3,4-Methylenedioxy-α-amyl-cinnamylaldehyde was prepared analogously from heptanal (11.4 g.) and piperonal (15 g.). The fraction 150–160° (0.8 mm.) of the condensation product was purified *via* the semicarbazone as above. From butyl alcohol long needles, m. p. 155°, were obtained.

Anal. Calcd. for $C_{16}H_{21}O_3N_3$: N, 13.9. Found: N, 14.0. The pure aldehyde had b. p. 158–159° (0.9 mm.).

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE
RECEIVED NOVEMBER 26, 1943

NEW COMPOUNDS

Some Aryl and Aralkyl Ureas

In connection with a study of the hypnotic properties of aryl ureas carried out by a pharmacological group in these Laboratories, a number of halogenated unsymmetrical aryl alkyl ureas have been prepared. Data on these and on some related unhalogenated ureas and symmetrically substituted ureas are presented in Table I.

TABLE I

SECONDARY ARYL AND ARALKYL UREAS $R_1R_2NCONH_2$

	R_1	R_2	M. p., °C.[a]	Appearance	Cryst. solvent[b]	Empirical formula	Analyses, % Calcd. C		Found C	H
							C	H	C	H
I	C_6H_5	CH_2CH_2OH	110		Æ	$C_9H_{12}O_2N_2$	59.97	6.71	59.68	7.05
II[c]	2-Me-4-Cl-C_6H_3	C_2H_5	93	Stout prisms	Æ-H	$C_{10}H_{13}ON_2Cl$	56.46	6.16	56.59	6.19
III[d]	2-Me-4-Br-C_6H_3	C_2H_5	88.5–89	Rect. prisms	E-H	$C_{10}H_{13}ON_2Br$	46.70	5.10	47.00	5.35
IV	The same	n-C_3H_7	94.5–95.5	Prisms	H	$C_{11}H_{15}ON_2Br$	48.70	5.58	48.76	5.78
V[e]	2-Me-5-Cl-C_6H_3	C_2H_5	166–167	Felted needles	A-Aq	$C_{10}H_{13}ON_2Cl$	56.46	6.16	56.52	6.37
VI[f]	The same	n-C_4H_9	79.5–80	Prisms	H	$C_{12}H_{17}ON_2Cl$	59.86	7.12	59.84	7.44
VII[g]	4-Me-2-Br-C_6H_3	C_2H_5	116	Tiny prisms	E	$C_{10}H_{13}ON_2Br$	46.70	5.10	46.82	5.21
VIII[h]	2-Et-4-Br-C_6H_3	C_2H_5	95	Small stout prisms	E-H	$C_{11}H_{15}ON_2Br$	48.70	5.58	48.45	5.86
IX[i]	4-Et-C_6H_4	C_2H_5	122–124	Stout prisms	Æ-H	$C_{11}H_{16}ON_2$	68.70	8.39	68.99	8.62
X[j]	4-Et-2-Br-C_6H_3	C_2H_5	114	Stout prisms	E-H	$C_{11}H_{15}ON_2Br$	48.70	5.58	48.65	5.76
XI	2,4-$Me_2C_6H_3$	C_2H_5	73–74	Prisms	H	$C_{11}H_{16}ON_2$	68.70	8.39	68.75	8.50
XII	$C_6H_5CH_2$	CH_3	135	Needle prisms	Æ	$C_9H_{12}ON_2$	65.82	7.37	65.99	7.32
XIII	The same	n-C_4H_9	61–62	Needles	H	$C_{12}H_{18}ON_2$	69.84	8.80	69.80	8.72
XIV[k]	2-EtO-5-Br-C_6H_3	C_2H_5	124–124.5	Needles	Æ-H	$C_{11}H_{15}O_2N_2Br$	45.98	5.27	46.24	5.50
XV	4-MeO-C_6H_4-CH_2	CH_3	140–141	Flattened needles	A-Aq	$C_{10}H_{14}O_2N_2$	61.82	7.27	62.12	7.46
XVI	4-MeO-3-Cl-$C_6H_3CH_2$	CH_3	169–169.5	Leaflets	A	$C_{10}H_{13}O_2N_2Cl$	52.49	5.73	52.52	5.64
XVII	4-MeO-3-Br-$C_6H_3CH_2$	CH_3	178	Leaflets	A	$C_{10}H_{13}O_2N_2Br$	43.95	4.80	44.22	5.10
XVIII	4-MeO-3-Cl-$C_6H_3CH_2CH_2$	CH_3	117.5–118	Prisms	Æ	$C_{11}H_{15}O_2N_2Cl$	54.41	6.23	54.49	6.38
XIX	4-MeO-3-Br-$C_6H_3CH_2CH_2$	CH_3	116.5–117	Prisms	Æ-H	$C_{11}H_{15}O_2N_2Br$	45.97	5.27	46.03	5.30
	Symmetrically substituted ureas									
XX	2-Me-4-Br-C_6H_3NHCONHEt		230–232	Tiny felted needles	HAc	$C_{10}H_{13}ON_2Br$	46.70	5.10	47.00	5.45
XXI	2,4-Me_2-C_6H_3NEtCONHEt		76	Stout prisms	H	$C_{13}H_{20}ON_2$	70.86	9.16	70.62	9.19
XXII	2-Et-C_6H_4NEtCON$(COC_6H_5)_2$		128–129	Needles	B	$C_{25}H_{24}O_3N_2$	74.97	6.04	75.00	6.38
							(N = 7.00)		(N = 6.95)	
	Secondary Aralkylamine Hydrochlorides $R_1R_2NH\cdot HCl$									
XXIII	4-MeO-3-Cl-$C_6H_3CH_2$	CH_3	201–201.5	Needle prisms	A	$C_9H_{13}ONCl_2$	48.64	5.90	48.76	6.03
XXIV	4-MeO-3-Br-$C_6H_3CH_2$ (hydrobromide)	CH_3	202–203	Needles	A	$C_9H_{13}ONBr_2$	34.73	4.21	35.08	4.44
XXV	4-MeO-3-Cl-$C_6H_3CH_2CH_2$	CH_3	196	Felted needles	Æ	$C_{10}H_{15}ONCl_2$	50.84	6.41	51.00	6.50
XXVI	4-MeO-3-Br-$C_6H_3CH_2CH_2$	CH_3	215–216	Fine needle prisms	A	$C_{10}H_{15}ONClBr$	42.78	5.39	42.94	5.49

[a] All melting points corrected. [b] A = ethanol; Æ = ethyl acetate; E = ether; H = hexane; Aq = water; HAc = acetic acid; B = benzene. [c] B. p. (13 mm.) of secondary amine, 136°. [d] B. p. (0.25 mm.) of secondary amine, 96–99°. [e] B. p. (27 mm.) of secondary amine, 141°. [f] B. p. (1 mm.) of secondary amine, 125°. [g] B. p. (17 mm.) of secondary amine, 137°. [h] B. p. (3 mm.) of secondary amine, 135°. [i] B. p. (22 mm.) of secondary amine, 122–123°. [j] B. p. (3 mm.) of secondary amine, 107°. [k] B. p. (0.25 mm.) of secondary amine, 111°.

The secondary amines corresponding to the ureas I, XI–XIII and XV are known. The amines corresponding to ureas XVI–XIX were characterized as salts and data thereon are also included in Table I. For the other secondary bases boiling points are given. The derived ureas are themselves satisfactory as compounds of characterization.

Preparation of Secondary Amines.—The 3-chloro and bromo anisyl methyl and homo anisyl methyl amines (leading to ureas XVI–XIX) were prepared by halogenation of N-methyl anisyl and N-methyl homo anisyl amines in hydrochloric acid solution (XXIV in hydrobromic acid).

Whereas non-halogenated aromatic secondary amines are readily prepared by alkylation with alkyl halides, isolation of the secondary amine as the nitrosamine followed by reduction with stannous chloride, the alkyl bromides and iodides are unsuitable for reaction with halogenated aromatic amines,[1] the halogen being removed or displaced with resulting complications. By use of alkyl sulfates and alkyl toluene-sulfonates the desired alkyl groups can be introduced satisfactorily.

Ethylation was accomplished by stirring the primary amine with ethyl sulfate and water on the steam-bath until the layers had disappeared after which the conventional nitrosamine procedure was followed.

The secondary propyl and butyl amines corresponding to ureas IV and VI were obtained by warming 1 mol of alkyl toluene sulfonate with 2 mols of primary amine for three hours at 110–120°. The partially cooled melts were sludged with benzene and the bulk of the primary amines separated as salts of *p*-toluenesulfonic acid. Addition to the filtrate of alcoholic hydrogen chloride equivalent to about half of the remaining base precipitated virtually all of the remaining primary amines, after which the hydrochlorides of the secondary amines could be separated without trouble. In some runs sulfonamide formation was encountered.

Preparation of Ureas.—The symmetrically substituted ureas XX and XXI were prepared from ethyl isocyanate and the appropriate aromatic bases.

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[1] Baltzly and Buck, THIS JOURNAL, **63**, 1757 (1941).

The unsymmetrically substituted ureas I–XIX were formed by the reaction of nitro-urea with the corresponding secondary amines. This reaction is not complete with aromatic secondary amines having ortho-substitution. Ordinarily unreacted amine can be separated by partitioning between ether or benzene and about 6% hydrochloric acid. When, however, there is halogen substitution the basicity of the amine is too low for this separation. Steam-distillation from saturated sodium chloride solution (at about 110°) proved to be adequate for the removal of the unreacted amine and it was then possible to crystallize the secondary ureas reported here. The *n*-butyl derivative analogous to the ureas III and IV was not obtained in crystalline form. Tested physiologically as a crude preparation it showed considerable hypnotic activity.

The dibenzoyl urea XXII resulted from benzoylation of the known N-ethyl-N-*o*-ethyl phenyl urea either by the Schotten–Baumann method or by heating with benzoyl chloride in pyridine.

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RECEIVED DECEMBER 10, 1943

Di-*n*-butyl-*n*-propylamine

This compound was prepared by the hydrolysis of γ-di-*n*-butylaminopropylmagnesium chloride with aqueous hydrochloric acid, and by the interaction of 2 moles of di-*n*-butylamine and 1 mole of *n*-propyl iodide in a sealed tube at 120° for four hours, removing the residual secondary amine by shaking with benzoyl chloride and 10% sodium hydroxide.

Both methods gave an identical product, with the following constants: b. p. (754 mm.) 193°; b. p. (8 mm.) 73–75°; d^{20}_4 0.7622; n^{25}_D 1.4248.

The picrate crystallized easily from 95% alcohol or from ether; m. p. 115.8–116.2°.

The picrate was analyzed for C and H. Calculated for $C_{17}H_{28}N_4O_7$: mol. wt., 400.42; C, 50.99; H, 7.05. Found: C, 50.90; H, 6.77.

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RECEIVED DECEMBER 23, 1943

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o-Phenylene Dioxyacetic Acid and its Ethyl Ester

The ethyl ester of *o*-phenylenedioxyacetic acid was prepared by refluxing dichloroethyl acetate with catechol in absolute ethanol solution in the presence of 2 moles of sodium and in an atmosphere of nitrogen until neutral to litmus. The reaction mixture was diluted with water, the ester extracted with ether, washed with sodium hydroxide solution and water, and isolated by fractionation; boiling point 115–117° at 12.5 mm.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.86; H, 5.15; mol. wt., 194. Found: C, 61.09; H, 5.70; mol. wt. (Rast), 191. The product gave no test for halogen nor phenolic hydroxyl.

The acid was prepared from its ester by hydrolysis with 1 *N* sodium hydroxide solution; melting point, 107–108° (uncor.) from ether–petroleum ether.

Anal. Calcd. for $C_8H_6O_4$: C, 57.84; H, 3.79. Found: C, 58.12; H, 3.91.

All attempts to effect direct preparation of *o*-phenylene dioxyacetic acid by condensation between catechol and dichloroacetic acid failed.

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RECEIVED NOVEMBER 23, 1943

A New Ammine of Basic Copper Chromate

The salt which most commonly separates from ammoniacal copper chromate solutions is $Cu(NH_3)_4CrO_4$. Other ammines have been described.[1] However, from solutions deficient in chromium and containing a considerable excess of ammonium hydroxide, there separates a previously undescribed compound, having the composition $2CuO\cdot 4NH_3\cdot CrO_3\cdot H_2O$. In a typical experiment, the crystals were obtained by adding to a suspension of 14.3 g. of basic copper carbonate in 20 ml. of water, 20 ml. of a solution containing 220 g. of ammonium dichromate per liter; 50 ml. of concentrated ammonium hydroxide was added and the mixture shaken thoroughly. Solution was complete except for a few bluish flecks. On standing at room temperature for several days, crystals of the new compound will frequently deposit. Once a crop has been obtained, preparation of the material may be ensured by seeding the solution with the compound. Cooling should be avoided, as at low temperatures green needles of $Cu(NH_3)_4CrO_4$ tend to separate. The yield, after washing with ammonium hydroxide, alcohol and ether, and drying, is about 6 g. The crystals of the new compound are 0.05–1.0 mm. on a side, thickly tabular, almost cubic in habit, greenish-black by reflected light and deep blue-green by transmitted light. The material slowly loses ammonia on exposure to the air, and stoppered preparations have a noticeable odor. On ignition at low temperatures, the crystals decompose with mild deflagration. The crystalline substance becomes coated with an orange-brown discoloration on exposure to air, and water decomposes it to a yellow basic copper chromate. It is insoluble in alcohol, ether, benzene and carbon tetrachloride, and soluble in ammonium hydroxide and acids, being decomposed by the latter; d^{25}_4 2.49.

Anal. Calcd. for $2CuO\cdot 4NH_3\cdot CrO_3\cdot H_2O$: CuO, 46.09; NH_3, 19.73; CrO_3, 28.96; H_2O, 5.22. Found: CuO, 46.21; NH_3, 19.55; CrO_3, 28.92; H_2O, 5.33.

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RECEIVED SEPTEMBER 29, 1943

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[1] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1931, Vol. 11, pp. 261–262.