double bond is known to be conjugated with the lactone grouping. Further, a study of the hydrogenolysis of the hydroxy-pyrone V has revealed that under comparable conditions the lactone ring is opened to form 3-hydroxy-5-phenylvaleric acid,[3] the constitution of which was established *via* analysis and dehydration to form γ-benzylcrotonic acid[3] (VII). The fact that the pyrone ring of I is stable toward Raney nickel in the absence of hydrogen renders it certain that its opening, and also that of the hydroxy-pyrone V, in the presence of hydrogen and nickel is due to reductive cleavage which must saturate the carbons α,β to the benzene ring. It follows from this that the initial product from the hydrogenolysis of the hydroxypyrone V should be given by structure VIII. Further reduction of VIII to yield VII most probably occurs through the keto form, which would equilibrate with VIII, since the enol ether IV is stable to further reduction under these conditions.

It is of interest that the hydroxy-pyrone V showed varying sensitivity toward different catalysts. Thus, although hydrogen with palladium supported with several different bases was without effect, and whereas Adams catalyst gave a mixture of unidentified products that resulted from the uptake of four moles of hydrogen,[4] and the Mozingo procedure[5] reduced the compound to such an extent that only volatile products were obtained, Raney nickel and hydrogen smoothly reduced the pyrone to the hydroxyacid.

Acknowledgment.—Our thanks are due Dr. Lester P. Kuhn, Ballistic Research Laboratory, Aberdeen Proving Grounds, Md., for infrared absorption spectra. We wish to thank Dr. and Mrs. G. Kleinspehn and Mr. J. Walter for analyses. One of the authors (J.R.S.) acknowledges with thanks receipt of a Grant-in-Aid from the Hynson, Westcott and Dunning Fund.

Experimental

Hydrogenolysis of 4-Hydroxy-6-phenyl-5,6-dihydro-2-pyrone.—Two grams (0.0105 mole) of the pyrone was dissolved in 50 ml. of absolute ethanol and 3 g. of Raney nickel[6] added. After shaking with hydrogen at 43 p.s.i. for five hours the catalyst was separated and the ethanol removed *in vacuo*. The residue solidified, and was taken up in base, leaving a trace of insoluble material. On acidification of the chilled filtrate lustrous white plates of 3-hydroxy-5-phenylvaleric acid separated. After washing, these had the reported m.p.[5] 129–130.5°, yield 1.3 g., or 63.7%. The material, after crystallization from water, was analyzed.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.00; H, 7.2. Found: C, 67.94; H, 7.3.

γ-Benzylcrotonic Acid.—The hydroxyacid V was submitted to distillation at atmospheric pressure, and the distillate dissolved in 15% aqueous sodium hydroxide. Extraction of this solution with ether removed a trace of neutral material. Acidification of the aqueous layer was followed by four extractions with ether. These were dried and evaporated to an oil that slowly solidified and consisted of a mixture of unchanged hydroxy acid and the crotonic acid. Separation by differential solubility in carbon bisulfide furnished pure γ-benzylcrotonic acid,[5] m.p. 102–102.5°.

Hydrogenolysis of 4-Ethoxy-6-phenyl-5,6-dihydro-2-pyrone.—Two grams (0.009 mole) of I[1] was dissolved in absolute ethanol and 3 g. of Raney nickel added. After shaking with hydrogen as described above, the solvent was removed, leaving crystals of 3-ethoxy-6-phenyl-2-pentenoic acid. After recrystallization from aqueous ethanol, white crystals, m.p. 114–115.5°, were obtained.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32; OC_2H_5, 20.46. Found: C, 71.04; H, 7.58; OC_2H_5, 20.50.

The product was soluble in carbonate solution, insoluble in bicarbonate solution, and showed ready oxidation with dilute potassium permanganate. This compound was shown to be identical with the crude acid earlier obtained from the reduction of 3-ethoxy-5-phenyl-2,4-pentadienoic acid,[1] after the impure material had been carefully recrystallized four times using Filter-Cel each time. Identity was established by mixed m.p., infrared absorption spectra, chemical tests and analysis.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.21; H, 7.59.

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[3] T. Hoffmann, *Ann.*, **283**, 308 (1894).

[4] Similar observations have been made with analogous compound by H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 3628 (1950).

[5] R. Mozingo, C. Spencer and K. Folkers, This Journal, **66**, 1859 (1944).

[6] Prepared according to the procedure in *Org. Syntheses*, **21**, 15 (1941), with the modification that the recommended digestion period of 12 hours on the steam-bath was changed to two hours on a hot plate at 100°.

Reactivities of 4-Substituted 2,6-Dimethylbenzoic Acids[1]

By John D. Roberts[1a] and Clare M. Regan

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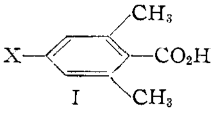
In an earlier investigation,[2] it was found that the substituent effects in 4- and 5-substituted 2-methylbenzoic acids paralleled closely those obtained with benzoic acids without the 2-methyl group. One possible interpretation of the results is that in either series of acids, the reactivity of a carboxyl group is not importantly determined by resonance-coupling of the carboxyl group with various 4-substituents. The argument is not strong in view of the certainly limited ability of a single ortho-methyl group to reduce coupling by sterically forcing the carboxyl out of the plane of the aromatic ring. To gain further evidence on this point, we have determined the apparent ionization constants in 50% water–50% ethanol (by volume) at 25.0° and the reactivities toward diphenyldiazomethane in absolute ethanol at 30.0° of a series of 4-substituted 2,6-dimethylbenzoic acids (I).



I

The procedures have been described earlier in detail.[3] The experimental data along with the physical constants of the compounds are summarized in Table I.

The values of the logarithms of the rate constants k_2 for the diphenyldiazomethane reactions are reasonably linear with the logarithms of the apparent ionization constants (pK_A) and indicate a

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[1] Supported in part by the program of research of the U. S. Atomic Energy Commission.

[1a] Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, Calif.

[2] J. D. Roberts and J. A. Yancey, This Journal, **73**, 1011 (1951).

[3] J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

TABLE I

PHYSICAL CONSTANTS, APPARENT IONIZATION CONSTANTS (25°) AND DIPHENYLDIAZOMETHANE REACTION RATE CONSTANTS (30°) OF 4-SUBSTITUTED 2,6-DIMETHYLBENZOIC ACIDS

Substituent	M.p., °C.	Half-point[a]	$K \times 10^6$ [b]	Concn. of acid,[c] moles/l.	Half-life,[c] min.	Av. k_2 l./mole min.
n-C_3H_7O–	93.0– 94.0	5.48	3.3	0.0423	6.92, 6.90	2.37
CH_3–	154.5–155.2	5.38	4.2	.0605	10.22, 10.25	2.80
CH_3CONH–	220 –222	5.21	6.2	.0389	5.33, 5.33	3.35
H–	115.5–116.2	5.18	6.6	.0231	8.25, 8.25	3.64
Br–	194.8–195.3	4.78	16.6	.0273	4.56, 4.58	5.53
H_2NCO–	246 –248	4.65	22.4	.0119	9.58, 9.58	6.09
CH_3O_2C–	191.0–192.0	4.56	27.5	.0126	7.92, 7.92	6.94

[a] Reading on *p*H scale of *p*H meter calibrated for aqueous buffer solutions at half-neutralization point using glass and saturated calomel electrodes without correction for liquid junction potentials in 50% water–50% ethanol (by volume) solutions. [b] Calculated assuming unit activities and readings of *p*H meter scale equal to logarithm of reciprocal of hydrogen ion concentrations.

linear free-energy relationship of the usual sort.[4] Plots of pK_A and log k_2 against the available Hammett σ-constants[4] are given in Figs. 1 and 2. It was assumed that the σ-constants of the *p*-*n*-propoxy and *p*-carbomethoxy groups are equal to those for *p*-methoxy[4,5] and *p*-carboethoxy[6] groups, respectively.

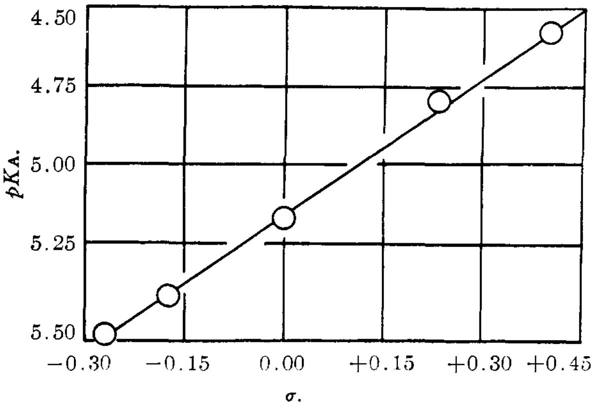

Fig. 1.—pK_A and σ for 4-substituted 2,6-dimethylbenzoic acids, points given for *n*-propoxy, methyl, hydrogen, bromo and carbomethoxy as 4-substituents.

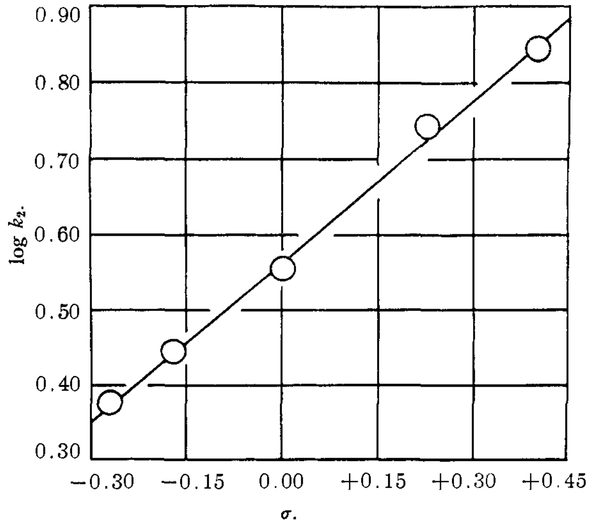

Fig. 2.—Log k_2 and σ for 4-substituted 2,6-dimethylbenzoic acids; points for substituents as in Fig. 1.

The plots of Figs. 1 and 2 show no pronounced upward trend with the electron-donating *n*-propoxy group as would be expected if electrical coupling between carboxyl group and substituent group (as expressed by II) were important in 4-substituted benzoic acids and sterically inhibitable by methyl groups ortho to the carboxyl. It is possible that such effects might be important in benzoic acids

II

with more strongly electron-donating *p*-substituents.

Acknowledgment.—We are indebted to Dr. M. S. Newman for information in advance of publication about his own research on this problem,[7] and to Dr. Newman and Dr. R. V. Heinzelman of the Upjohn Company for generous samples of the acids used in this work.

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(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chaps. III, VII and IX.

(5) The assumption looks quite reasonable since *p*-methoxy and *p*-ethoxy have almost identical σ-constants.[4]

(6) J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2267 (1953).

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A Method for Growing Barium Titanate Single Crystals

BY J. P. REMEIKA

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New types of storage elements for digital computers and telephone switching systems are under investigation which have as a basic requirement a rectangular hysteresis loop characteristic.[1] This property may be obtained in ferromagnetic as well as in ferroelectric materials. The most promising of the ferroelectrics is barium titanate which may be used either as a single crystal or as a ceramic.[2] Our work on ferroelectric storage elements has indicated that the hysteresis loops obtained from

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