Acknowledgment. The author wishes to thank the Humble Oil and Refining Company for inviting him to their Baytown laboratories for the summer of 1956 and placing their research facilities at his disposal. He is especially grateful to Mr. J. A. Anderson, Jr., and Dr. J. T. Horeczy, in whose sections he worked, for facilitating many things; Doctors E. M. Amir and R. H. Perry for sharing their laboratory with him, and Messrs. E. J. Hoffman and R. L. Heinrich for sharing their office with him.

BAYTOWN, TEX.

[CONTRIBUTION FROM COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY]

Solvolyses of Some Sterically Hindered Aliphatic Esters[1]

JAMES G. TRAYNHAM AND MERLE A. BATTISTE[2]

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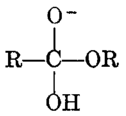
Solvolyses, mainly in alkaline solutions, of several methyl, isopropyl, and *s*-octyl branched aliphatic esters have been studied. Even when the normal reaction path through an addition intermediate (I) was severely hindered, evidence for the alternate path (alkyl-oxygen fission) was not obtained.

Alkaline hydrolyses of primary and secondary alkyl esters usually occur by acyl-oxygen fission,[3] probably through an addition intermediate (I).[4]



$$R—\overset{O^-}{\underset{OH}{C}}—OR$$

I

With tertiary alkyl,[5] allyl,[6] and diarylcarbinyl[7] esters, alkyl-oxygen fission[8] occurs predominantly or exclusively. For these systems the alternative mode of fission has been attributed to ion formation.[3] A bimolecular displacement reaction, however, leads to alkyl-oxygen fission in the hydrolysis of β-lactones.[9] Even with methyl esters under conditions that mask the usual reaction, slow alkyl-oxygen fission has been observed.[10]

With two modes of fission possible (by three paths: acyl-oxygen, alkyl-oxygen by ionization, and alkyl-oxygen by displacement), the difference in energy requirements in each case will control the course of the reaction. With saturated primary and secondary alkyl esters, the addition intermediate appears to be favored energetically. In other systems, the formation of relatively stable carbonium ions or relief of strain in a small ring compound appear to be favored over the addition intermediate. When normal acyl-oxygen fission merely regenerates reactants (*e.g.*, methyl benzoate and methoxide in anhydrous methanol[11]), alkyl-oxygen fission, much less favored but not prohibitively so, occurs slowly.

In several types of reactions, including hydrolysis of certain aromatic esters, steric factors have been found to outweigh all other factors in controlling the reaction course among several alternatives. Thus in olefin-forming eliminations with highly-branched alkyl derivatives, the less-substituted olefin predominates.[10] And highly-hindered aromatic esters which are not hydrolyzed by the usual procedure quickly respond, through acylium ion formation, to treatment with concentrated sulfuric acid.[12] The effects of extensive branching on the rates of esterification and hydrolysis have been examined in some detail.[13] We though it of interest to examine the importance of steric factors in controlling the course of the hydrolysis reaction with aliphatic esters.

The change in mode of fission as the alkyl group is changed from primary to tertiary may arise in part from an increase in energy requirements for formation of the addition intermediate (I). Formu-

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(1) Taken from the M.S. thesis of M. A. Battiste, Louisiana State University, August, 1956. Presented in part at the Southwide Chemical Conference, Memphis, Tenn., December 7, 1956.

(2) University research assistant, 1955–56.

(3) For excellent reviews, see C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, p. 752 ff, Cornell University Press, Ithaca, N. Y., 1953; and J. Hine, *Physical Organic Chemistry*, p. 266 ff, McGraw-Hill Book Co., Inc., New York, N. Y., 1956.

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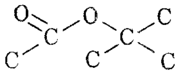
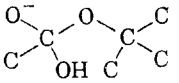
(13) See M. S. Newman, in *Steric Effects in Organic Chemistry*, ed. by M. S. Newman, pp. 205–225, John Wiley and Sons, Inc., New York, N. Y., 1956.

las II–V illustrate the relationship between *t*-butyl acetate, its addition intermediate and hydrocarbons of similar structure. Homomorphs[14] of di-*t*-butylmethane (V) have been shown to be appreciably strained. Although oxygen is smaller than methyl (and II and III are not properly regarded as true homomorphs of IV and V, respectively), the increase in strain in going from II to III is probably quite similar to that for the transition IV to V. At least it seems reasonable that a significant contribution to the difference in energy requirements for the two modes of fission with such branched esters may arise from the unfavorable strain in the addition intermediate leading to acyl-oxygen fission. By considering changes in steric interaction accompanying changes in hybridization of the carbonyl carbon, Taft[15a] has described similar conclusions about the role of steric effects in the formation of the addition intermediate.



II



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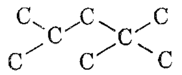
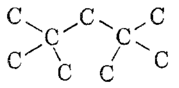
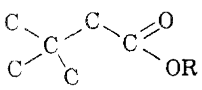


IV

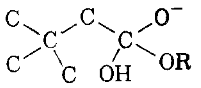


V

Strained structures may be obtained with non-tertiary alkyl esters when the acid chain rather than the alkyl chain is branched (formulas VI and VII).



VI



VII

In order to evaluate the importance of this strain in promoting alkyl-oxygen fission, we have studied solvolyses, mainly in alkaline solutions, of several *s*-octyl, methyl, and isopropyl esters prepared from branched aliphatic acids. The acids chosen were trimethylacetic, *t*-butylacetic and diisopropylacetic acids. Both racemic and optically active esters were solvolized under a variety of conditions: hydroxide in aqueous alcohol, methoxide in anhydrous methanol, 2-propoxide in anhydrous 2-propanol, and dilute acid in aqueous methanol or acetone. Normal acyl-oxygen fission would give alcohol with complete retention of configuration, alkyl-oxygen fission by ionization would give alcohol or ether with inversion and extensive racemization, and alkyl-oxygen fission by displacement would give alcohol or ether with inversion of configuration.

In nearly all experiments only alcohol with complete retention of configuration was obtained. In one early experiment, based on the expectation that the *s*-octyl *t*-butylacetate would be more resistant to hydrolysis than it proved to be, concentrated alkali in slightly aqueous 2-propanol was employed and the product alcohol was appreciably racemized (15% loss of activity). However these same conditions racemized (−)2-octanol no less extensively. Under no conditions was ether obtained and in no other experiment was the rotation of product 2-octanol significantly different from that of starting 2-octanol. With *s*-octyl diisopropylacetate, saponification in anhydrous methanol proceeded to a maximum of 12% after 20 days refluxing. Despite this extremely slow rate, we were unable to detect any methyl *s*-octyl ether (which would have indicated alkyl-oxygen fission). Even when conditions were chosen which would mask the normal path—*i.e.*, alkoxide in anhydrous alcohol with the corresponding alkyl ester—no ether nor carboxylate could be detected in the resulting reaction mixtures. These results clearly indicate that even when bimolecular attack at the carbonyl carbon is severely hindered and the rate of acyl-oxygen fission is unusually slow, alkyl-oxygen fission in these substituted acetates is still highly unfavored.

The occurrence of alkyl-oxygen fission by displacement in the reaction of methoxide with methyl benzoate,[10] in contrast to its absence in our experiments with methyl *t*-butylacetate, may result from the greater electron-withdrawing influence of phenyl over alkyl. The slightly greater electron depletion at the methyl carbon in the benzoate may well facilitate nucleophilic attack at that carbon sufficiently to account for the contrasting observations. Strong support for this suggestion is found in the data of Hammett and Pfluger[15b] on the reaction of trimethylamine with methyl esters to give quaternary ammonium salts by alkyl-oxygen fission.

$$RCO_2CH_3 + N(CH_3)_3 \longrightarrow RCO_2^- + N(CH_3)_4^+$$

The order of rates of these reactions parallels the order of acid strengths (*e.g.*, benzoate faster than acetate), providing evidence that electron-withdrawal in R increases the rate of alkyl-oxygen fission. Somewhat more direct support is derived from a single preliminary experiment in our laboratory which we hope to extend and report in detail later. Methyl trifluoroacetate, in which electron-withdrawing effects in the acid chain are essentially maximum, reacted with methoxide in refluxing anhydrous methanol to give a rather rapid evolution of gas, presumed to be methyl ether.

The lower susceptibility of secondary carbons (compared with primary carbons) to nucleophilic displacements would make such reactions even less

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TABLE I

PHYSICAL PROPERTIES OF ACIDS, ACID CHLORIDES, AND ESTERS

Compound	B.P., (Mm.) °C.	n_D^{20}	d_4^{20}	α_D^{20}
Trimethylacetic acid	82–85 (20)	...	...	...
Trimethylacetyl chloride	104–105	1.4142	1.003	...
s-Octyl trimethylacetate	92–93 (11)	1.4172	0.842	$-8.85°^a$
		1.4175		$+10.53°^b$
Methyl trimethylacetate	98–99	1.3894	0.850	...
Isopropyl trimethylacetate	68–69 (104)	1.3888	0.830	...
t-Butylacetic acid	98–99 (25)	1.4110	0.915	...
t-Butylacetyl chloride	68–71 (100)	1.4229	0.964	...
s-Octyl *t*-butylacetate	114 (10)	1.4247	0.848	$-6.25°^a$
				$+7.49°^b$
Methyl *t*-butylacetate	124–126	1.3994	0.870	...
Isopropyl *t*-butylacetate	82–83 (69)	1.4025	0.838	...
Diisopropylacetic acid	108 (12)	1.4264	...	...
Diisopropylacetyl chloride	88–89 (54)	...	...	...
s-Octyl diisopropylacetate	137 (12)	1.4333	...	$+7.81°^b$
Methyl diisopropylacetate	72–74 (34)	1.4159	...	...

[a] From (−)2-octanol, α_D^{20} −6.45°. [b] From (+)2-octanol, α_D^{20} +7.88°.

likely among the *s*-octyl and isopropyl esters studied here.

The differences in energy requirements of the alternative modes of reaction for unbranched aliphatic esters are greater then than the steric strains imposed on the addition intermediate among the esters included in this study. A tentative inference is that, although steric factors do indeed play a significant role in determining the *rates* of normal ester hydolyses, polar factors seem to play the predominant role in determining the *course* of the reactions of esters of primary and secondary alcohols in basic solution.

EXPERIMENTAL[16]

Preparation of materials. Trimethylacetic acid and *t*-butylacetic acid were obtained (in 82% and 85% yields) by hypobromite oxidation[17] of pinacolone and methyl neopentyl ketone,[18] respectively. Diisopropylacetic acid was prepared in 50% yield by hydrolysis of diisopropylcyanoacetic acid with concentrated HCl in a sealed tube heated at 160–170° for 14–18 hr.[19] The diisopropylcyanoacetic acid[20] (m.p. 95.5–97.5°) was obtained by alkaline hydrolysis of the ethyl ester[20] [b.p. 85–87° (3 mm.), n_D^{20} 1.4350, d_4^{20} 0.953] which was prepared[20] in 61–77% yield from ethyl cyanoacetate and isopropyl bromide or iodide.

The acids were converted to the corresponding acid chlorides (66–90% yields) with excess thionyl chloride. Heating the acid chloride with the appropriate alcohol, followed by the usual work-up, gave esters in good yields. The physical properties of these compounds are described in Table I.

Anhydrous methanol was prepared from reagent grade alcohol and magnesium turnings.[21] Anhydrous 2-propanol was prepared by distilling reagent grade alcohol from calcium metal.[21]

2-octanol was resolved in the customary manner;[22] b.p. 91° (18 mm.), n_D^{20} 1.4260, d_4^{20} 0.821, α_D^{20} −6.45° and +7.88°.

Solvolysis experiments. (A) Hydroxide in aqueous alcohol. 1. Methanol. A solution was prepared by dissolving 5.18 g. (0.024 mole) of (+)*s*-octyl trimethylacetate in 60 ml. of aqueous 90% methanol which was 0.75*M* in sodium hydroxide. After being refluxed for 4 days, the mixture was diluted with water and extracted with petroleum ether (b.p. 60–70°). Drying and distilling gave 2.9 g. (93%) of (+)2-octanol; n_D^{20} 1.4261, α_D^{20} +7.86°.

Similar treatment of 6.10 g. (0.027 mole) of (+)*s*-octyl *t*-butylacetate led to 3.13 g. (90%) of (+)2-octanol; n_D^{20} 1.4262, α_D^{20} +7.82°. From the alkaline aqueous solution, *t*-butylacetic acid was obtained in 96% yield.

Hydrolysis of 5.13 g. (0.020 mole) of (+)*s*-octyl diisopropylacetate under similar conditions was attempted, but after 13 days refluxing only traces of 2-octanol could be isolated. Analysis of the product fractions by use of refractive indices indicated that the extent of hydrolysis did not exceed 5%.

2. 2-Propanol. A sample of (−)*s*-octyl *t*-butylacetate was added to about 4 times its volume of an alkaline solution prepared by dissolving potassium hydroxide (27% by wt.) in slightly aqueous 98% 2-propanol. The solution was refluxed for 41 hr. Dilution with water, extraction with petroleum ether, and distillation gave (−)2-octanol in 88% yield; n_D^{20} 1.4260, α_D^{20} −5.30°.

(B) Methoxide in anhydrous methanol. To a solution prepared by dissolving about 0.1 g.-atom of sodium in 60 ml. of anhydrous methanol was added about 0.05 mole of ester. The solution was protected by drying tubes from atmospheric moisture while being refluxed for an appropriate time (48 hr. unless specified otherwise). It was then cooled, acidified with dilute sulfuric acid, and diluted with water to dissolve all salts. The mixture was extracted twice with petroleum ether (b.p. 30–40°).[23] The combined organic material was washed with dilute carbonate solution, dried over

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[16] All optical rotations were measured with pure liquids in 1-dm. jacketed tubes.

[17] A. H. Homeyer, F. C. Whitmore, and V. H. Wallingford, *J. Am. Chem. Soc.*, **55**, 4209 (1933).

[18] Prepared by procedure of W. A. Mosher and J. C. Cox, Jr., *J. Am. Chem. Soc.*, **72**, 3701 (1950).

[19] J. von Braun and F. Fischer, *Ber.*, **66**, 101 (1933). The sealed tube was not specified by these authors but was found necessary in our experiments.

[20] F. C. B. Marshall, *J. Chem. Soc.*, 2754 (1930).

[21] A. I. Vogel, *Practical Organic Chemistry*, 3rd ed., pp. 169–70, Longmans, Green and Co., New York, N. Y., 1956.

[22] A. W. Ingersoll, *Org. Reactions*, **II**, 400 (1944). Only slightly more than 0.5 mole of brucine was used for each mole of *s*-octyl hydrogen phthalate in the resolution step.

[23] Methanol formed azeotropes with some of the esters and had to be excluded from the organic extract as much as possible. Petroleum ether was better than ethyl ether as the extracting solvent for this reason.

potassium carbonate, and distilled. In no experiment was any methyl *s*-octyl ether found. (The ether was prepared independently from methyl iodide and sodium *s*-octoxide; b.p. 78–82° (42 mm.), n_D^{21} 1.4108.)

The aqueous carbonate solution was acidified to permit isolation of any organic acid. No significant amount of acid could be found in these experiments.

1. (−)*s-Octyl trimethylacetate* gave a 57% yield of methyl trimethylacetate (n_D^{20} 1.3894) and a 92% yield of (−)2-octanol (α_D^{20} −6.46°, n_D^{20} 1.4260).

2. (−)*s-Octyl t-butylacetate* gave a 61% yield of methyl *t*-butylacetate (n_D^{20} 1.3996) and a 93% yield of (−)2-octanol (α_D^{20} −6.44°, n_D^{20} 1.4255). The infrared spectrum of the alcohol indicated slight contamination by ester.

3. *s-Octyl diisopropylacetate*, even after 20 days, was recovered in 88% yield. Small amounts (less than 0.2 g.) of methyl diisopropylacetate and 2-octanol were also obtained.

4. *Methyl t-butylacetate* was recovered unchanged after 14 days refluxing. No attempt to trap methyl ether was made, but no *t*-butylacetic acid could be detected.

(*C*) *2-Propoxide in 2-propanol.* A solution prepared from 0.18 g.-atom of sodium metal, 275 ml. of anhydrous 2-propanol, and 0.13 mole of isopropyl *t*-butylacetate was refluxed for 5 days while being protected from atmospheric moisture. From the organic material extracted from the acidified mixture, no isopropyl ether nor *t*-butylacetic acid could be obtained. The unreacted ester was recovered.

(*D*) *Acid hydrolyses. 1.* (+)*s-Octyl trimethylacetate* (5.32 g., 0.025 mole) was dissolved in 60 ml. of aqueous 90% methanol which was 0.6*M* in HCl. The solution was refluxed for 4 days, diluted with water, and extracted with petroleum ether. The extract was washed with dilute carbonate solution and with water. Drying and distillation gave, in addition to about 6% recovery of *s*-octyl ester, a 12% yield of methyl trimethylacetate[24] and a 90% yield of (+)2-octanol (α_D^{20} +7.88°, n_D^{20} 1.4257).

2. (+)*s-Octyl t-butylacetate* (6.2 g., 0.027 mole) was treated in a similar fashion. There were obtained about 7% recovery of starting ester, 76% yield of methyl *t*-butylacetate and 83% yield of (+)2-octanol (α_D^{20} +7.77°, slight recemization).

3. When a solution of (+)*s-octyl diisopropylacetate* (4.7 g., 0.018 mole) in 60 ml. of aqueous 90% acetone, 0.6*M* in HCl, was refluxed for 12 days, no detectable reaction occurred.

Acknowledgment. We have appreciated helpful discussions with Dr. Harold Shechter about this study before experiments were begun, and with Dr. H. C. Brown and Dr. Samuel Siegel near its completion.

BATON ROUGE, LA.

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[24] Some loss resulting from the difficulty of cleanly separating ester and petroleum ether may account for this low yield.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

1,5-Diaryl-2,3-pyrrolidinediones. VIII. Synthesis and Structure Proof

WALTER L. MEYER[1] AND WYMAN R. VAUGHAN

Received April 26, 1957

1,5-Diphenyl-2,3-pyrrolidinedione (XI) has been synthesized and its structure has been proven. This material was found o be identical with the previously unidentified thermal decarboxylation product of 1,5-diphenyl-4-carbethoxy-2,3-pyrolidinedione, and distinctly different from the substance previously assigned this structure, which is now known to be 5-phenyl-3-anilino-2(5*H*)-furanone.

Many reports of 1,5-diaryl-2,3-pyrrolidinediones as the products of the reaction of a benzylideneaniline with pyruvic acid or of a benzylidenepyruvic acid with an aromatic amine have appeared in the literature since Schiff and Gigli[2] first reported 1,5-diphenyl-2,3-pyrrolidinedione itself. Although the formulation of these compounds has been accepted almost without question,[3] several curious aspects of their chemical behavior[4] and dissimilarities in properties and infrared spectra between these and 2,3-pyrrolidinediones with other types of substitution[4–6] suggested that a critical examination of the structure of the supposed 1,5-diaryl-2,3-pyrrolidinediones was in order.[7,8]

Previous investigators[9,10] have attempted degradative studies on the presumed 1,5-diphenyl-2,3-pyrrolidinedione (I) without conclusive results.

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[1] National Science Foundation Predoctoral Fellow, 1954–1957. Abstracted from a portion of the Ph.D. dissertation of Walter L. Meyer, University of Michigan, 1957.

[2] R. Schiff and L. Gigli, *Ber.*, **31**, 1306 (1898).

[3] *Cf.*, however, K. Garzarolli-Thurnlackh, *Monatsh.*, 20, 480 (1899).

[4] (a) W. R. Vaughan and L. R. Peters, *J. Org. Chem.*, **18**, 393 (1953); (b) W. R. Vaughan and L. R. Peters, *J. Org. Chem.*, **18**, 405 (1953); (c) W. R. Vaughan and D. I. McCane, *J. Org. Chem.*, **20**, 143 (1955); (d) W. R. Vaughan, *J. Org. Chem.*, **20**, 1619 (1955).

[5] (a) P. L. Southwick and L. L. Seivard, *J. Am. Chem. Soc.*, **71**, 2532 (1949); (b) P. L. Southwick and R. T. Crouch, *J. Am. Chem. Soc.*, **75**, 3413 (1953); (c) P. L. Southwick, E. P. Previc, J. Casanova, Jr., and E. H. Carlson, *J. Org. Chem.*, **21**, 1087 (1956).

[6] (a) R. Schiff and C. Bertini, *Ber.*, **30**, 601 (1897); (b) L. J. Simon and A. Conduché, *Ann. chim. phys.*, [8] 12, 5 (1907).

[7] For a preliminary report on the results of this study see W. L. Meyer and W. R. Vaughan, *J. Org. Chem.*, **22**, 98 (1957).

[8] Since the publication of our preliminary report,[7] results of a study which reached the same conclusions have appeared, see H. H. Wasserman and R. C. Koch, *Chemistry & Industry*, 428 (1957).

[9] H. Bücherer and R. Russischwili, *J. Prakt. Chem.*, **128**, 89 (1930).

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