2-picoline, 2,6-lutidine, quinoline, and morpholine, since the picrates of these amines have quite low solubility in alcohol. On the contrary, the formation of the picrates of aliphatic amines in alcohol was not too successful, as the picrates have about the same or even more solubility in alcohol than the picric acids themselves. Ethyl ether was found to be a satisfactory solvent for the precipitation of picrates of aliphatic amines and picrates of 1-naphthylamine. The picrates of aniline were easily prepared from boiling water. The melting points of the picrates were determined in an evacuated capillary tube using a copper melting point block. Values obtained in an open melting point heated block were as much as 40° lower. To obtain reasonable duplication, the melting points were recorded using a temperature gradient of 1°/min.

CHICAGO 26, ILL.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF PUERTO RICO AT MAYAGUEZ AND DALHOUSIE UNIVERSITY]

Saponification of Methyl-Substituted α-Butyrolactones

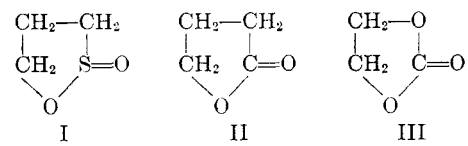
OWEN H. WHEELER[1a] AND DONALD S. GAMBLE[1b]

Received December 8, 1960

The rates of saponification of γ-butyrolactone and monomethyl and *gem*-dimethyl γ-butyrolactones have been measured in 92.3% ethanol at 0° and 25°. The observed differences in rate cover a range of only about 4-fold, much less than anticipated from data on esters, and suggest that the steric effect of the methyl groups is relatively unimportant in the hydrolysis of these lactones.

The effect of alkyl groups on the ease of ring opening of carbon rings is still not fully understood,[2] and little experimental work has been published on this, although Bordwell and co-workers[3] have recently reported a study of the unimolecular solvolysis of sultones (I) (cyclic sulfonates). Many ring-opening reactions, however, proceed by bimolecular hydrolysis and this paper reports a study of the effect of methyl groups on the rates of saponification of γ-butyrolactone (II) (see Table I).

The basic hydrolysis of γ-butyrolactones is very rapid in aqueous solution[4] and was accordingly studied in 92% ethanol, in which solvent the rate



I II III

can be conveniently followed by titration (see experimental), which also served as a check on the purity of the lactones used. The mechanism of basic hydrolysis of γ-butyrolactone has been well established as involving an initial nucleophilic attack of hydroxyl (or ethoxyl) ion on the carbonyl carbon atom, followed by acyl-oxygen fission.[5] No uncatalyzed solvolysis has been detected.[6] The observed rates of saponification (Table I) covered a range of some 4-fold, all the methylated γ-butyrolactones hydrolyzing at 25° at a lower rate than γ-butyrolactone itself, in the order H $<$ α CH_3 $<$ γ CH_3 $\sim$ β CH_3 $<<$ γ,γ$(CH_3)_2$ $<$ ββ $(CH_3)_2$ $<<$ αα $(CH_3)_2$. The differences are considerably less than those which might be expected from the rates of saponification of esters. Thus the relative rates for ethyl propionate, isovalerate and pivalate (analogous in substitution of γ-butyrolactone and β-methyl and α,α-dimethyl-γ-butyrolactone) are 100:12:1.3 (in 85% ethanol at 25°).[7] Similar small differences have been noted in the saponification of γ-butyrolactone and γ-methyl and γ,γ-dimethyl-γ-butyrolactone in 43% acetone at 20° (ratio 100:39:12.6),[8] for γ-butyrolactone and α-methyl, γ-methyl, and γ,γ-dimethyl-γ-butyrolactone at 25° (ratio 100:69:50:18),[9] and in the acid-catalyzed hydrolysis.[9,10] The energies of activation for the saponification of the butyrolactones are more constant[8] than for ester hydrolysis, although the log PZ factors are more variable (ethyl propionate and pivalate have Eact. 14.7 and 17.1 kcal and log PZ 8.0 and 8.2, respectively[7c]).

The ring of γ-butyrolactone is probably nearly planar, although eclipsed non-bonded interactions between the hydrogen atoms on the β- and γ-

(1)(a) University of Puerto Rico at Mayaguez, P. R.; (b) Dalhousie University, Halifax, N. S., Canada. Taken from M.Sc. Thesis, September, 1959.

(2) *Cf.* N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).

(3) F. G. Bordwell, C. E. Osborne, and R. D. Chapman, *J. Am. Chem. Soc.*, **81**, 2698 (1959).

(4) D. S. Hegan and J. H. Wolfenden, *J. Chem. Soc.*, 508 (1938).

(5) *Cf.* E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Henry Holt, New York, N. Y., 1959, p. 318.

(6) F. D. Coffin and F. A. Long, *J. Am. Chem. Soc.*, **74**, 5767 (1952).

(7)(a) H. A. Smith and H. S. Levenson, *J. Am. Chem. Soc.*, **61**, 1172 (1939); (b) D. P. Evans, J. J. Gordon, and H. B. Watson, *J. Chem. Soc.*, 1439 (1938); (c) J. D. R. Thomas and H. B. Watson, *J. Chem. Soc.*, 3958 (1956), value for pivalic ester at 25° calculated from value at 40°.

(8) C. M. Stevens and D. S. Tarbell, *J. Org. Chem.*, **19**, 1996 (1954).

(9) H. Sebelius, Inaugural dissertation, Lund, 1927, reported by W. Hückel, *Theoretical Principles of Organic Chemistry*, Elsevier, New York, 1958, p. 892. The solvent is not given (presumably water) and the original reference was not available to us.

(10) O. H. Wheeler and E. E. Granell, unpublished results.

TABLE I

RATE CONSTANTS FOR SAPONIFICATION OF BUTYROLACTONES[a]

	$k \times 10^3$ L. Mole^{-1} Sec.$^{-1}$ 25°	0°	Eact. Kcal.	log PZ	Rel. Rate[b]
γ-Butyrolactone	47.7 ± 2.0	2.90 ± 0.02	18.2	12.0	100
α-Methyl lactone	44.7 ± 1.6	3.13 ± 0.09	17.2	11.2	93
β-Methyl lactone	41.3 ± 0.8	2.95 ± 0.11	17.1	11.1	87
γ-Methyl lactone	41.7 ± 1.5	2.87 ± 0.10	17.3	11.3	87
α,α-Dimethyl lactone	12.7 ± 0.3	0.861 ± 0.01	17.4	10.9	27
β,β-Dimethyl lactone	20.0 ± 0.3	1.49 ± 0.03	16.8	10.6	42
γ,γ-Dimethyl lactone	23.9 ± 0.2	1.13 ± 0.035	19.7	12.8	57

[a] In 92.3% ethanol. [b] Relative rates at 25° to γ-butyrolactone = 100.

carbon atoms can be reduced by raising these carbon atoms respectively above and below the plane of the other three atoms,[11] and such a conformation will reduce unfavorable interactions between methyl groups and ring hydrogen atoms in the substituted γ-butyrolactones. The preferred direction of attack of base is most probably from a general direction above the plane of the ring and behind the carbonyl carbon atom, away from the electrostatic repulsion of the lone pair of electrons on the ring oxygen atom.[12] While the butyrolactone ring exists in a near planar form, approach of a reagent in his manner will not be impeded by the ring hydrogen atoms. The enhanced rate of hydrolysis of butyrolactones as compared to acyclic esters[13] is consistent with this mode of attack.[12b] A single methyl group in either the α-, β-, or γ-positions leads to a very slight decrease in rate at 25°, with even smaller differences at 0° (there was even a slight enhancement in the rate for the α-methyl isomer). That a single methyl group in the β-, γ-position should not effect the ease of attack on the carbonyl carbon atom is consistent with the "half-chair" conformation of the ring. In the case of the α-methyl group the small inductive effect of the methyl group should further decrease the rate of nucleophilic attack, although this was not in fact observed. Appreciable differences in the rates of hydrolysis were only found for the *gem*-dimethyl butyrolactones. The order at both 25° and 0° was $\beta,\beta < \gamma,\gamma < \alpha,\alpha$. The relatively slow rate of saponification of the α,α-dimethyl lactone is no doubt due partially to the electronic (-I) effect of the methyl groups, which by increasing the electron density on the carbonyl-carbon atom decreases the facility of nucleophilic attack of base. Models show that the *gem*-dimethyl groups will exert a small shielding effect to the approach of base on the carbonyl-carbon atom and this effect should be greatest for α-substitution but still be appreciable for β and γ-substitution.

The shielding effect of methyl groups also has been noted in the saponification of cyclic ethylene carbonates (III),[14] where the differences were of the same order as those encountered here (4:1 for ethylene carbonate and its α,α,β-trimethyl derivative[14b]), although the slow rate of alkaline hydrolysis of tetramethylethylene carbonate (about 1/180 times as low as ethylene carbonate) was explained as due to increase of strain in the transition state (formed by the addition of base to the carbonyl group) resulting from steric repulsion from the methyl groups.[14b] It has been suggested that ring strain in cyclic carbonyl compounds themselves is reflected in shifts in the carbonyl stretching frequency.[15] However all the γ-butyrolactones studied here had γ C=O 1775 ± 3 cm.$^{-1}$

The effect of methyl groups in reducing the ease of unimolecular solvolysis of sultones (I) must clearly be of a different origin to that mentioned above, and has been attributed[3] to the steric hindrance of the methyl groups to the free-rotation of the carbon-skeleton in the opening of the ring.

EXPERIMENTAL

Lactones. γ-Butyrolactone and γ-valerolactone were commercial samples (Eastman Kodak, white label). α-Methyl-γ-butyrolactone was prepared from diethyl methyl-malonate[16] and recovered from the aqueous solution by continuous ether extraction. β-Methyl and β,β-dimethyl-γ-butyrolactone were prepared by heating the silver salts of β-methyl and β,β-dimethyl glutaric acids with iodine.[17] It was found important to dry the salts thoroughly and to use an efficient condenser to avoid loss of lactone with iodine vapor. α,α-Dimethyl-γ-

(11) Cyclopentanone probably exists in such a "half-chair" form. F. V. Brutcher, Jr., T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4918 (1959).

(12)(a) D. G. H. Ballard and C. H. Bamford, *J. Chem. Soc.*, 355 (1958); (b) H. K. Hall, Jr., M. K. Brandt and R. M. Mason, *J. Am. Chem. Soc.*, **80**, 6423 (1958).

(13) R. Huisgen, *Angew. Chem.*, **69**, 341 (1957); R. Huisgen and H. Olt, *Tetrahedron*, **6**, 253 (1959).

(14)(a) R. Kempa and W. H. Lee, *J. Chem. Soc.*, 1576 (1959); (b) L. A. Pohoryles, I. Levin, and S. Sorel, *J. Chem. Soc.*, 3082 (1960).

(15) H. K. Hall, Jr., and R. Zbinden, *J. Am. Chem. Soc.*, **80**, 6428 (1958).

(16) H. Adams and E. F. Rogers, *J. Am. Chem. Soc.*, **63**, 228 (1941).

Note added in manuscript. Dr. H. Shechter has informed us that he has also carried out a study of the saponification of methyl substituted γ-butyrolactones and obtained similar results.

(17) S. S. G. Sircar, *J. Chem. Soc.*, 898 (1928); F. J. M. Pattison and B. C. Saunders, *J. Chem. Soc.*, 2745 (1949).

butyrolactone[18] and γ,γ-dimethyl-γ-butyrolactone[19] were prepared by published methods. The lactones were all freshly distilled at reduced pressure immediately before use, and their physical constants were in excellent agreement with published values. Their infrared spectra were determined in carbon tetrachloride solution using a Baird-Atomic double beam instrument.

Kinetics. Preliminary experiments showed that the saponification of γ-butyrolactone in 80% ethanol was too rapid (0.16 mole^{-1} sec.$^{-1}$) to be conveniently followed by titration and to be rather too slow (0.0087 mole^{-1} sec.$^{-1}$) in absolute ethanol. The measurements were accordingly carried out in 92.3% ethanol (d_{25}^{25} 0.8096), which had been purified by treatment with zinc dust and sodium hydroxide.

The lactone (0.2–0.3 g.) was dissolved in purified 92% ethanol (100-x ml.), allowed to equilibrate in a constant temperature bath at 25.08 ± 0.02° or in an ice water bath at 0.00 ± 0.02° and 0.04*M* sodium hydroxide (x ml.) in the same solvent and at the same temperature added. Aliquots (10 ml.) were withdrawn at intervals, added to excess 0.06*N* hydrochloric acid (5 ml.) and ice-cold distilled water (20 ml.) and the excess acid immediately titrated with standard 0.045*N* sodium hydroxide solution, using phenolphthalein as indicator. The purity of the lactone was determined by dissolving samples (0.04–0.06 g.) in 0.045*N* aqueous sodium hydroxide (15 ml.) and titrating the excess base with standard acid after 2–3 days. The purity was always at least 95% and was taken into account in calculating the kinetics. The rate constants were determined from the slope of the second order rate plots in the usual manner. Each run was carried out at least three times and the means and their mean errors are given in Table I. The E act and log PZ values are probably accurate to ± 0.2 units.

(18) B. E. Hudson, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, **63**, 3156 (1941).

(19) R. T. Arnold, J. S. Buckley, Jr., and J. Richter, *J. Am. Chem. Soc.*, **69**, 2322 (1947); J. Cason, P. B. Brewer, and E. L. Pippen, *J. Org. Chem.*, **13**, 239 (1948); R. L. Frank, R. Armstrong, J. Kiviatek, and H. A. Price, *J. Am. Chem. Soc.*, **70**, 1379 (1948).

Acknowledgment. This work was supported in part by a grant from the National Research Council of Canada.

MAYAGUEZ, PUERTO RICO
HALIFAX, N. S., CANADA

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Electron Exchange Polymers. XV. NMR Spectra of Some Methylated Hydroquinones and Their Derivatives[1]

KENNETH A. KUN[2] AND HAROLD G. CASSIDY

Received November 7, 1960

NMR spectra are reported on the *tau* scale for 1,4-dimethoxybenzene; 2-methyl-, 2,5-dimethyl-, 2,3,5-trimethyl-, and 2,3,5,6-tetramethyl-1,4-dimethoxybenzenes; 2-vinyl-3,6-dimethyl- and 2-vinyl-3,5,6-trimethyl-1,4-dimethoxybenzenes; 2-(2-hydroxyethyl)-, 2-(2-hydroxyethyl)-3,6-dimethyl-, 2-(2-hydroxyethyl)-3,5-6-trimethyl-, and 2-(1-hydroxyethyl)-3,5,6-trimethyl-1,4-dimethoxybenzene; and α,α'-bis(2,5-dimethoxy-3,4,6-trimethylphenyl)diethyl ether. The chemical shifts of the aromatic, methoxyl, and methyl protons are interpreted.

The use of NMR spectra has increased rapidly since the initial work of Purcell and co-workers,[3] and its application to structural organic chemistry by Gutowsky and co-workers.[4] Detailed discussions of theory and applications may be found in the works of Pople and co-authors,[5] Roberts,[6] Conroy,[7] and Jackman.[8] With this rapidly increasing use of NMR it seemed of interest to report the chemical shifts of the aromatic methoxyl and methyl protons of several methylated hydroquinones and their derivatives.

Measurements described in this paper were made with a 60 mc./sec. Varian NMR spectrometer using analytical grade carbon tetrachloride as the solvent. All chemical shifts were measured with reference to an internal standard, tetramethylsilane, and are given on the "tau" (τ) scale as described by Tiers.[9] The numbers of parentheses indicate relative intensities. Concentrations of 40% by volume were used. As a result, no bulk-susceptibility corrections are required, but some dilution effects characteristic of aromatic compounds are no doubt present.[5]

(1) (a) Taken from the Dissertation submitted by Kenneth A. Kun to the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree. (b) For other papers in this series see K. A. Kun and H. G. Cassidy, *J. Polymer Sci.*, **44**, 383 (1960).

(2) Present address: Rohm and Haas Company, Research Laboratories, Bristol, Pa.

(3) E. M. Purcell, H. C. Torrey, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

(4) L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York (1959).

(6) J. D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill, New York (1959).

(7) H. Conroy, "Nuclear Magnetic Resonance in Organic Structural Elucidation," in *Advances in Organic Chemistry, Methods and Results*, R. Raphael, ed., Interscience, New York (1960).

(8) L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York (1959).

(9) (a) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958); (b) G. V. D. Tiers, *Characteristic Nuclear Magnetic Resonance "Shielding Values" for Hydrogen in Organic Structures. Part I. Tables of τ-Values for a Variety of Organic Compounds. Exploratory NMR Studies.* Project 737602, Central Research Department, Minnesota Mining & Manufacturing Co., St. Paul, Minn.