Chemistry of Pseudoureas[1]

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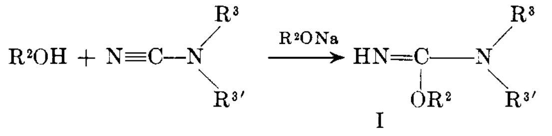
Trisubstituted pseudoureas undergo a novel base-catalyzed transalkylation of the O-alkyl group, but the reaction fails with di- and tetrasubstituted analogs. When both of the 3-substituents of trisubstituted pseudoureas are secondary groups, the compounds do not transalkylate but are unstable in alkaline medium. Steric factors displace the equilibrium towards formation of the cyanamide. Disubstituted pseudoureas are likewise unstable in alkaline medium because of displacement of the equilibrium by formation of a stable monosubstituted cyanamide anion. The di- and trisubstituted pseudoureas were prepared from cyanamides or carbodiimides and alcohols by means of alkaline or acid catalysis. Tetrasubstituted pseudoureas were synthesized from trisubstituted ureas *via* chloroformamidines. Generalizations concerning the infrared spectra of the pseudoureas are presented and comparisons are made with the spectra of similarly substituted ureas.

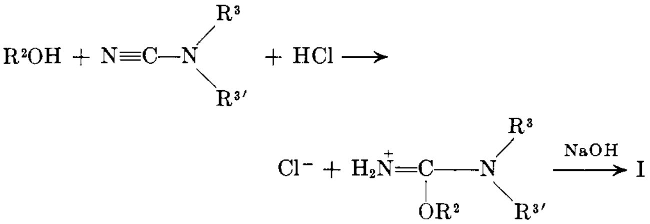
Several pseudoureas tested in an agricultural chemical evaluation program exhibited biological activity against commercially important pests; consequently, preparation of a wide variety of compounds of this class was undertaken. A review of the literature revealed that 2,3,3-trisubstituted pseudoureas have been prepared by the reaction of disubstituted cyanamides and alcohols in the presence of more than equivalent amounts of sodium alkoxide.[2]



$$R^2OH + N{\equiv}C{-}N(R^3)(R^{3'}) \xrightarrow{R^2ONa} HN{=}C(OR^2){-}N(R^3)(R^{3'})$$

I

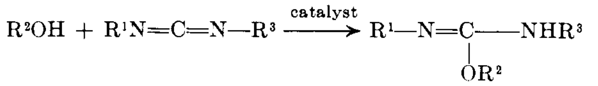
Elderfield and Green[3] observed that a small amount of potassium hydroxide also catalyzed this reaction. McKee[2] reported the use of hydrogen chloride to synthesize di- and 2,3,3-trisubstituted pseudoureas *via* the pseudouronium salts (II).



$$R^2OH + N{\equiv}C{-}N(R^3)(R^{3'}) + HCl \longrightarrow Cl^- + H_2\overset{+}{N}{=}C(OR^2){-}N(R^3)(R^{3'}) \xrightarrow{NaOH} I$$

II

Carbodiimides[4,5] have been converted to 1,2,3-trisubstituted pseudoureas (III) by reaction with alcohols or phenols.

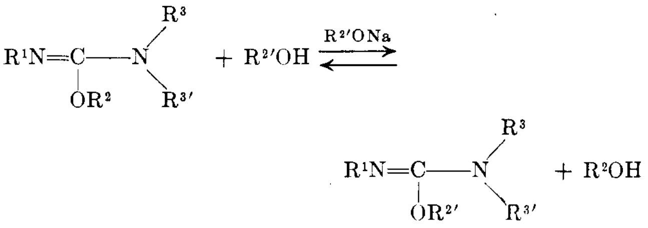


$$R^2OH + R^1N{=}C{=}N{-}R^3 \xrightarrow{\text{catalyst}} R^1{-}N{=}C(OR^2){-}NHR^3$$

III

We obtained pseudoureas of the type I (Table I), the most numerous of the types prepared, by four methods. Disubstituted cyanamides (Table II) reacted with alcohols in the presence of more than an equivalent quantity of sodium alkoxide by a modification of the method first reported by McKee.[2] Pseudoureas were prepared in which R^3 and $R^{3'}$ were identical primary aliphatic groups with from one to twelve carbons, as well as allylic, benzyl, or pentamethylene. The R^2 groups included primary alkyls with one to six carbons or, alternately, olefinic, alkoxy substituted alkyls, or secondary butyl group. Catalytic amounts of sodium alkoxides were found to be sufficient to induce the reaction of a cyanamide with a primary, secondary, or tertiary alcohol. We had already completed our work when Schaefer and Peters[6] reported two similar preparations catalyzed by small amounts of sodium alkoxide. Our yields were usually 60–90%; more than a catalytic amount of sodium alkoxide appeared to be unnecessary.

Transalkylation and Equilibria.—We have found that trisubstituted pseudoureas undergo novel transalkylation reactions of synthetic value where R^1 or R^3 is H. A methyl or ethyl group could be replaced by a higher molecular weight primary or secondary group, and the equilibrium was displaced by distilling the resulting methyl or ethyl alcohol. The transalkylation reaction did not occur even at elevated temperatures in the absence of the alkoxide catalyst. 2-Ethylhexyl, neopentyl, 2,2,4-trimethylpentyl, cyclohexyl, benzyl, and tetrahydrofurfuryl groups were introduced into the 2-position by this procedure. Although these compounds sometimes may be accessible by other routes, 3,3-dimethallyl-2-tetrahydrofurfurylpseudourea and 2-benzyl-3,3-dimethylpseudourea were prepared by this method after the usual syntheses with a dialkycyanamide and either of the corresponding alcohols in alkaline medium had failed. These results indicate that a bulky group can more easily approach the back side of the 2-position of a pseudourea than it can attack a cyanamide.



$$R^1N{=}C(OR^2){-}N(R^3)(R^{3'}) + R^{2'}OH \underset{}{\overset{R^{2'}ONa}{\rightleftarrows}} R^1N{=}C(OR^{2'}){-}N(R^3)(R^{3'}) + R^2OH$$

Some observations which follow have led to the conclusion that the mechanism of the transalkylation of 2,3,3-trisubstituted pseudoureas probably involves a reversible equilibrium.

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[1] Abstracts, 142nd National Meeting of the American Chemica Society, Atlantic City, N. J., September 1962, p. 75Q.

[2] R. H. McKee, *Am. Chem. J.*, **26**, 209 (1901); **36**, 208 (1906); **42**, 1 (1909).

[3] R. C. Elderfield and M. Green, *J. Org. Chem.*, **17**, 431 (1952).

[4] E. Schmidt, M. Seefelder, R. G. Jennin, W. Striewsky, and H. von Martius, *Ann.*, **571**, 83 (1951).

[5] F. B. Dains, *J. Am. Chem. Soc.*, **21**, 136 (1899).

[6] F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 412 (1961).

TABLE 1

PSEUDOUREAS

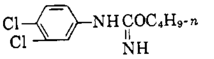
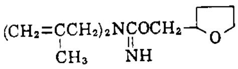
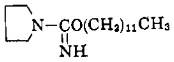
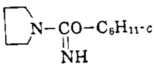
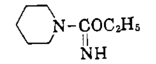
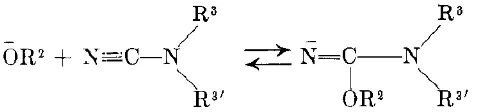
Formula	Method[a]	Yield, %	B.p., °C. (mm.)	$n^{25}D$ (or m.p., °C.)	d^{25}_4	Found				Calcd.			
						Neut. equiv.	C	H	N	Neut. equiv.	C	H	N
$n\text{-}C_4H_9NH\underset{\overset{\|}{NH}}{C}OCH_2\underset{\overset{\vert}{C_2H_5}}{C}HC_4H_9\text{-}n$	D	20	86 (0.005)	1.4591	0.9062	238	68.2	12.2	12.5	228	68.4	12.4	12.3
$C_6H_5NH\underset{\overset{\|}{NH}}{C}OCH_2\underset{\overset{\vert}{C_2H_5}}{C}HC_4H_9\text{-}n$	D	37	95 (0.004)	1.5156	1.0068	250	72.2	9.7	11.2	248	72.5	9.7	11.3
	D	44				267	50.7	5.3	11.0	261	50.6	5.4	10.7
$(n\text{-}C_3H_7)_2N\underset{\overset{\|}{NH}}{C}OC_3H_7\text{-}n$	B	72	108 (10)	1.4450	0.8939	190	64.1	11.5	14.9	186	64.5	11.9	15.0
$(n\text{-}C_3H_7)_2N\underset{\overset{\|}{NH}}{C}OCH_2\underset{\overset{\vert}{CH_3}}{C}{=}CH_2$	B	62	118 (12)	1.4569	.9052	206	66.8	10.9	14.1	198	66.6	11.2	14.1
$(i\text{-}C_3H_7)_2N\underset{\overset{\|}{NH}}{C}OC_4H_9\text{-}n$	D	39	62 (0.2)	1.4491	.9005	205	65.8	12.0	14.0	200	66.0	12.1	14.0
$(n\text{-}C_4H_9)_2N\underset{\overset{\|}{NH}}{C}OC_3H_7\text{-}n$	B	72	79 (0.15)	1.4474	.8825	215	67.6	12.0	12.9	214	67.2	12.2	13.1
$(n\text{-}C_4H_9)_2N\underset{\overset{\|}{NH}}{C}OC_4H_9\text{-}n$	A	85	117 (2)	1.4500	.8871	234	68.0	12.4	12.4	228	68.3	12.4	12.3
$(n\text{-}C_4H_9)_2N\underset{\overset{\|}{NH}}{C}OCH_2\underset{\overset{\vert}{C_2H_5}}{C}HCH_4H_9\text{-}n$	C	89	94 (0.025)	1.4535		285	71.7	13.1	10.0	284	71.8	12.8	9.9
$(n\text{-}C_4H_9)_2N\underset{\overset{\|}{NH}}{C}OCH_2\overset{CH_3}{\underset{\overset{\vert}{CH_3}}{\overset{\vert}{C}}}C_4H_9\text{-}i$	C	75	74 (0.002)	1.4538	.8810	286	71.6	12.7	9.7	285	71.8	12.8	9.9
$(n\text{-}C_4H_9)_2N\underset{\overset{\|}{NH}}{C}O{-}C_6H_{11}\text{-}c$	C	74	94 (0.001)	1.4692	.9320	259	70.7	12.1	11.1	254	70.8	11.9	11.0
$(n\text{-}C_6H_{13})_2N\underset{\overset{\|}{NH}}{C}OC_4H_9\text{-}n$	B	68	117 (0.15)	1.4520	.8131	288	72.0	13.1	10.0	285	71.8	12.8	9.9
$(CH_2{=}CHCH_2)_2N\underset{\overset{\|}{NH}}{C}OCH_2CH{=}CH_2$	A	58	94 (5)	1.4809	.9555	182	66.6	8.9	15.8	180	66.7	8.9	15.5
$(CH_2{=}CHCH_2)_2N\underset{\overset{\|}{NH}}{C}OC_4H_9\text{-}n$	A	43	100 (5)	1.4796	.9005	196	67.6	10.6	14.6	196	67.3	10.3	14.3
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}CH_2)_2N\underset{\overset{\|}{NH}}{C}OCH_3$	A	73	71 (0.7)	1.4730	.9414	191	66.1	10.1	15.2	182	65.9	10.0	15.4
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}CH_2)_2N\underset{\overset{\|}{NH}}{C}OC_2H_5$	A	83	73 (0.5)	1.4665			67.1	10.3	15.3		67.3	10.2	14.3
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}{-}CH_2)_2N\underset{\overset{\|}{NH}}{C}OC_4H_9\text{-}n$	A	82	102 (2.2)	1.4684	.9134	228	69.4	10.7	12.6	224	69.6	10.8	12.5
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}CH_2)_2N\underset{\overset{\vert}{NH}}{C}O\underset{\overset{\vert}{CH_3}}{C}HC_2H_5$	A	74	59 (0.005)	1.4656	.9056	229	69.8	10.8	12.3	224	69.6	10.8	12.5
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}CH_2)_2N\underset{\overset{\|}{NH}}{C}OCH_2C(CH_3)_3$	C	86	83 (0.5)	1.4623	.8992	257	70.7	10.8	11.8	238	70.5	11.0	11.8
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}CH_2)_2N\underset{\overset{\|}{NH}}{C}OCH_2\underset{\overset{\vert}{C_2H_5}}{C}HC_4H_9\text{-}n$	A	57	110(0.2)	1.4698	.9043	335	72.8	11.4	10.0	281	72.8	11.5	9.7
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}CH_2)_2N\underset{\overset{\|}{NH}}{C}OCH_2\underset{\overset{\vert}{CH_3}}{C}{=}CH_2$	A	18	87 (1)	1.4731	.9136	232	69.9	10.3	13.0	222	70.2	10.0	12.6
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}CH_2)_2N\underset{\overset{\|}{NH}}{C}OCH_2CH_2OC_4H_9\text{-}n$	A	68	128 (1.8)	1.4692	.9409	281	67.2	10.5	10.7	268	67.2	10.4	10.4
$(CH_2{=}\underset{\overset{\vert}{CH_3}}{C}CH_2)_2N\underset{\overset{\|}{NH}}{C}O(CH_2CH_2O)_2C_4H_9\text{-}n$	A	72	140 (0.6)	1.4723	.9626	320	65.6	10.6	9.0	313	65.3	10.3	9.0
	C	82	83 (0.004)	1.4883	1.0095	259	66.6	9.6	11.3	252	66.5	9.6	11.1
$(c\text{-}C_6H_{11})_2{-}N\underset{\overset{\|}{NH}}{C}O{-}C_6H_{11}\text{-}c$	D	14	115 (0.003)	(80)		306	74.4	11.3	9.4	307	74.5	11.2	9.1
$(C_6H_5CH_2)_2N\underset{\overset{\|}{NH}}{C}OCH_3$	A	62	128 (0.01)	(51–53)					10.8				11.0
$(C_6H_5CH_2)_2N\underset{\overset{\|}{NH}}{C}OC_2H_5$	A	57	133 (0.01)	1.5652	1.0823				10.1				10.4
$C_6H_5\overset{n\text{-}C_4H_9}{\overset{\vert}{N}}\underset{\overset{\|}{NH}}{C}OC_4H_9\text{-}n$	B	76	102 (0.1)	1.5040	0.9758	265	72.7	9.7	12.1	248	72.5	9.7	11.8
$(CH_3)_2\underset{\overset{\vert}{NO_2}}{C}CH_2\overset{n\text{-}C_4H_9}{\overset{\vert}{N}}\underset{\overset{\|}{NH}}{C}OC_4H_9\text{-}n$	B	70	83 (0.02)	1.4650	1.0126	291	56.9	10.0	15.0	273	57.1	10.0	15.4
	B	90	146 (0.001)	1.4710		292	72.3	12.1	9.8	283	72.3	12.1	9.9

TABLE I (*Continued*)

Formula	Method[a]	Yield, %	B.p., °C. (mm.)	$n^{25}D$ (or m.p., °C.)	d^{25}_4	Found Neut. equiv.	Found C	Found H	Found N	Calcd. Neut. equiv.	Calcd. C	Calcd. H	Calcd. N
	B	89	77 (0.001)	1.4980	1.032	196	67.3	10.3	14.5	196	67.3	10.3	14.3
	A	66	109 (15)	1.4794	1.0015		61.4	10.2	17.6		61.5	10.3	18.0
$n\text{-}C_4H_9NH\underset{\overset{\|}{NC_4H_9\text{-}n}}{C}OC_4H_9\text{-}n$	E	65	58 (0.001)	1.4478		234	68.2	12.5	12.1	228	68.4	12.4	12.3
$n\text{-}C_4H_9NH\underset{\overset{\|}{NC_4H_9\text{-}n}}{C}O—C_6H_{11}\text{-}c$	E	73	106 (0.001)	1.4715		278	71.0	12.1	10.9	254	70.8	11.9	11.0
$n\text{-}C_4H_9NH\underset{\overset{\|}{NC_4H_9\text{-}n}}{C}OC_6H_5$	F	44		1.5068	0.9832	286	72.4	9.8	11.4	248	72.5	9.7	11.3
$c\text{-}C_6H_{11}—NH\underset{\overset{\|}{N—C_6H_{11}\text{-}c}}{C}OCH_3$	E	89	85 (0.025)	1.4945		241	70.7	11.2	11.8	238	70.5	11.0	11.7
$c\text{-}C_6H_{11}—NH\underset{\overset{\|}{N—C_6H_{11}\text{-}c}}{C}O—C_6H_{11}\text{-}c$	E	60		(85)		312	74.3	11.1	9.0	307	74.5	11.2	9.1
$c\text{-}C_6H_{11}—NH\underset{\overset{\|}{NC_6H_{11}\text{-}c}}{C}O—CH_2\overset{C_2H_5}{\overset{\|}{C}}H—C_4H_9\text{-}n$	C	96	128 (0.025)	1.4815		341	74.9	12.2	8.1	337	74.9	12.0	8.3
$n\text{-}C_4H_9NH\underset{\overset{\|}{NC_6H_5}}{C}OC_4H_9\text{-}n$	E	85	80 (0.005)	1.5088	0.9823	254	72.6	9.8	11.2	248	72.5	9.7	11.3
$C_6H_5NH\underset{\overset{\|}{NC_6H_5}}{C}OCH_2\underset{\overset{\|}{C_2H_5}}{C}HC_4H_9\text{-}n$	E	41	120 (0.001)			341	77.1	8.4	8.4	325	77.7	8.7	8.6

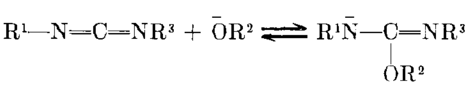
[a] Methods: (A) Reaction of the cyanamide with the alcohol in the presence of 1.1 equivalents of sodium alkoxide. Method does not work with phenol, furfuryl alcohol, or *t*-butyl alcohol. (B) As in A but with 0.1 equivalent of sodium alkoxide. Method does not work with phenol or furfuryl alcohol. (C) Transalkylation of the 2-methyl or 2-ethyl group of a trisubstituted pseudourea with an alcohol in the presence of 0.1 equivalent of sodium alkoxide. Method does not work with phenol, furfuryl alcohol, or *t*-butyl alcohol. (D) Saturation of a mixture of the cyanamide and the alcohol with hydrogen chloride. Method does not work with phenol. (E) Reaction of a carbodiimide with an alcohol catalyzed by 0.1 equivalent of sodium alkoxide. (F) Saturation of a mixture of a carbodiimide and phenol with hydrogen chloride.



When both of the 3-substituents of a 2,3,3-trisubstituted pseudourea were secondary alkyl groups, the compounds behaved differently. Such pseudoureas could not be prepared from the cyanamides by alkaline catalysts but were obtained by using the anhydrous hydrogen chloride method[2] *via* the pseudouronium salts (II). Attempts to transalkylate this type of pseudourea in the presence of an alkaline catalyst caused complete conversion to the corresponding cyanamide and alcohol. Thus, the equilibrium of alkoxides and dialkylcyanamides with 2,3,3-trisubstituted pseudoureas favors cyanamide formation when two secondary alkyl groups are attached to a single nitrogen, probably because of the large size of the secondary alkyl groups. Since Curd, Davey, and Richardson[7] were able to prepare 2,3-dimethyl-3-isopropylpseudourea from isopropylmethylcyanamide under alkaline conditions, the equilibrium must still favor pseudourea formation where both a secondary group and a primary group are on the same nitrogen.

An attempt was made to transalkylate 2,3,3-trisubstituted pseudoureas with two secondary groups on the 3-position by means of hydrogen chloride catalysis. Only 10% of a 2-methyl group was replaced by *n*-butyl, as indicated by gas phase chromatography of the alkyl iodides[8] resulting from reaction of the product with hydriodic acid.

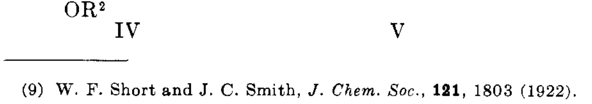
With two secondary groups on different nitrogen atoms, as in 1,2,3-trisubstituted pseudoureas (III), the transalkylation reaction under alkaline conditions proceeded readily and in high yield. This transalkylation process and the synthesis of 1,2,3-trisubstituted pseudoureas from carbodiimides[4,5] are strong evidence for equilibrium between carbodiimides and alkoxide ions similar to the one involving cyanamides. Although



$$R^1—N{=}C{=}NR^3 + \bar{O}R^2 \rightleftharpoons R^1\bar{N}—\underset{\overset{|}{OR^2}}{C}{=}NR^3$$

phenol was added to carbodiimides under acid conditions, as previously reported,[9] phenoxide could not be used to make trisubstituted pseudoureas.

Monoalkylcyanamides[2] and alcohols reacted only in the presence of hydrogen chloride; attempted syntheses in the presence of alkoxides failed. The disubstituted pseudoureas (IV) so formed could not be transalkylated with base but partly decomposed instead to the alcohol and a polymer of the monoalkylcyanamide. The extent of the decomposition depended upon the quantity of the intended catalyst which was used; with a small amount of base most of the pseudourea was recovered unchanged. The alkalinity of the reaction mixture decreased during the heating period to a value only a little higher than that of a solution of pseudourea in alcohol. These observations are in



$$R^3NH\underset{\overset{|}{OR^2}}{C}{=}NH + R^{2\prime}O^- \rightleftharpoons R^3\bar{N}—C{\equiv}N + R^2OH + R^{2\prime}OH$$

IV V

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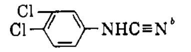
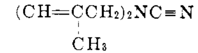
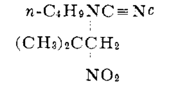
(7) F. H. S. Curd, D. G. Davey, and D. N. Richardson, *J. Chem. Soc.*, 1732 (1949).

(8) H. Kratzl and K. Gruber, *Monatsch. Chem.*, **89**, 618 (1958).

(9) W. F. Short and J. C. Smith, *J. Chem. Soc.*, **121**, 1803 (1922).

TABLE II

CYANAMIDES

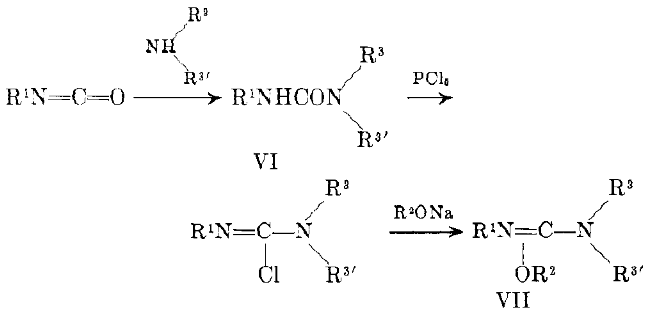
Formula	Method[a]	Yield, %	B.p., °C. (mm.)	n^{25}D (or m.p., °C.)	d^{25}_{4}	Found C	Found H	Found N	Calcd. C	Calcd. H	Calcd. N
 Cl Cl NHC≡N[b]	B	33		(125–132)		44.8	2.4	14.7	45.0	2.15	15.0
$(n\text{-}C_6H_{13})_2NC\equiv N$	A	88	175 (14)	1.4438	0.8687	74.5	12.3	13.1	74.2	12.5	13.3
$(n\text{-}C_7H_{15})_2NC\equiv N$	A	87	120 (0.2)	1.4469							
 $(CH{=}\underset{CH_3}{C}CH_2)_2NC\equiv N$	A	83	95 (5.5)	1.4650	0.9027			18.8			18.7
$(c\text{-}C_6H_{11})_2{-}NC\equiv N$	B	74	147 (0.5)	(46)							
 $n\text{-}C_4H_9NC\equiv N^{c}$ / $(CH_3)_2\underset{NO_2}{C}CH_2$	B	76	111 (0.2)	1.4577	1.0387	54.5	8.7	21.1	54.3	8.6	21.1

[a] Methods: (A) Reaction of an alkyl chloride with cyanamide in aqueous alcoholic alkali. (See E. B. Vliet, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 203.) Failed with tetrahydrofurfuryl bromide. (B) Reaction of an amine with cyanogen bromide. [b] Precipitated from alkaline solution between pH 9.4–1.0; purest fraction obtained below pH 8.0. calcd.: Cl, 37.9; neut. equiv., 187. Found: Cl, 35.1, neut. equiv., 203 (as an acid by titration with sodium methylate in nonaqueous medium). [c] *n*-Butyl-2-methyl-2-nitropropylamine, prepared by method of M. Senkus, *J. Am. Chem. Soc.*, 68, 10 (1946).

harmony with the postulated equilibria and the acidity of monoalkylcyanamides.

Monoalkylcyanamides formed a stable anion (V); further reaction in a basic medium was prevented.

1,2,3,4-Tetrasubstituted pseudoureas (VII) did not transalkylate. In the presence of more than an equivalent amount of sodium alkoxide, no reaction occurred and the original pseudourea was recovered unchanged. The lack of a hydrogen on either nitrogen prevented the formation of a reactive intermediate with sodium alkoxide. Failure of this transalkylation is further evidence against a mechanism involving direct displacement by an alkoxide ion on an uncharged pseudourea or an addition elimination sequence on the pseudourea themselves. The tetrasubstituted pseudoureas were prepared by the following series of reactions.[10]



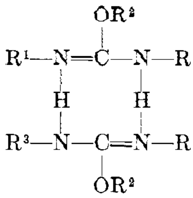
This synthesis succeeded only when R¹ was aromatic. Sodium *n*-butoxide could not be replaced successfully as a reactant by sodium phenoxide.

General Properties.—The basic properties of the pseudoureas permitted titrations with hydrogen bromide in glacial acetic acid to a crystal violet end point. This distinguished pseudoureas from unchanged cyanamides and by-product ureas. Amines, possible by-products of comparable basicity, were so much more volatile than the pseudoureas that they could not be present in the distilled product fractions. The usually liquid pseudoureas are more volatile than the normally solid ureas.

Ability to form crystalline pseudouronium salts of different solubility characteristics from typical impurities sometimes served as a means of purification.

As a general rule, pseudoureas containing a 2-phenyl group were more difficult to form, less stable to heat and hydrolysis, and more difficult to purify than other pseudoureas.

The characteristic infrared frequencies of pseudoureas (Table III) were compared with each other and with those of similarly substituted ureas (Table IV). The NH stretching region of pseudoureas, 3200–3460 cm.⁻¹, resembles the spectra of amidines.[11,12] The intensity of the NH stretching band increased in the order, trisubstituted pseudoureas < disubstituted pseudoureas < substituted ureas. Hydrogen bonding in 1,2,3-trisubstituted pseudoureas caused the appearance of a second band in this region.[13] The strong C═N stretching absorption of pseudourea[14] was observed between 1680–1590 cm.⁻¹. The capability of forming a cyclic hydrogen-bonded dimer (VIII) by some 1,2,3-trisubstituted pseudoureas and 2-alkyl-3-aryl disubstituted pseudoureas was evidenced by the fact that these compounds absorbed at the highest frequencies in this region. The C═O stretching band of the ureas occurred in nearly the same region, 1680–1613 cm.⁻¹. In contrast to the pseudoureas, the ureas showed a strong NH bending band between 1600–1513 cm.⁻¹. The C—O—C stretching band of the pseudoureas appeared as a strong, broad band in the region 1126–1062 cm.⁻¹. This strong band, characteristic of open chain ethers,[15] was absent from the spectra of ureas. The C—N stretching frequency ofs peudourea falls between 1345–1290 cm.⁻¹ and is attributed[11] to the HN═C—N(R)₂ structure. Ureas have a similar band



VIII

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[10] Beilstein's "Handbuch der Organischen Chemie," Vol. IV, p. 122; Vol. XII, 4th Ed., p. 443.

[11] J. C. Grivas and A. Taurins, *Can. J. Chem.*, **37**, 795 (1959).

[12] J. C. Grivas and A. Taurins, *ibid.*, **39**, 414 (1961).

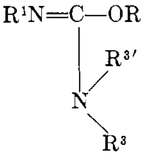
[13] L. S. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Company, Ltd., London, 1958, p. 206.

[14] J. Pitha, *et al.*, *Collection Czech. Chem. Commun.*, **26**, 834 (1961).

[15] R. N. Jones and C. Sandorfy, "Technique of Organic Chemistry," Vol. IX, 1956, p. 435.

TABLE III

CHARACTERISTIC INFRARED ABSORPTION BANDS OF PSEUDOUREAS



$$R^1N{=}C(OR^2)N(R^3)(R^{3'})$$

R¹	R²	R³	R³′	NH stretching, cm.⁻¹	C=N stretching, cm.⁻¹	C—O—C stretching,[a] cm.⁻¹	C—N stretching, cm.⁻¹
H	2-Ethylhexyl	Butyl	H	3210	1634	1098	1316
H	2-Ethylhexyl	Phenyl	H	3420, 3330, 3240	1657	1112, 1098, 1067	1323
H	Butyl	3,4-Dichlorophenyl	H	3420, 3330, 3240	1657	1126, 1101, 1068	1330
H	Ethyl	Methyl	Methyl	3290	1623	1096, 1060	1337
H	Benzyl	Methyl	Methyl	3290	1623	1093, 1058	1346
H	Butyl	Ethyl	Ethyl	3310	1618	1110, 1085, 1080	1316, 1295
H	Propyl	Propyl	Propyl	3320	1623	1094, 1078	1304
H	Methallyl	Propyl	Propyl	3320	1620	1085	1302
H	Methyl	*i*-Propyl	*i*-Propyl	3330	1613	1096, 1080	1309
H	Butyl	*i*-Propyl	*i*-Propyl	3330	1613	1085	1311
H	Methyl	Butyl	Butyl	3330	1626	1094, 1078	1302
H	Propyl	Butyl	Butyl	3330	1623	1094, 1082	1302
H	Butyl	Butyl	Butyl	3330	1613	1094, 1079	1297
H	Amyl	Butyl	Butyl	3330	1623	1104, 1087, 1075	1304
H	2-Ethylhexyl	Butyl	Butyl	3330	1625	1110, 1098, 1074	1300
H	2,2,4-Trimethylamyl	Butyl	Butyl	3330	1623	1094, 1073	1302
H	Methallyl	Butyl	Butyl	3330	1618	1099, 1081	1299
H	Cyclohexyl	Butyl	Butyl	3330	1616	1094, 1067	1290
H	*i*-Butyl	*i*-Butyl	*i*-Butyl	3330	1623	1094, 1072	1307
H	Butyl	Hexyl	Hexyl	3330	1623	1094, 1082	1299
H	Butyl	Octyl	Octyl	3340	1618	1094, 1080	1307
H	Butyl	Allyl	Allyl	3300	1613	1080	1308
H	Allyl	Allyl	Allyl	3330	1618	1105, 1072	1294
H	Methyl	Methallyl	Methallyl	3330	1630	1092, 1084	1299
H	Ethyl	Methallyl	Methallyl	3330	1629	1095, 1080	1295
H	Butyl	Methallyl	Methallyl	3310	1623	1093, 1081	1295
H	2-Butyl	Methallyl	Methallyl	3300	1618	1093, 1075	1316
H	*t*-Butyl	Methallyl	Methallyl	3300	1616	1093, 1085, 1062	1316
H	Neopentyl	Methallyl	Methallyl	3330	1623	1089, 1081	1295
H	2-Ethylhexyl	Methallyl	Methallyl	3310	1622	1078	1279
H	Methallyl	Methallyl	Methallyl	3330	1626	1085	1299
H	2-(Butoxy)ethyl	Methallyl	Methallyl	3280	1618	1126, 1080	1289
H	2-[2-(Butoxy)ethoxy]-ethyl	Methallyl	Methallyl	3310	1625	1120, 1084	1280
H	Tetrahydrofurfuryl	Methallyl	Methallyl	3310	1622	1073	1295
H	Butyl	3-Chlorobut-2-enyl	3-Chlorobut-2-enyl	3310	1623	1094	1299
H	Methyl	Cyclohexyl	Cyclohexyl	3320	1620	1094, 1078	1307
H	Ethyl	Cyclohexyl	Cyclohexyl	3330	1602	1092, 1068	1297
H	Cyclohexyl	Cyclohexyl	Cyclohexyl	3330	1590	1119, 1083, 1063	1299
H	Methyl	Benzyl	Benzyl	3300	1623	1083	1307
H	Ethyl	Benzyl	Benzyl	3320	1626	1094, 1077	1307
H	Cyclohexyl	Benzyl	Benzyl	3330	1622	1080	1316
H	Butyl	2-Chlorobenzyl	2-Chlorobenzyl	3310	1629	1087	1305
H	Butyl	Butyl	Phenyl	3290	1627	1085	1300
H	Butyl	Butyl	2-Nitro-*i*-butyl	3330	1621	1096	1302
H	Dodecyl		Tetramethylene	3300	1622	1096, 1082	1328
H	Cyclohexyl		Tetramethylene	3300	1614	1067	1325
H	Ethyl		Pentamethylene	3300	1614	1096, 1075, 1068	1337
H	Cyclohexyl		3-Oxapentamethylene	3330	1626	1122, 1070	1299
Butyl	Butyl	Butyl	H	3460, 3310	1664	1112, 1087, 1075	1299
Butyl	Cyclohexyl	Butyl	H	3400, 3280	1667	1116, 1093, 1062	1289
Butyl	Phenyl	Butyl	H	3390, 3180	1678	1116, 1099, 1078	1290
Cyclohexyl	2-Ethylhexyl	Cyclohexyl	H	3420	1660	1125, 1100, 1062	1295
Cyclohexyl	Cyclohexyl	Cyclohexyl	H	3420	1663	1125, 1104, 1091, 1078, 1064	1289
Phenyl	Butyl	Butyl	H	3390	1653	1119, 1105, 1072	1299
Phenyl	Phenyl	Butyl	H	3390	1662	1116, 1092, 1072	1300
Phenyl	2-Ethylhexyl	Phenyl	H	3370	1658	1116, 1083	1309
Phenyl	Phenyl	Phenyl	H	3360	1667	1107, 1074	1328
Phenyl	Butyl	Butyl	Butyl	. . .	1626	1111, 1105, 1087	1309
Phenyl	Butyl	Phenyl	Phenyl	. . .	1645	1118, 1074	1305

[a] Where several bands are in the C—O—C stretching region, these are given, although only one may be caused by the group in question.

between 1305–1283 cm.⁻¹ except for urea[16] itself; dodecylurea has only a weak band in this region.

Experimental

Preparation of Cyanamides[17] with Cyanogen Bromide.[18]—Bromine (1 mole) and water (16 ml.) were stirred in a flask cooled in an ice–salt bath. Provision was made for reducing the escape of bromine vapor by means of a narrow bore condenser. A solution of sodium cyanide (1.05 moles) in water (350 ml.) was

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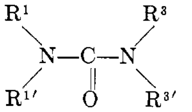
(16) J. E. Stewart, *J. Chem. Phys.*, **26**, 248 (1957).

(17) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1003 (1953).

(18) W. W. Hartman and E. E. Dreger, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 150.

TABLE IV

CHARACTERISTIC INFRARED ABSORPTION BANDS OF SOME UREAS



R^1	$R^{1'}$	R^3	$R^{3'}$	NH stretching, cm.$^{-1}$	C=O stretching, cm.$^{-1}$	NH bending, cm.$^{-1}$	C—N stretching, cm.$^{-1}$
H	H	H	H	3450, 3330	1680	1635, 1600	. . .
Dodecyl	H	H	H	3360, 3300	1650	1562	1300
Octyl	Octyl	H	H	3300	1613	1575	1300
Methallyl	Methallyl	H	H	3300	1650	1590	1290
Amyl	H	Amyl	H	3300	1635	1570	1284
Butyl	Butyl	Butyl	H	3300	1625	1535	1300
Butyl	Butyl	Phenyl	H	3260	1636	1530	1302
Butyl	Phenyl	Butyl	H	3350	1650, 1645	1513	1283
Phenyl	Phenyl	Butyl	H	3300	1650	1525, 1515	1300
Butyl	Phenyl	Phenyl	H	3300, 3200	1650	1530	1305, 1295
Phenyl	Phenyl	Phenyl	H	3350	1676	1515	1300
Butyl	Butyl	Butyl	Butyl	. . .	1637	. . .	1304

added slowly while the reaction temperature was held below 25°. After 2 hr., the amine (1 mole) was added slowly at about 0°, and then a solution of 10 *N* sodium hydroxide (1 mole) was added. A solvent such as ethyl acetate, diethyl ether, or hexane was sometimes added either along with the amine or after the addition of the sodium hydroxide. After another 2 hr., the organic phase was separated and the aqueous phase was extracted with solvent. The combined organic phases were washed with a little dilute sodium hydroxide solution and then distilled, or in some cases crystallized. Butyl[19] and phenyl cyanamides were not purified but were used as solutions in 2-ethylhexanol.

Preparation of Pseudoureas from Substituted Cyanamides. A.—Sodium (1.1 g.-atoms) was dissolved in 500 ml. of an alcohol and a dialkylcyanamide (1 mole) was added with sufficient benzene to keep the refluxing pot temperature at about 100°. The mixture was refluxed usually for 3 hr., and then the sodium alkoxide was neutralized with glacial acetic acid. The mixture was washed with water and then distilled. There were some variations in the neutralization procedure, depending on the solubility of the alcohol in water and the sensitivity of the pseudourea to hydrolysis. In some cases, 1,1-dialkylureas were obtained as by-products.

B.—The procedure was the same as in A except that only 0.1 g.-atom of sodium was used.

C.—Sodium (0.1 g.-atom) was dissolved in 500 ml. of an alcohol higher than ethanol, and 1 mole of a 2-methyl- or 2-ethylpseudourea was added. Sufficient benzene was present to hold the pot temperature near 100° while the mixture was slowly distilled through a 120 × 3.5 cm. column packed with 5-mm. glass helices. The mixture was alternately on total reflux or was distilled at a reflux of 20:1 to remove the lower boiling alcohol as the azeotrope with benzene. When no more methyl or ethyl alcohol could be obtained, the sodium alkylate in the pot was neutralized with glacial acetic acid, and the mixture was distilled to obtain the product.

D.—The mono- or disubstituted cyanamide (0.3 mole) in 250 ml. of the alcohol was saturated with dry hydrogen chloride at room temperature. After standing for 1 to 15 days, the mixture was made alkaline with aqueous sodium hydroxide and extracted with benzene. The product was obtained by distillation of the benzene solution. In some cases the reaction mixture was heated up to 100° for several hours instead of allowing it to stand at room temperature.

2-Phenyl-1,3-disubstituted Pseudoureas.—A carbodiimide (0.25 mole) and phenol (1.0 mole) was saturated with dry hydrogen chloride at 75–80° and then heated at 115° fo. 3 hr. The mixture was extracted with ether, and the insoluble solids were recrystallized from benzene to obtain the pseudouronium hydrochloride. A portion was dissolved in a large volume of water or 1 *N* hydrochloric acid. When the aqueous or acid solution was made alkaline, the pseudourea was precipitated.

Pseudoureas from Substituted Chloroformamidines and Sodium Alkoxides.—Sodium (0.1 g.-atom) was dissolved in butanol (1 mole) and a solution of trisubstituted chloroformamidine (0.08 mole) in benzene was added slowly. The mixture was refluxed for 2 hr., washed with water, neutralized, and distilled.

Infrared Spectra.—The spectra were determined with a Perkin-Elmer Model 421 instrument. Liquids were spread as films between sodium chloride plates; solids were incorporated into pellets with potassium bromide at a concentration of about 0.5%.

Acknowledgments.—The analyses were done by the Analytical Section of our laboratory under the supervision of John E. Zarembo.

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[19] A. D. Ainsley, F. H. S. Curd, and F. L. Rose, *J. Chem. Soc.*, 98, (1949).