reaction. D-Fructose diethyl mercaptal exists and has been made by an indirect method.[10] The hexosamines are essentially insoluble in concentrated hydrochloric acid and the procedure is not applicable to them. The acetylated diethyl mercaptals of the ethyl[11] and methyl[11,12] esters of D-galacturonic acid have been recorded.

An obvious disadvantage of the method is the odor of the ethyl mercaptan but this can be minimized by the employment of small quantities of material and by the use of good fume cupboards. The purified substances are odorless.

TABLE I

CHARACTERIZING PROPERTIES OF THE KNOWN FULLY ACETYLATED DIETHYL MERCAPTALS OF ALDOMONOSACCHARIDES

Fully acetylated diethyl mercaptal of	M. p., °C.	$[\alpha]^{20-25}$D ($c < 5$, $CHCl_3$)
D-Arabinose[a]	80	+30°
L-Arabinose[b]	79-80	−30
D-Xylose[c]	46-48	+13
D-Lyxose[d]	36-37	+40.5
D-Glucose[e]	45-47	+11
D-Galactose (trimorphous)[f]	76.5-77	+11
	80.5-81[g]	+11
	90.5-91	+11
6-Desoxy-L-galactose (L-fucose)[h]	99-100	+ 5
D-Mannose[i]	52-53	+32
6-Desoxy-L-mannose (L-rhamnose)[i]	59-61	−42
D-Gluco-D-*gulo*-heptose[j]	99-100	−12
D-Gala-L-*gluco*-heptose[k]	105	+27
D-Gala-L-*manno*-heptose[l]	145-146	+56
D-Manno-D-*gala*-heptose[m]	77	− 2.2
D-Gala-L-*gala*-octose[n]	106	+30
Methyl D-galacturonate[o,p]	112.5-113.5	+20.5
Ethyl D-galacturonate[p]	80-81	+11

[a] M. L. Wolfrom, D. I. Weisblat, W. H. Zophy and S. W. Waisbrot, THIS JOURNAL, **63**, 201 (1941). [b] M. L. Wolfrom and Mildred R. Newlin, *ibid.*, **52**, 3619 (1930). [c] Ref. 8. [d] M. L. Wolfrom and F. B. Moody, *ibid.*, **62**, 3465 (1940). [e] W. Schneider and Johanna Sepp, *Ber.*, **51**, 220 (1918); M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929); first nuclei difficult to obtain but the deacetylated form crystallizes with ease. [f] M. L. Wolfrom, *ibid.*, **52**, 2464 (1930); L. H. Welsh and G. L. Keenan, *ibid.*, **64**, 183 (1942). [g] Stable form. [h] M. L. Wolfrom and J. A. Orsino, *ibid.*, **56**, 985 (1934). [i] N. W. Pirie, *Biochem. J.*, **30**, 374 (1936); Mildred R. Newlin, Ph.D. dissertation, The Ohio State University (1932); in the publication of Pirie, L-rhamnose diethyl mercaptal tetraacetate is recorded incorrectly as being dextrorotatory. [j] M. L. Wolfrom, M. Konigsberg, F. B. Moody (and Mildred R. Newlin), THIS JOURNAL, **62**, 2348 (1940); higher sugar nomenclature of C. S. Hudson, *ibid.*, **60**, 1537 (1938). [k] R. M. Hann and C. S. Hudson, *ibid.*, **56**, 2080 (1934). [l] R. M. Hann and C. S. Hudson, *ibid.*, **59**, 1898 (1937). [m] Edna Montgomery and C. S. Hudson, *ibid.*, **56**, 2463 (1934). [n] R. M. Hann, W. D. Maclay and C. S. Hudson, *ibid.*, **61**, 1270 (1939). [o] Ref. 12. [p] Ref. 11.

Experimental

Identification of D-Mannose as D-Mannose Diethyl Mercaptal Pentaacetate.—The general procedure employed was an adaptation of that reported previously[8] from this Laboratory. D-Mannose (50 mg.) was dissolved in 0.5 cc. of concentrated hydrochloric acid (*ca.* 12 *N*) in an ice-bath and 0.5 cc. of ethyl mercaptan added. The mixture was stirred or shaken mechanically for one hour and was then neutralized in the cold with concentrated ammonium hydroxide (*ca.* 15 *N*) and concentrated to dryness at 40° under reduced pressure. The salt residue was dried by adding absolute ethanol and removing this by distillation under reduced pressure at 40°, the process being repeated several times. The dried residue was treated with 3 cc. of a 2:1 (by volume) mixture of acetic anhydride and dry pyridine. After standing overnight at room temperature, the solution was poured into 10 cc. of water and extracted twice with 10-cc. portions of chloroform. The chloroform extract was washed four times with 10 cc. of a saturated aqueous sodium bicarbonate solution and finally with water. The sirup obtained on solvent removal from the dried chloroform extract was crystallized from methanol solution by the gradual addition of water; yield of D-mannose diethyl mercaptal pentaacetate practically quantitative, m. p. 51–52°.

Identification of D-Galactose in a Crude Hydrolyzate.—A fraction of solid material (50 mg.) obtained by the acid hydrolysis of a galactose-containing polysaccharide and containing *ca.* 25% of D-galactose (as determined by the mucic acid assay) was treated as described above and the product isolated in the same manner; yield of D-galactose diethyl mercaptal pentaacetate 15 mg., m. p. 78–79°.

As a confirmatory derivative, the above acetate was deacetylated to D-galactose diethyl mercaptal. To 9 mg. of the D-galactose diethyl mercaptal pentaacetate dissolved in 2 cc. of anhydrous methanol was added 0.5 cc. (*ca.* 10% excess) of 0.2 *N* barium methoxide in methanol (prepared by refluxing barium oxide with anhydrous methanol) and the solution refluxed for one hour. Carbon dioxide gas was then introduced until precipitation was complete and the precipitated barium carbonate was removed by centrifugation. The residue obtained on solvent removal from the centrifugate was extracted with 2 cc. of warm ethanol (acetone is likewise useful as a solvent in which the sugar mercaptals have some solubility) and crystallized from aqueous ethanol; yield of D-galactose diethyl mercaptal 3 mg., m. p. 138–139° (micro stage).

CHEMICAL LABORATORY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

RECEIVED JANUARY 9, 1945

NEW COMPOUNDS

Esters of Mesitoic Acid

2-Mesitoyl-4-methylphenyl Mesitoate.—A mixture of 22 g. of 2-mesitoyl-4-methylphenol[1] and 20 g. of mesitoyl chloride was warmed until hydrogen chloride ceased to be evolved. The reaction mixture was dissolved in ether, and the resulting solution washed successively with water, dilute sodium hydroxide solution and water. Evaporation of the ether left the ester as a solid which, after being recrystallized from ethanol, melted at 135–136°; yield 32%.

Anal. Calcd. for $C_{27}H_{28}O_3$: C, 80.97; H, 7.05. Found: C, 81.31; H, 7.09.

Phenyl Mesitoate.—The phenyl ester was prepared in 83% yield from phenol and mesitoyl chloride. It formed colorless needles; m. p. 37–38° (cor.).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.28; H, 6.75.

---

[10] M. L. Wolfrom and A. Thompson, THIS JOURNAL, **56**, 880 (1934).

[11] R. J. Dimler and K. P. Link, *ibid.*, **62**, 1216 (1940).

[12] H. A. Campbell and K. P. Link, *J. Biol. Chem.*, **120**, 471 (1937).

[1] Fuson, Scott and Speck, THIS JOURNAL, **63**, 2845 (1941).

β-Naphthyl Mesitoate.—This ester was prepared in 96% yield from mesitoyl chloride and β-naphthol. It crystallized from alcohol in colorless needles; m. p. 112–113° (cor.).

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.42; H, 6.37.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
REYNOLD C. FUSON
STANLEY B. SPECK

RECEIVED NOVEMBER 27, 1944

The Inner Carbonate of 2,3-Butanediol

Hammond[1] and Mitchell[2] have patented methods for the preparation of the alkyl carbonates and chlorocarbonates by the interaction of the aliphatic monohydric alcohols and phosgene. These procedures have been applied by the present authors to the interaction of 2,3-butanediol and phosgene.

Procedure.—A vertical glass tube, 46 mm. by 450 mm. in dimensions, was filled with glass beads and electrically heated so that a thermometer imbedded in the glass beads was maintained at 150°. Liquid 2,3-butanediol was dropped into the top of the tube at the rate of 44 g. per hour while phosgene gas was introduced into the bottom of the tube at the rate of 200 ml. per minute. The products boiling above 150° were collected at the bottom of the tube. The resulting material was heated, on a boiling water-bath under a reflux condenser, for two hours to complete the reaction. During the heating period copious evolution of hydrogen chloride took place. The resulting product was distilled at reduced pressure, a large fraction distilling at 96° at 8 mm. pressure; yield, 75%.

Anal. Calcd. for $C_5H_8O_3$: C, 51.7; H, 7.0. Found: C, 51.5; H, 7.1.

Properties.—The molecular weight in phenanthrene was 116; $n^{26}{}_D$ 1.4226, $d^{26}{}_4$ 1.129, b. p. 240° (740 mm.). The compound is colorless and insoluble in water. It is an excellent solvent for cellulose nitrate and cellulose acetate.

CHEMISTRY DEPARTMENT
IOWA STATE COLLEGE
AMES, IOWA
J. J. KOLFENBACH
E. I. FULMER
L. A. UNDERKOFLER

RECEIVED DECEMBER 18, 1944

---

[1] J. A. Hammond, U. S. Patents 1,603,689 (October 19, 1926); 1,618,824 (February 22, 1927).

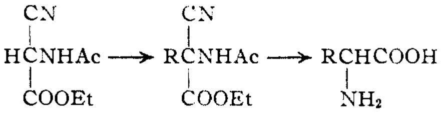
[2] H. G. Mitchell, U. S. Patents 1,603,703 (October 19, 1926); 1,638,014 (August 9, 1927).

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF AMINO ACIDS FROM ACETAMIDOCYANOACETIC ESTER

Sir:

Recently considerable interest has been shown in the preparation of amino acids from acetamidomalonic ester. We have found that ethyl acetamidocyanoacetate (I)[1] possesses even greater advantages as a general reagent. Alkylation is effected under the same conditions employed for acetamidomalonic ester.[2] Direct hydrolysis of the condensation product proceeds in either acid or basic media to yield the amino acid.



$$\underset{\text{I}}{\overset{\text{CN}}{\underset{\text{COOEt}}{\text{HCNHAc}}}} \longrightarrow \underset{\text{II}}{\overset{\text{CN}}{\underset{\text{COOEt}}{\text{RCNHAc}}}} \longrightarrow \underset{\text{NH}_2}{\text{RCHCOOH}}$$

Alkylation of I with gramine gave 98% of ethyl α-acetamido-α-cyano-β-(3-indolyl)-propionate (II, R = skatyl), m. p. 196–198° (calcd. N, 14.02. Found: N, 13.78). Alkaline hydrolysis gave *dl*-tryptophan, m. p. 288–290° (cor.). A 71% yield of pure amino acid was obtained from crude indole.

When 4-chloromethylimidazole hydrochloride was condensed with I, a 66% yield of ethyl α-acetamido-α-cyano-β-imidazolepropionate (II, R = 4-imidazolemethyl), m. p. 100–103° anhydrous or 111° as monohydrate, was obtained (calcd. anhydrous: N, 22.39. Found: N, 21.98. Calcd. monohydrate: C, 49.25; H, 6.01. Found: C, 49.40; H, 5.89). Hydrolysis with sulfuric acid gave a 61% yield of *dl*-histidine, m. p. 285°. The dihydrochloride melted at 232°.[3] The overall yield of *dl*-histidine from cane sugar was 18%.

Methylation of monothioethylene glycol with dimethyl sulfate gave 80% of β-methylthiolethanol. Chlorination with thionyl chloride and condensation with I without isolation of the methylthiolethyl chloride or chlorination with hydrogen chloride followed by condensation with I gave 60% of the theoretical amount of ethyl α-acetamido-α-cyano-γ-methylthiolbutyrate (II, R = methylthiolethyl), m. p. 118° (calcd. N, 11.47. Found: N, 11.62). Basic hydrolysis gave 80% of recrystallized *dl*-methionine. The N-benzoyl derivative melted at 150°.

Alkylation of I with isopropyl bromide gave 66% of ethyl α-acetamido-α-cyano-β-methylbutyrate (II, R = isopropyl), m. p. 149° (calcd.: N, 13.20. Found: N, 13.52). Alkaline hydrolysis gave 65% of pure *dl*-valine, m. p. 289–290°. Acid hydrolysis gave an 80% yield, but the melting point was lower. The N-acetyl derivative melted at 147° and the N-benzoyl derivative at 131°.

Condensation of benzyl chloride with I gave 83% of ethyl α-acetamido-α-cyano-β-phenylpropionate (II, R = benzyl); m. p. 134° (calcd. N, 10.75. Found: N, 10.57). Hydrolysis with sodium hydroxide gave a 75% yield of *dl*-phenylalanine, m. p. 275–277°.

---

[1] Cerchez and Colesiu, *Compt. rend.*, **194**, 1954 (1932).

[2] (a) Albertson, Archer and Suter, THIS JOURNAL, **67**, 36 (1945); (b) Albertson and Archer, *ibid.*, **67**, 308 (1945).

[3] Pyman, *J. Chem. Soc.*, **99**, 1395 (1911).