ture.[6] Furthermore, a straight line relationship is obtained in a plot of long-spacing values and molecular weights. Thus, the relationships of long-spacing values, molecular weights, and melting points of the diacid diglycerides, solvent crystallized in the β-form, indicate that they represent a truly homologous series.

Transition temperatures for the different polymorphic forms for each diglyceride obtained from warming and cooling curves and capillary tube determinations are given in Table II. Since X-ray diffraction patterns were not obtained on forms other than those obtained on crystallization from solvent, the system of nomenclature used is the same as that previously reported.

Acknowledgment.—The assistance of Miss Gretta L. Scott in obtaining some of the X-ray diffraction data is gratefully acknowledged.

Summary

X-Ray diffraction and thermal data are reported for a series of three symmetrical diacid diglycerides, two of which, namely, 1-palmityl-3-laurin and 1-myristyl-3-caprin, are new compounds.

The side-spacing diffraction data for 1-myristyl-3-caprin and 1-palmityl-3-laurin correspond to Malkin's type *a* pattern for the *beta* form of monoacid diglycerides, while the data for 1-stearyl-3-myristin seemed to correspond more nearly to Malkin's type *b* pattern.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF SARAH LAWRENCE COLLEGE]

The Reversible Esterification of Carboxylic Acids with Isobutene and Trimethylethylene. Quantitative Studies and Synthetic Applications

BY ROLF ALTSCHUL

The literature contains only scattered publications dealing with esterifications of carboxylic acids with olefins, such as the catalyzed additions of fatty acids to butene-2 and pentene-2,[1] to trimethylethylene,[2,3] or to isobutylene.[1,4]

The thermal and the acid-catalyzed decompositions of tertiary esters represent the reverse reaction, and these constitute in contrast a generally recognized phenomenon[5] and have been fully characterized in the presence of hydroxylic reagents, leading to hydrolysis with water,[6] formation of ethers with anhydrous alcohols,[7] or acetolysis with acetic acid.[8]

In the past the opposing reactions have been studied separately under irreversible conditions by either expelling the volatile alkenes at elevated temperature, by exposing them to solvolysis, or by conducting esterifications with an excess of carboxylic acid sufficient to mask the attainment of an equilibrium state.

If such additions or decompositions are carried out reversibly in an inert solvent, an equilibrium results, analogous to that between alcohols and acids. In the following, we will present in turn the study of the equilibrium system and of the rates and mechanism, followed by a brief appraisal of its value as a general preparative tool.

Equilibrium.—Equation 1 represents the relevant equilibrium

$$\text{Acid} + \text{Olefin} \underset{k_1}{\overset{k_2}{\rightleftarrows}} \text{Ester} \qquad (1)$$

$$K = (\text{Ester})/(\text{Acid}) \times (\text{Olefin}) = k_2/k_1 \qquad (2)$$

Quantitative measurements were carried out on the esterifications of benzoic acid, *p*-nitrobenzoic acid and acetic acid with isobutylene and, for the first acid, with trimethylethylene leading to *t*-butyl benzoate (I), *t*-butyl *p*-nitrobenzoate (II), *t*-butyl acetate (III), and *t*-amyl benzoate (IV),

TABLE I

EQUILIBRIUM BETWEEN ISOBUTENE, BENZOIC ACID AND *t*-BUTYL BENZOATE IN DIOXANE SOLUTIONS CONTAINING SULFURIC ACID AT 25 ± 0.1° AND 35 ± 0.1°

Initial concn., moles/liter					
(Ester)	(Bz acid)	(*i*-Bu)	(H_2O)	(H_2SO_4)[a]	K
			At 25°		
0.928	0.629	0	0.062	0.545	1.39
.928	.0	0	.119	1.040	1.52
.928	.280	0	.119	1.040	1.43
.928	.0	0	.238	1.141	1.39
.928	.0	0	.149	1.302	1.59
.0	.247	0.855	.0	0.483	1.59
					Av. 1.47 ± 0.08
			At 35°		
0.928	0	0	0	1.075	1.18
.696	0	0	0	0.664	1.04
1.392	0	0	0	.664	0.98
1.113	0	0	0	1.128	1.10
0.928	0	0	0	0.441	0.94
.0	0.620	0.540	0	.664	.93
					Av. 1.03 ± .08

[a] Concentration of sulfuric acid given as equivalents/liter,

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(1) Zavgorodnii, *C. A.*, **33**, 5805 (1939).

(2) Kondakow, *J. Russ. Phys. Chem. Soc.*, **25**, 442 (1893).

(3) Timofejev and Andreasov, *Chem. Zentr.*, **96**, II, 1652 (1925).

(4) Scovill, Burk and Lankelma, THIS JOURNAL, **66**, 1039 (1944).

(5) (a) Bilger and Hibbert, *ibid.*, **58**, 823 (1936); (b) Tronov and Sibgatulin, *Ber.*, **62B**, 2850 (1929); (c) Barkenbus, Roswell and Mitts, THIS JOURNAL, **62**, 1251 (1940); (d) Zaki, *J. Chem. Soc.*, 983 (1928).

(6) Day and Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941). This paper presents an extensive summary of data on ester hydrolyses.

(7) Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941).

(8) Cohen, *ibid.*, **66**, 1395 (1944).

respectively. For a suitable reaction medium anhydrous dioxane was chosen with its adequate solvent power capable of accommodating ample quantities of isobutylene. Varying amounts of sulfuric acid served as catalyst.

With benzoic acid, isobutylene and (I) as a model system, the behavior was explored thoroughly at two temperatures by approaching equilibrium from both directions and by varying the concentrations of the constituents and of the catalyst. Establishment of true equilibria, *independent* of sulfuric acid concentrations over the measured range, is demonstrated by the data (Table I).

Two independent methods were applied to analysis of the solutions: acidimetric titrations afforded the values of carboxylic acid concentrations, while an iodimetric procedure for the determination of olefin was developed. The former was generally reproducible to within 1%, whereas the latter was accurate to 5% provided the isobutylene concentration was kept below 0.6 mole/liter. Within these limits, there was close agreement between the equilibrium concentrations calculated from the two analyses.[9]

A large-scale run served to substantiate the acidimetric procedure further by permitting an additional gravimetric determination of acid and ester. The agreement between both methods was good (maximum deviation 0.9%). This experiment, moreover, provided a sufficient quantity of ester to be characterized fully through its physical constants and its great resistance to saponification. Less than 15% of the available benzoic acid was liberated after agitation with 17% aqueous alkali in a sealed tube at 110° for twenty hours. We were thus dealing with a tertiary ester formed in accordance with Markownikow's rule.

Additional preliminary experiments clarified the distinct effect of small amounts of water on the reaction course. While anhydrous dilute solutions of isobutene in dioxane were stable in the presence of catalytic amounts of sulfuric acid—hence precluding polymerization near room temperature—introduction of known quantities of water rapidly consumed an equivalent amount of unsaturation. This is attributed most reasonably to hydration which, upon completion, yields once more a stable solution. For instance, the molarity of a solution of *i*-butene in dioxane dropped from 0.70 to 0.48 mole/liter within less than four hours after addition of 0.213 mole/liter of water and 0.850 equivalent/liter of sulfuric acid. From then on the *i*-butene concentration remained practically static for at least twenty eight hours (0.47 mole/liter). Inclusion of water with the original test runs presented a convenient means of varying the olefin concentrations (Table I) but was abandoned for the later determinations conducted under strictly anhydrous conditions with 100% sulfuric acid as the catalyst, replacing the concentrated acid which contains about 23 mole per cent. of water. Table II presents the equilibrium constants at 2 temperatures along with a rough estimate of ΔH for the exothermic addition reactions.

TABLE II

SUMMARY OF EQUILIBRIUM CONSTANTS AND HEATS OF REACTION IN DIOXANE SOLUTION AT TWO TEMPERATURES

Ester	(H_2SO_4) equil./l.	K	Temp., °C.	ΔH, kcal./m.
I	0.48–1.30	1.47	25	
II	0.89–1.04	3.57	25	
III	1.22	1.43	25	
IV	1.25–1.67	6.25	25	
I	0.66–1.13	1.03	35	−6.5
II	0.66–1.13	2.38	35	−7.5
III	1.10	0.91	35	−8.4
IV	1.10	4.76	35	−5.2

All constant at one temperature fall within a fairly narrow range, in accord with similar observations for the equilibria between various acids and alcohols.[10] Attainment of the equilibrium state was established when progressive titrations of samples ceased to show a trend. This condition was usually reached within a day or two, and subsequent readings remained constant over all measured periods (up to eight days). As a consequence, slow isomerization to secondary esters, conceivably due to partial addition contrary to Markownikow's rule, may be rejected. Such a rearrangement would be expected to cause a drift toward lower acid concentrations since a sample of *s*-butyl acetate showed no decomposition at all after three days at 25° nor after an additional equal period at 35° in a 1.84 *N* solution of sulfuric acid in dioxane.

In accordance with the numerical values of K for I and III at 35°, a system is stationary at a one molar level with approximately equal concentration of its 3 components. The other runs (Table II) adjusted themselves toward more complete esterification.[11]

Rates and Mechanism.—Speculations as to the mechanism for reactions of tertiary esters must account for their susceptibility to acid catalysis and their simultaneous resistance to basic reagents. The latter trait in particular is

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(9) The vapor pressure of isobutylene is sufficiently low under these conditions to permit only negligible quantities of the gas to stray into the vapor phase.

More reliable data were generally obtained when the equilibrium was approached by means of ester dissociation, as the alternative required either the analysis of an initial solution too rich in olefin to fall within the limitations of the iodimetric assay, or the employment of so low a starting concentration as to amplify normal deviations of the primary analytical data into unduly large differences for K.

(10) Hammett, "Physical Organic Chemistry," McGraw-Hill Co., New York, N. Y., 1940, Chapter VII.

(11) In a manner similar to the gravimetric experiment with (I) above, a sample of *t*-amyl benzoate was isolated and identified from a run starting with olefin and acid: $n^{25}\text{D}$ 1.4903, d_{27} 0.962, mol. wt., 188 ± 6. Less than 7% of the ester was hydrolyzed after treatment with excess 20% aqueous sodium hydroxide for three and one-half hours.

so emphatic that it is of diagnostic value for the distinction between isomeric esters.[12]

Their ready participation in acid-sponsored reactions is credited to the relatively great stability of tertiary carbonium ions as a driving force and the consequent labilization of the alkyl-oxygen link. Choosing as their criterion the nature of reaction products, Cohen and Schneider located this point of breakage in an elegant fashion by isolating *t*-butyl methyl ether from acid-catalyzed solvolyses of *t*-butyl esters in anhydrous methanol.[7] This reaction occurred at the expense of orthodox ester interchange, commonly observed for less branched esters and presumably proceeding through cleavage of the acyl-oxygen bond.[13]

The following mechanism has been advanced for the alcoholysis of *t*-butyl esters[7]

$$RCOOC(CH_3)_3 + H^+ \rightleftarrows R^+C(OH)O{\cdot}C(CH_3)_3 \quad (3)$$

$$R^+C(OH)OC(CH_3)_3 \rightleftarrows RCOOH + {}^+C(CH_3)_3 \quad (4)$$

$${}^+C(CH_3)_3 + CH_3OH \rightleftarrows C(CH_3)_3OCH_3 + H^+ \quad (5)$$

Operating in the absence of hydroxylic reagents we can modify the last step

$${}^+C(CH_3)_3 \rightleftarrows C(CH_3)_2{=}CH_2 + H^+ \quad (6)$$

In order to check the validity of this hypothesis and in order to clarify further the role of the catalyst, the rates of ester dissociation (k_1, equation 1) were measured in the absence of water. We also looked for a clue as to the correlation between these rate constants and the ionization constants K_a of the parent acids. A special kinetic formulation is required to represent the course of a reversible reaction. Such an equation was derived in accordance with the principals outlined in the literature.[14,15] If X equals the concentration of carboxylic acid, its net rate of formation can be written as

$$\mathrm{d}X/\mathrm{d}t = k_1(A - X) - k_2X^2 \quad (7)$$

where A is the concentration of ester at the zero point. Integration, substitution and rearrangement lead to

$$C + k_1t = (K_\mathrm{d} \ln Q)/(2X_\mathrm{e} + K_\mathrm{d}) \quad (8)$$

where

$$Q = (X + X_\mathrm{e} + K_\mathrm{d})/(X_\mathrm{e} - X) \quad (9)$$

C is the integration constant, X_e stands for the equilibrium concentration of acid, and K_d as dissociation constant is the reciprocal of the respective equilibrium constants (Table II). Since Q can be readily evaluated at the zero point, elimination of C presents no problem.[15]

Dissociations were followed at 35° by progressive acidimetric titrations of the carboxylic acid concentrations rising from zero to X_e within approximately three hours for the fastest run and within about eighty hours for the slowest. Table III presents the results of three typical runs.

TABLE III

RATES OF DISSOCIATION OF THREE ESTERS IN DIOXANE CONTAINING SULFURIC ACID AS A CATALYST AT 35 ± 0.1°

Hours	X	Hours	X	Hours	X[a]
Run no. 45		Run no. 46		Run no. 48	
0	0	0	0	0	0
0.58	0.144	0.52	0.504	5.0	0.086
1.50	.263	.80	.675	7.8	.139
1.93	.293	1.20	.820	18.5	.299
2.50	.318	1.80	.910	30.0	.397
3.32	.351	24.5	.960	51.5	.535
4.00	.364			66.3	.577
28	.385			114	.628

[a] Concentrations are given as moles/liter; complete experimental conditions for each run are listed in Table IV.

With the decompositions generally leveling off at 60–65%, this system affords a favorable case for study of reversible rates. Figure 1, showing the graphs for the runs above, demonstrates how closely equation 8 represents the kinetic picture over the entire course since the last point on each curve signifies well over 90% completion. Autocatalysis due to the liberated acidic products can hence be ruled out. In accord with the proposed mechanism, the rate is first order with respect to ester concentration.

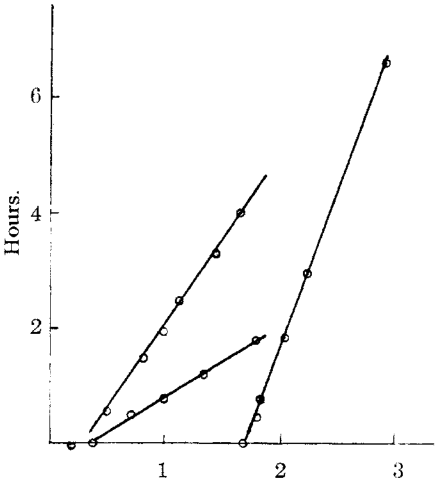

Fig. 1.—Rates of sulfuric acid–catalyzed ester dissociations in dioxane at 35°: left to right no. 45 (a = 0), no. 46 (a = 0), no. 48 (a = 1.3). The ordinate is reduced by a factor of ten for no. 48.

Table IV summarizes all rate constants at various catalyst concentrations.

The nitrobenzoate (II) unexpectedly trailed the other *t*-butyl esters. The ratio of their k_1 constants at uniform catalyst level (1.128 equiv./l.)

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[12] A spectacular example is represented by *t*-butyl 2,4,6-trimethylbenzoate which succumbs easily to hydrolysis with 18% hydrochloric acid but is recovered almost untouched after similar treatment with 20% aqueous alkali (*cf.* ref. 7). Steric hindrance is commonly held responsible for the stability of these compounds toward base.

[13] That this type of reactivity is restricted mainly to tertiary isomers is supported by our observation above showing complete stability of *s*-butyl acetate under conditions favoring rapid dissociation of its isomer.

[14] Ref. 10, Chapter IV.

[15] Conant and Bartlett, THIS JOURNAL, **54**, 2881 (1932).

TABLE IV

RATE CONSTANTS OF SULFURIC ACID-CATALYZED REVERSIBLE ESTER DISSOCIATIONS IN DIOXANE AT 35 ± 0.1°

Ester	Run no.	(H_2SO_4) equiv./l.	(A) moles/l.	k_1 hrs.$^{-1}$	k_1/(H_2SO_4)^3
I	48	0.441	0.928	0.018	0.21
	41	.664	.696	.053	.18
	42	.664	1.392	.059	.20
	43	1.128	0.556	.27	.19
	47	1.128	1.113	.26	.18
II	40	0.664	0.615	.01	.036
	44	1.128	.491	.052	.034
III	46	1.128	1.473	.66	...
IV	45	1.128	1.012	.18	...

points to an inverse dependence on the corresponding acid ionization constants.[16]

A rigid quantitative relationship can obviously not be established from the available data. Instead, the qualitative prediction of more complete esterification and slower ester decomposition for the stronger carboxylic acids seems justified. The trend is borne out by Table II.

However, the more essential result lies in the relationship between k_1 and the sulfuric acid concentrations; the dependence is close to the third power over a 2.5-fold range. While the tentative mechanism (equations 3-5) partially conforms to our experimental data, its first step (equation 3) must be an oversimplification as written, with definitely more than one, and probably three, protons instrumental in it, perhaps in the form of a dioxonium complex. We hesitate to be more specific at this time.

Preparative Applications.—The preceding results furnish certain clues as to the optimum conditions for esterification with olefins: (a) *low* reaction temperature, (b) high concentrations and a liberal excess of the more abundant reactant, (c) a relatively large quantity of catalyst, and (d) anhydrous conditions. Esters I, II and III were prepared accordingly.[17] The fraction of converted starting material was moderate, with the yields ranging from 85 to 93% allowing for recovered acid. This method appears to be an advantageous route to tertiary esters especially when parent acid chlorides are difficultly accessible and hence prohibit recourse to the alternate procedure with pyridine.[18]

Experimental

Quantitative Measurements.—Preceding the runs, separate solutions of sulfuric acid, carboxylic acid and olefin in pure dioxane were standardized volumetrically (described below) immediately before use. Solutions of ester in the solvent were made up by volume. Thermostated aliquot volumes were mixed in small constricted tubes, sealed immediately in a manner to permit a minimum of empty space. The ampules were stored in a thermostat and later analyzed as follows: (a) Acidimetric. Aliquot portions were run into a moderate excess of 0.1 *N* carbonate-free sodium hydroxide followed by backtitration with 0.1 *N* hydrochloric acid using phenolphthalein. Blank tests established that no other constituents interfered. (b) Iodimetric. Aliquot portions were added to a moderate excess of 0.1 *M* bromine in glacial acetic acid, and the tightly stoppered flask was kept at room temperature for four minutes. Twenty cc. of roughly 1 *M* potassium iodide was added, followed by immediate titration with thiosulfate. Blank tests showed that no other constituents interfered. This method was developed using known solutions of freshly distilled trimethylethylene and afforded checks to within 1% of the given molarity. For isobutene it was reproducible within the provisions outlined in the text. All equilibrium runs were analyzed by both methods.

Gravimetric Run with I.—Twenty-five cc. of I was added to 40 cc. of a 2.002 *N* solution of sulfuric acid in dioxane and stored in a g. s. Erlenmeyer flask at 25°. Acidimetric readings showed that equilibrium was reached within less than twenty-three hours, with the benzoic acid at 1.140 moles/liter.[19] Sixty-one cc. of the residual solution was split quantitatively into a neutral and an acid fraction by repeated extractions with ether and saturated aqueous sodium bicarbonate. From the former there was isolated 10.8 g. of pure ester, $n^{25}D$ 1.4880, d_{25} 0.990; this corresponded to a concentration of 0.994 mole/liter for the parent solution (calcd. 1.003 mole/liter). The bicarbonate layer afforded 8.41 g. of benzoic acid in the usual manner (dried *in vacuo* to constant weight); m. p. 121-122°, remaining unchanged when mixed with an authentic sample. This quantity gave a value of 1.13 moles/liter for the original solution and, combined with the ester value, it amounted to 99.2% of the starting material.

Hydrolysis of the recovered ester was complete after three and one-half hours when 5.95 g. of the oil was boiled with 20 cc. of 10 *N* sulfuric acid. Quantitative collection afforded 4.09 g. of benzoic acid, m. p. 119-121°, and corresponding to a molecular weight of 179 ± 3 for the ester (calcd. 178.1). However when 0.20 g. of the material was stirred in a sealed tube with 2 cc. of 17% aqueous sodium hydroxide at 110° for twenty hours, very little hydrolysis took place. Quantitative isolation of acid in the usual manner resulted in less than 20 mg. of crude benzoic acid, m. p. 105-112°, corresponding to 14.5% of the available benzoate.

1,4-Dioxane.—The commercial product was purified according to standard procedure.[20] The final solvent, m. p. 11.7-11.8°, was stored in paraffin-sealed, glass-stoppered bottles over sodium wire with a minimum contact with air.

100% Sulfuric Acid.—Small amounts of C. P. oleum of unknown strength were mixed with varying quantities of C. P. concentrated sulfuric acid in order to adjust the compositions by means of melting point determinations. Following these preliminary tests, 179 cc. of oleum was added slowly to 260 cc. of concentrated sulfuric acid, yielding the desired solution, m. p. 10.5°.

Isobutene.—The compressed gas was dried with calcium chloride.

***t*-Butyl Benzoate.**—One batch was prepared from benzoyl chloride, pyridine, and *t*-butyl alcohol,[21] b. p. 75-79° (2-3 mm.), $n^{23}D$ 1.4893, d_{24} 0.993. It gave a negative test with alcoholic silver nitrate.

In an alternate preparation, 0.087 mole (10.8 g.) of commercial C. P. benzoic acid was suspended in 16 cc. of a

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[16] The products of k_1K_a are 1.9 and 2.1 × 10^{-6} for I and II, respectively. K_a equals 6.8 × 10^{-5} and 40 × 10^{-5}, respectively at 25°.

[17] Presence of an ether solvent is often indispensable since side reactions (presumably polymerization) seem to occur otherwise; this was observed for acetic acid under a variety of conditions.

[18] Extensive transesterifications can also be visualized. The alcohol constituents of labile esters can be traded for suitable olefins, while the acyl components are exchangeable for other acids present in excess. The acetolysis of *t*-butyl benzoate is reported, *cf.* ref. 8.

[19] This experiment contributed no value for *K*, as it was not analyzed for isobutene content.

[20] (a) Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1941, p. 368; (b) Bartlett and Dauben, THIS JOURNAL, **62**, 1339 (1940).

[21] Norris and Rigby, THIS JOURNAL, **54**, 2088 (1932).

dioxane solution containing 1.3 cc. of concentrated sulfuric acid. A fairly rapid stream of *i*-butene was passed for eighty minutes into the suspension contained in a large test-tube at room temperature, affording a clear solution with slight evolution of heat during the period. The flask was stoppered and kept overnight; ether was added, followed by extractions as usual to remove unreacted acid. From the alkaline layer 0.050 mole (57.5%) of benzoic acid, m. p. 119–120°, was recovered, while 0.030 mole (5.3 g., or 35%) of ester was isolated from the organic layer, thus accounting for 92% of the starting material: $n^{25}\text{D}$ 1.4876, d_{23} 0.984, mol. wt. 182 ± 5 (determined through acid hydrolysis of 3.0 cc. of ester).

***t*-Butyl Acetate**.—This ester was prepared once according to the literature,[21] b. p. 95.5–96.5° (755 mm.), $n^{27}\text{D}$ 1.3827, d_{26} 0.855.

A second esterification started from 0.70 mole (40 cc.) of glacial acetic acid in solution in 28 cc. of dioxane containing 2.5 cc. of concentrated sulfuric acid. A moderately slow stream of *i*-butene was bubbled into the solution at room temperature for sixteen hours for a weight gain of 8.0 g. (0.14 mole). After a few hours of standing of the stoppered tube separation was effected as usual. Recovery of unreacted acid was not attempted. Upon distillation there resulted 0.12 mole (14 g.) of pure ester, b. p. 96.3–97.2° (766 mm.), $n^{26}\text{D}$ 1.3842, d_{26} 0.849. The yield, based on the added olefin, was 85%.

Benzoic Acid.—The commercial C. P. product was crystallized from water and dried *in vacuo*, m. p. 122°.

2-Methylbutene-2.—Dehydration of *t*-amyl alcohol led to the olefin[22]; it was distilled through a 3-ft. Widmer column, b. p. 38.1–38.8° (762 mm.).

***p*-Nitrobenzoic Acid**.—Alkaline permanganate oxidation of *p*-nitrotoluene led to the acid which was recrystallized from acetic acid, m. p. 232–233° (uncor.).

***t*-Butyl *p*-Nitrobenzoate**.—The ester was prepared through the addition reaction rather than through the pyridine–acid chloride synthesis for which a 29% yield is reported.[23] Certain modifications of procedure were indicated due to the limited solubility of the aromatic acid. Accordingly, 0.053 mole (8.8 g.) of the solid was suspended in 20 cc. of 3.8 *N* sulfuric acid in dioxane (prepared by adding 7 cc. of 100% sulfuric acid to 73 cc. of pure dioxane) in a large test-tube. This mixture was saturated with a fairly rapid stream of dry *i*-butene in the course of one hour at room temperature and was then separated by decantation of the clear solution. This was followed by three successive additions of 20-cc. portions of the catalyst solution in their turn to the residual unreacted acid, each to be saturated again for one hour at least. The supernatant layers were poured into ether, extracted first with water and then with 2 portions of 12% aqueous sodium hydroxide. Combination of the corresponding layers from all shifts afforded 0.033 mole of recovered acid (5.5 g., or 62.7%), isolated from the alkaline portion. The organic layer furnished 0.016 mole (31%) of the pure product after crystallization from dioxane–petroleum ether, or from benzene–petroleum ether, m. p. 115–116° (reported 115–117°). This accounted for 94% of the starting material.

***t*-Amyl Benzoate**.—The ester was prepared by means of the pyridine–benzoyl chloride procedure rather than by base-catalyzed transesterification of methyl benzoate in *t*-amyl alcohol[5d]; b. p. 99–103.5° (1.5–2 mm.); $n^{25}\text{D}$ 1.4910; d_{26} 0.972. It gave a negative test with silver nitrate.

***s*-Butyl Acetate**.—Butanol-2, acetic anhydride and a catalytic amount of sulfuric acid afforded the pure ester in 60% yield after a very vigorous reaction; b. p. 111–111.5° (761 mm.), $n^{27}\text{D}$ 1.3848, d_{27} 0.863.

All purified esters were stored over anhydrous potassium carbonate.

Acetic Acid.—Commercial glacial acetic acid was purified as usual.[24] The final product was stored in paraffin-sealed bottles; m. p. 16.6°.

Summary

Three representative carboxylic acids were added to the double bonds of *i*-butene and trimethylethylene to yield the corresponding tertiary esters in strict accordance with Markownikow's rule without formation of isomers. This exothermic reaction leads to an equilibrium in dioxane solutions with sulfuric acid as a catalyst. The equilibrium constants were determined at two temperatures, affording an estimate of the heats of reaction.

The mechanism is discussed in relation to kinetic measurements of four reversible ester dissociations for which an adequate mathematical formulation is derived. The dissociation rates were determined quantitatively as a function of the catalyst concentration, and a qualitative relationship between these rate constants and the parent acid ionization constants is indicated.

Based on the preceding clues, an appraisal of this esterification procedure in terms of its general preparative value is presented along with an outline of the optimum experimental conditions.

Some aspects of the problem are under further investigation.

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(22) See Reference 20a, Experiment 7.

(23) Hückel, Nerdel and Reimer, *J. prakt. Chem.*, **149**, 311 (1937).

(24) Weissberger and Proskauer, "Organic Solvents," The Clarendon Press, Oxford, 1935, p. 146.