0.16
13*	IV	29.9	1	9.58	0.33[j]	0.20	38	III	29.9	2	5.08	0.73	0.14
14*	IV	39.9	1	12.7	0.37[j]	0.23	39	III	40.1	1	6.37	0.90	0.16
15	IV	29.9	2	10.4	1.19	0.18	40*	IV	29.9	2	7.98	1.07	0.16
16*	VI	29.9	2	9.79	0.74	0.20	41	V	29.9	1	3.8[k]	0.53	0.14
17*[l]	VII	29.9	2	*m*	0.38	0.04	42*	X	29.9	2	12.9	1.16	0.17
18	VIII	4.9	2	2.63	0.26	0.15	43	IX	19.9	1	10.9	0.33	0.18
19	VIII	29.9	2	7.43	0.68	0.14	44	IX	29.9	2	13.3	0.55	0.19
20	VIII	40.1	1	9.70	1.16	0.16	45	IX	39.9	1	17.3	0.62	0.20
21*	XIII	29.9	2	*m*	0.48	0.05	46	XIV	29.9	2	*m*	0.48	0.03
							In propionic acid[b]						
22	XI	29.9	2	25.3	1.32	0.19	47*	XII	9.9	1	10.8	0.18	0.18
23	XII	19.9	1	19.0	0.48	0.18	48*	XII	19.9	2	13.5	0.31	0.19
24	XII	29.9	1	21.0	0.72	0.20	49*	XII	29.9	2	19.1	0.23	0.20

[a] Unless otherwise designated, reactions were run using 50 ml. of solvent, 75.0 mg. of platinum oxide from the same premixed batch, and 5 mmoles of hydrocarbon. [b] Unstarred runs in this solvent were made in batch P_1 propionic acid; starred runs, in batch P_2 propionic acid. [c] Unstarred runs in this solvent were made in batch A_1 acetic acid; starred runs, in batch A_2 acetic acid. [d] Not listed chronologically. [e] Where two trials are reported, they were made in succession; where three or more trials are reported, only two were made consecutively. [f] This series of trials was made over a period of 18 months in order to check the retention of activity of the catalyst. It includes runs from two different bottles of A_1 acetic acid and one run using 2.58 mmoles of hydrocarbon. [g] From the nearly identical rate constants found in runs 28 and 29, it appears that some irregularity may occur in the hydrogenation of I between 29.9° and 35.0° in A_1 acetic acid. [h] Using P_1 propionic acid to which 1% of water was added. [i] Using a fresh batch of catalyst. [j] k_2 appears to be insensitive to changes in temperature in runs 12–14. [k] This represents a maximum value, inasmuch as the earlier part of the short linear portion coincides with the log plot for reduction of the catalyst (as noted from run 46). [l] See ref. 6. [m] No *bona fide* first linear portions ascribable to hydrogenation of the substrate were present in the log plots of these runs. However, preliminary reduction and sorption of hydrogen by the catalyst is observed.

and XIV) were particularly low values (0.04 ± 0.01 at 29.9°) obtained. Moreover, of all the compounds studied, only these three absorbed less than an equimolar amount (compared to the size of hydrocarbon sample used) of hydrogen during a 40-min. run. The intercept values compare favorably with that of 0.02–0.04 obtained as a blank for reduction–saturation of the catalyst–solvent combination alone. However, in the absence of hydrocarbon substrate, the catalyst readily was observed to coagulate after only a few minutes of reaction time. In contrast, during any regular run, no coagulation was visually apparent until near the termination of the run, if at all. Since XIII and XIV can give only reduction of the naphthalene moiety, we have used the intercept of 0.04 ± 0.01 as an operative value representing the appropriate blank (at 29.9°) for the regular runs. At this temperature an intercept of 0.18 ± 0.03 would correspond to absorption of 1 mole of hydrogen per mole of hydrocarbon (plus blank). Intercepts found were 0.17 ± 0.03 for all compounds except the aforementioned three.

As suggested previously[4] and in accordance with the results noted in the preceding paragraph, the second linear portion of the curve is considered generally to represent only a first-order reduction process[19] for the naphthalene moiety. Consistent with this assignment are the facts that, for runs made under the same conditions, k_2 values are nearly identical for the conjugated and unconjugated pair of 2-cyclopentenylnaphthalenes II and X (runs 32 and 42), as well as for (runs 44 and 46) 1-cyclohexylnaphthalene (XIV) and the unconjugated 1-cyclohexenylnaphthalene (IX). The slightly higher value of k_2 (run 38) for the conjugated 1-cyclohexenylnaphthalene (III) as compared to values for the latter pair may be ascribed to some overlapping of the first and second linearities in the curve for this compound.[20] The curve for VII is nearly superimposable on those for XIII and XIV, despite the fact that VII is a *bona fide* naphthyl alkene.[21] Though lack of material

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(19) Since studies with varying amounts of catalyst and investigations of the time dependence of concentrations of hydrocarbons were not made, this really must be considered a pseudo first-order process.

(20) J. W. Cook and C. A. Lawrence [*J. Chem. Soc.*, 1431 (1936)] reported simultaneous reduction of the cyclohexenyl double bond and the naphthalene ring in preparative studies.

(21) This was the first indication that VII has the structure shown rather than that of 5-methyl-1-(1-naphthyl)cyclopentene assigned previously.[5]

prevented checking this point, it seems likely that preferential hydrogenation of the naphthalene ring (rather than of the cycloalkenyl double bond) occurs in VII.

With assignment of the second linearity to exclusive reduction of the naphthalene moiety, one thence must ascribe the first linearity (where present) to reduction of the alkenyl double bond plus, in general, some simultaneous reduction of the naphthalene moiety. Except for the initial portion of the curve where reduction–activation of the platinum oxide catalyst occurs, one may represent the slope of the kinetic curve at any point by the semiempirical equation (1) that follows

$$\frac{d\log(p_0/p)}{dt} = k_Ag_A + k_Ng_N \qquad (1)$$

where k_A is an inherent partial rate constant referring to reduction of the alkenyl double bond only, k_N is an inherent partial rate constant referring to reduction of the naphthalene ring only, and g_A and g_N are parameters which vary with t and with the hydrocarbon used. g_A and g_N may take values ≥ 0. Interest and simplicity are attached to those periods of time when both g_A and g_N remain effectively constant, for then one obtains a simple integral equation (2) for a first-order reaction.

$$\log(p_0/p) = (k_Ag_A + k_Ng_N)t \qquad (2)$$

Thus, during the second linearity we take $g_A = 0$ and $g_N = 1$, *i.e.*, $k_N = k_2'$. The case corresponding to $g_A = g_N = 1$ for the first linearity has been discussed by Klemm and Hodes,[4] who noted that under such circumstances extrapolation of the second linearity to $t = 0$ would give an intercept corresponding precisely to that amount of hydrogen required for the blank plus reduction of the alkenyl double bond, *i.e.*, $k_A + k_N = k_1'$. In such case the naphthyl and alkenyl moieties appear to act independently. For the case where $0 < g_A < 1$ and $g_N > 1$, the naphthyl moiety may be considered to usurp some of the catalytic sites otherwise open to the alkenyl moiety. Generally one would expect this situation to lead to the result $k_1' < k_A + k_N$ and to a low value for the intercept. On the other hand, for $g_A > 1$ and $0 < g_N < 1$, the alkenyl moiety may be considered to usurp catalytic sites otherwise open to the naphthyl moiety. Again such situation should lead to the result $k_1' > k_A + k_N$ and to a high value for the intercept. Examination of Table I shows that, as expected (except in a few cases), large values for the intercept (at 29.9°) are associated with large values of k_1, and vice versa.

Examination of Table I also shows the effects of structural factors in the hydrocarbon on k_1. Using only data for the reaction temperature 29.9°, it is apparent that k_1 decreases with increasing substitution on the alkenyl double bond.[22,23] Thus (for values of k_1), in solvent P_1, monosubstituted alkenes (k_1 = 21–25.3; runs 22, 24) > trisubstituted alkenes (7.4–11.5; runs 3, 9, 15, 19); in P_2, mono- (19.1; run 49) > tri- (9.5–9.8; runs 13, 16) > tetra- (0; run 17); in A_1, di- (13.3; run 44) > tri- ($\leq$9.1; runs 27, 35, 38, 41); and in A_2, di- (12.9; run 42) > tri- (7.9–10; runs 31, 32, 40). Comparing values of k_1 for the same alkene run in two different solvents, both at 29.9°, one can get an estimate of the relative effect on k_1 of the solvent. Taking P_1 as the standard solvent for comparison one gets k_1 (in P_1) = 1.1 k_1 (in P_2); *cf.* runs 13, 15; 24, 49 = 1.27–1.46 k_1 (in A_1); *cf.* runs 3, 27; 9, 35 = 1.04–1.30 k_1 (in A_2); *cf.* runs 3, 31; 9, 32; 15, 40. On this basis one obtains for our compounds the relative specific rates k_1 in solvent P_1 of monosubstituted alkenes (21–25) > disubstituted alkenes (13–20) > trisubstituted alkenes (up to 12) > tetrasubstituted alkenes (0).

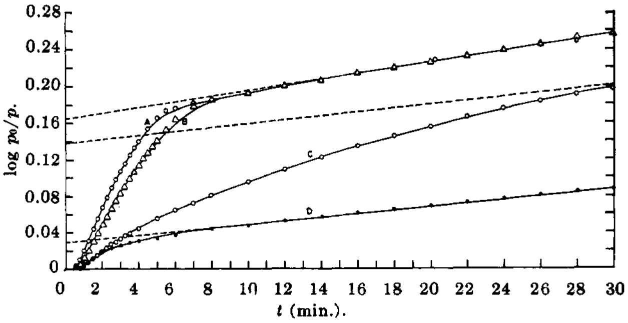

Fig. 2.—Hydrogenation kinetic runs at 29.9°. Curves A and B for 1-(2-naphthyl)cyclopentene (II) in P_1 propionic acid and in A_1 acetic acid, respectively; curve C for 1-(1-naphthyl)cycloheptene in A_1 acetic acid; curve D for 1-cyclohexylnaphthalene in A_1 acetic acid.

Double bond migration to form more stable alkenes has been reported[22] to occur on various catalysts in the presence of hydrogen. Comparison of runs 32 and 42 shows that in the 2-cyclopentenylnaphthalene system (where the conjugated isomer II should be considerably more stable[24] than the nonconjugated one X) k_1 for X is greater than for II. Although these data do not militate against any bond migration of the type X → II prior to hydrogenation, it is clear that if such migration does occur its rate cannot be enormously faster than that for hydrogenation of X directly. The situation is even clearer in the 1-cyclohexenylnaphthalene system (IX, III; compare runs 43–45 with 37–39, respectively) where k_1 is nearly three times as large for the unconjugated arrangement as for the conjugated one. In this case, however, because of appreciable twisting around the pivotal bond[24] there may be little, if any, increase in stability to be gained by the transformation of IX → III.

In solvent P_1 at 29.9° (runs 9, 15, 16, and 24), one observes the order of reactivity, as based on conjugated alkenyl substituents in the 2-naphthyl position, vinyl >> cyclopentenyl $\geq$ cyclohexenyl $\geq$ cycloheptenyl (estimated). Also in A_1 at 29.9° (runs 22, 27, 38, and 41) one obtains the order, for substituents in the 1-naphthyl position, vinyl (estimated) >> cyclopentenyl > cyclohexenyl > cycloheptenyl. These orders are consistent with bulkiness of the groups, but apparently not with conjugative powers of the groups as measured by polarographic reduction and ultraviolet spectra.[25] In addition, for P_1 solvent one estimates, for the isomeric conjugated 1- and 2-alkenyl naphthalenes, the order cycloheptenyl (>2.5) > cyclohexenyl (1.6–2.2) > cyclopentenyl (1.1) > vinyl (0.83) for the ratio k_1 (2 isomer) to k_1 (1 isomer). The values near 1.0 for the vinyl

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[22] G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, Chapter 11.

[23] B. B. Corson in "Catalysis," Vol. III, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, pp. 89–90.

[24] Compare ultraviolet absorption spectra as reported by L. H. Klemm, H. Ziffer, J. W. Sprague, and W. Hodes, *J. Org. Chem.*, **20**, 190 (1955), and in ref. 8.

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

and cyclopentenyl cases are consistent with the postulation that in these compounds there is little energetic difference to the attainment of coplanarity (assumed to be desirable for most facile adsorption)[4] onto the catalytic surface between the corresponding 1 and 2 isomers. Steric hindrance to attainment of coplanarity in the 2 isomers should be less than in the 1 isomers for the cyclohexenyl and cycloheptenyl pairs, however. The slower rate of hydrogenation of VIII as compared to IV (runs 15 and 19) seems to be ascribable to steric hindrance effects only (either greater hindrance to the attainment of coplanarity in VIII or hindrance to adsorption due to the sidewise projecting methyl group in this compound, or both).[24]

Syntheses of Jasmone and the Related Compounds. I. Preparation of Dihydrojasmone and the Homologs from γ,γ-Dialkylparaconic Acids[1]

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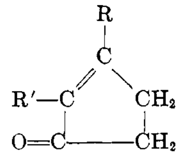
Received October 7, 1963

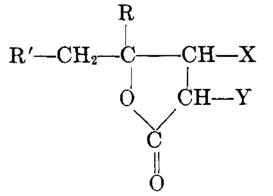
γ,γ-Dialkylparaconic acids (III) were synthesized by hydrolysis of γ,γ-dialkyl-α,β-dicarbethoxybutyrolactones (IV), or by means of lactonization of the Stobbe half-esters (IX). The butyrolactones (IV) were obtained by the condensation of ethyl β,β-dialkylglycidates (V) with sodiomalonate. Treatment of the paraconic acids (III) with polyphosphoric acid gave the corresponding 2,3-dialkyl-2-cyclopenten-1-ones (I), including dihydrojasmone. As by-products, unsaturated dibasic acids (VII) and acid anhydrides (VIII) were separated.

A new route to dihydrojasmone (I, R = CH_3 and R′ = C_5H_{11}) and its homologs from lactonic intermediates (III and IV) was studied. The cyclopentenones (I) previously have been obtained by dehydration of γ-butyrolactones (II),[2–8] but lactonic acids (III) or esters (IV), which can be prepared more readily than II, were found also to be converted into I in good yields. A number of cyclopentenones (I) were synthesized by this procedure.

The paraconic acids (III) were obtained in two ways. The first route involves the reaction of ethyl γ,γ-dialkylglycidates (V) with sodiomalonate.[9]

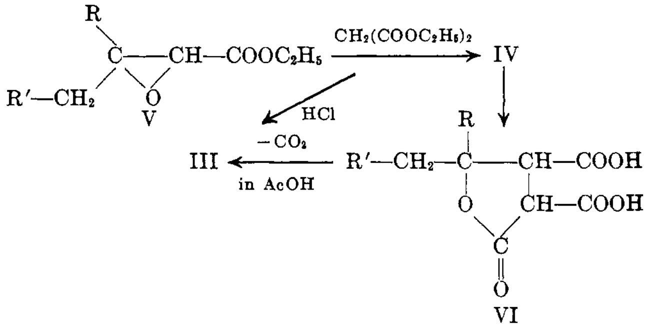


I



II, X = Y = H
III, X = COOH, Y = H
IV, X = Y = $COOC_2H_5$

In this reaction 70–80% yields of γ-methyl-γ-alkyl-α,β-dicarbethoxybutyrolactones (IV) were obtained. The new lactone diesters (IV) are listed in Table II. The lactone diesters (IV) were converted into the paraconic acids (III) by means of hydrolysis to VI followed by decarboxylation.[10] Pyridine[10] or 20% sulfuric acid,[11] when used as a decarboxylating agent, afforded the paraconic acids (III) in yields of 40–60%. Glacial acetic acid was found to give much better yields of 70–80%. The paraconic acids[12] (III) were obtained, however, in one step from the lactone diesters (IV) by the action of concentrated hydrochloric acid in 78% yield.



Hydrolysis of the lactone diesters (IV) in the presence of excess of 5 *N* sodium hydroxide followed by decarboxylation gave unsaturated dibasic acids (VII) through the fission of the lactone ring.

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[1] Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tôkyô, April, 1961.

[2] R. L. Frank, P. G. Arvan, J. W. Richter, and C. R. Vanneman, *J. Am. Chem. Soc.*, **66**, 4 (1944).

[3] F. B. LaForge and W. F. Barthel, *J. Org. Chem.*, **10**, 222 (1945).

[4] R. L. Frank, R. Armstrong, J. Kwiatek, and J. A. Price, *J. Am. Chem. Soc.*, **70**, 1379 (1948).

[5] M. Elliott, *J. Chem. Soc.*, 2231 (1956).

[6] C. Rai and S. Dev, *Experientia*, **11**, 114 (1955); *J. Indian Chem. Soc.*, **34**, 266 (1957).

[7] E. Demole, E. Lederer, and D. Mercier, *Helv. Chem. Acta*, **45**, 685 (1962).

[8] L. Givaudan, German Patent 639,455 (1936); *Chem. Abstr.*, **31**, 1434 (1937).

[9] The reaction of β,β-dimethylglycidate with sodiomalonate has been recorded. See A. Haller and G. Blanc, *Compt. rend.*, **142**, 1471 (1906); G. V. Chelintsev and E. D. Osetrova, *J. Gen. Chem. USSR*, **7**, 2373 (1937); *Chem. Abstr.*, **32**, 2099 (1938). The reaction by the carbanion of malonate occurred at the α-position of glycidate. However, R. E. Parker, *Chem. Rev.*, **59**, 737 (1959), described that anions from amines combined with the β-carbon, while Y. Liwschitz, Y. Rabinsohn, and D. Perera, *J. Chem. Soc.*, 1116 (1962), showed the α-attack by ammonia. The present results of the reaction sequences confirmed the α-attack by malonate.

[10] W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubband, *J. Am. Chem. Soc.*, **83**, 606 (1961).

[11] S. F. Birch and J. F. Thorpe, *J. Chem. Soc.*, 1821 (1922).

[12] Infrared spectra of the neat paraconic acids (III) have a single carbonyl band at about 1735 cm.$^{-1}$. Absorption in chloroform showed two bands at 1780–1755 cm.$^{-1}$ for lactone carbonyl and at 1720–1700 cm.$^{-1}$ for carboxylic acid carbonyl, respectively. Ethyl γ-methyl-γ-hexylparaconate have a lactone carbonyl band at 1776 cm.$^{-1}$ and an ester carbonyl band at 1729 cm.$^{-1}$. The lowering of the lactone carbonyl frequency of neat γ,γ-dialkylparaconic acids (III) may be due to intermolecular hydrogen bonding. See C. Katsuta and N. Sugiyama, *Bull. Chem. Soc. Japan*, **35**, 1194 (1962).