The following mechanism is suggested:

(1) H_3O^+ is adsorbed according to a Langmuir adsorption. The H_3O^+ concentration of the dilute solutions of the weak acids is proportional to $\sqrt{c}$ (c = total acid concentration), the coefficient of adsorption being somewhat dependent on the nature of the anion which, for reason of electroneutrality, must remain close to the adsorbed H_3O^+, presumably forming an ion-pair. As long as only one species of acid is present, this mechanism is indistinguishable from molecular adsorption following an "exponential" isotherm.

(2) When two or more acids are present, the adsorbed H_3O^+ acts as an anion-exchanger with respect to the acids in solution according to the mechanism

$$[H_3O^+{}_{ads} + A_1^-] + HA_2 \overset{k_3}{\rightleftarrows} [H_3O^+{}_{ads} + A_2^-] + HA_1$$

(3) In mixtures of two acids, the coefficient $k_{1,2}$ of adsorption of H_3O^+ is taken as the appropriate mean of the single solute coefficients k_1 and k_2, *i.e.*

$$k_{1,2} = (c_1k_1 + c_2k_2)/(c_1 + c_2) \qquad (2)$$

which covers at the same time differences in the dissociation constants of the two acids. Equation 2 is an approximation only, but exact treatment would be unjustifiably laborious; it implies that total adsorption of acids (q) can be calculated from the single-solute data without the introduction of the new constant k_3 (see Fig. 1 line C.).

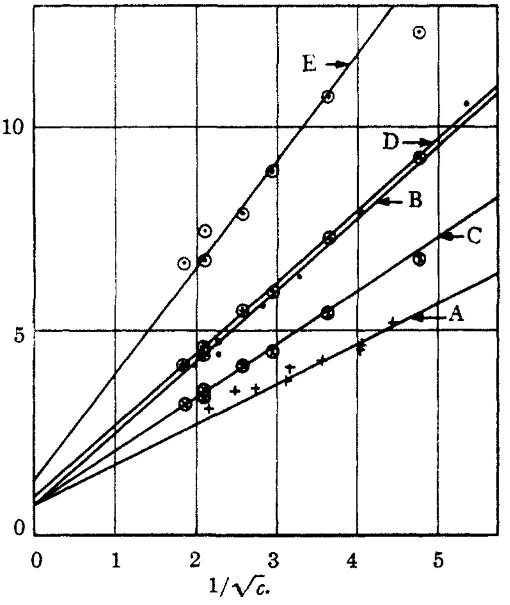

Fig. 1.—Adsorption from mixture of acetic and propionic acids calculated from adsorption data of the pure acids (c = total acid concentration in moles/liter, q in millimoles/g.): A, + + +, propionic acid (single solute) (eqn. 3); B, . . ., acetic acid (single solute) (eqn. 3); C, ⊗⊗⊗, total adsorption from mixture (eqn. 3); D, ⊕⊕⊕, propionic acid (from mixture) (eqn. 5a); E, ⊙⊙⊙, acetic acid (from mixture) (eqn. 4a); (curve E shows $1/q$-values halved).

The assumption of a Langmuir adsorption for H_3O^+ means then that the total adsorption of acids is in all cases represented by the equation

$$q = \frac{Qk\sqrt{c}}{1 + k\sqrt{c}} \qquad (3)$$

where k is k_1, k_2 or $k_{1,2}$ according to whether one deals with single or multiple solutes. In the example of the acetic and propionic acids, the constants $Q = 1.43$, $k_1 = 0.399$ and $k_2 = 0.690$ are obtained from Nestler and Cassidy's single solute experiments, *i.e.*, from the slopes and intercepts of line A and B of the figure. For the 5:4 molar mixture of acids used, the value $k_{1,2} = 0.528$ follows from eqn. 2 as the mean of k_1 and k_2. The only new constant to be obtained from the binary adsorption data is thus the ion-exchange constant $k_3 = 0.27$ (from Table I). These constants are to be applied to concentrations in mole/liter and to specific adsorptions (q) in millimole/g.

The final equations for q_1 and for q_2 in mixed adsorption taking account of the anion-exchange, then follow from eqn. (1) and (3) combined with the fact that $q_1 + q_2 = q$

$$q_1 = \frac{Qk_{1,2}\sqrt{c}}{(1 + k_{1,2}\sqrt{c})}\frac{k_3c_1}{(c_2 + k_3c_1)} \qquad (4)$$

$$q_2 = \frac{Qk_{1,2}\sqrt{c}}{(1 + k_{1,2}\sqrt{c})}\frac{c_2}{(c_2 + k_3c_1)} \qquad (5)$$

and for the fixed molar ratio of 5:4 we obtain for acetic (subscript 1) and propionic (subscript 2) acids the equations

$$q_1 = 0.191\,\sqrt{c}/(1 + 0.528\sqrt{c}) \qquad (4a)$$

$$q_2 = 0.565\,\sqrt{c}/(1 + 0.528\sqrt{c}) \qquad (5a)$$

For a check of the experimental data it is convenient to plot $1/q$ against $1/\sqrt{c}$, whence the equations 3, 4a and 5a result in straight lines. The experimental data of Nestler and Cassidy are shown as points in the figure and they agree well, within the limits of their accuracy, with the calculated lines.

This calculation does not exclude the possibility that some acid is adsorbed in undissociated form as well, but such an assumption alone does not explain the data satisfactorily, while the ion-exchange model alone does. This discussion is intended to emphasize the need to differentiate between exponential isotherms due to dissociation phenomena and those due to a statistical distribution of adsorbing sites of different affinity. This difference, though not apparent in single solute isotherms, becomes important for the adsorption of mixtures.

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Dicyclic Hydrocarbons. II. 2-Alkylbicyclohexyls

BY I. A. GOODMAN AND P. H. WISE

The syntheses and physical properties of a series of 2-substituted alkylbiphenyls have recently been reported from this Laboratory.[1] The alkyl substituents included methyl, ethyl, propyl, isopropyl and butyl. In this communication we wish to present the results of the catalytic hydrogenation of these hydrocarbons, including data on the separation of the geometrical isomers, and the analyses and physical properties of the five pairs of isomers which were obtained. The

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[1] I. A. Goodman and P. H. Wise. THIS JOURNAL, 72, 3076 (1950).

Table I

Physical Properties, Yields and Analyses of 2-Alkylbicyclohexyls

Bicyclohexyl hydrocarbon	M.p., °C.	B.p., °C. at 760 mm.	$n^{20}D$	d^{20}, g./ml.	ΔH_f, kcal./mole	Est. purity, mole %	Heat of comb.,[c] kcal./mole	Relative yield, %	Carbon, %		Hydrogen, %		Viscosity, centistokes[d]			
									Calcd.	Found	Calcd.	Found	32° F.	100° F.	140° F.	210° F.
2-Methyl[a]	−26.43	249.87	1.4791	0.88447	4.4	98.9	1855	41	86.58	86.65	13.42	13.35	8.84	3.11	2.08	1.22
2-Methyl[b]	−10.27	255.00	1.4836	.89450	4.6	99.2	1870	59	86.58	86.58	13.42	13.41	12.85	4.20	2.69	1.51
2-Ethyl[a]	Glass	266.23	1.4827	.89065	...	..	1995	34	86.51	86.60	13.49	13.48	16.33	4.20	2.58	1.40
2-Ethyl[b]	−0.35	269.54	1.4851	.89624	5.4	99.9	2015	66	86.51	86.46	13.49	13.47	18.53	4.75	2.89	1.54
2-Propyl[a]	Glass	279.40	1.4807	.88527	...	..	2145	35	86.46	86.44	13.54	13.56	28.32	5.38	3.05	1.56
2-Propyl[b]	0.25	282.22	1.4838	.89205	5.7	99.8	2160	65	86.46	86.47	13.54	13.56	34.08	6.20	3.46	1.71
2-Isopropyl[a]	Glass	277.18	1.4843	.89305	...	..	2140	49	86.46	86.45	13.54	13.54	46.82	6.94	3.75	1.80
2-Isopropyl[b]	−9.13	283.06	1.4901	.90365	5.7	99.9	2165	51	86.46	86.50	13.54	13.53	29.12	6.54	3.78	1.91
2-Butyl[a]	Glass	294.15	1.4799	.88227	...	..	2300	40	86.40	86.42	13.60	13.48	42.37	6.74	3.64	1.76
2-Butyl[b]	−6.51	296.56	1.4827	.88819	6.5	..	2300	60	86.40	86.44	13.60	13.48	51.18	7.65	4.05	1.91

[a] Low-boiling isomer. [b] High-boiling isomer. [c] ASTM procedure: D240-39. [d] ASTM procedure: D445-46T.

synthesis of 2-methylbicyclohexyl and 2-ethylbicyclohexyl from cyclohexylidenecyclohexanone has been reported,[2] but no reference is made to the existence of geometrical isomerism in these hydrocarbons.

The general application of von Auwers' rule[3] has been shown to be susceptible to error[4,5] as indicated by the recent change in the name of the *cis* and *trans* isomers of 1,3-dimethylcyclohexane. Consequently, since the pertinent thermodynamic properties have not been investigated, no specific assignment of *cis* and *trans* configurations can be made, and the products isolated are referred to simply as the low- and high-boiling isomers.

The high-boiling isomer of each isomeric pair and the low-boiling isomer of 2-methylbicyclohexyl could be successfully crystallized. An estimation of their purities on the basis of their time–temperature melting curves and heats of fusion is shown in Table I. Because of the short length of the equilibrium portion of the melting curve for the high-boiling isomer of 2-butylbicyclohexyl, the estimation of purity of this compound was not deemed valid and is not recorded.

For the low-boiling isomers which could not be crystallized, fractions were combined on the basis of constant refractive index and density values. A systematic evaluation of purity could not be made for these isomers, but the distinct plateaus of refractive index and density values indicated purities of the same order of magnitude as those recorded for the compounds obtained in the crystalline state.

All of the physical properties were determined by methods previously described,[1] and the estimated mole % purities were determined according to the method of Glasgow, Streiff and Rossini.[6]

Experimental[7]

Materials and Procedure.—The 2-alkylbiphenyls used in this investigation had physical properties similar to those previously reported.[1] The quantity of each hydrocarbon hydrogenated varied according to the amount available for such use. Hydrogenations were carried out in a 3-liter bomb at 1500–2000 p.s.i. and 190–210°. A volume of methylcyclohexane equal to that of the hydrocarbon was used as solvent, and 10–12% by weight of UOP nickel was used as catalyst except for the hydrogenation of 2-butylbiphenyl. Small amounts of halogen-containing olefin were present in this material; consequently 18–20% by weight of UOP nickel was used in this case.

The quantities of material hydrogenated were as follows: 2590 g. (15.4 moles) of 2-methylbiphenyl; 1925 g. (10.6 moles) of 2-ethylbiphenyl; 1100 g. (5.6 moles) of 2-propylbiphenyl; 950 g. (4.8 moles) of 2-isopropylbiphenyl; and 1015 g. (4.8 moles) of 2-butylbiphenyl. Yields of completely hydrogenated product were essentially quantitative, although the rate of hydrogenation was much lower for the 2-butylbiphenyl than for any of the other hydrocarbons (23 hours compared to an average of 5 hours for each of the others), because of the presence of halogen impurity.

Purification.—Separation and purification of the five isomeric mixtures was effected by passage of the hydrogenation products through silica gel columns followed by careful fractionation at reduced pressure through six-foot Podbielniak distillation columns.

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Paper Chromatography in the Separation of Estradiol-17α from Estradiol-17β and of Equilin from Equilenin

By Erich Heftmann

It has recently been shown that paper chromatography may be used for the identification of mixtures of estrone, estradiol-17β ("α"-estradiol) and estriol.[1] The same method is applicable to the binary mixtures of estradiol-17α and estradiol-17β and of equilin and equilenin with only a minor change in the developing solvent. The separation of the 17-epimers of estradiol and of dihydroequilenin by partition chromatography on Celite has also been accomplished by Haenni.[2]

Experimental

Conditions for the preparation of the *p*-nitrobenzeneazodimethoxyaniline derivatives of the estrogens and for the development of the chromatogram are exactly as previously described,[1] except that equilin and equilenin couple more readily without heating than the other estrogens studied and that the development with the modified solvent mixture takes only 1.25 hours. The new solvent mixture is prepared by equilibration of 200 cc. of petroleum ether (boiling range 35–60°), 100 cc. of toluene, 10 cc. of ethanol and 90 cc. of distilled water. The R_f values of estrogen derivatives in the new solvent mixture and in the solvent mixture previously described are given in Table I.

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