through the extractor, a total of 300 ml. being employed. The solvent was well dispersed by the stirrer, and rose to form a static layer in the exit arm of the U-tube, from which it drained at the same rate at which fresh solvent was added. Qualitative tests showed no detectable cerium remaining in the water phase. The butyl phosphate extracted bromine as well as cerium.

Uranyl and thorium nitrates were observed to be readily extracted by butyl phosphate. These elements can be separated by extraction of cerium(III) solutions. The extraction of iron, zirconyl and lanthanum nitrates by butyl phosphate was also studied. The results showed that excellent separation from iron, fair separation from zirconium, and rather poor separation from lanthanum can be expected.

Iron(II) nitrate solutions, containing 1 mg. to 5 g. of iron per 100 ml., and 1.0 *F* in nitric acid, were extracted with butyl phosphate, the organic layer washed with ammonium nitrate–nitric acid solution, and re-extracted with hydrogen peroxide. The amount of iron thus recovered was determined spectrophotometrically with 1,10-phenanthroline and the ratio of the amount of iron in the original aqueous phase to the amount from the organic phase taken as a "separation factor." This factor varied from 2000 for low iron concentrations to 1.6 × 10^6 for the high concentrations. Similar experiments with zirconium, using a radioactive isotope (Zr^{95}, half-life 65 days) showed separation factors of 200 to 600, while with lanthanum (La^{140}, half-life 40 hours), factors of only 80 to 100 were observed. Lanthanum nitrate solution (500 mg. of La per 100 ml.) was extracted exhaustively by the stirrer U-tube technique described above, using sodium bromate, when 4 to 7% was found to be carried over.[8]

The high degree of extraction by butyl phosphate over a wide range of conditions suggested formation of a compound between the solvent and cerium(IV) nitrate.

Absorption spectra of aqueous and butyl phosphate solutions each 0.05 *F* in cerium(IV) nitrate were identical except for a slight shift toward the longer wave lengths for the non-aqueous solution. The absorption curves had no maxima, and both solutions were transparent for wave lengths above 580 mμ. The solvents were non-absorbing for wave lengths above 400 mμ. Kjeldahl analyses of the organic phase showed that no ammonium compound was present. Treatment of small known quantities of the solvent with a large excess of cerium(IV) nitrate solution, followed by extraction with carbon tetrachloride and determination of the Ce(IV) content, showed Bu_3PO_4/Ce ratios of 2.5 ± 0.1. Butyl phosphate extracts of ammonium hexanitratocerate(IV) from solutions containing no additional nitric acid were analyzed for nitrate by the nitron method,[9] and for cerium(IV), which gave NO_3/Ce ratios of 3.3 ± 0.2. While these values do not coincide with the ratios demanded by a simple formula, there was also no assurance of complete conversion of the reactants into a single compound. The analytical work was not pursued sufficiently to establish unambiguously the identity of the extracted substance or substances.

CONTRIBUTION NO. 53 FROM THE
INSTITUTE FOR ATOMIC RESEARCH
IOWA STATE COLLEGE
AMES, IOWA
RECEIVED APRIL 19, 1949

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[8] Electrolytic oxidation is preferred to the use of bromates, for the latter seemed to permit greater extraction of iron, zirconium, and lanthanum. This may be attributable to the formation of bromides. It was observed that the behavior of zirconyl halides toward butyl phosphate extraction was quite different from that of the nitrate.

[9] Busch, *Ber.*, **38**, 861 (1905); Gutbier, *Z. angew. Chem.*, **18**, 494 (1905).

NEW COMPOUNDS

The Diacetate of 2-Methyl-1,3-pentanediol

Investigations in this Laboratory led to the preparation of the diacetate of 2-methyl-1,3-pentanediol. This new compound is of interest as it was reported by previous investigators[1] that the reaction of 2-methyl-1,3-pentanediol with acetic anhydride yields only the monoacetyl derivative.

Procedure.—One-half mole of 2-methyl-1,3-pentanediol and one-half mole of acetic anhydride were refluxed with a trace of sulfuric acid for three hours. At the end of this period, toluene was added to the reaction flask and a water-trap placed in the reflux system. The water from the reaction was then removed by refluxing with the toluene. The glycol diacetate was recovered in good yield after removal of the toluene and subsequent fractionation through a five-bulb Snyder column.

The physical constants of the diacetate of 2-methyl-1,3-pentanediol are: b. p., 225° (uncor.); d^{20}_4 1.0025; n^{20}_D 1.4253; *anal.* 99% ester content as the diacetate of 2-methyl-1,3-pentanediol; mol. ref. 51.68 found; 51.56 calcd.

PETROLEUM RESEARCH AND DEVELOPMENT LABORATORY
CELANESE CORPORATION OF AMERICA
CLARKWOOD, TEXAS GUILES FLOWER, JR.[2]
RECEIVED MARCH 9, 1949

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[1] Kling and Roy, *Bull. soc. chim.*, [4] **1**, 698 (1907); Kling and Roy, *Compt. rend.*, **144**, 1112 (1907).

[2] Present address: Dictaphone Corporation, Bridgeport 5, Connecticut.

Esters of 5-Methyl-2-thenoic Acid

The esters of 5-methyl-2-thenoic acid listed in Table I were prepared by refluxing 10 g. (0.07 mole) of the acid[1] in an excess (125 ml.) of the required alcohol containing 6–7 ml. of concd. sulfuric acid. After refluxing for four hours, the esters were worked up in the usual manner, and vacuum-distilled.

TABLE I

ESTERS OF 5-METHYL-2-THENOIC ACID

Ester	B. p., °C. (5 mm.)	d^{20}_4	n^{20}_D	Yield, %	Sulfur, %[b] Calcd.	Sulfur, %[b] Found
Methyl	77–79[a]	1.1736	1.5380	71	20.53	20.70
Ethyl	87–89	1.1234	1.5233	82	18.83	18.99
n-Propyl	95–98	1.0936	1.5075	80	17.40	17.47
i-Propyl	87–88	1.0766	1.5092	44	17.40	17.14
n-Butyl	106.5–108.5	1.0668	1.4955	88	16.17	16.18
i-Butyl	102–105	1.0610	1.5082	76	16.17	16.33
n-Amyl	116–118	1.0456	1.5054	64	15.10	15.29

[a] Rinkes reported a b. p. 102° (16 mm.) (*Rec. trav. chim.*, 52, 538 (1933)). [b] Analyses by Mrs. Betty Jarvis.

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[1] Prepared by the method of Hartough and Conley, THIS JOURNAL, **69**, 3096 (1947), in an average of 69%.

INDIANA UNIVERSITY HERSCHEL G. GROSE
BLOOMINGTON, INDIANA E. E. CAMPAIGNE
RECEIVED MAY 21, 1949

3-(4- and 5-Methyl-2-pyridylamino)-acrylic Acids[1]

These two new derivatives of acrylic acid were prepared for biological testing at the request of the Chemical-Bio-

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[1] This work was carried out under a Grant-in-Aid from the Research Corporation.

logical Coördination Center of the National Research Council. Preparation was accomplished by heating 5 g. of either the corresponding ethyl 2-pyridylaminomethylenemalonate (I)[2] or the 3-carbethoxy-2H-pyrido-1,2-a-pyrimidine-4-one (II)[2] with 250 ml. of 1% aqueous sodium hydroxide solution at 90° for five minutes with II or thirty minutes with I. The solution was filtered hot and made acid to congo red with dilute hydrochloric acid while still hot. The precipitated acid was twice recrystallized from pyridine.

3-(4-Methyl-2-pyridylamino)-acrylic Acid.—M. p. 238° with decarboxylation; yield from I 43%, from II 61%.

Anal. Calcd. for $C_9H_{10}O_2N_2$: N, 15.72; neut. equiv., 178. Found: N, 15.65[3]; neut. equiv., 176.

3-(5-Methyl-2-pyridylamino)-acrylic Acid.—M. p. 258° with decarboxylation; yield from I 36%, from II 67%.

Anal. Calcd. for $C_9H_{10}O_2N_2$: N, 15.72; neut. equiv., 178. Found: N, 15.74[3]; neut. equiv., 180.

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(2) G. R. Lappin, THIS JOURNAL, **70**, 3348 (1948).

(3) Microanalysis by the Clark Microanalytical Laboratory, Urbana, Ill.

CHEMICAL LABORATORY
ANTIOCH COLLEGE
YELLOW SPRINGS, OHIO GERALD R. LAPPIN

RECEIVED MAY 16, 1949

Some Quaternary Salts of Carbamates of Amino Alcohols[1]

A series of compounds of the general formula $[R_3'N—A—OCONR_2]^+I^-$ has been prepared (Table I). The unsubstituted carbamates (both R = H) were prepared by method 1, the N-methylcarbamates (R = CH_3, and R = H) by method 2, and the N,N-dimethylcarbamates (both R = CH_3) by method 3.

TABLE I

QUATERNARY SALTS OF CARBAMATES OF AMINO ALCOHOLS

Compound	M. p., °C.	Formula	Iodide analyses, %	
			Calcd.	Found
2-Di-*n*-butylaminoethyl carbamate butiodide	99–100	$C_{15}H_{33}IN_2O_2$	31.70	31.47
3-Di-*n*-butylaminopropyl carbamate butiodide	122–123	$C_{16}H_{35}IN_2O_2$	30.62	30.64
3-Di-*n*-amylaminopropyl carbamate amyl iodide	108–110	$C_{19}H_{41}IN_2O_2$	27.80	27.40
2-Diethylaminoethyl N-methylcarbamate ethiodide	90–92	$C_{10}H_{23}IN_2O_2$	38.42	38.52
2-Di-*n*-butylaminoethyl N-methylcarbamate butiodide	100–101.5	$C_{16}H_{35}IN_2O_2$	30.62	30.43
2-Pentamethyleneaminoethyl N-methylcarbamate methiodide	103–105	$C_{10}H_{21}IN_2O_2$	38.66	38.99
3-Di-*n*-butylaminopropyl N-methylcarbamate butiodide	110.5–112	$C_{17}H_{37}IN_2O_2$	29.62	29.36
3-Di-*n*-amylaminopropyl N-methylcarbamate amyliodide	78–83	$C_{20}H_{43}IN_2O_2$	26.97	27.05
1-(3,4-Methylenedioxybenzyl)-2-[(3,4-methylenedioxybenzyl)-methylamino]-ethyl N-methylcarbamate methiodide	155–157	$C_{22}H_{27}IN_2O_6$	23.40	23.30
3-Dimethylamino-*d*-bornyl N-methylcarbamate methiodide	187–189	$C_{15}H_{29}IN_2O_2$	32.02	31.91
2-Diethylaminoethyl N,N-dimethylcarbamate ethiodide	106–107	$C_{11}H_{25}IN_2O_2$	36.86	37.08
Octahydro-N-[2-(dimethylcarbamyloxy)-ethyl]-2-methylpyrrocolinium iodide	150–151.5	$C_{14}H_{27}IN_2O_2$	33.19	33.23

(1) Reaction of a dialkylamino alcohol with phosgene gave the dialkylaminoalkyl chloroformate, which reacted with ammonia to give the urethan. Condensation with an alkyl iodide gave the quaternary salt.[2]

$$R_2N(CH_2)_nOH \xrightarrow{COCl_2} R_2N(CH_2)_nOCOCl \xrightarrow{NH_3}$$
$$R_2N(CH_2)_nOCONH_2 \xrightarrow{RI} [R_3N(CH_2)_nOCONH_2]^+I^-$$

(2) Reaction of a dialkylamino alcohol with methyl isocyanate gave a carbamate, which reacted with an alkyl iodide to give the quaternary salt.

$$R_2N(CH_2)_nOH \xrightarrow{CH_3NCO} R_2N(CH_2)_nOCONHCH_3 \xrightarrow{RI}$$
$$[R_3N(CH_2)_nOCONHCH_3]^+I^-$$

(3) Reaction of a chloro alcohol and phosgene gave the chloroalkyl chloroformate, which was converted to the iodoalkyl carbamate by reaction first with dimethylamine and then with sodium iodide in acetone. Condensation of the iodoalkyl carbamate with a tertiary amine gave the quaternary salt.[3]

$$Cl(CH_2)_nOH \xrightarrow{COCl_2} Cl(CH_2)_nOCOCl \xrightarrow{(CH_3)_2NH}$$
$$Cl(CH_2)_nOCON(CH_3)_2 \xrightarrow{NaI} I(CH_2)_nOCON(CH_3)_2 \xrightarrow{R_3N}$$
$$[R_3N(CH_2)_nOCON(CH_3)_2]^+I^-$$

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

(2) Dalmer and Diehl, U. S. Patent 1,894,162; *C. A.*, **27**, 2533 (1933).

(3) Sprinson, THIS JOURNAL, **63**, 2249 (1941).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY L. KAPLAN
STANFORD, CALIF. C. R. NOLLER

RECEIVED APRIL 27, 1949

Stilbestrol Esters

Since a new series of testosterone esters[1] was found to have greater androgenic activity than testosterone propionate, similar stilbestrol esters have been prepared to determine whether these esters have any advantage over stilbestrol dipropionate. Two representative esters have been prepared.

Diethylstilbestrol Di-ethoxyacetate.—A solution of 1 g. of diethylstilbestrol (1 mole) in 15 cc. of dry ether and 6 cc. of dry pyridine was prepared. To this was added 2 cc. of ethoxyacetyl chloride (5 mole) in 10 cc. of dry ether. The reaction mixture was refluxed for one hour and 100 cc. more ether was added. This was poured into water and the ether layer separated, washed with dilute sulfuric acid, dilute sodium carbonate solution and water. Evaporation of the ether left 1.40 g. of reddish white powder, m. p. 129–136°. The product was taken up in a large amount of ether and filtered through activated alumina (Aluminum Ore Co. mm. 80 mesh). The red color was adsorbed on the alumina. Evaporation of the ether left a residue which was twice crystallized from 95% ethanol giving a product (1.05 g.) melting at 136.5–137.5°.

Anal. Calcd. for $C_{26}H_{32}O_6$: C, 70.89; H, 7.32. Found: C, 71.16; H, 7.57.

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(1) Mooradian and Lawson, in press.