removed by this method. The combined filtrates may be concentrated and a small additional amount of the acid recovered on cooling.

The crude acid as thus obtained is transferred to a 3-liter distilling flask and mixed with 600 cc. of benzene. The benzene is then distilled until 300 cc. of distillate has been obtained or until the distillate is no longer turbid. More benzene may be added if necessary. By this procedure the small quantities of water in the crude acid are removed and any free nitric acid is converted into nitrobenzene. After cooling, the contents of the flask are filtered and the product allowed to air-dry for 12–24 hours. This method results in yields of 85–90% of a product melting at 198° (open tube) and having a neutral equivalent of 209. If the material is not dried thoroughly the melting point may drop as low as 150°. Pure 3-nitrophthalic acid may be obtained by one crystallization of the above-described product from glacial acetic acid. When recrystallizing the crude product it is well to allow the cooled mixture to stand for at least 48 hours, as crystal formation is rather slow. The material obtained by this method melts at 206° (open tube) and has a neutral equivalent of 210.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

THE SUBSTITUTED THIO-UREAS. V. THE SYNTHESIS OF THIO-UREAS FROM AMINO-ETHANOLS AND OF THIAZOLIDINE DERIVATIVES

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This investigation is a continuation of a general study[1] of the action of alkylene bromides upon the disubstituted thio-ureas, RNHCSNHR′, where the groups R and R′ are different, with the purpose of ascertaining the effects of various groups upon the constitution of the resulting thiazolidines.

The most satisfactory method for the identification of the bases thus obtained was found to be their comparison with thiazolidines of known structure. This necessitated, therefore, the synthesis of a number of these thiazoles from the ethanol thio-ureas, whose reactions were studied somewhat in detail, as well as the preparation of a number of intermediates whose properties are recorded briefly.

Experimental Part

Preparation of Intermediates

Aryl-(alkyl)-amino-ethanols. ***p*-Xylyl-amino-ethanol,** $2,4\text{-}(CH_3)_2C_6H_3NHCH_2CH_2OH$.—Ethylene chlorohydrin and *p*-xylidine (2 molecular equivalents) were heated

[1] Dains, Brewster, Blair and Thompson, THIS JOURNAL, 44, 2637 (1922).

at 135° for 12 hours. The mixture was then made alkaline with sodium hydroxide and the excess of amine distilled with steam. The residue in the flask was extracted with ether, dried and distilled.

The ethanol boiled at 206° (40 mm.) and on cooling solidified. When crystallized from gasoline, it melted at 57°.

Anal. Calcd. for $C_{10}H_{15}ON$: N, 8.49. Found: 8.35, 8.31.

p-**Bromophenylamino-ethanol**, $BrC_6H_4NHCH_2CH_2OH$.—This was made by passing ethylene oxide (from the chlorohydrin and potassium hydroxide) into the cooled bromo-aniline and heating the mixture at 75° under a pressure of 90 cm. of mercury. The oxide slowly reacted with the amine as was shown by the decrease in pressure. The ethanol which melted at 93° was purified by crystallization from hot water, as it decomposed on distillation.

Anal. Calcd. for $C_8H_{10}ONBr$: N, 6.48. Found: 6.29, 6.25.

The **methyl-, ethyl- and benzylamino-ethanols** were also made by the action of ethylene oxide upon the amines, either in 33% solution or pure (benzyl).[2]

Mustard Oils. ***p*-Xylyl Isothiocyanate**,[3] C_8H_9NCS.—Di-*p*-xylyl-thio-urea was not decomposed by boiling with concd. hydrochloric acid, but the mustard oil was obtained in good yield on warming the thio-urea with an excess of acetyl chloride and distilling the product with steam. The pure isothiocyanate boiled at 249–251°.

Anal. Calcd. for C_9H_9NS: N, 8.59. Found: 8.57, 8.67.

Ethyl Isothiocyanate, C_2H_5NCS.[1]—A 33% solution of ethylamine (45 g.) was added slowly to a mixture of carbon disulfide (27 g.) and sodium hydroxide (15 g.) in water solution. The mixture, which was kept in an ice-bath and well stirred during the addition of the amine, soon solidified due to the separation of sodium ethyl dithiocarbamate.

The whole mass was then added to a solution of lead nitrate (110 g.) in 400 cc. of

TABLE I

DISUBSTITUTED THIO-UREAS

Thio-urea RNHCSNHR′	M. p. °C.	Nitrogen, % Calcd.	Found	Source
α-*p*-Bromophenyl-β-*p*-tolyl- $C_{14}H_{13}N_2SBr$	184	8.73	8.75 8.56	From *p*-bromo-aniline and *p*-tolyl isothiocyanate
α-*p*-Bromophenyl-β-α-naphthyl- $C_{17}H_{13}N_2SBr$	188	7.63	7.38 7.41	From *p*-bromophenyl isothiocyanate and α-naphthylamine
α,β-Di-*p*-xylyl-[3] $C_{17}H_{20}N_2S$	155	9.86	9.88	From *p*-xylidine and carbon disulfide
α-Phenyl-β-*p*-xylyl- $C_{15}H_{16}N_2S$	133	10.92	10.99 10.89	From phenyl isothiocyanate and *p*-xylidine and from aniline and *p*-xylyl isothiocyanate
α-*p*-Tolyl-β-*p*-xylyl- $C_{16}H_{18}N_2S$	140	10.37	10.32 10.38	From *p*-tolyl isothiocyanate and *p*-xylidine
α-*o*-Tolyl-β-*p*-xylyl- $C_{16}H_{18}N_2S$	139	10.37	10.35 10.52	From *o*-tolyl isothiocyanate and *p*-xylidine
Mono-*p*-xylyl-[3] $C_9H_{12}N_2S$-	141	15.52	15.42 15.52	From *p*-xylyl isothiocyanate and ammonia

[2] Knorr, *Ber.*, **22**, 2088 (1889). Markwald, *Ber.*, **34**, 3549 (1901). Knorr and Matthes, **31**, 1069 (1898). Liebermann, *Ber.*, **16**, 533 (1883). Gabriel and Stelzner, *Ber.*, **29**, 2382 (1896).

[3] Dyson and George, *J. Chem. Soc.*, **125**, 1705 (1924).

water and distilled with steam. The yield was 15 g. The same method was used in the preparation of the methyl and benzyl mustard oil, although in the latter case no solid sodium benzyl dithiocarbamate separated.

Disubstituted Thio-ureas, $RNHCSNHR'$.—The following thio-ureas, used in the later work in this paper and not listed in Richter's "Lexikon der Kohlenstoff-Verbindungen" were made by dissolving the components in ethyl alcohol and allowing the solution to stand at ordinary temperatures. The thio-ureas were purified by recrystallization from the same solvent.

Di-aryl-(aryl-alkyl)-ethanol-thio-ureas,[4] $RN(CH_2CH_2OH)CSNHR'$.—Thio-ureas of this type were readily formed by the action alone or in alcohol solution of alkyl-(aryl)-amino-ethanols upon aryl-(alkyl) isothiocyanates.

When the products were obtained as oils or gums no effort was made to purify them for analysis, but instead they were converted directly into the desired thiazolidines.

Diphenyl-ethanol-thio-urea, $C_6H_5N(CH_2CH_2OH)CSNHC_6H_5$.—Molecular proportions of the anilino-ethanol and phenyl isothiocyanate gave the thio-urea which crystallized from alcohol in white flakes; m. p., 108°.

Anal. Calcd. for $C_{15}H_{16}ON_2S$: N, 10.28. Found: 10.17, 10.10.

Reactions of Diphenyl-ethanol-thio-urea

In general, these reactions are typical of all corresponding thio-ureas.

1. Heated with halogen acids, the ring closed with the formation of diphenyl-thiazolidine, $SC(C_6H_5N)NC_6H_5CH_2CH_2$.

2. Phosgene or other acid chlorides brought about the same ring closure as in Reaction 1.

3. Heat alone caused the ring to close, although the reaction was not a smooth one. For instance, when a mixture of molecular *p*-tolyl isothiocyanate and *p*-tolylamino-ethanol was heated at 110° for seven hours, the

TABLE II

ETHANOL THIO-UREAS

	Derivatives of α-Ethanol-γ-β-R-R'-thio-urea $RNCH_2CH_2OH.CS.NHR'$	M. p. °C.	Nitrogen, % Calcd.	Found	Source
I	α-Phenyl-β-*p*-tolyl- $C_{16}H_{18}ON_2S$	101	9.79	9.88 9.67	Phenylamino-ethanol and *p*-tolyl isothiocyanate
II	α-*p*-Tolyl-β-phenyl- $C_{16}H_{18}ON_2S$	120	9.79	9.77 9.71	*p*-Tolylamino-ethanol and phenyl isothiocyanate
III	α,β-Di-*p*-tolyl- $C_{17}H_{22}ON_2S$	130	9.33	9.61	*p*-Tolylamino-ethanol and *p*-tolyl isothiocyanate
IV	α-Phenyl-β-*o*-tolyl- $C_{16}H_{18}ON_2S$	94	9.79	9.55	Phenylamino-ethanol and *o*-tolyl isothiocyanate
V	α-*p*-Tolyl-β-*o*-tolyl- $C_{17}H_{20}ON_2S$	Oil			*p*-Tolylamino-ethanol and *o*-tolyl isothiocyanate

[4] Ref. 1, p. 2369.

TABLE II (*Concluded*)

	Derivatives of α-Ethanol-γ-β-R-R′-thio-urea $RNCH_2CH_2OH.CS.NHR'$	M. p. °C.	Nitrogen, % Calcd.	Found	Source
VI	α-Phenyl-β-*o*-methoxyphenyl- $C_{16}H_{18}.O_2N_2S$	Oil			Phenylamino-ethanol and *o*-methoxyphenyl isothiocyanate
VII	α-*o*-Methoxyphenyl-β-phenyl- $C_{16}H_{18}O_2N_2S$	143	9.21	9.35	*o* - Methoxyphenylamino - ethanol and phenyl isothiocyanate
VIII	α-Phenyl-β,α-naphthyl-[a] $C_{19}H_{18}N_2OS$				Phenylamino-ethanol and α-naphthyl isothiocyanate
IX	α-*p*-Bromophenyl-β-phenyl- $C_{15}H_{15}ON_2SBr$	98	7.98	7.81 7.74	*p* - Bromophenylamino - ethanol and phenyl isothiocyanate
X	α-Phenyl-β-*p*-bromophenyl- $C_{15}H_{15}ON_2SBr$	131	7.98	7.88 7.74	Phenylamino-ethanol and *p*-bromophenyl isothiocyanate
XI	α-*p*-Tolyl-β-*p*-bromophenyl- $C_{16}H_{17}ON_2SBr$	137	7.67	7.70 7.81	*p*-Tolylamino-ethanol and *p*-bromophenyl isothiocyanate
XII	α-*p*-Bromophenyl-β-*p*-tolyl- $C_{16}H_{17}BrON_2S$	Oil			*p* - Bromophenylamino-ethanol and *p*-tolyl isothiocyanate
XIII	α-*p*-Bromophenyl-β,α-naphthyl- $C_{19}H_{17}BrON_2S$	60	6.98	6.79 6.83	*p* - Bromophenylamino-ethanol and α-naphthyl isothiocyanate
XIV	α,α-Naphthyl-β-*p*-bromophenyl- $C_{19}H_{17}BrN_2OS$	Oil			α - Naphthylamino-ethanol and *p* - bromophenyl isothiocyanate
XV	α-*p*-Bromophenyl-β-allyl- $C_{12}H_{15}BrN_2OS$	96	8.88	8.83	*p*-Bromophenylamino-ethanol and allyl isothiocyanate
XVI	α-*p*-Xylyl-β-*p*-tolyl- $C_{18}H_{22}N_2OS$	107	8.72	8.92 8.55	*p*-Xylylamino-ethanol and *p*-tolyl isothiocyanate
XVII	α-*p*-Xylyl-β-*o*-tolyl- $C_{18}H_{22}N_2OS$	Oil			*p*-Xylylamino-ethanol and *p*-tolyl isothiocyanate
XVIII	α-*p*-Xylyl-β-*p*-xylyl- $C_{18}H_{22}ON_2S$	Oil			*p*-Xylylamino-ethanol and *p*-xylyl isothiocyanate
XIX	α-Phenyl-β-methyl- $C_{10}H_{14}N_2OS$	69	13.34	13.39 13.00	Phenylamino-ethanol and methyl isothiocyanate
XX	α-Methyl-β-phenyl- $C_{10}H_{14}N_2OS$	95	13.34	13.47 13.60	Methylamino-ethanol and phenyl isothiocyanate
XXI	α-Ethyl-β-phenyl- $C_{11}H_{16}N_2OS$	152	12.50	12.62 12.74	Ethylamino-ethanol and phenyl isothiocyanate
XXII	α-Phenyl-β-ethyl- $C_{11}H_{16}N_2OS$	97	12.50	12.20	Phenylamino-ethanol and ethyl isothiocyanate
XXIII	α-Benzyl-β-phenyl- $C_{16}H_{18}N_2OS$	110	9.79	9.52	Benzylamino-ethanol and phenyl isothiocyanate
XXIV	α-Phenyl-β-benzyl- $C_{16}H_{18}N_2OS$	Oil			Phenylamino-ethanol and benzyl isothiocyanate

[a] Not isolated in pure condition.

reaction product contained di-*p*-tolyl-thiazolidine, di-*p*-tolyl-thio-urea and di-*p*-tolyl-urea.

4. When desulfurized in benzene solution with mercuric oxide, diphenyl-oxazolidine, $OC(NC_6H_5)NC_6H_5CH_2CH_2$, was formed.

5. Heated with lead hydroxide in alcohol solution with ammonia or aniline, the same oxazolidine resulted with no trace of the expected guanidine.

6. Ethylene chlorohydrin in potassium hydroxide solution on boiling acted as a desulfurizing agent and gave the diphenyl-oxazolidine.

Di-aryl(alkyl)-thiazolidines. $S—C(NR)NRCH_2CH_2$

These were formed by heating the corresponding ethanol-thio-ureas with hydrochloric acid until solution resulted and then precipitating the base with alkali. The thiazolidines are usually solids soluble in organic solvents, and were best purified by recrystallization from ethyl alcohol.

Compounds obtained as oils were easily identified by means of their picrates or perchlorates, which were prepared by dissolving the base in dil. hydrochloric acid, adding a water solution of picric or perchloric acid, and recrystallizing the salt from alcohol. The following table gives a list of these thiazolidines. Under the source is indicated the thio-urea from which they were made. The letters "E. d." indicate that they are

TABLE III

DI-ARYL-(ALKYL)-THIAZOLIDINES

	Derivatives of 2-R-imino-3-R'-thiazolidine $S—C(NR)NRCH_2CH_2$	M. p. °C.	Nitrogen, % Calcd.	Found	Source Ethanol disubstituted thio-ureas, $R(CH_2CH_2OH)NCSNHR'$
XXV	2-*p*-Tolyl-3-phenyl, $C_{16}H_{16}N_2S$[5]	113			I
XXVI	2-Phenyl-3-*p*-tolyl, $C_{16}H_{16}N_2S$[6]	127	10.44	10.39 10.42	II
XXVII	2,3-Di-*p*-tolyl, $C_{17}H_{18}N_2S$	110			II E. d.
XXVIII	2-*o*-Tolyl-3-*p*-tolyl, $C_{17}H_{18}N_2S$[7]	110	9.93	9.84 9.75	V
XXIX	2-Phenyl-3-*o*-methoxyphenyl, $C_{16}H_{16}ON_2S$[8]	144	9.86	9.55 9.75	VII
XXX	2-*o*-Methoxyphenyl-3-phenyl, $C_{16}H_{16}ON_2S$	103	9.86	9.84 9.90	VI
XXXI	2-*α*-Naphthyl-3-phenyl, $C_{19}H_{16}N_2S$[9]	130			VIII E. d.
XXXII	2-Phenyl-3-*p*-bromophenyl, $C_{15}H_{13}N_2SBr$	113	8.41	8.53 8.25	IX
XXXIII	2-*p*-Bromophenyl-3-phenyl, $C_{15}H_{13}N_2SBr$	112	8.41	8.62 8.64	X
XXXIV	2-*p*-Bromophenyl-3-*p*-tolyl, $C_{16}H_{15}N_2SBr$	97	8.07	7.96 8.11	XI

TABLE III (*Concluded*)

	Derivatives of 2-R-imino-3-R′-thiazolidine S—C(NR)NRCH₂CH₂	M. p. °C.	Nitrogen, % Calcd.	Found	Source Ethanol disubstituted thio-ureas, R(CH₂-CH₂OH)NCSNHR′
XXXV	2-*p*-Tolyl-3-*p*-bromophenyl, $C_{16}H_{15}N_2SBr$	145	8.07	8.20 8.28	XII E. d.
XXXVI	2-α-Naphthyl-3-*p*-bromophenyl, $C_{19}H_{15}N_2SBr$	127	7.28	7.04 7.11	XIII
XXXVII	2-*p*-Bromophenyl-3-α-naphthyl, $C_{18}H_{15}N_2SBr$	165	7.28	7.21	XIV E. d.
XXXVIII	Phenyl-*p*-xylyl-. Picrate, $C_{23}H_{21}O_7N_5S$	Oil[a] 159	13.38	13.25 13.33	Phenyl - *p* - tolyl-thio-urea and E. d.
XXXIX	2-*p*-Tolyl-3-xylyl, $C_{18}H_{20}N_2S$	112	9.46	9.56 9.37	XVI
XL	2-*p*-Xylyl-3-*p*-tolyl, $C_{18}H_{20}N_2S$	90	9.46	9.30 9.37	From *p* - tolyl - *p*-xylyl-thio - urea and E. d.
XLI	2-*o*-Tolyl-3-*p*-xylyl-. Picrate, $C_{24}H_{23}O_7N_5S$	179[a]	13.33	13.37 13.31	XVII
XLII	2-*p*-Xylyl-3-*o*-tolyl-. Picrate, $C_{24}H_{23}O_7N_5S$	147[a]	13.33	13.32 13.15	From *o* - tolyl - *p*-xylyl-thio - urea and E. d.
XLIII	2,3-Di-*p*-xylyl, $C_{19}H_{22}N_2S$	86	9.04	8.97 9.09	XVIII, di-xylyl-thio - urea and E. d.
XLIV	2,3-Di-*p*-xylyl-5-methyl-Picrate, $C_{26}H_{27}N_5O_7S$	151[a]	12.66	12.58 12.53	From dixylyl-thio-urea and propylene dibromide
XLV	2-Methyl-3-phenyl, $C_{10}H_{12}N_2S$	45	14.58	14.36 14.38	XIX E. d.
XLVI	2-Phenyl-3-methyl, $C_{10}H_{12}N_2S$	89	14.58	14.36 14.40	XX
XLVII	2-Phenyl-3-ethyl, oil $C_{11}H_{14}N_2S.HClO_4$	90[a]	9.10	8.75	XXI
XLVIII	2-Ethyl-3-phenyl, $C_{11}H_{14}N_2S.HClO_4$	42, 68	13.60	13.50 13.70	XXII E. d.
XLIX	2-Phenyl-3-benzyl, $C_{16}H_{16}N_2S$	100	10.45	10.60	XXIII
L	2-Benzyl-3-phenyl, $C_{16}H_{16}N_2S.HClO_4$[6]	85[a]	7.61	7.73	XXIV
LI	2-Phenyl, $C_9H_{10}N_2S$[10]				From α - phenyl-β - ethanol-thio-urea[11]

[a] Oil.

[5] Ref. 1, p. 2640.

[6] Kucera, *Monatsh.*, **35,** 153 (1914).

[7] Will and Bielschowski gave a melting point of 82°. *Ber.*, **15,** 1315 (1882).

[8] Foerster, *Ber.*, **21,** 1868 (1888).

[9] This synthesis confirms the work of Foerster, Ref. 7.

[10] Menne, *Ber.*, **33,** 659 (1900).

[11] Knorr and Rossler, *Ber.*, **36,** 1280 (1903)

also formed by the action of ethylene dibromide upon the thio-urea, RNHCSNHR′, containing the two groups shown in the first column.

The Action of Ethylene Dibromide on the α,β-Disubstituted Thio-ureas Where the Two Groups are Unlike

It is evident and has long been known that two possible isomers can be formed in this reaction: $RNHCSNHR' + C_2H_4Br_2 = SC(NR)NR'CH_2CH_2$ or $SC(NR')NRCH_2CH_2$.

The problem in question was whether the two groups exert any selective influence, so that one base would be formed in preference to the other.

The reactions were carried out by heating the thio-urea with an excess of ethylene dibromide at 110–130° for one-half to one hour, distilling the excess of dibromide with steam and precipitating the base formed with alkali. In nearly every case small amounts of mustard oils were formed, indicating the occurrence of side reactions other than thiazolidine synthesis. Table IV lists the results obtained. It should be noted in addition that in nearly every case some evidence was obtained of the second possible isomer, although not in amounts sufficient for accurate identification.

TABLE IV

Ethylene dibromide and RNHCSNHR′	Thiazolidine formed
Phenyl-*p*-tolyl	A mixture from which was isolated 2-phenyl-imino-3-*p*-tolyl. No. XXVI
Phenyl-*o*-tolyl	A mixture of bases
Phenyl-*o*-methoxyphenyl	2-Phenyl-3-*o*-methoxyphenyl. No. XXIX. This confirmed the earlier work of Foerster
Phenyl-α-naphthyl	Foerster isolated the two possible bases. Our synthesis of XXX was additional proof of the structure
Phenyl-*p*-bromophenyl	2-Phenylimino-3-*p*-bromophenyl. No. XXXII
p-Tolyl-*p*-bromophenyl	2-*p*-Tolylimino-3-*p*-bromophenyl. No. XXXV
α-Naphthyl-*p*-bromophenyl	2-*p*-Bromophenyl-3-α-naphthyl. No. XXXVII
Allyl-*p*-bromophenyl	No thiazolidine; only decomposition products
p-Xylyl-*p*-tolyl	2-*p*-Xylyl-*p*-tolyl. No. XL. Isomer of No. XXXIX
p-Xylyl-*p*-tolyl	2-*p*-Xylyl-3-*o*-tolyl. No. XLII. Isomer of No. XLI
Benzyl-phenyl	2-Benzyl-3-phenyl. No. L
Methyl-phenyl	A dithio-ethylene ether and, at higher temperatures, 2-methyl-3-phenyl-thiazolidine
Ethyl-phenyl	A dithio-ethylene ether and, at higher temperatures, the 2-ethyl-3-phenyl-thiazolidine

Discussion of Results

A thio-urea of the type used could react in the two enol forms, (I) RNHC(SH)NR′ and (II) RNHC(SH)NHR′.

It is probable that where the two groups R and R′ are nearly alike, approximate amounts of the two enol forms I and II will be present and

a nearly equimolecular mixture of thiazolidines will be formed. Such seemed to be the case. However, when the group R′ was more positive than group R, the experimental evidence pointed to an increase in the enol form I, which then gave with ethylene dibromide a larger amount of thiazolidine with R′ at Position 2. $SC(NR')NRCH_2CH_2$. This was especially noticeable where R′, which might be either phenyl or *p*-tolyl, was compared to R, which was in this case an *o*-anisidyl or *p*-bromophenyl group and where benzyl occurred with a phenyl group in the same thio-urea.

The case was accentuated with methyl-phenyl-thio-urea and ethyl-phenyl-thio-urea where at 110° the ethylene dibromide reacted with two molecular equivalents of the thio-urea giving a dithio-ethylene ether, while at higher temperatures (140–150°), ring closure occurred with the formation of the 2-methyl-(or 2-ethyl)-3-phenyl-thiazolidine.

Action of Ethylene Dibromide on Monophenyl-thio-urea and α-Alkyl-β-phenyl-thio-ureas.—The results showed the increased reactivity of the enol (SH) form, since that group alone combined with the dibromide at 110°, yielding dithio ethers with no evidence of thiazolidine formation.

Monophenyl-thio-urea.—The γ-ethylene ether of the monophenyl-thio-urea, $C_6H_5NHC(NH)SCH_2CH_2S(NH)NHC_6H_5$,[12] was heated at 125° with aniline to displace ammonia if possible and form a tetraphenyl derivative. Instead, while ammonia was actually replaced by the aniline group, the thio-ethylene bonding was also broken, with the formation of diphenyl-thiazolidine (m. p., 136°).

The following dithio-ethylene ethers resulted when the alkylphenyl-thio-ureas were heated with ethylene dibromide at 110° for two hours.

TABLE V

DI-THIO-ETHYLENE ETHERS

Ethylene ether of R-R′-thio-urea $RNH(NR')SCH_2$	M. p. °C.	Nitrogen, % Calcd.	Found	From ethylene dibromide and the alkyl-aryl thio-ureas
Phenyl-methyl-	139	15.60	15.28	Phenyl-methyl-thio-urea
$C_{18}H_{22}N_4S_2$	213			*Mol. wt.* Calcd.: 356. Found: 355, 350
HBr salt				
Phenyl-ethyl-	130	14.50	14.20	Phenyl-ethyl-thio-urea
$C_{20}H_{26}N_4S_2$				*Mol. wt.* Calcd.: 386. Found: 370
HBr salt[13]	196			
Perchlorate	160			
Phenyl-*n*-butyl-	92	12.67	12.45	Phenyl-*n*-butyl-thio-urea
$C_{24}H_{34}N_4S_2$				
Propylene ether of phenyl-methyl-	120	15.01	15.16	From propylene dibromide and phenyl-methyl-thio-urea
$C_{19}H_{24}N_4S$	195			
HBr salt				

[12] Bertram, *Ber.*, **25**, 59 (1892).

[13] Ref. 6, p. 150.

In the case of phenyl-methyl-thio-urea and ethylene and propylene dibromide, the hydrobromide separated from the reaction mixture and could be obtained in a pure form by simply washing with chloroform.

To obtain the free base, this salt was dissolved in water and made alkaline with ammonium hydroxide. When the hydrobromic acid salt did not separate on cooling, the excess of ethylene dibromide was distilled with steam and the filtered solution from the flask made alkaline, thus freeing the base.

Oxazolidine Formation

In the earlier part of this paper, it was shown that one of the characteristic reactions of the ethanol-thio-ureas was their ready conversion into the corresponding oxazolidines, which were prepared by heating the ethanol thio-ureas with an excess of yellow mercuric oxide until desulfurization was complete. The solution, filtered from the mercuric sulfide, was evaporated and the base purified by recrystallization from benzene or alcohol.

The following derivatives illustrate this property and further identify these thio-ureas.

TABLE VI

DI-ARYL-OXAZOLIDINES

2,3-Diaryl-oxazolidines $OC(NR)NR'CH_2CH_2$	M. p. °C.	Nitrogen, % Calcd.	Found	Source
2,3-Diphenyl, $C_{15}H_{14}ON_2$	124	11.77	11.89	From the diphenyl-ethanol-thio-urea with m. o.[a] or with ethylene chlorohydrin
Di-*p*-tolyl, $C_{17}H_{18}ON_2$	136	10.35	10.25	From III and m. o.
2-Phenyl-3-*p*-bromophenyl, $C_{15}H_{13}ON_2Br$	149	8.83	8.94 8.79	From IX and m. o.
2-*p*-Bromophenyl-3-phenyl, $C_{15}H_{13}ON_2Br$	138	8.83	8.97 8.74	From X and m. o.
2-*p*-Bromophenyl-3-*p*-tolyl, $C_{16}H_{15}ON_2Br$	108	8.72	8.50 8.57	From XI and m. o.

[a] M. o. = mercuric oxide.

Summary

1. A study has been made of the synthesis of the disubstituted ethanol thio-ureas and their reactions.

2. These ethanol-thio-ureas have been converted into oxazolidines and thiazolidines of known structure.

3. The action of ethylene dibromide upon α,β-disubstituted thio-ureas has shown that the groups of the thio-urea tend to exert a selective action, the more positive group going to Position 2 of the resulting thiazolidine.

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