in DMF) is essentially the same as for the alkali metal ions. The available conductance, emf, and spectroscopic data (*8*) suggest that the proton in *N,N*-dimethylformamide is strongly solvated by a single DMF molecule and that a Grotthus-type conduction mechanism is not operative for the solvated proton in DMF.

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ORGANIC SECTION

Preparation and Properties of 1-Benzyloxy-3-arylureas, 1-Benzyloxy-3-alkylureas, and 1,5-Diphenyl-3-benzyloxybiuret

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Preparation and properties of 15 1-benzyloxy-3-arylureas, two 1-benzyloxy-3-alkylureas, and 1,5-diphenyl-3-benzyloxybiuret are described.

Preparation and properties of 15 1-benzyloxy-3-arylureas, represented by the general formula I, are reported here. These were prepared to study their oxidation with lead tetraacetate which, in general, gave 1-benzyloxybenzimidazolones or 1,2-dibenzyloxy-1,2-diarylcarbamylhydrazines (*2, 3*).

$$C_6H_5CH_2ONHCONHAr$$

I

The preparations were carried out by reaction of aryl isocyanate with benzyloxyamine, a reaction first described by Voltmer (*2*). Benzyloxyamine hydrochloride was prepared by a modification of the procedure used by Mamalis et al. (*7*), treatment of *N*-acetylbenzyloxyamine with ethanol saturated with hydrogen chloride. Benzyloxyamine was isolated by ether extraction of an aqueous alkaline mixture of the amine hydrochloride. The amine was then allowed to react with equimolar amounts of phenyl isocyanate.

When an equimolar quantity of benzyloxyamine was added to phenyl isocyanate (*8*), two products were obtained and were separated by column chromatography on alumina. The second product to be eluted with methanol was the desired 1-benzyloxy-3-phenylurea. The first product was eluted with ether and was shown by elemental analysis to be an addition product of 2 moles of phenyl isocyanate with 1 mole of benzyloxyamine. Such a reaction product was described by Kjellin and Kuylenstjerna (*5*) with a reported melting point of 240°. However, our product had an observed melting point of 140°. The proposed structure of this product is II, and to prove this, II was hydrogenated at 2 atm pressure, room temperature, and with a Raney nickel catalyst. The product mp 209–210° was identical to 1,5-diphenylbiuret (*4, 6*) by ir and mixed melting point.

$$C_6H_5NHCON(OCH_2C_6H_5)CONHC_6H_5$$

II

Alternately, when an equimolar amount of aryl isocyanate was added slowly to benzyloxyamine to keep the benzyloxyamine in excess until the last of the isocyanate was added, only the urea product was isolated. Finally, when the benzyloxyamine was added to a 4*m* ratio of phenylisocyanate, only 1,5-diphenyl-3-benzyloxybiuret was isolated.

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Experimental

Absorption spectra. The infrared spectra were obtained with a Perkin-Elmer grating infrared spectrometer, Model 621. The nuclear magnetic resonance spectra (nmr) were taken on a Varian A60 instrument.

Benzyloxyamine. *N*-acyl-*O*-benzylhydroxylamine was prepared by the procedure described previously (*1*) on a 2-mole scale. The product, which was not purified, was dissolved in 500 ml of methanol. The methanol solution was cooled in an ice bath, and gaseous hydrogen chloride was bubbled through until no further precipitate of benzyloxyamine hydrochloride could be obtained. The amine salt was removed by vacuum filtration and treated with an aqueous solution of sodium hydroxide. From the ether extract of the aqueous solution, an oily, clear-colored organic material was obtained. Vacuum distillation of this material afforded 160 grams (65% yield based on hydroxylamine hydrochloride) of benzyloxyamine (bp 109°/20 mm).

1-Benzyloxy-3-arylureas and 1-Benzyloxy-3-alkylureas, general method. A solution containing 4.06×10^{-2} mole of aryl or alkyl isocyanate in 50 ml of dry benzene was added dropwise to 5.00 grams (4.06×10^{-2}) mole of benzyloxyamine dissolved in 50 ml of dry benzene. The resulting mixture was stirred for 3 hr at room temperature. The 1-benzyloxy-3-arylurea or 1-benzyloxy-3-alkylurea was separated by filtration, or in those cases where a precipitate was not formed, the benzene was removed in vacuo on a rotary evaporator, and the residue was recrystallized from an appropriate solvent. The physical properties of the 1-benzyloxy-3-arylureas obtained by this

Table I. Summary of Physical Data and Solvents of Recrystallization for 1-Benzyloxy-3-arylureas

Aryl group	Mp, °	Solvent of recrystallization	Major infrared absorptions[a]	Nmr spectrum[b]	Analysis	
					Calcd	Found
C_6H_5	107–8	Ethanol-water	3318 (N—H), 3193 (N—H), 1657 (C=O)	4.87 (CH_2), 6.80–7.70 (10, ArH), 8.72 (N—H), 9.50 (N—H)	C 69.41 H 5.82 N 11.56	C 69.53 H 5.81 N 11.48
p-$NO_2C_6H_4$	141–2	Chloroform	3403 (N—H), 3163 (N—H), 1693 (C=O)	4.92 (CH_2), 7.27–8.37 (9, ArH), 9.46 (N—H), 9.93 (N—H)	C 58.53 H 4.56 N 14.63	C 58.67 H 4.52 N 14.69
p-ClC_6H_4	136–7	Benzene	3380 (N—H), 3175 (N—H), 1675 (C=O)	4.89 (CH_2), 7.22–7.81 (9, ArH), 8.94 (N—H), 9.62 (N—H)	C 60.76 H 4.73 N 10.13	C 60.91 H 4.74 N 10.11
p-$CH_3C_6H_4$	108–9	Ethanol-water	3330 (N—H), 3200 (N—H), 1660 (C=O)	2.25 (CH_3), 4.88 (CH_2), 7.00–7.66 (9, ArH), 8.66 (N—H), 9.46 (N—H)	C 70.29 H 6.29 N 10.93	C 70.36 H 6.21 N 10.96
p-$CH_3OC_6H_4$	120–1	Benzene	3265 (N—H), 1640 (C=O)	3.72 (CH_3), 4.88 (CH_2), 6.78–7.62 (9, ArH), 8.64 (N—H), 9.43 (N—H)	C 66.16 H 5.92 N 10.29	C 66.36 H 5.81 N 10.30
m-ClC_6H_4	106–7	Benzene	3310 (N—H), 3210 (N—H), 1655 (C=O)	4.98 (CH_2), 6.86–7.88 (9, ArH), 9.01 (N—H), 9.69 (N—H)	C 60.76 H 4.73 N 10.13	C 61.18 H 4.72 N 10.03
m-$NO_2C_6H_4$	140–1	Chloroform	3330 (N—H), 3175 (N—H), 1675 (C=O)	4.92 (CH_2), 7.30–8.75 (9, ArH), 9.37 (N—H), 9.84 (N—H)	C 58.53 H 4.56 N 14.63	C 58.80 H 4.49 N 14.81
m-$CH_3C_6H_4$	98–9	Benzene	3320 (N—H), 3195 (N—H), 1660 (C=O)	2.28 (CH_3), 4.88 (CH_2), 6.73–7.63 (9, ArH), 8.65 (N—H), 9.50 (N—H)	C 70.29 H 6.29 N 10.93	C 70.09 H 6.32 N 10.94
o-$NO_2C_6H_4$	120–1	Benzene	3293 (N—H), 3150 (N—H), 1685 (C=O)	4.98 (CH_2), 7.08–8.75 (9, ArH), 10.82 (2, N—H)	C 58.53 H 4.56 N 14.63	C 58.70 H 4.48 N 14.69
o-ClC_6H_4	110–1	*n*-Hexane-CCl_4	3405 (N—H), 3150 (N—H), 1690 (C=O)	4.93 (CH_2), 6.92–8.29 (9, ArH), 8.32 (N—H), 10.06 (N—H)	C 60.76 H 4.73 N 10.13	C 60.87 H 4.75 N 10.21
o-FC_6H_4	101–2	*n*-Hexane-CCl_4	3410 (N—H), 3140 (N—H) 1675 (C=O)	4.91 (CH_2), 6.85–8.17 (9, ArH), 8.36 (N—H), 9.81 (N—H)	C 64.60 H 5.03 N 10.77	C 64.58 H 5.08 N 10.80
o-$CH_3C_6H_4$	125–6	Benzene	3403 (N—H), 3170 (N—H), 1673 (C=O)	2.16 (CH_3), 4.90 (CH_2), 6.86–7.72 (9, ArH), 8.08 (N—H), 9.61 (N—H)	C 70.29 H 6.29 N 10.93	C 70.05 H 6.12 N 10.87
o-$CH_3OC_6H_4$	91–2	*n*-Hexane-CCl_4	3393 (N—H), 3150 (N—H), 1670 (C=O)	3.86 (CH_3), 4.90 (CH_2), 6.86–8.30 (9, ArH), 8.25 (N—H), 9.90 (N—H)	C 66.16 H 5.92 N 10.29	C 66.40 H 5.97 N 10.26
$\propto$-$C_{10}H_7$	138–9	Benzene	3280 (N—H), 1647 (C=O)	4.95 (CH_2), 7.30–8.00 (12, ArH), 8.76 (1, N—H), 9.60 (1, N—H)	C 73.96 H 5.52 N 9.58	C 74.29 H 5.63 N 9.58
3,4-diClC_6H_3	118–9	Benzene	3185 (N—H), 1660 (C=O)	4.90 (CH_2), 7.29–8.07 (8, ArH), 9.12 (N—H), 9.76 (N—H)	C 54.03 H 3.89 N 9.00	C 53.99 H 3.93 N 8.90

[a] All infrared samples were run as Nujol mulls, and the infrared absorptions are expressed in cm^{-1}. [b] All nmr samples were run in DMSO-d_6 solutions. Chemical shifts are expressed in ppm relative to TMS.

Table II. Summary of Physical Properties and Solvents of Recrystallization for 1-Benzyloxy-3-alkylureas

Alkyl group	mp, °	Solvent of recrystallization	Major infrared absorptions[a]	Nmr spectrum[b]	Analysis Calcd	 Found
n-Butyl	47–8	*n*-Hexane	3380 (N—H), 3190 (N—H) 1650 (C=O)	0.68–1.58 (7, CH_2CH_3), 2.97–3.40 (CH_2), 4.79 (CH_2), 5.55 (N—H), 7.27 (N—H), 7.30–7.51 (5, ArH)	C 64.86 H 8.16 N 12.60	C 65.10 H 8.02 N 12.69
Allyl	68–9	*n*-Hexane–CCl_4	3440 (N—H), 3155 (N—H) 1670 (C=O)	3.54–3.87 (CH_2), 4.75 (CH_2), 4.84–6.20 (CH_2=CH), 6.83 (N—H), 7.37 (5, ArH), 9.07 (N—H)	C 64.06 H 6.84 N 13.58	C 64.19 H 6.84 N 13.75

[a] All infrared samples were run as Nujol mulls, and the infrared absorptions are expressed in cm^{-1}. [b] All nmr samples were run in DMSO-d_6 solutions. Chemical shifts are expressed in ppm relative to TMS.

method and the solvents used for recrystallization are listed in Table I. The physical properties of the 1-benzyloxy-3-alkylureas are listed in Table II. In all cases, the yields of 1-benzyloxy-3-substituted ureas were in excess of 90%.

1,5-Diphenyl-3-benzyloxybiuret. To a solution of 2.31 grams (18.7 mmol) of benzyloxyamine in 25 ml of dry benzene was added 8.90 grams (74.8 mmol) of phenyl isocyanate. The mixture was refluxed for 1 hr, and the volatile material was removed under an air stream. The solid residue was dissolved in hot carbon tetrachloride which was then evaporated. This crude product was chromatogramed on alumina, and 6.74 grams, 99%, mp 136–40°, was eluted with ether. A pure sample, mp 140–140.8°, was obtained by repeated chromatography.

Anal. Calcd for $C_{21}H_{19}N_3O_3$: C, 69.80; H, 5.32; N, 11.63. Found: C, 69.85, H, 5.32; N, 11.55. Major infrared absorption (CCl_4 solution) NH 3400, 3200 cm^{-1} C=O 1740 and 1680 cm^{-1}. Nmr in CCl_4 solution 4.83 (CH_2), 7.07 (15 ArH), 9.98 (2 NH).

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