2,4-Dinitrophenylhydrazone	M. p.,[5] °C.	Color	Nitrogen, % Found	Nitrogen, % Calcd.	Max.,[6] (chlf.), mμ	Log E_m (chlf.)	Max. (alk.), mμ
Isoandrosterone	215–216	Orange-yellow	11.17	11.27	372	5.04	400
Etiocholan-3β-ol-17-one	178–180	Yellow	11.41	11.27	370	5.05	400
Dehydroepiandrosterone[3]	237–238	Yellow-orange	12.10	12.38	370	5.02	395
17-Methyltestosterone[3]	218–221	Red-orange	12.24	12.00	395	5.25	430
Equilenin[4]	268–270	Orange-yellow	13.44	13.01	370	5.01	350, 390

Acknowledgment.—The authors are indebted to Dr. Arthur St. André of Ciba Pharmaceutical Products, Inc., who supplied the hormones used in this investigation.

(3) Johnston, *Science*, **106**, 91 (1947).

(4) Veitch and Milone, *J. Biol. Chem.*, **157**, 417 (1945).

(5) The melting points were determined on a Fisher–Johns apparatus.

(6) Spectroscopic Analysis.—Solutions of the five DNPH derivatives in chloroform (1 ml. equivalent to 25 micrograms of free hormone) were subjected to analysis in the Beckman quartz spectrophotometer in the region 255 mμ to 500 mμ. The effect of alkali on the spectra was determined by treatment of the steroid DNPH derivatives (1 ml. of chloroform solution equivalent to 75 micrograms of free hormone) with 0.1 *N* alcoholic potassium hydroxide, and measurement of per cent. transmittance in a Coleman spectrophotometer in the region 350 to 600 mμ. The maxima were shifted toward the visible region of the spectrum in each case, with the exception of equilenin DNPH, which exhibited two maxima, one toward the ultraviolet, the other toward the visible. A similar discrepancy in the shifting of spectra with alkali has been noted by Roberts and Green.[7]

(7) Roberts and Green, THIS JOURNAL, **68**, 214 (1946).

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Some Acetylenic Compounds[1]

Propargyl Formate.—A mixture of 56 g. of propargyl alcohol and 46 g. of anhydrous formic acid was heated to boiling, and 30 g. of powdered calcium chloride was added. After standing overnight in a stoppered flask, the liquid was decanted and distilled through a 40-cm. Vigreux column. A main fraction was taken from 95–110° and a second fraction from 110–118°. The second fraction was reesterified with 12 g. of formic acid and 8 g. of calcium chloride. Most of the product distilled below 110°. The fractions boiling at 95–110° were combined, cooled in ice, two volumes of ether added and the solution washed with cold aqueous sodium bicarbonate. After drying over calcium chloride and fractionating through a 40-cm. Vigreux column, 28 g. (35%) distilled at 105–109°; $n^{18.5}D$ 1.4203.

Anal.[2] Calcd. for $C_4H_4O_2$: C, 57.14; H, 4.80. Found: C, 56.75, 56.74; H, 5.44, 5.45.

Methyl Bromopropiolate.—To a solution of 75 g. of bromopropiolic acid in 600 cc. of methanol was added slowly 185 g. of concentrated sulfuric acid with shaking and cooling under tap water. After standing six days the solution was poured onto 1.5 kg. of ice and extracted with five 200-cc. portions of ether. The extracts were dried over anhydrous magnesium sulfate and the ether and alcohol removed under reduced pressure. The product was distilled twice at 5 mm. pressure from a Claisen flask having a 20-cm. fractionating side arm to give 62 g. (75%), b. p. 40–45° at 5 mm., $n^{25}D$ 1.4884.

Anal. Calcd. for $C_4H_3O_2Br$: C, 29.47; H, 1.85. Found: C, 29.50, 29.52; H, 1.99, 2.01.

(1) These compounds were prepared for the Office of Scientific Research and Development under Contract OEMsr-136 with Stanford University.

(2) All carbon–hydrogen microanalyses by Huffman Microanalytical Laboratories, Denver, Colo.

The product is unstable and soon turns dark red. After standing a month, about one-third had polymerized.

2-Chloroethyl Propiolate.—This ester was prepared from 43 g. of propiolic acid, 175 g. of anhydrous ethylene chlorohydrin and 18 g. of concentrated sulfuric acid by the procedure given for methyl bromopropiolate. The yield after two fractionations was 43 g. (53%), b. p. 79–82° at 17 mm.; $n^{20}D$ 1.4588.

Anal. Calcd. for $C_5H_5O_2Cl$: C, 45.30; H, 3.80. Found: C, 45.30, 45.17; H, 3.90, 3.86.

Allyl Propiolate.—A mixture of 100 g. of propiolic acid, 500 g. of allyl alcohol, and 45 g. of concentrated sulfuric acid was allowed to stand for two days and the ester isolated as above. The yield was 46 g. (30%), b. p. 70–73° at 60 mm.; $n^{18.5}D$ 1.4378.

Anal. Calcd. for $C_6H_6O_2$: C, 65.44; H, 5.49. Found: 65.42, 65.49; H, 5.72, 5.67.

Isopropyl Acetylenedicarboxylate.—A mixture of 50 g. of acetylenedicarboxylic acid, 200 g. of dry isopropyl alcohol, 5 g. of *p*-toluenesulfonic acid and 0.2 g. of hydroquinone was placed in a 500-cc. flask fitted with a 40-cm. Vigreux column and a condenser set for distillation. The mixture was heated on an oil-bath, the temperature of which was raised slowly from 110 to 135° until 145 g. of isopropyl alcohol had distilled at 80–81° during two hours. The mixture was cooled, poured into 400 cc. of water, extracted with three 100-cc. portions of ether, washed with sodium bicarbonate solution, and dried over calcium chloride. The ether was evaporated, 0.2 g. of hydroquinone added, and the product distilled at reduced pressure from a modified Claisen flask. The yield was 39 g. (45%), b. p. 103–107° at 4 mm.; $n^{18.5}D$ 1.4408.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.09, 60.20; H, 7.23, 7.27.

Allyl Acetylenedicarboxylate.—This ester was prepared from 50 g. of acetylenedicarboxylic acid, 200 g. of allyl alcohol, 3 g. of *p*-toluenesulfonic acid, and 0.2 g. of hydroquinone by a procedure analogous to that for isopropyl acetylenedicarboxylate. The yield was 61 g. (70%) b. p. 112–118° at 4 mm., $n^{18.5}D$ 1.4718.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.84; H, 5.19. Found: C, 61.62, 61.68; H, 5.39, 5.30.

Methoxytetrolic Acid.—In a 2-liter three-necked flask equipped with a gas inlet reaching to the bottom of the flask, a mercury-sealed stirrer, and a reflux condenser cooled with ice water, was placed 30 g. of magnesium turnings and 300 cc. of absolute ether. Methyl chloride was added from a cylinder until all of the magnesium had reacted. The gas inlet was replaced by a dropping funnel, and 75 g. of methyl propargyl ether was added. The mixture was refluxed for six hours. After cooling in an ice-bath and adding 300 cc. of dry benzene, the dropping funnel was replaced by the gas inlet and carbon dioxide passed through the mixture for four hours at 0° and four hours at 20°. The mixture was cooled to 0° and 500 cc. of cold 10% sulfuric acid was added, keeping the temperature below 5° during the addition. After reaching room temperature the ether layer was separated, and the aqueous layer was extracted with three 100-cc. portions of ether. The ether solutions were combined and extracted with aqueous sodium carbonate. The carbonate extract was acidified with 20% sulfuric acid and extracted with four 50-cc. portions of ether. The ether was evaporated, and the residue distilled at reduced pressure from a modified Claisen flask. The yield was 60 g. (49%), b. p. 114–118° at 3 mm.; $n^{20}D$ 1.4669.

Anal. Calcd. for $C_5H_6O_3$: C, 52.63; H, 5.30. Found: C, 52.25, 52.18; H, 5.31, 5.39.

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Some Substituted Benzalmalononitriles[1]

The substituted benzalmalononitriles listed in Table I were prepared essentially by the procedure of Corson and Stoughton.[2]

TABLE I

SUBSTITUTED BENZALMALONONITRILES

Substituents	Reaction solvent[a]	Cryst. solvent[a]	Yield, %	M. p., °C.	Formula	Analyses,[b] % Carbon Calcd.	Carbon Found		Hydrogen Calcd.	Hydrogen Found	
3-Chloro	*t*-Amyl	*n*-Butyl	85	116–117	$C_{10}H_5ClN_2$	63.68	63.86	63.79	2.67	2.75	2.73
4-Chloro	*i*-Propyl	Ethyl	80	162–163	$C_{10}H_5ClN_2$	63.68	63.79	63.69	2.67	2.84	2.76
2-Bromo	*n*-Butyl	*n*-Butyl	95	90–90.5	$C_{10}H_5BrN_2$	51.53	51.63	51.62	2.16	2.32	2.15
3-Bromo	*t*-Amyl	*n*-Butyl	81	109.5–110	$C_{10}H_5BrN_2$	51.53	51.64	51.62	2.16	2.24	2.23
3-Iodo	*t*-Amyl	*n*-Butyl	85	107–108	$C_{10}H_5IN_2$	42.88	43.01	42.93	1.80	1.90	1.91
4-Nitro	Ethyl	Ethyl	41	159–160	$C_{10}H_5N_3O_2$	60.30	60.42	60.30	2.53	2.66	2.68
3-Hydroxy	Ethyl	*t*-Amyl	59	151.5–153	$C_{10}H_6N_2O$	70.58	70.37	70.50	3.55	3.65	3.64
2-Methyl	*i*-Propyl	*n*-Butyl	51	104–106	$C_{11}H_8N_2$	78.55	78.55	78.57	4.79	4.79	4.93
3-Methyl	*i*-Propyl	*n*-Butyl	38	133–134	$C_{11}H_8N_2$	78.55	78.52	78.66	4.79	4.87	4.94
2,6-Dichloro	Ethyl	Hexane	56	89–90	$C_{10}H_4Cl_2N_2$	53.84	53.91	53.93	1.81	2.01	1.88
2-Chloro-5-nitro	*i*-Propyl	Ethyl	78	119–120	$C_{10}H_4ClN_3O_2$	51.41	51.51	51.60	1.73	1.87	1.86
2,4,6-Trichloro-3-hydroxy	*i*-Propyl	Benzene	70	135–136	$C_{10}H_3Cl_3N_2O$	43.90	44.12	44.05	1.10	1.26	1.26
4-(2-Chloroethyl-mercapto)	Ethyl	*t*-Amyl	..	87–88	$C_{12}H_9ClN_2S$	57.94	57.84	57.70	3.67	3.73	3.63
4-Methoxymethyl	Ethyl	Ethyl	61	72–73	$C_{12}H_{10}N_2O$	72.71	72.79	72.78	5.10	5.13	5.15
2-Thiophenal-malononitrile	Ethyl	Ethyl	50	95–96	$C_8H_4SN_2$	59.98	60.06	60.00	2.52	2.61	2.62
1-Naphthalmalono-nitrile	Ethyl	Ethyl	70	170–171.5	$C_{14}H_8N_2$	82.33	82.54	82.66	3.95	4.09	4.15

[a] Alcohols except as noted. [b] Microanalyses by Huffman Microanalytical Laboratories, Denver, Colo.

(1) These compounds were prepared for the Office of Scientific Research and Development under Contract OEMsr-136 with Stanford University.

(2) Corson and Stoughton, THIS JOURNAL, **50**, 2825 (1928).

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Some Acylamino Acid Esters and Amides

The following previously undescribed esters and amides of butyrylglycine and acetylalanine have been prepared and characterized.

Acetylalanine N-*n*-butylamide was prepared from the ethyl ester and *n*-butylamine, m. p. 114–115.2° from nitromethane.

Anal. Calcd. for $C_9H_{18}O_2N_2$: C, 58.04; H, 9.74; N, 15.05. Found: C, 58.10; H, 9.26; N, 14.88.

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N,N-Dicyclohexylformamide

In the course of the preparation of tertiary amines from N,N-dialkyl amides, there was occasion to prepare N,N-dicyclohexylformamide, a white, wax-like compound. To the best of our knowledge, the preparation of this substance has not been reported previously.

Fifty ml. of water and 108.4 g. of 85% formic acid were added to a 500-ml., 3-neck, round-bottom flask equipped with a dropping funnel in one side neck, a water-cooled reflux condenser in the other side neck and a mercury-sealed mechanical agitator in the center neck. The solution was warmed to 50°, when the dropwise addition of 90.5 g. of dicyclohexylamine was begun. After the amine was completely added, the solution was allowed to agitate for fifteen minutes, when it was transferred to a Claisen flask. The water and some of the excess formic acid were removed by distillation at atmospheric pressure, followed

TABLE I

BUTYRYLGLYCINE DERIVATIVES

Compound			Ethyl ester	N-*n*-Butylamide	Anilide
Prepn. method			Esterify acid	Ester and amine	Na salt and aniline
M. or b. p., °C.			B. 136° (5 mm.)	M. 147.5–148.5	M. 158.5–159.5
Analyses, %	Carbon	Calcd.	55.5	60.0	65.43
		Found	55.23	60.09	65.5
	Hydrogen	Calcd.	8.73	10.06	7.32
		Found	8.58	9.75	7.22
	Nitrogen	Calcd.	8.08	14.0	12.72
		Found	7.95	14.16	12.96