between. F-Strain should become a dominant factor only with reference acids having greater steric requirements than the proton.

Conclusions.—By using the alkyl and halo substituted pyridine bases as a reference system free of significant *ortho* effects, it has been possible to arrive at a quantitative measure of the *ortho* effects of these groups in other aromatic systems. In the case of the halogens, evidence has been advanced to support the conclusion that hydrogen bonding, steric inhibition of resonance and F-strain all contribute to the *ortho* effects in the acids and base examined. The important effects appear to be: 1, benzoic acids, steric inhibition of resonance; 2, phenylboric acids, F-strain in the anion complex; 3, phenols and thiophenols, hydrogen bonding; 4, anilines, hydrogen bonding and F-strain (in the anilinium ion); 5, dimethylanilines, no data available: hydrogen bonding (in the anilinium ion) and steric inhibition of resonance (in the free base) expected to be important.

Recently Taft[35] has made a brilliant attempt to extend the scope of the Hammett equation[36,37] to include *ortho* substituents. We shall not attempt to discuss Taft's treatment here, but we will comment on certain of his conclusions which bear on the subject matter of the present paper.

Taft finds that the ionization constants for the

(35) R. W. Taft, Jr., THIS JOURNAL, **74**, 2729, 3120 (1952); **75**, 4231, 4538 (1953).
(36) L. P. Hammett, ref. 5, pp. 184–193.
(37) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

ortho substituted benzoic acids can be related linearly to the σ-values he has developed, that is, to what he calls the electron displacement parameter. From this observation he draws the conclusion that "the relative ionization of those benzoates listed (CH_3O-, CH_3-, C_6H_5-, $Cl-$, $Br-$, $I-$, O_2N-) are determined by polar effects of substituents and are not dependent to an appreciable degree upon steric factors." He also finds a linear relationship for the dissociation of *ortho* substituted anilines utilizing his σ-values.

From the treatment presented in the present paper, it would appear that the various types of *ortho* effects cannot be considered entirely negligible in comparison with the polar effects. Consequently, it would appear that Taft's σ-constants may represent a composite of a major contribution by the polar factor with relatively minor contributions by the different *ortho* effects. These σ-constants may be expected to operate satisfactory only in cases where the polar factor continues to dominate the situation. Taft has pointed out that his treatment may be expected to fail when steric effects are not nearly constant relative to polar effects.[35]

Many apparently erroneous interpretations of *ortho* effects have appeared in the literature, in part because no suitable reference system has been available to permit a quantitative estimate of the magnitude of the *ortho* effect. The pyridine bases appear to provide a reasonably satisfactory reference system of this kind.

LAFAYETTE, INDIANA

Base-catalyzed Methanolysis of *l*-Menthyl *m*- and *p*-Alkylbenzoates

BY MELVIN S. NEWMAN AND ELIOT K. EASTERBROOK[1]

The rates for the sodium methoxide catalyzed methanolysis of *p*-alkyl *l*-menthyl benzoates fall in the order, $CH_3 < C_2H_5 < i\text{-}C_3H_6 < t\text{-}C_4H_9$, which indicates that the hyperconjugative effect is predominant. In the *m*-series the same order is obtained. To account for this order in the *m*-series a steric effect is suggested. The rates for all of the compounds fall very close together and all rates are slower than that for *l*-menthyl benzoate.

Two mechanisms of electron release by alkyl groups are recognized—the inductive and hyperconjugative. We were interested in observing the effect of methyl, ethyl, *i*-propyl and *t*-butyl groups in the *meta* and *para* positions relative to a carboxylic acid derivative in a typical reaction of the carbonyl addition type. In this paper we report on the base-catalyzed methanolysis of *l*-menthyl benzoates in absolute methanol at 30 and 40°.

This reaction was chosen for a study of the polar effects of alkyl groups on a carbonyl addition reaction since the ρ-value of +2.62 computed from published data[2] indicated that the methanolysis of *l*-menthyl benzoates at 30° was more sensitive to polar effects than the alkaline hydrolysis at 30° of

(1) This paper is based on the Ph.D. thesis of E. K. E., Ohio State University 1953. E. K. E. was holder of the Visking Chemical Corporation fellowship, 1952–1953.
(2) R. W. Taft. Jr., M. S. Newman and F. H. Verhoek, THIS JOURNAL, **72**, 4511 (1950).

ethyl benzoates in 87.83% by weight ethanol for which a ρ-value of 2.498 had been calculated.[3]

The *m*-alkylbenzoic acids, except for *m*-toluic acid, were prepared from the corresponding alkylbenzenes. Nitration afforded a mixture of *o*- and *p*-nitroalkylbenzenes which, without isomer separation, were reduced to the corresponding amino compounds. By means of acetylation, bromination, deacetylation and deamination, these amines were converted into the corresponding *m*-bromoalkylbenzenes. The latter were converted to nitriles which were hydrolyzed to acids. The *m*-isopropylbenzoic acid thus obtained melted at 49–50°. Since at the time a m.p. of about 20° had been reported,[4] this compound was prepared by an alternate method from *m*-bromobenzoyl chloride. The

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 189.
(4) W. S. Calcott, J. W. Tinker and V. Weinmayer, THIS JOURNAL, **61**, 1010 (1939). Later a m.p. of 47–48° was reported—see ref. 14.

melting point was 49–50°, alone and mixed with the other sample. On oxidation isophthalic acid was obtained.

The p-alkylbenzoic acids were prepared by two methods: one, by bromination of the alkylbenzene, followed by conversion to the nitrile and hydrolysis of the latter: and the other, by reaction of the alkylbenzene with chloroacetyl chloride followed by alkaline cleavage of the phenacylpyridinium chloride formed from the phenacyl chloride and pyridine. The melting points and ionization constants (determined by the mid-point titration method) of the acids are listed in Table I.

TABLE I

IONIZATION CONSTANTS AND MELTING POINTS OF m- AND p-
ALKYLBENZOIC ACIDS

RC₆H₄COOH R =	M.p., °C.[a]	$K_{ion} \times 10^{5 b}$
H	121.5–122.5	10.0
p-CH₃	179.6–180.4	6.0
p-C₂H₅	112.8–113.6	6.0
p-i-C₃H₇	116.6–117.1	5.9
p-t-C₄H₉	166.0–166.8	6.0
m-CH₃	110.2–111.0	7.2
m-C₂H₅	47.0–47.6	6.6
m-i-C₃H₇	49.2–50.2	6.1
m-t-C₄H₉	126.8–127.6	6.0

[a] The acids were recrystallized to constant melting points from dilute alcohol. [b] The solvent was 48% (by weight) dioxane–water.

Experimental

Nitration of t-Butylbenzene.[b]—A solution of 62 g. of concd. nitric acid in 95 g. of concd. sulfuric acid was added dropwise to 83 g. of stirred t-butylbenzene at 10–20°. After the addition, stirring was continued for two hours and the reaction mixture then left at 20–25° for 15 hours. The organic product was isolated after dilution, washed with alkali and distilled to yield 105 g. (95%) of a yellow oil, b.p. 98–102° at 3–4 mm. This mixture of o- and p-nitro-t-butylbenzene was used for reduction. Similarly there were obtained 65% of o- and p-nitroethylbenzene, b.p. 108–115° at 8 mm.,[6] and 53% of o- and p-nitroisopropylbenzene, b.p. 92–98° at 3 mm.[7]

t-Butylanilines.—A solution of 35 g. of the above mixed nitro-t-butylbenzenes in 75 ml. of alcohol, freshly distilled over potassium hydroxide, was reduced at 40–20 p.s.i. over 0.2 g. of platinic oxide.[8] Four hours was required for the absorption of the theoretical amount of hydrogen. The t-butylaniline mixture, b.p. 79–83° at 3 mm., was obtained in 95% yield. Similarly, an 88% yield of ethylanilines, b.p. 89–95° at 9 mm., and a 67% yield of isopropylanilines, b.p. 70–81° at 1 mm., were obtained.

3-Bromo-4(2)-amino-t-butylbenzenes.—A solution of 83 g. of the above mixed o- and p-t-butylanilines in 300 ml. of acetic anhydride was refluxed for four hours and cooled to 25°. The addition of 96 g. of bromine was carried out in one hour with the temperature held in the range 40–50°. The solution was left at 25° for 15 hours and then poured into 4 l. of water which contained 25 g. of sodium bisulfite. The crude air-dried brominated aniline was refluxed for 4 hours with 250 ml. of alcohol and 250 ml. of concd. hydrochloric acid. After concentration, the cooled mixture was filtered and the crude hydrochloride was suspended in 400 ml. of water. The free base was liberated by the addition of 10% caustic and was obtained in 74% yield as an oil, b.p. 106–112° at 2–3 mm. Similarly there were obtained a 51% yield of 3-bromo-4(2)-aminoethylbenzenes, b.p. 105–110° at 2 mm.,[9] and a 44% yield of 3-bromo-4(2)-aminoisopropylbenzenes, b.p. 107–112° at 2–3 mm.[7]

(5) Compare D. Craig, THIS JOURNAL, **57**, 196 (1935).

(6) E. L. Cline and E. E. Reid, *ibid.*, **49**, 3154 (1927).

(7) E. C. Sterling and M. T. Bogert, *J. Org. Chem.*, **4**, 20 (1939).

(8) J. T. Baker and Co., commercial catalyst.

(9) H. Kondo and S. Uyeo, *Ber.*, **70**, 1094 (1937).

m-Bromo-t-butylbenzene.—To a solution containing 83.2 g. of 3-bromo-4(2)-amino-t-butylbenzene, 758 ml. of glacial acetic acid, 505 ml. of water and 152 ml. of concentrated hydrochloric acid, was added carefully a solution of 31.5 g. of sodium nitrite in 191 ml. of water. The temperature was maintained at 5° or below. The clear diazonium salt solution was added to 758 ml. of cold 30% hypophosphorous acid. The resultant solution was stored for two days in a refrigerator at 5° and at room temperature for one day. During this storage, a reddish oil separated, which was then taken into ether. Distillation afforded 51.3 g. (59.2%) of m-bromo-t-butylbenzene, b.p. 103–105° at 17 mm.[10]

In a similar manner there also were obtained m-bromo-ethylbenzene (76.5%), b.p. 91–94° at 20 mm.,[11] and m-bromoisopropylbenzene (83.2%), b.p. 94–99° at 20 mm.[7]

m-t-Butylbenzonitrile.[12]—Into a one-liter 3-necked flask, equipped with a reflux condenser and a thermometer were placed 51.5 g. of m-bromo-t-butylbenzene, 26.9 g. of cuprous cyanide and 25 ml. of pyridine. This mixture was held at 180–190° for 18 hours. The hot mixture was poured into a mixture of 150 ml. of aqueous ammonia, 150 ml. of water and 150 ml. of benzene. There was obtained 33.5 g. (87.2%) of m-t-butylbenzonitrile, b.p. 93–96° at 4 mm.

Similarly there were obtained m-ethylbenzonitrile (76%), b.p. 91–92° at 7–8 mm., and m-isopropylbenzonitrile (82%), b.p. 102–104° at 9 mm.

m-t-Butylbenzoic Acid.[13]—The m-t-butylbenzonitrile (33.5 g.) was added dropwise with stirring into a 500-ml. 3-necked flask containing a mixture of 100 ml. of water and 100 ml. of concd. sulfuric acid. The mixture was gently refluxed during the addition of the nitrile and for four hours afterward. After dilution of the reaction mixture with 100 ml. of water, the solid which formed on cooling was collected by filtration, dissolved in 10% sodium hydroxide and reprecipitated by acidification with dilute hydrochloric acid. Two recrystallizations from dilute alcohol produced 27.4 g. (73%) of m-t-butylbenzoic acid, m.p. 126.8–127.6° (127°).[14]

Likewise there were obtained 97% of m-ethylbenzoic acid,[14] m.p. 47.0–47.6°, and 90% of m-isopropylbenzoic acid,[14] m.p. 49.2–50.2°.

Alternate Synthesis of m-Isopropylbenzoic Acid.—m-Bromobenzoyl chloride (200 g.) was added slowly to a stirred solution of 2.4 moles of methylmagnesium bromide in 1 l. of ether held at 20–25°. After two hours the mixture was treated with 20% acetic acid. Vacuum distillation through a 4-inch packed column afforded 73.8 g. (41%) of α-methyl-m-bromostyrene,[15] b.p. 78–82° at 5 mm., and 94.4 g. (48%) of dimethyl-m-bromophenylcarbinol, b.p. 107–108° at 3 mm. The crude carbinol was dehydrated to the styrene in 83% yield by two distillations over small amounts of iodine. The bromostyrene was catalytically reduced to m-bromoisopropylbenzene in 87% yield over platinic oxide catalyst. Over-reduction should be avoided as bromine is lost. The sample of m-bromoisopropylbenzene thus produced was converted through the nitrile to the acid as described above. This acid was identical to that produced by the synthesis through the nitro compound.

p-Ethylbenzoic Acid.—This acid, m.p. 112.8–113.6°, was prepared routinely by the sequence ethylbenzene, p-bromoethylbenzene, p-ethylbenzonitrile (b.p. 88–90° at 5–6 mm., 77% yield), p-ethylbenzoic acid.

p-Isopropylbenzoic and p-t-Butylbenzoic Acids.—A solution of 158 g. of chloroacetyl chloride in 156 g. of cumene was added slowly to a stirred suspension of 180 g. of aluminum chloride in 200 ml. of carbon disulfide. The temperature was maintained at −10 to 5°. The mixture was allowed to warm to 20–25° during 15 hours and was then poured on ice and hydrochloric acid. The organic layer was diluted with ether, dried over calcium chloride, and distilled to remove solvents. The residue was taken into ether and heated with a slight excess of pyridine. The pyridinium salt was collected, dissolved in hot water and

(10) H. R. Snyder, R. R. Adams and A. V. McIntosh, THIS JOURNAL, **63**, 3282 (1941).

(11) M. Crawford and F. H. C. Stewart, *J. Chem. Soc.*, 4443 (1952).

(12) M. S. Newman, *Org. Syntheses*, **21**, 89 (1941).

(13) Compare A. Tomisek, B. Graham, A. Griffith, C. S. Pease and B. E. Christensen, THIS JOURNAL, **68**, 1588 (1946).

(14) M. Crawford and F. H. C. Stewart, *J. Chem. Soc.*, 4443 (1952), report the m.p. of m-isopropylbenzoic acid as 47–48°; see ref. 4.

(15) W. E. Ross and R. C. Fuson, THIS JOURNAL, **59**, 1408 (1937).

treated with 10% sodium hydroxide (much darkening).[16] After extraction with ether, acidification precipitated a solid which recrystallization did not decolorize. On vacuum distillation 81 g. (50% over-all from isopropylbenzene) of good *p*-isopropylbenzoic acid, m.p. 116–117°, was obtained. Similarly *p-t*-butylbenzoic acid, m.p. 166–167°, was obtained in 26% yield.

Preparation of Esters.—The acid chlorides, prepared with phosphorus pentachloride, were refluxed with one equivalent of *l*-menthol in dry benzene for 10–12 hours to give over-all yields of 80–85% of the esters. The esters, all of which were viscous non-crystalline oils, were doubly distilled from a Claisen flask with a 10-inch Vigreux column at 0.5–0.8 mm. In the second distillation only a middle constant-boiling cut was retained. Physical constants and analyses for each ester are listed in Table II.

TABLE II

PHYSICAL CONSTANTS AND ANALYSES FOR SUBSTITUTED *l*-MENTHYL BENZOATES

Substituent and position[a]	B.p., °C.[b]	n^lD	*t*, °C.	Analyses,[c] % Calcd. C	H	Found C	H
p-CH₃	137	1.5084	26	78.7	9.6	78.7	9.4
p-C₂H₅	151	1.5078	26	79.1	9.8	79.1	9.8
p-i-C₃H₇	155	1.5044	29	79.4	10.1	79.5	10.1
p-t-C₄H₉	168.5	1.5050	27	79.7	10.2	79.8	10.3
m-C₂H₅	144	1.5060	27	79.1	9.8	79.1	9.8
m-i-C₃H₇	145	1.5032	25	79.4	10.1	79.5	10.1
m-t-C₄H₉	159	1.5012	30	79.7	10.2	79.7	10.2

[a] See ref. 2 for *m*-methyl isomer. [b] All b.p.'s were at 0.5–0.8 mm. [c] All analyses by the Galbraith Laboratories, Knoxville, Tenn.

The menthol, solutions, apparatus and procedure were similar to those used previously, as was the accuracy of measurement.[2]

Results

The fundamental relationship between reaction rate and observed rotations is log $(a_\infty - a) = (k_1/2.303)t + c$, where a = observed rotation, a_∞ = final rotation, k_1 = first-order constant, t = time and c = integration constant. For each experiment the logarithm of the rotation calculated for *l*-menthol at the appropriate concentration (a_∞) minus the observed rotation (a) was plotted against time. Each of the plots yielded straight lines. From the slopes (method of least mean squares) of these lines, the first-order rate constants (k_1) were calculated and are listed in Table III.

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE METHANOLYSIS OF SUBSTITUTED *l*-MENTHYL BENZOATE IN THE PRESENCE OF SODIUM METHYLATE

Temp., °C.	Ester, mole/l.	MeONa, mole/l.	k_1, sec.⁻¹ × 10⁵
l-Menthyl *p*-toluate			
39.95	0.09061	0.1165	18.75
	.08465	.09816	14.90
	.09206	.08402	12.62
l-Menthyl *m*-ethylbenzoate			
39.95	0.08975	0.06573	17.56
	.08885	.03300	8.28
	.08711	.08190	21.62
	.08773	.05171	13.22
	.08716	.08605	22.73
30.0	.0893	.0978	10.85

(16) S. H. Babcock, F. I. Nakamura and R. C. Fuson, THIS JOURNAL, **54**, 4407 (1932); F. Kröhnke, *Ber.*, **66**, 604 (1933).

l-Menthyl *p*-ethylbenzoate

39.95	0.08649	0.09888	16.88
	.08732	.1165	14.39
	.08768	.06893	11.09
	.08811	.05191	7.85
30.0	.0880	.1087	7.23

l-Menthyl *m*-isopropylbenzoate

39.95	0.08406	0.1033	30.50
	.08385	.08724	25.41
	.08437	.07137	20.14
	.08502	.05177	14.19
30.0	.0883	.0969	11.32

l-Menthyl *p*-isopropylbenzoate

39.95	0.08373	0.1069	18.58
	.08471	.06566	10.85
	.08469	.09586	17.22
	.08444	.09200	16.06
30.0	.0850	.0969	6.84

l-Menthyl *m-t*-butylbenzoate

39.95	0.07991	0.1025	29.57
	.08105	.06932	19.52
	.08121	.05216	13.46
	.08113	.08615	25.29
30.0	.0879	.1006	11.39

l-Menthyl *p-t*-butylbenzoate

39.95	0.08034	0.1071	19.95
	.08115	.09516	17.93
	.08059	.07679	14.27
	.08124	.05783	10.27
30.0	.0808	.1088	8.38

For the 40° reactions, the first-order constants, k_1 (− slope) were plotted *vs.* the sodium methylate concentrations for each ester. The plots all gave straight lines which passed through the origin. The specific rate constants (given in Table IV) then were calculated from the slopes of these lines (method of least mean squares). At 30° the specific rate constants were obtained by dividing the first-order constants by the appropriate concentration of sodium methoxide.

TABLE IV

RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE BASIC METHANOLYSIS OF SUBSTITUTED *l*-MENTHYL BENZOATES

Substituent and position	$k_{30.00}$, × 10⁴ sec.⁻¹	$k_{39.95}$, × 10⁴ sec.⁻¹	E^a	log PZ^a	$S\ddagger - S_0\ddagger^a$
H	0.519	1.294	17,600	8.33	0
p-CH₃–	.218	0.616	18,030	8.33	0
m-CH₃–	.388	1.000	17,740	8.37	−0.16
p-C₂H₅–	.255	0.734	20,040	9.86	−7.00
m-C₂H₅–	.415	1.051	17,630	8.32	+0.04
p-i-C₃H₇–	.271	0.741	19,070	9.18	−3.78
m-i-C₃H₇–	.432	1.211	19,530	9.71	−6.16
p-t-C₄H₉–	.296	0.768	18,070	8.49	−0.71
m-t-C₄H₉–	.435	1.233	19,800	9.91	−7.05

[a] In examining the values obtained for the activation energy, log *PZ* factor and entropy, one should consider the fact that these values may be somewhat in error. First of all the activation energies, from which the log *PZ* factors and entropies were obtained, were calculated over only one temperature range. Secondly, the specific rate constants at 30° could be in error, since they were obtained from the determination of the first-order rate constant at only one concentration of sodium methylate.

Activation energies were calculated from the Arrhenius equation for the interval 30.00–39.95°. The log PZ factors for each ester were calculated using the activation energy and the corresponding rate constant at 39.95°. These values are given in Table IV.

Discussion

Inspection of the rates of methanolysis of the l-menthyl substituted benzoates reveals (see Table IV) that there is very little difference in rate from the slowest, p-methyl, to the fastest, m-t-butyl. All react more slowly than l-menthyl benzoate. The order for the para series, $CH_3 < C_2H_5 < i$-$C_3H_7 < t$-C_4H_9, is that to be expected if the hyperconjugative effect of the alkyl groups is of more importance than the direct inductive effect. It is assumed that electron release to the carbonyl group retards the rate of methanolysis. This assumption is supported by the results previously obtained in a study of alkaline methanolysis.[2]

Since hyperconjugation involving a $meta$ group is not thought to be of importance, the results for the $meta$ series are unexpected. Here the same order, $CH_3 < C_2H_5 < i$-$C_3H_7 < t$-C_4H_9, is observed

as for the $para$ series. To account for the facts we suggest that a steric effect is operative. Examination of accurate scale models reveals that when the carboxyl function is held so that the two oxygens are coplanar with the ring a t-butyl group in the $meta$ position interferes with the l-menthyl group when the two are on the same side. Since this interference is absent in the methyl ester methanolysis should be accompanied by a release of strain. Since the release of strain should be greatest for the m-t-butyl and least for the m-methyl groups the observed order of reactivity can be explained by the assumptions that the release of strain is more important than the inductive effect and that the hyperconjugative effect is negligible.

The steric effect above outlined is different from that used to account for the rates of alkaline hydrolysis of a few m- and p-alkyl substituted ethyl benzoates in aqueous acetone[17] and also different from that used to account for the low base strength of 2,6-di-t-butylpyridine.[18]

(17) C. C. Price and D. C. Lincoln, This Journal, 73, 5836 (1951).
(18) H. C. Brown and B. Kanner, ibid., 75, 3865 (1953).

Columbus 10, Ohio

Ruthenium-catalyzed Hydrogenation of Acids to Alcohols

By J. E. Carnahan, T. A. Ford, W. F. Gresham, W. E. Grigsby and G. F. Hager

Carboxylic acids have been hydrogenated smoothly to the corresponding alcohols in the presence of a ruthenium catalyst.

Catalytic hydrogenation of carboxylic acids to the corresponding alcohols has been accomplished heretofore with copper catalysts[1] at temperatures above 300°, with promoted copper catalysts[2] at temperatures above 240°, or with cobalt catalysts[3] at temperatures above 220°. However, direct hydrogenation of carboxyl groups has not been used widely in synthetic work because better yields could generally be obtained through hydrogenation of the corresponding esters.

The present work[4] shows that ruthenium catalysts can be used for the direct hydrogenation of carboxylic acids to the corresponding alcohols in good yields at temperatures in the neighborhood of 150°. The reaction has been applied to monocarboxylic acids, dicarboxylic acids and a hydroxy

(1) W. Schrauth, O. Schenck and K. Stickdorn, Ber., 64, 1314 (1931); W. Normann, Z. angew. Chem., 44, 714 (1931); W. Normann and H. Prückner, German Patent 594,481 (1934); W. Normann, German Patent 648,510 (1937).
(2) W. A. Lazier, U. S. Patent 1,839,974 (1932); U. S. Patent 2,066,533 (1937); U. S. Patent 2,094,127 (1937); U. S. Patent 2,094,611 (1937); G. Schiller, U. S. Patent 2,121,367 (1938); G. Von Schuckman, U. S. Patent 2,332,834 (1943); E. A. Duintjer, "Über die katalytische Reduktion der Carboxylgruppe ungesättigter Fettsäuren," dissertation, Eidgenössischen Technischen Hochschule in Zürich, 1941; A. Guyer, A. Bieler and K. Jaberg, Helv. Chim. Acta, 30, 39 (1947).
(3) I. G. Farbenindustrie, British Patent 356,731 (1930); H. R. Arnold and W. A. Lazier, U. S. Patent 2,116,552 (1938); G. Schiller, U. S. Patent 2,121,367 (1938).
(4) T. A. Ford, U. S. Patent 2,607,807 (1952); W. F. Gresham, U. S. Patent 2,607,805 (1952).

acid (Table I). Either ruthenium dioxide or ruthenium-on-carbon catalyst was effective. Platinum and palladium were ineffective under similar conditions or under even more severe conditions (experiments 10, 11 and 12).

The specific conditions required for the ruthenium-catalyzed hydrogenation varied somewhat depending upon the acid being hydrogenated. In general, the optimum temperature appeared to be about 150°. In one series of experiments (experiments 13, 14, 15 and 16) using the same reactants and pressures, better yield was obtained at 149–155° for 1 hour than was obtained at 250–255° or at 97–111° or at 144–145° for only 0.18 hour. In another series (experiments 17, 18 and 19) with a different catalyst, better yield was obtained at 146–151° for 0.16 hour than at 129–136° for 0.33 hour. In the same series, experiment 19 shows that hydroxyacetic acid can be hydrogenated in reasonable yields at pressures below 100 atmospheres; however, isolated carboxyl groups are less reactive and pressures in excess of 500 atmospheres have been required for best results. In experiment 9, about the same yield was obtained with twice as much catalyst. On the other hand, the difference in yields between experiments 8 and 14 can be attributed to the different quantities of catalyst used. Water (experiment 5) and carbon dioxide (experiment 3) were satisfactory as diluents.

The chief side reaction appeared to be hydrogen-