quite sharply, but upon continued heating it resolidified and melted again at 222–223°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.61; H, 5.55.

The ether solution containing the neutral fraction was evaporated to dryness leaving 0.173 g. of residue, melting at 194–200°, which upon recrystallization gave a melting point of 215–218° and proved to be identical with the compound formed by heating the acidic fraction.

The analytical sample of 12-methylol-9,10-ethanoanthracene-9-carboxylic acid lactone melted at 222–223°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.54; H, 5.44.

9,12-Dicyano- and 9,11-Dicyano-9,10-ethanoanthracene.—A mixture of 4.00 g. (0.0197 mole) of 9-cyanoanthracene, 20 ml. (0.307 mole) of acrylonitrile and 0.1 g. of hydroquinone was heated in a sealed tube for 18 hours at 135–145°. Upon cooling, the material in the unopened tube solidified into a large mass of yellow needles. Since this indicated unreacted 9-cyanoanthracene was present the tube was heated for 22 hours more at 190–200°. This time when the tube was cooled, no yellow crystals appeared. The excess acrylonitrile was evaporated, and the residue was dissolved in methanol and the solvent allowed to evaporate slowly. Two types of crystals were formed in this process: a white, fine grained, agglomerate which melted at 196–198° in crude form, and large beautiful prismatic crystals of slightly yellow color, m.p. 165–166°, weighing as much as 0.125 g. each. By a process of separating the crystals manually and by recrystallization from methanol, 1.70 g. (33%) of the crystals melting at 204–205° (the 9,11-dicyano) and 0.95 g. (18.5%) of white crystals melting at 166.5–167.5° (the 9,12-dicyano) were obtained.

Anal. 9,11-Dicyano isomer. Calcd. for $C_{18}H_{12}N_2$: C. 84.35; H, 4.72; N, 10.93. Found: C, 84.40; H, 4.85; N, 10.76. 9,12-Dicyano isomer: Found: C, 84.40; H, 4.77; N, 10.78.

In a second run 3.5 g. (0.0173 mole) of 9-cyanoanthracene, 30 ml. (0.46 mole) of acrylonitrile and 0.1 g. of hydroquinone were heated in a sealed tube for 23 hours at 190–200°. Upon evaporation of excess acrylonitrile a light tan residue remained. Treatment as before led to 0.36 g. (8.1%) of the 9,12-dicyano isomer, m.p. 166.5–167.5°, and 0.75 g. (16.9%) of the 9,11-dicyano isomer, m.p. 204–205°.

A mixture of 0.274 g. (0.001 mole) of the adduct of 9-cyanoanthracene and acrylamide, m.p. 216–219°, and 10 ml. of acetic anhydride was refluxed for one hour. The addition of 2–3 ml. of water and cooling gave 0.167 g. (65%) of product, m.p. 163–164°. A mixed melting point with the lower melting dinitrile showed no depression.

Two grams of 12-cyano-9,10-ethanoanthracene-9-carboxaldehyde,[2] 2 g. of hydroxylamine hydrochloride, 10 ml. of ethanol and 10 ml. of water were refluxed for two hours, cooled and dried with an air jet. After extraction with water the residue was recrystallized from aqueous methanol and 1.26 g. of oxime, m.p. 196–197°, was obtained. Repeated recrystallization gave an analytical sample melting at 206–207°.

Anal. Calcd. for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.62; H, 5.04; N, 10.19.

When this oxime was dehydrated with acetic anhydride the product was found to be identical with the lower melting adduct of 9-cyanoanthracene and acrylonitrile prepared above.

Hydrolysis of 9,12- and 9,11-Dicyano-9,10-ethanoanthracene.—The lower melting isomer was hydrolyzed by heating 0.71 g. in 15 ml. of ethylene glycol with 1.12 g. of potassium hydroxide for 40 hours at 150°. The product was recrystallized from aqueous methanol after acidification and 0.75 g. (92%) of solid, which first started to melt at 224° and was completely melted at 230–231°, was recovered. Mixed melting with the 9,12-dicarboxylic acid previously obtained from the acrylamide adduct showed no depression. After drying over phosphorus pentoxide at 120° the neutralization equivalent was 150, calcd. 147.

When 0.80 g. of the higher melting dicyano isomer was hydrolyzed 0.44 g. (47%) of an acid melting at 268–270° was obtained, lit. 266–268°.[4]

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.28; H, 4.93.

Acknowledgment.—Carbon–hydrogen analyses were performed by Galbraith Microanalytical Laboratories and Microchemical Specialties. Nitrogen analyses were done by Mrs. D. E. Ramey. The acrylamide was a gift of the American Cyanamid Co. and the acrylic acid a gift of the B. F Goodrich Chemical Co.

BOULDER, COLORADO

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of Branched Primary and Secondary Alkyl Acetates

BY SHALOM SAREL[1] AND MELVIN S. NEWMAN

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The preparation and properties of a number of highly branched primary and secondary alcohols and of the corresponding acetates are described.

In connection with the study of the rates of alkaline hydrolysis of acetates of branched alcohols in the accompanying paper it was necessary to prepare the required esters. This paper describes the methods of preparation and properties of the necessary compounds.

All of the primary alcohols were prepared by the reduction of acids or esters with lithium aluminum hydride. In general the yield was better when the free acid rather than the methy or ethyl ester was used.[2] For example, only a 65% yield of pure neopentyl alcohol was obtained on reduction of ethyl trimethylacetate whereas reduction of the acid afforded the desired alcohol in 92% yield.

Reduction of hindered acids or esters was quite sluggish and often incomplete. For example, after 8 hours of reflux with excess reagent triethylacetic acid was reduced in only 65% yield and 25% of acid was recovered. Similarly after 12 hours diisopropylacetic acid was reduced in 86% yield and 10% of acid was recovered (see Table I for the other data).

The more highly hindered acids were made by three methods: (1) alkylation of acetonitrile followed by hydrolysis,[3] (2) alkylation of ethyl cyano-

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[1] Formerly Shalom Israelashvili. The work herein reported was supported by a grant from the Office of Naval Research.

[2] See J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2515 (1951).

[3] (a) K. Ziegler and H. Ohlinger, *Ann.*, **495**, 84 (1932); (b) N. Sperber, D. Papa and E. Schwenk, THIS JOURNAL, **70**, 3091 (1948); (c) C. Schuerch, Jr., and E. H. Huntress, *ibid.*, **70**, 2824 (1948).

TABLE I

PREPARATION OF ALCOHOLS BY LITHIUM ALUMINUM HYDRIDE REDUCTION[a]

Alcohol	Refluxing period, hr.	Yield, %	Boiling point		n^{25}D	d^{25}	RLD	
			°C.	Mm.			Calcd.	Found
2,3-Dimethyl-1-butanol[b]	0.5	80	145–146	740	1.4173	....		
2,3,3-Trimethyl-1-butanol[c,d]	4	68	158–159	740	1.4230	0.8238	36.05	35.86
3-Methyl-2-ethyl-1-butanol[e]	4	83	84–85	38	1.4234	.8327	36.05	35.61
3,3-Dimethyl-2-ethyl-1-butanol[f]	6	96	88–89	38	1.4348	.8425	40.66	40.32
3-Methyl-2-isopropyl-1-butanol[g]	6	75[g]	171–172	741	1.4342	.8425	40.66	40.30
	12	86.5						
3,3-Dimethyl-1-butanol[h]	0.25	83.5	144–145	740	1.4115	.8097	31.43	31.35
Cyclopropanemethanol[i]	.25	70	123	740	1.4297	.9098		20.47
Cyclobutanemethanol[j]	.25	80	140–141	740	1.4430			
Cyclopentanemethanol[c,k]	.25	76.5	160–161	740	1.4570			
2,2-Dimethyl-1-propanol[l,m]	.50	85	112–114	740	M.p. 51–51.6°			
2,2-Dimethyl-1-butanol[n]	.75	90	134–135	740	1.4192			
2-Methyl-2-ethyl-1-butanol[c,o]	4	82	152	740	1.4288			
2,2-Diethyl-1-butanol[p]	8	65[q]	92	25	1.4411			
3,3-Dimethyl-2-butanol[r]	2	86	118.5–120	741	1.4153	0.8122	31.43	31.50

[a] The carboxylic acids were used. [b] A. Gorski, *J. Russ. Phys. Chem.*, **45**, 168 (1913); *Chem. Zentr.*, **84 I**, 2022 (1913); P. Sutter, *Helv. Chim. Acta*, **21**, 1268 (1938), gives $n^{20.5}$D 1.4195 for 2,3-dimethyl-1-butanol. [c] Methyl esters were used. [d] P. G. Stevens and J. A. McCoubrey, THIS JOURNAL, **63**, 2847 (1941), give b.p. 159.5–162° at 761 mm., n^{25}D 1.4288 for 2,3,3-trimethyl-1-butanol, but without an analysis. *Anal.* Calcd. for $C_7H_{16}O$: C, 72.4; H, 13.8. Found: C, 72.2; H, 13.9. [e] W. Dirscherl and H. Nahn, *Ber.*, **76**, 635 (1943), give b.p. 65–66.5°, at 14 mm. for 3-methyl-2-ethyl-1-butanol. [f] The *t*-butylethylacetic acid, m.p. 76.0–76.5°, used in the reduction was supplied by The Dow Chemical Co., Midland, Michigan. *Anal.* of the alcohol, Calcd. for $C_8H_{18}O$: C, 73.8; H, 13.9. Found: C, 73.9; H, 13.9. [g] Yield was based upon amount of acid used; recovered acid amounted to 15%. *Anal.* Calcd. for $C_8H_{18}O$: C, 73.8; H, 13.9. Found: C, 73.9; H, 13.8. [h] M. Delacre, *Bull. acad. sci. Belg.*, 20 (1906); *Chem. Zentr.*, **77**, 1233 (1906), gives b.p. 142.6–143.6° at 760 mm. [i] L. I. Smith and S. McKenzie, Jr., *J. Org. Chem.*, **15**, 74 (1950), gives b.p. 122–123° at 670 mm., n^{25}D 1.4300, for cyclopropanemethanol; J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2515 (1951), reported a 68% yield in the reduction of cyclopropanecarboxylic acid with $LiAlH_4$. [j] H. Pines, H. G. Rodenberg and V. N. Ipatieff, *ibid.*, **75**, 6065 (1953), give b.p. 142–143.5°, n^{20}D 1.4450, for cyclobutanemethanol, which has been prepared similarly in 76% yield. [k] N. Turkiewicz, *Ber.*, **72**, 1060 (1931), gives b.p. 161–163° at 760 mm., n^{20}D 1.4552, for cyclopentanemethanol. [l] Ethyl esters were used. [m] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2549 (1947), reported a 92% yield in the reduction of pivalic acid with $LiAlH_4$. [n] F. Hovorka, H. P. Lankelma and W. R. Smith, *ibid.*, **62**, 2372 (1940), gives b.p. 136.7°, n^{25}D 1.4188, for 2,2-dimethyl-1-butanol. [o] R. V. Rice, G. L. Jenkins and W. C. Harden, *J. Am. Pharm. Assoc.*, **27**, 303 (1938), give b.p. 150–151° at 760 mm., n^{20}D 1.4251, for 2-methyl-2-ethyl-1-butanol. *Anal.* Calcd. for $C_7H_{16}O$: C, 72.4; H, 13.8. Found: C, 72.1; H, 14.0. [p] Ref. *o* gives b.p. 76–77° at 11 mm., n^{20}D 1.4400 for 2,2-dimethyl-1-butanol. [q] Yields based upon acid used. On basis of acid consumed the yield was 90%. [r] F. C. Whitmore and P. L. Meunier, THIS JOURNAL, **55**, 3722 (1933), gives b.p. 118.7–119.7° at 741 mm., n^{20}D 1.4148, for 3,3-dimethyl-2-butanol.

acetate followed by hydrolysis and decarboxylation[4] and (3) Faworsky rearrangement. The hydrolysis of hindered nitriles to the corresponding acid is difficult. Previously this result has been accomplished in two stages, hydrolysis to amide followed by treatment of the amide with sulfuric and nitrous acids.[5] In the case of trialkylacetonitriles the use of alkyl nitrites and hydrogen chloride in dioxane at 80° was found necessary.[3b] We have found that hydrolysis to the amide stage can be effected quite rapidly and in good yield by heating a 96% sulfuric acid solution of the hindered nitrile to 145–155° for one hour. The conversion of hindered amides to acids is carried out by treating a 75% sulfuric acid solution of the amide at 80–85° with solid sodium nitrite during about one hour.

The conversion of ethyl diisopropylcyanoacetate to diisopropylacetic acid has been accomplished previously[4] by partial alkaline hydrolysis to cyanoacid followed by acidic hydrolysis to the amido acid and finally the malonic acid. The latter was decarboxylated. Alternatively we have converted the cyanoester to cyanoacid by partial alkaline hydrolysis and thence by decarboxylation to diisopropylacetonitrile. This nitrile was then hydrolyzed to the corresponding acid by the two-step method described above.

The bromination of methyl neopentyl ketone and of 3-ethyl-2-pentanone to yield monobromoketones suitable for Faworsky rearrangement to *t*-butylmethylacetic acid and diethylmethylacetic acid, respectively, offered unexpected difficulties. In the former case a 66% yield of bromoketone was obtained by bromination for 40 minutes at 0° without solvent. Hydrogen bromide was removed as formed in a stream of dry nitrogen which also served to introduce the bromine. The duration of bromination in this case proved critical as doubling of the optimum period caused a marked diminution in yield. In our hands the yields after 80 minutes were as follows: recovered ketone, about 25%; monobromoketone, about 50%; and dibromoketone, about 25%. It is noteworthy that the yield of monobromoketone is rarely over 50% when bromination of aliphatic ketones is carried out under the conditions originally described by Faworsky[6] which involve relatively lengthy periods of bromination. The proportion of monobromoketone in the aliphatic series stands in contrast to that observed by Kröhnke who noted that only small changes in yield of phenacyl bromide oc-

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(4) F. C. B. Marshall, *J. Chem. Soc.*, 2754 (1930).

(5) L. Bouveault, *Bull. soc. chim.*, [3] **9**, 368 (1893); J. J. Sudborough, *J. Chem Soc.*, **67**, 601 (1895).

(6) (a) A. Faworsky, *J. prakt. Chem.*, [2] **88**, 646, 680 (1913); (b) see also A. A. Sacks and J. G. Aston, THIS JOURNAL, **73**, 3902 (1951).

curred on varying the time of bromination of acetophenone.[7]

The highest yields of esters in the Faworsky rearrangement were obtained from those bromoketones whose carbonyl groups were most highly hindered. Thus, 4-bromo-2,5-dimethyl-3-hexanone and 1-bromo-3-ethyl-2-pentanone were converted into methyl diisopropylacetate and methyl diethylmethylacetate in 83 and 76% yields, respectively, by treatment with sodium methoxide in ether. According to Loftfield's cyclopropanone mechanism[8] for the Faworsky rearrangement this advantageous steric effect is to be expected as side reactions involving carbonyl addition should occur to a smaller extent with hindered bromoketones.

The physical properties of the 2-ethyl-2-methyl-1-butanol prepared by reduction of methyl diethylmethylacetate did not agree with the properties previously reported (see footnote *o*, Table I). The alcohol was oxidized to diethylmethylacetaldehyde in 88% yield by means of chromic oxide in pyridine.[9] This method of oxidation has also been used to prepare trimethylacetaldehyde from neopentyl alcohol in high yield.[10]

Experimental[11]

Dimethylethylacetic acid, b.p. 186–186.5° at 751 mm.,[12] was prepared in 40% yield by carbonation of *t*-amylmagnesium chloride[13] (obtained in 85% yield). Attempted carbonation of triethylcarbinylmagnesium chloride (prepared in 80% yield) afforded only 5% of triethylacetic acid.

Triethylacetic acid was prepared by the hydrolysis of triethylacetonitrile,[14] b.p. 164–166°, n^{25}D 1.4155, which was prepared in 58% yield by alkylation of acetonitrile with ethyl bromide and sodamide in dry ether.[3] The acid distilled at 131–132° at 20 mm., and crystallized on cooling to give colorless crystals, m.p. 35°. The yield from nitrile was 70%. Three recrystallizations from petroleum ether (b.p. 35–40°) afforded pure acid,[15] m.p. 38.9–39.5°.

Methylisopropylacetic acid, b.p. 188–189° at 740 mm., n^{25}D 1.4127,[16] was prepared in 60% over-all yield by the malonic ester synthesis.[17]

Ethylisopropylacetic acid, b.p. 198–200° at 745 mm., n^{25}D 1.4145, was prepared by the malonic ester synthesis,[18] in 78.5% over-all yield.

Diisopropylacetic acid was prepared by malonic ester synthesis from ethyl cyanoacetate[4] in 40% over-all yield. Alternatively, ethyl diisopropylcyanoacetate was hydrolyzed to cyanodiisopropylacetic acid which was decarboxylated to diisopropylacetonitrile. The nitrile was converted to the acid by partial hydrolysis to the amide followed by nitrous acid treatment to give diisopropylacetic acid. **Diisopropylacetonitrile**, b.p. 169–170° at 745 mm. (reported[4] b.p. 170–171°), was prepared according to Marshall[4] in 51% over-all yield.

Diisopropylacetamide.—Diisopropylacetonitrile (11.8 g.) was mixed with 25 g. of sulfuric acid (96%) and heated gradually to 140–150° over a period of 45 minutes. The temperature was held at 145–155° for 0.5 hour, and the cooled reaction mixture was poured on ice. An ether extract of the amide was washed with alkali and water and dried over anhydrous magnesium sulfate. After removal of solvent 13 g. (85%) of crude diisopropylacetamide was obtained. Recrystallization from benzene afforded colorless needles, m.p. 148.0–148.5° (reported[4] m.p. 149°). The crude diisopropylacetamide (12 g.) was mixed with 25 g. of sulfuric acid (75%) and heated to 80–85°. Solid sodium nitrite (25 g.) was added portionwise over a period of one hour. The reaction mixture was worked up in the usual way to give 9.8 g. (83%) of diisopropylacetic acid, b.p. 214° at 740 mm., n^{25}D 1.4260, d^{25}_{25} 0.9125.

Methyl diisopropylacetate, b.p. 72.5° at 25 mm., n^{20}D 1.4159, was prepared in 83% yield by treatment of α-bromoisobutyl isopropyl ketone,[19] b.p. 63° at 5 mm., n^{26}D 1.4513, with a suspension of alcohol-free sodium methoxide[20] in dry ether as described.[19] The required bromoketone was obtained in 42% yield by treatment of isobutyroin with phosphorus tribromide.[19]

***t*-Butylacetic acid**, b.p. 181–181.8° at 741 mm., n^{25}D 1.4084, was prepared in 57% over-all yield from ethyl *t*-butylmalonate as described.[21]

Cyclopropanecarboxylic Acid.—Freshly distilled methyl cyclopropyl ketone was added to 750 ml. of a stirred solution containing 1.15 moles of potassium hydrochlorite[22] in a flask fitted with a reflux condenser at a rate sufficient to maintain the temperature at 70°. After the addition was complete, stirring was continued for 30 minutes. The acid,[23] b.p. 181–182°, n^{27}D 1.4355, d^{24}_{24} 1.0847, was isolated by continuous ether extraction in 95% yield.

Methyl *t*-butylmethylacetate was prepared by alkaline rearrangement of α-bromomethyl neopentyl ketone as above.

α-Bromomethyl Neopentyl Ketone.—Bromine vapor in dry nitrogen was bubbled through methyl neopentyl ketone[24] (0.375 mole) held at 0°. The hydrogen bromide was removed as formed by the nitrogen stream. The reaction mixture was treated with water and the organic layer separated and dried over potassium carbonate. When one equivalent of bromine was introduced over a period of 40 minutes a 65.5% yield of bromoketone,[25] b.p. 91° at 32 mm., n^{26}D 1.4658, was obtained. When the bromine was added over a period of 80 min. a more complex mixture of products was formed and the yield of desired bromoketone was smaller. Methyl *t*-butylmethylacetate was obtained in 51% yield from the bromoketone, b.p. 150–152° at 740 mm., n^{25}D 1.4092, d^{25} 0.8749.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.2; [*RL*]D, 40.79. Found: C, 66.5; H, 11.4; [*RL*]D 40.75.

Methyl Methyldiethylacetate.—To a clear solution of dimethylcadmium[26] (0.25 mole) in ether, freshly distilled diethylacetyl chloride (0.5 mole) in ether was added dropwise to maintain gentle reflux. The reaction mixture was processed in the usual manner to give an 80% yield of 3-ethyl-2-pentanone, b.p. 137–138° at 745 mm., n^{25}D 1.4060. The semicarbazone was obtained in 94% yield as colorless plates from ethanol–water, m.p. 96° (reported[27] m.p. 97°). Bromination of 3-ethyl-2-pentanone (0.18 mole) over a period of one hour as described above, afforded a 48% yield of 1-bromo-3-methyl-2-pentanone, b.p. 90° at 32 mm., n^{25}D 1.4635, and 10 g. of a pink oil, b.p. 120–122° at 7 mm., n^{27}D 1.4870, probably consisting of dibromoketones. When bromination was carried on in carbon tetrachloride the monobromoketone was obtained only in 40% yield. Methyl methyldiethylacetate was obtained as a colorless pleasant-smelling liquid, b.p. 62–63° at 25 mm., n^{25}D 1.4089, d^{25} 0.8824, in 76% yield by treatment of 1-bromo-3-ethyl-2-pentanone with sodium methoxide (as above).

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.1; *ML*D, 40.79. Found: C, 66.4; H, 11.3; *ML*D, 40.34.

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[7] F. Kröhnke, *Ber.*, **69B**, 921 (1936).

[8] R. B. Loftfield, THIS JOURNAL, **73**, 4707 (1951).

[9] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *ibid.*, **75**, 422 (1953).

[10] Work done by G. Kahle.

[11] Analysis by Clark Microanalytical Laboratories, Urbana, Ill.

[12] M. Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933).

[13] Compare S. V. Puntambeker and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524.

[14] C. Schuerch, Jr., and E. H. Huntress, THIS JOURNAL, **70**, 2824 (1948).

[15] Work done by Toshio Miwa.

[16] Ref. 3 gives b. p. 191.7°, at 760 mm., n^{20}D 1.4146 for methylisopropylacetic acid.

[17] F. Fichter and P. Sutter, *Helv. Chim. Acta*, **21**, 896 (1938).

[18] A. W. Crossley and H. R. Lesueur, *J. Chem. Soc.*, 85 (1900).

[19] A. A. Sacks and J. G. Aston, THIS JOURNAL, **73**, 3902 (1951).

[20] Mathieson Chemical Corporation product.

[21] S. Widequist, *Arkiv. Kemi Mineral. Geol.*, **23B**, No. 4 (1946); J. W. C. Crawford, *J. Chem. Soc.*, 2660 (1953).

[22] M. S. Newman and H. L. Holmes, "Organic Syntheses," Coll Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 429.

[23] P. Bruylants, *Bull. soc. chim. Belg.*, **38**, 133 (1929).

[24] G. W. Moersch and F. C. Whitmore, THIS JOURNAL, **71**, 819 (1949).

[25] J. G. Aston, *et al.*, *ibid.*, **64**, 300 (1942), report b.p. 106° at 88 mm.

[26] H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55**, 528 (1936).

[27] J. Colonge, *Bull. soc. chim.*, [4] **41**, 327 (1927).

TABLE II

SOME DERIVATIVES OF ALCOHOLS

Alcohol	2-Naphthylurethan, M.p., °C.	3,5-Dinitrobenzoate, m.p., °C.	Solvent of recrystn.	Crystal form	Formula	Analyses, % Calculated C	H	N	Found C	H	N
2,3-Dimethyl-1-butanol	70.5–71.0		Skellysolve B	Prisms	$C_{17}H_{21}O_2N$	75.3	7.8		75.5	7.6	
2,3,3-Trimethyl-1-butanol	Oil	163.8[c]	Benzene	Prisms	$C_{15}H_{16}O_4Cl_4$	44.8	4.0		44.6	4.0	
2-Ethyl-3-methyl-1-butanol		47–49[a]	Skellysolve F	Pale yel. crystals							
2-Ethyl-3,3-dimethyl-1-butanol	86.8–87.2		Skellysolve B	Prisms	$C_{19}H_{29}O_2N$	76.3	8.4	4.7	76.5	8.5	4.6
3,3-Dimethyl-1-butanol		83.0–83.6[b]	Ethanol	Prisms							
3-Methyl-2-isopropyl-1-butanol	65.8–67.4		Skellysolve F	Prismatic rods	$C_{19}H_{25}O_2N$			4.7			4.8
Cyclopropanemethanol	119.5		Skellysolve C	Needles	$C_{15}H_{15}O_2N$			5.8			5.7
Cyclobutanemethanol	112.5		Skellysolve C	Needles	$C_{16}H_{17}O_2N$			5.5			5.5
Cyclopentanemethanol	87.4–87.8		Skellysolve B	Needles	$C_{17}H_{19}O_2N$			5.2			5.5
2-Methyl-2-ethyl-1-butanol		144–146[d]	Benzene	Prisms							

[a] W. Dirscherl and H. Nahm, *Ber.*, **76**, 635 (1943), gave a m.p. 47.5–49°. [b] P. Sutter, *Helv. Chim. Acta*, **21**, 1269 (1938), reported a m.p. 83.5° for 3,3-dimethyl-1-butyl 3,5-dinitrobenzoate. [c] Tetrachloroacid phthalate derivative. [d] R. V. Rice, G. L. Jenkins and W. C. Harden, THIS JOURNAL, **59**, 2000 (1937), gave a m.p. 144–145°.

TABLE III

ACETATES OF PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

Acetate of	Formula	Boiling point °C.	Mm.	$n^{25}D$	d^{25}	$[R_L]_D$ Calcd.	Found	Yield, %	Acetyl method used	Analyses, % Calcd. C	H	Found C	H
2-Methyl-1-butanol[a]	$C_7H_{14}O_2$	138–139	741	1.3996	0.8719	36.17	36.17	77	1	..	..	..	..
2,3-Dimethyl-1-butanol	$C_8H_{16}O_2$	156–157	740	1.4068	.8790	40.79	40.50	92	2	66.7	11.2	67.0	11.5
2,3,3-Trimethyl-1-butanol	$C_9H_{18}O_2$	170–171	741	1.4125	.8687	45.41	45.30	89	2	68.3	11.4	68.0	11.4
2-Ethyl 1-butanol[b]	$C_8H_{16}O_2$	160	740	1.4090	.8764	40.79	40.68	85	1	..	..	..	..
3-Methyl-2-ethyl-1-butanol	$C_9H_{18}O_2$	88–89	30	1.4156	.8774	45.41	45.23	95	1	68.3	11.4	68.4	11.4
3,3-Dimethyl-2-ethyl-1-butanol	$C_{10}H_{20}O_2$	100	40	1.4220	.8770	50.00	49.90	97	1	69.7	11.7	69.9	11.5
2-Ethyl-1-hexanol[c]	$C_{10}H_{20}O_2$	104	40	1.4182	.8688	50.00	49.97	93	1	..	..	..	..
3,3-Dimethyl-1-butanol	$C_8H_{16}O_2$	156–157	741	1.4038	.8683	40.79	40.60	81	2	66.7	11.2	66.9	11.1
3-Methyl-2-isopropyl-1-butanol	$C_{10}H_{20}O_2$	130	110	1.4200	.8803	50.00	49.50	72	1	69.7	11.7	69.7	11.6
Cyclopropanemethanol[d]	$C_6H_{10}O_2$	133.5	740	1.4156	.9603	29.97	29.80	89	1	..	..	..	..
Cyclobutanemethanol	$C_7H_{12}O_2$	150	741	1.4245	.9508	34.40	34.43	87	1	65.6	9.4	65.4	9.4
Cyclopentanemethanol	$C_8H_{14}O_2$	172.5	741	1.4340	.9577	38.60	38.70	91	1	67.6	9.9	67.6	10.2
Cyclohexanemethanol[e]	$C_9H_{16}O_2$	108	40	1.4422	.9541	43.25	43.35	77	1	..	..	..	..
2,2-Dimethyl-1-propanol[f]	$C_7H_{14}O_2$	127	740	1.3927	.8539	36.17	36.36	76	1	..	..	..	..
2,2-Dimethyl-1-butanol	$C_8H_{16}O_2$	152–153	740	1.4050	.8704	40.79	40.60	92	1	66.7	11.2	66.8	11.1
2-Methyl-2-ethyl-1-butanol	$C_9H_{18}O_2$	100	80	1.4150	.8815	45.41	44.95	75	1	68.3	11.4	68.3	11.3
2,2-Diethyl-1-butanol	$C_{10}H_{20}O_2$	103–104	40	1.4269	.8900	50.00	49.68	92	1	69.7	11.7	69.4	11.6
Isopropyl alcohol[g]	$C_5H_{10}O_2$	88.0	745	1.3750				90	1	..	..	..	..
3,3-Dimethyl-2-butanol[h]	$C_8H_{16}O_2$	138–138.5	738	1.4002				63	1	..	..	..	..
Diisobutylcarbinol[i]	$C_{11}H_{22}O_2$	125–126	60	1.4117				90	1	..	..	..	..
3-Methyl-2-pentanol	$C_8H_{16}O_2$			1.4027				68	1	66.7	11.2	66.6	11.2
t-Butyl alcohol[j]	$C_6H_{12}O_2$	96.5–97.0	745	1.3840				52	1	..	..	..	..

[a] J. P. W. Houtman, J. Van Steenis and P. M. Heertjes, *Rec. trav. chim.*, **65**, 781 (1946), give b.p. 140° at 760 mm., $n^{20}D$ 1.4019, for 2-methylbutyl acetate. [b] A. J. Van Pelt, Jr., and J. P. Wibaut, *ibid.*, **60**, 55 (1941), give b.p. 64.5–65.6° at 20 mm., $n^{20}D$ 1.4109 for 2-ethylbutyl acetate. [c] I. Heilbron, "Dictionary of Organic Compounds," Vol. II, 1953, p. 507, gives b.p. 95° at 25 mm., $n^{20}D$ 1.4204 for 2-ethyl-1-hexyl acetate. [d] J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5034 (1951), give b.p. 136–136.5° at 760 mm., $n^{25}D$ 1.4150–1.4162 for cyclopropanemethyl acetate. [e] R. T. Arnold and J. F. Dowdell, *ibid.*, **70**, 2590 (1948), give b.p. 195–196° at 745 mm., for cyclohexylmethyl acetate. [f] O. R. Quayle and H. M. Norton, *ibid.*, **62**, 1170 (1940), give b.p. 127° for 760 mm., $n^{20}D$ 1.3893 for neopentyl acetate. [g] H. E. French and G. G. Wrightsman, *ibid.*, **60**, 50 (1938), give b.p. 87.9–88.2° for 742 mm., $n^{25}D$ 1.3750 for isopropyl acetate. [h] Ref. *c*, Vol. II p. 322, gives b.p. 141° at 756 mm., $n^{25}D$ 1.4001, for *d*-pinacolyl acetate. [i] V. Grignard, *Chem. Zentr.*, **72, II,** 622 (1901), gives b.p. 183° at 750 mm., 122–123° at 88 mm., for diisobutylcarbinyl acetate. [j] W. M. D. Bryant and D. M. Smith, THIS JOURNAL, **58**, 1016 (1936), gives b.p. 97.9°, $n^{25}D$ 1.3840, for *t*-butyl acetate.

Methyl cyclopentanecarboxylate, b.p. 154–154.5° at 740 mm., $n^{25}D$ 1.4353, was obtained in 63% yield from 2-chlorocyclohexanone by treatment with a suspension of alcohol-free sodium methoxide in ether (compare ref. 8).

Formation of Alcohols by Means of $LiAlH_4$.—The carboxylic acids or their esters were smoothly converted to primary alcohols by means of the general technique described below.[28] In all cases a 20–30% excess of lithium aluminum hydride was used in ether. The period of reflux varied from 15 minutes to 12 hours. The excess of lithium aluminum hydride was decomposed with saturated sodium chloride solution or water. When ethanol or methanol was used for this purpose lower yields of desired alcohol were obtained because of difficulties in separating the two alcohols unless an efficient column were used. The amount of carboxylic acids used varied from 0.05 to 1.0 mole. The alcohols were carefully dried and distilled fractionally through an efficient column. The boiling points, indices, yields and analysis of the alcohols prepared are given in Table I and a list of some new solid alcohol derivatives is given in Table II.

Oxidation of 2-Methyl-2-ethyl-1-butanol to Methyldiethylacetaldehyde.—The alcohol (5 g.) in 5 ml. of dry pyridine was added to a slurry of chromic oxide–pyridine complex in 50 ml. of pyridine[9] and allowed to stand overnight at room temperature. The mixture was then heated under reflux for 3 hours and poured into cold dilute sulfuric acid. After drying the ether extract, it was fractionally distilled at atmospheric pressure to yield 4.4 g. (88%) of a liquid,[29] b.p. 132–133°, $n^{27}D$ 1.4100. The yellow 2,4-dinitrophenylhydrazone[30] melted at 122.8–123.5° after two recrystallizations from methanol. *Anal.* Calcd. for $C_{13}H_{18}N_4O_4$: N, 19.0; Found: N, 19.0.

3-Methyl-2-butanol,[31] b.p. 107–108° at 680 mm., $n^{20}D$ 1.4075, was prepared in 65% yield by lithium aluminum

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(28) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

(29) A. Faworssky and J. Zalessky-Kibardina, *Bull. soc. chim.*, [4] **37**, 1232 (1925), give b.p. 130–135° for methyldiethylacetaldehyde.

(30) O. L. Brady, *J. Chem. Soc.*, 757 (1931).

(31) W. J. Bailey and C. King, THIS JOURNAL, **77**, 76 (1955), report b.p. 108–110° at 742 mm., $n^{20}D$ 1.4067, for the alcohol and b.p. 128–129° at 742 mm., $n^{20}D$ 1.3958, for the acetate.

hydride reduction of methyl isopropyl ketone, followed by careful fractionation. The pure acetate,[31] b.p. 124.0–124.5° at 680 mm., $n^{20}\mathrm{D}$ 1.3960, was obtained in 68% yield from the alcohol by the acetyl chloride–pyridine method (see below) and careful fractionation of the acetate.

2-Methyl-3-pentanol[32] was prepared from ethylmagnesium bromide and isobutyraldehyde in 67% yield and agreed well with the b.p. and index of refraction reported. Acetylation by the acetyl chloride–pyridine method (see below) afforded the pure acetate (see Table III).

Formation of Acetates.—Two different methods were used for acetylation of the alcohols: (1) acetyl chloride–pyridine method and (2) reaction with isopropenyl acetate using a catalytic amount of acid.[33] The following modification of the acetyl chloride–pyridine method was used: to an equimolar mixture of alcohol and dry pyridine in dry ether (about 250 ml. per mole) was added dropwise with stirring acetyl chloride in ether at a rate to maintain gentle reflux. After the addition was complete, refluxing of the stirred reaction mixture was continued for 30 minutes to 6 hours (depending on the alcohol structure). The acetates were carefully dried over anhydrous calcium sulfate and fractionally distilled through a packed column. The physical constants, yields and analyses of the acetates prepared are given in Table III. The amounts of alcohols used varied from 0.05 to 1.0 mole.

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[32] F. Hovorka, H. P. Lankelma and A. E. Axelrod, THIS JOURNAL, **62**, 187 (1940).

[33] H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Rates of Alkaline Hydrolysis of a Series of Primary and Secondary Alkyl Acetates

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The rates of alkaline hydrolysis of a number of branched primary and secondary alkyl acetates in 70% dioxane–water have been measured. The possible utility of the information thus gained in the improvement of condensation reactions is discussed.

We became interested in a study of steric hindrance to ester hydrolysis because of possible applications of knowledge thus gained to improvement of synthetic reactions. There are many examples of the use of bifunctional (or polyfunctional) reagents in which one function is the esterified carboxyl group. The yields of desired products are often reduced by side reactions which stem from undesired condensation reactions involving the ester function.

It seemed likely that such side reactions might be decreased by modifying the ester function to provide a greater degree of steric hindrance. This modification could be effected by choice of the proper alkyl moiety in the ester group. However, the use of too hindered an ester would be unwise as hydrolysis at a later stage might prove too difficult.

A notable example of judicious choice of alkyl moiety in an ester has been provided by the studies on the Stobbe condensation in which[3] the use of *t*-butyl succinate was shown far superior to that of methyl or ethyl succinate. However, it is not known to what extent the polar or steric properties of the *t*-butyl group are responsible for the results. Another example of the utility of *t*-butyl esters is found in the condensation of *t*-butyl acetate with ketones.[4] A study of the effect of the alkyl group in Reformatsky reactions involving alkyl α-bromopropionates has also been made.[5]

In order to provide a background of quantitative data upon which future (or past) work might be analyzed we have chosen to study the alkaline hydrolysis of alkyl acetates as a typical example of a reaction known to proceed by carbonyl addition.[6] An immediate object of this research was to find which primary or secondary alkyl acetates would saponify at rates comparable to that of *t*-butyl acetate. Thus one would have alcohols to substitute for *t*-butyl alcohol in the preparation of esters desired for synthetic work. Such substitutions are often desirable because of the difficulty of preparing certain *t*-butyl esters.

Little attention has been paid to the effect of steric factors in the alkyl moiety of an ester on the rate of alkaline hydrolysis. In a general way it is known that esters of tertiary alcohols are saponified at a slower rate than those of secondary alcohols, and the latter at a slower rate than esters of primary alcohols.[7] However, this rate order is probably determined by polar as well as steric factors in the alkyl portion since the alkoxide ions released during hydrolysis are of widely different base strengths: *e.g.*, primary $RO^- <$ secondary $RO^- <$ tertiary RO^-. Therefore, in order to evaluate steric effects, one should limit comparison of hydrolysis rates to esters of the same class of alcohol.

Accordingly we have measured the rates of alkaline hydrolysis of a series of primary and secondary acetates in 70% dioxane–water at 20 and 30°. The data is listed in Table I together with that for a few esters included for comparative purposes.

Experimental

Solvents and Reagents.—Dioxane was purified by the method described.[8] Sodium hydroxide solution in 70% dioxane was prepared by diluting 1.0 *N* aqueous solution with distilled water so that the total volume was short of 300

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[3] G. H. Daub and W. S. Johnson, THIS JOURNAL, **72**, 501 (1950).

[4] C. R. Hauser and W. H. Puterbaugh, *ibid.*, **75**, 1068 (1953).

[5] M. S. Newman and F. J. Evans, Jr., *ibid.*, **77**, 946 (1955).

[6] M. L. Bender, *ibid.*, **73**, 1626 (1951).

[7] For example, the relative rates of hydrolysis of 1-butyl, 2-butyl and *t*-butyl acetates in water at 20° are 3.93, 0.82 and 0.08, respectively; see M. S. Newman "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 220-222.

[8] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.