resulting semisolid was dissolved in water containing a small quantity of hydrochloric acid and extracted 3 times with ether. Evaporation of the ether extract gave 100 g. of a heavy oil (60% yield). A benzene solution of the oil was chromatographed twice on alumina and the solution evaporated to an oil to a constant micro melting point of 62.7 to 63.5°. The over-all yield of purified material was 44 g. (29%). The ultraviolet spectrum showed a λ_{max} of 245 and an ϵ_{max} of 11,680.

Anal. Calcd. for $C_{17}H_{19}NOS$: C, 71.57; H, 6.66; N, 4.91. Found: C, 71.73; H, 6.52; N, 5.10.

n-Butyl-N-p-methoxyphenyl thiolcarbamate. This compound was prepared by the same procedure as that used for *n*-butyl thiolcarbanilate.[3] The product, micro melting point 62.5–63°, was obtained in a yield of 100%. After recrystallization from petroleum ether the micro melting point was 64.0°.

Anal. Calcd. for $C_{12}H_{17}NO_2S$: C, 60.25; H, 7.11; N, 5.86. Found: 59.98; H, 7.29; N, 5.90.

Acknowledgment. The authors are grateful to Dr. H. Kwart for helpful discussions and suggestions and to Dr. H. K. Hall, Jr., for samples of amines.

NEWARK, DEL.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION OF G. D. SEARLE & CO.]

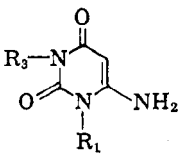
Peroxide Desulfurization of Thioureas

MAX J. KALM

Received November 2, 1960

Investigation of the hydrogen peroxide desulfurization of thioureas to the corresponding ureas has led to a convenient method for synthesizing intermediates which lead to physiologically active uracils. The method has been extended to the synthesis of 5-ureidouracils. Some of the limitations of the reaction are discussed.

The preparation of a variety of 1,3-disubstituted 6-aminouracils[1] and the discovery of their usefulness as oral diuretic agents[2] has led to further studies in the synthesis of uracil derivatives. New synthetic routes to the oral diuretic agents Mincard[3] (I) and Rolicton[3] (II) were investigated as well as to other uracil derivatives which might prove to be more potent diuretic agents.



I. $R_1 = CH_2{=}CH{-}CH_2{-}$; $R_3 = C_2H_5{-}$
II. $R_1 = CH_2{=}C(CH_3){-}CH_2{-}$; $R_3 = CH_3{-}$

The syntheses of Mincard[3] and Rolicton[3] from urea and cyanoacetic acid followed by alkaline cyclization has been described in detail[1] and these steps give good yields of the desired products. The preparation of the starting ureas was reinvestigated because the starting material in the preparation of Rolicton,[3] *N*-2-methylallyl-*N'*-methylurea, is most readily prepared from 2-methylallylamine, a substance which is not readily available in commercial quantities.

As the corresponding thiourea can be readily prepared by reaction of 2-methyallyl chloride with an alkali thiocyanate followed by condensation of the resultant isothiocyanate with an amine,[4] the conversion of thioureas to ureas was now thoroughly investigated.

There are several methods in the literature for the conversion of thioureas to the correspondig urea. Oxidizing agents which have been employed successfully are alkali bromates and iodates,[5] benzoperoxide,[6] and sodium peroxide,[7] or alkaline hydrogen peroxide.[8] The last two reagents seemed to give the best yields and their use involved mild conditions. It seemed most logical therefore to investigate the peroxide desulfurization of 2-methylallylthiourea and *N*-2-methylallyl-*N'*-methylthiourea.

Although it has been reported that the alkali peroxides are not as good reagents as alkaline hydrogen peroxide for the conversion of thioureas to ureas,[8] it was shown in the case of the above thioureas that both reagents gave about the same yield of comparable quality urea. The alkaline hydrogen peroxide method was found preferable only because the handling of large quantities of

(1) V. Papesch and E. F. Schroeder, *J. Org. Chem.*, **16**, 1879 (1951).

(2) C. G. Van Arman and H. R. Dettelbach, *Fed. Proc.*, **14**, 392 (1955); R. V. Ford *et al.*, *Am. J. Med. Sci.*, **234**, 640 (1957); N. I. Nissen and B. Zachau-Christiansen, *Acta Med. Scandinav.*, **160**, 385 (1958); C. M. Kagawa and C. G. Van Arman, *J. Pharm. and Exptl. Therap.*, **129**, 343 (1960); and C. G. Van Arman, H. R. Dettelbach, and C. M. Kagawa, *Arch. Int. Pharmacodyn.*, **CXXVI**, 400 (1960).

(3) Registered trademark.

(4) N. E. Searle, U. S. Pat. **2,462,433**, February 22, 1949.

(5) H. H. Capps and W. M. Dehn, *J. Am. Chem. Soc.*, **54**, 4301 (1932).

(6) L. Vanino and A. Schinner, *Ber.*, **47**, 699 (1914).

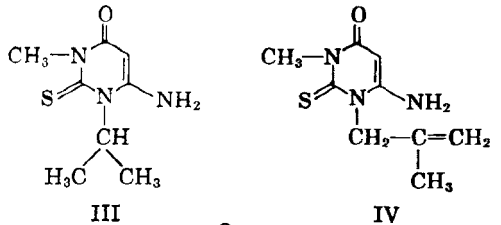
(7) R. T. C. Loh and W. M. Dehn, *J. Am. Chem. Soc.*, **48**, 2956 (1926).

(8) R. Kitamura, *J. Pharm. Soc. Japan*, **54**, 1 (1954); **55**, 300 (1955).

sodium peroxide provided problems not encountered with hydrogen peroxide.

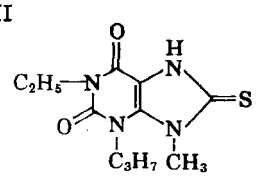
One problem which required solution before the desulfurization could be adapted to large scale processes involved the isolation of the urea from the reaction mixture. Initially, the product was isolated by first removing the water by distillation, and then extracting the solids with acetone leaving the inorganic salts as a residue. This method of isolation is not suited for production equipment and the product was always contaminated with a small amount of impurity, which seemed to be an oxidation product of the urea, probably resulting from oxidation of the double bond in the methyallyl side chain. The solution to this problem was to reduce the quantity of water used in the desulfurization, making possible the extraction of the product with chloroform. This method of work-up also provided a purer product since the oxygenated impurity was not extracted by the solvent.

In an attempt to extend this reaction to compounds containing the thiourea moiety in a ring, 1 - isopropyl - 3 - methyl - 6 - amino - 2 - thiouracil[9,10] (III), 1-(2-methylallyl)-3-methyl-6-amino-2-thiouracil (IV), and 1-propyl-3-ethyl-9-methyl-8-thioxanthine[10] (V) were subjected to alkaline hydrogen peroxide desulfurization. In each case the bulk of the material used underwent extensive decomposition during the course of the reaction. This was evidenced by solubilization of the material in water and by the isolation of only small amounts of sulfur containing product.



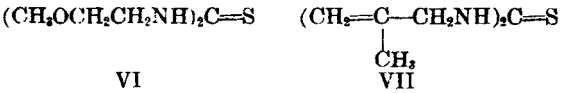
III

IV

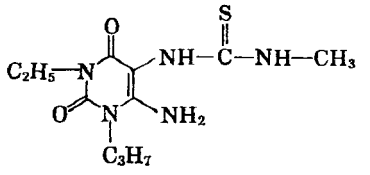


V

Two other simple thioureas which were readily converted to the corresponding ureas were *N,N'*-bis(2-methoxyethyl)thiourea[11] (VI) and *N,N'*-bis(2-methylallyl)thiourea (VII). A third urea which was successfully desulfurized was 1-propyl-3-ethyl-5-methylthioureido-6-aminouracil[10] (VIII). This compound, although containing the uracil structure, was not destroyed by alkaline hydrogen peroxide. The thiocarbonyl in this compound is not a part of the ring and the decomposition observed with the thiouracils III and IV was not noted in this case.

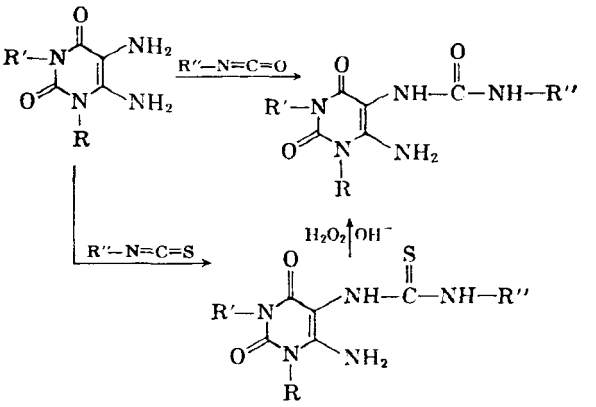


VI VII



VIII

The desulfurization of the thioureidouracil VIII provided an easy method for the preparation of ureido substituted uracils which are not readily prepared otherwise. The preparation of such thioureidouracils from a diaminouracil and an isothiocyanate has been described previously.[12] The ureidouracils can of course be prepared by direct reaction of a diaminouracil and an isocyanate but the new method provides a novel alternate method especially in cases where the isocyanate is difficult to prepare or is unstable. The two methods for preparing the 5-ureido-6-aminouracils are shown:



A large variety of 5-ureido derivatives of I and II were prepared using the synthetic schemes shown above. The thiourea intermediates which were prepared for this purpose are shown in Table I, while the ureido derivatives are shown in Tables II and III

The unsubstituted urea of the series of compounds shown in Table II was also prepared, using the reaction between a diaminouracil and potassium isocyanate in the presence of mineral acid.[13,14]

All the compounds discussed were submitted for screening in a wide variety of biological tests. Surprisingly, the 5-ureidouracils were devoid of the diuretic activity which provided the usefulness for the 5-unsubstituted compounds. Several of

(9) V. Papesch and E. F. Schroeder, U. S. Pat. 2,615,020, October 21, 1952.

(10) These compounds were synthesized by Dr. E. F. Schroeder of these laboratories.

(11) Supplied by the Stauffer Chemical Company.

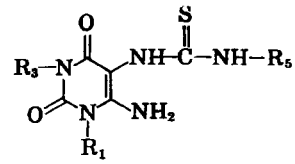
(12) F. F. Blicke and R. L. Schaaf, *J. Am. Chem. Soc.*, 78, 5857 (1956).

(13) E. Fisher, *Ber.*, 30, 559 (1897).

(14) K. Sembritzki, *Ber.*, 30, 1814 (1897).

TABLE I

1,3-DISUBSTITUTED 5-THIOUREIDO-6-AMINOURACILS

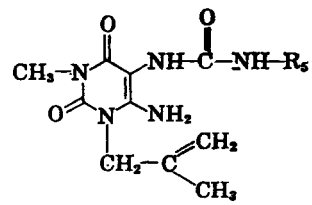


No.	R_5	Formula	M.P.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
	A. 1-(2-Methylallyl)-3-methyl-5-thioureido-6-aminouracils (R_1 = CH_2=C(CH$_3$)–CH_2–; R_3 = CH_3–)							
IX	$(CH_3)_2CH$–	$C_{12}H_{21}N_5O_2S$	[a]	51.3	22.49	21.99	10.29	10.19
X	CH_2=CH–CH_2–	$C_{13}H_{19}N_5O_2S$	206–207	87.0	22.64	22.64	10.36	10.35
XI	C_4H_9–	$C_{14}H_{23}N_5O_2S$	209–210	83.7	21.52	21.42	9.85	10.03
XII	CH_2=C(CH$_3$)–CH_2–	$C_{14}H_{21}N_5O_2S$	193–194	66.2	21.66	21.63	9.91	10.05
	B. 1-Allyl-3-ethyl-5-thioureido-6-aminouracils (R_1 = CH_2=CH–CH_2–; R_3 = C_2H_5–)							
XIII	CH_3–	$C_{11}H_{17}N_5O_2S$	205–206	95.0	24.72	24.42	11.32	11.47
XIV	C_4H_9–	$C_{14}H_{23}N_5O_2S$	197.5–198.5	80.2	21.52	21.48	9.85	9.95
XV	CH_2=C(CH$_3$)–CH_2–	$C_{14}H_{21}N_5O_2S$	198–199.5	80.0	21.66	21.59	9.91	10.08

[a] M.p. greater than 200°. Product cyclizes on melting.

TABLE II

1-(2-METHYLALLYL)-3-METHYL-5-UREIDO-6-AMINOURACILS



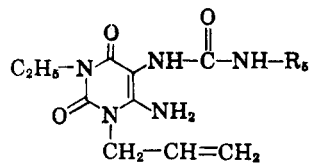
No.	R_5	Formula	M.P.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
XVI	CH_3–	$C_{11}H_{17}N_5O_3$	211–212.5	16.2[a]					26.20	25.92
XVII	C_2H_5–	$C_{12}H_{19}N_5O_3$	212–214	75.5[b]	51.23	50.95	6.81	6.75	24.90	24.62
XVIII	$(CH_3)_2CH$–	$C_{13}H_{21}N_5O_3$	>260	64.8[a]	52.86	52.65	7.17	7.73	23.72	23.60
XIX	CH_2=CH–CH_2–	$C_{13}H_{19}N_5O_3$	189–191	27.1[a]					23.88	23.92
XX	C_4H_9–	$C_{14}H_{23}N_5O_3$	174.5–176.5	46.4[a]	54.35	54.58	7.49	7.62	22.64	22.51
XXI	CH_2=C(CH$_3$)–CH_2–	$C_{14}H_{21}N_5O_3$	192–193	60.7[a]	54.71	54.64	6.89	7.11	22.79	22.60
XXII	C_5H_{11}–	$C_{15}H_{25}N_5O_3$	182–183	78.8[b]	55.71	55.33	7.79	7.80	21.66	22.02
XXIII	C_7H_{15}–	$C_{17}H_{29}N_5O_3$	175–176	85.4[b]					19.93	19.89
XXIV	C_6H_5–	$C_{16}H_{19}N_5O_3$	234–236	95.0[b]	58.34	58.32	5.81	6.14	21.27	21.21

[a] Prepared by desulfurization of the corresponding thiourea. [b] Prepared by reaction of the 5,6-diaminouracil with an isocyanate.

the substances showed good appetite inhibition activity and this activity was not due to emetic properties of the compounds. Several of the compounds tested affected blood pressure when administered intravenously but there was no consistency in this blood pressure effect as some exhibited hypotensive activity while others were hypertensive agents.

TABLE III

1-ALLYL-3-ETHYL-5-UREIDO-6-AMINOURACILS



No.	R_5	Formula	M.P.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
XXV	CH_3—	$C_{11}H_{17}N_5O_3$	209–210	13.6[b]	49.43	49.38	6.41	6.38	26.20	26.10
XXVI	C_2H_5—	$C_{12}H_{19}N_5O_3$	199–199.5	82.4[c]	51.23	51.45	6.81	6.85		
XXVII	$(CH_3)_2CH$—	$C_{13}H_{21}N_5O_3$	~209[a]	28.6[b]	52.86	52.65	7.17	6.87	23.72	23.49
XXVIII	C_4H_9—	$C_{14}H_{23}N_5O_3$	181–184	75.3[b]	54.35	54.61	7.49	7.64		
XXIX	C_5H_{11}—	$C_{15}H_{25}N_5O_3$	179–180.5	82.1[c]	55.71	55.84	7.79	8.07	21.66	21.72
XXX	C_7H_{15}—	$C_{17}H_{29}N_5O_3$	146.5–148.5	86.3[c]	58.09	57.95	8.32	8.31	19.93	19.84

[a] Compound cyclizes on melting forming higher melting xanthine. [b] Prepared by desulfurization of the corresponding thiourea. [c] Prepared by reaction of the 5,6-diaminouracil with an isocyanate.

EXPERIMENTAL[15]

Alkyl and alkenyl isothiocyanates. The methyl, allyl, *n*-butyl, and 2-methylallyl esters were purchased. The isopropyl ester was prepared in 70% yield by a known method.[16]

Alkyl isocyanates. The ethyl ester was purchased. The *n*-amyl and *n*-heptyl esters were prepared by a known procedure[17] in yields of 52.5% and 72%, respectively. The *n*-amyl isocyanate had b.p. 86–87° (140 mm.) and the *n*-heptyl isocyanate had b.p. 99–103° (48 mm.).

Substituted thioureas. The thioureas were prepared by known procedures,[4,18,19] some being used for the conversion to the corresponding ureas without complete characterization. The thioureas thus prepared were 2-methylallylthiourea,[4,19] *N*-2-methylallyl-*N'*-methylthiourea and *N,N'*-bis-(2-methylallyl)thiourea (VII) in yields of 66.2%, 90%, and 92% respectively

The *N-2-methylallyl-N'-methylthiourea* had m.p. 63–64°.

Anal. Calcd. for $C_6H_{12}N_2S$: N, 19.43; S, 22.23. Found: N, 19.10; S, 22.40.

1-(2-Methylallyl)-3-methyl-6-amino-2-thiouracil (IV). A solution of 45 g. (0.313 mole) of *N*-2-methylallyl-*N'*-methylthiourea, 40.3 g. (0.469 mole) of cyanoacetic acid, and 35.5 ml. (0.375 mole) of glacial acetic acid was heated at 50–55° for 2 hr. To the resulting red solution was slowly added 195 ml. of water and the water–acetic acid mixture was stripped of solvents at reduced pressure. An additional 100 ml. of water was added to the residue and this was again removed at reduced pressure. The residue was treated with 258 ml. of water and sufficient solid sodium carbonate to make the mixture alkaline. After warming at 80° for several minutes sufficient methanol was added to solubilize the product and this solution was treated with Darco G-60. Following removal of the Darco the methanol was removed by distillation and the residue was set aside for crystallization. Recrystallization from 95% ethanol gave 12.2 g. (18.5%) of *1-(2-methylallyl)-3-methyl-6-amino-2-thiouracil* (IV) as a light yellow solid with m.p. 212.5–213.5°.

Anal. Calcd. for $C_9H_{13}N_3OS$: N, 19.89; S, 15.18. Found: N, 19.80; S, 15.08.

Substituted ureas. The desulfurization of the substituted thioureas was carried out with both sodium peroxide and alkaline hydrogen peroxide.

1. *Sodium peroxide desulfurization.* To a stirred mixture of 0.08 mole of the thiourea and 100 ml. of water is added 0.32 mole of sodium peroxide in 0.5 g. portions at 3-min. intervals. The internal temperature increases as addition proceeds. On completion of the addition the mixture is heated on a steam bath for several minutes and is then allowed to cool to room temperature. Dilute sulfuric acid is used to neutralize the solution which is then evaporated to dryness. The residue is extracted with several portions of acetone and the extracts are evaporated to yield the desired urea.

2. *Hydrogen peroxide desulfurization. Method A.* To a mixture of 0.15 mole of thiourea and 0.3 mole of sodium hydroxide in 120 ml. of water at 40° is added, dropwise, 0.6 mole of 30% aqueous hydrogen peroxide. The internal temperature is maintained at 40–45° by external cooling. On completion of the addition the mixture is briefly heated to 80° and on cooling to room temperature it is neutralized with dilute sulfuric acid. After evaporation to dryness the residue is extracted with several portions of acetone and removal of the acetone yields the desired urea.

Method B. To a mixture of 0.15 mole of thiourea and 0.3 mole of sodium hydroxide in 50 ml. of water is added, dropwise, 0.6 mole of 35% hydrogen peroxide. An internal temperature of 45–55° is maintained by external cooling. Excess hydrogen peroxide is destroyed by addition of solid sodium bisulfite and sufficient sodium hydroxide is added to maintain a *p*H of 8–9. The product is then extracted with several portions of chloroform. Evaporation of the solvent yields the desired urea.

2-Methylallylurea. Using sodium peroxide, this urea was obtained in 88% yield, the product having m.p. 105–115°.

Anal. Calcd. for $C_5H_{10}N_2O$: N, 24.55. Found: N, 24.85.

N-2-Methylallyl-N'-methylurea. Using hydrogen peroxide Method B, this urea was obtained in 70–98% yields, the product having m.p. 64.5–65.5°.

Anal. Calcd. for $C_6H_{12}N_2O$: C, 56.22; H, 9.44; N, 21.86. Found: C, 56.29; H, 9.61; N, 21.80.

N,N'-Bis(2-methylallyl)urea. Using hydrogen peroxide Method B, this urea was obtained in 89% yield, the product having m.p. 120–122°.

Anal. Calcd. for $C_9H_{16}N_2O$: N, 16.65. Found: N, 16.50.

N,N'-Bis(2-methoxyethyl)urea. Using hydrogen peroxide

(15) In most instances, no attempt was made to obtain maximum yields in these syntheses. The yields reported in this section and in Tables I to IV constitute, for the most part, results from a single experiment. All melting points are uncorrected.

(16) M. L. Moore and F. S. Crossley, *Org. Syntheses*, **21**, 81 (1941).

(17) C. F. H. Allen and A. Bell, *Org. Syntheses*, **24**, 94 (1944).

(18) T. O. Otterbacher and F. C. Whitmore, *J. Am. Chem. Soc.*, **51**, 1909 (1929).

(19) H. A. Bruson and J. W. Eastes, *J. Am. Chem. Soc.*, **59**, 2011 (1937).

Method A, this urea was obtained in 97% yield, the product having m.p. 57–61°.

Anal. Calcd. for $C_7H_{16}N_2O_3$: N, 15.90. Found: N, 15.48.

1,3-Disubstituted 5,6-diaminouracils were prepared by the procedure of Blicke and Godt[20] except that the nitrosation was carried out at 85°.

1-(2-Methylallyl)-3-methyl-5,6-diaminouracil was obtained in 48.6% yield and had m.p. 149–153°.

Anal. Calcd. for $C_9H_{14}N_4O_2$: C, 51.42; H, 6.71; N, 26.65. Found: C, 51.62; H, 6.64; N, 26.52.

1-Allyl-3-ethyl-5,6-diaminouracil was obtained in 40.2% yield and had m.p. 138.5–141.5°.

Anal. Calcd. for $C_9H_{14}N_4O_2$: N, 26.65. Found: N, 26.52.

General procedure for the preparation of 1,3-disubstituted 5-thioureido-6-aminouracils. To a solution of 0.1 mole of the appropriate 1,3-disubstituted 5,6-diaminouracil in 100 ml. of chloroform is added 0.1 mole of the desired isothiocyanate. When the exothermic reaction has subsided the solution is heated under reflux for 1 hr. The product may precipitate during heating, or cooling in an ice bath may be necessary to effect crystallization. The thioureido derivatives can be recrystallized from 95% ethanol. Compound IX to XV were prepared by this procedure and the physical properties, yields, and analytical data are shown in Table I.

General procedure for the preparation of 1,3-disubstituted 5-ureido-6-aminouracils. A. *By desulfurization of the thiourea.* The appropriate 1,3-disubstituted 5-thioureido-6-aminouracil (0.03 mole) is suspended in 0.06 mole of sodium hydroxide in 100 ml. of water and the mixture is heated to 40°. There is added, dropwise, 0.12 mole of 30% hydrogen peroxide and on completion of addition, which is exothermic, the mixture is heated at 75–80° for several minutes. On cooling, the product is removed by filtration and the urea may be recrystallized from either 95% ethanol or chloroform and benzene. Compounds XVI, XVIII to XXI, XXV, XXVII, and XXVIII were prepared in this manner and the physical properties, yields, and analytical data are shown in Tables II and III.

(20) F. F. Blicke and H. C. Godt, Jr., *J. Am. Chem. Soc.*, **76**, 2798 (1954).

B. *By reaction of an isocyanate and a diaminouracil.* To a solution of 0.024 mole of the appropriate 1,3-disubstituted 5,6-diaminouracil in 50 ml. of chloroform is added 0.024 mole of the desired isocyanate. On completion of the exothermic reaction the solution is heated under reflux for 30 min. Some benzene is added to induce crystallization and the product is recrystallized from either 95% ethanol or chloroform and benzene. Compounds XVII, XXII to XXIV, XXVI, XXIX, and XXX were prepared in this manner, and the physical properties, yields, and analytical data are shown in Tables II and III.

1-(2-Methylallyl)-3-methyl-5-ureido-6-aminouracil. To a solution of 10 g. (0.0476 mole) of 1-(2-methylallyl)-3-methyl-5,6-diaminouracil in 4.24 ml. (0.0476 mole) of concd. hydrochloric acid diluted with 44 ml. of water was added 7.72 g. (0.0952 mole) of potassium cyanate. A vigorous exothermic reaction ensued accompanied by precipitation of the product. The mixture was stirred for 1 hr. followed by filtration of the product and washing with water. The yield of urea was 10 g. (82.5%). It was impossible to determine the melting point of the product since it ring closes on heating. Recrystallization also proved impossible due to insolubility of the material. The spectral data were consistent with the proposed structure.

Anal. Calcd. for $C_{10}H_{15}N_5O_3$: N, 27.66. Found: N, 27.19.

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CHICAGO 80, ILL.

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Oxidation of Alkylbenzenes with Sulfur and Water

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It has been found that sulfur and water will oxidize the methylbenzenes to their respective carboxylic acids by heating to 200° to 400° under autogenous pressure. Mixing of all three components at reaction temperature minimizes side reactions. Sulfur dioxide and sulfuric acid will also function, if initiated with small amounts of hydrogen sulfide. The reactions with sulfur and water are reversible. Intermediate sulfur compounds can be isolated in most cases. By control of conditions, *o*-xylene can be made to yield thiophthalide, an intermediate, as the major product. Some of the theoretical implications are considered.

The use of sulfur, water, and a base, such as caustic or ammonia, as an oxidizing agent for organic compounds has been studied and reported previously.[1] Other forms of sulfur, such as sulfite, thiosulfate, and sulfate triggered by hydrogen sulfide function similarly.[2] Products are carboxylic salts. If ammonia is the base used, amides are also produced. Sulfuric or other mineral acid is required to liberate the free carboxylic acids.

Current studies show that with the methylbenzenes sulfur and water can be used as the oxidant and a base is not required. The free carboxylic acids are obtained directly, according to the reaction:

$$C_6H_5CH_3 + 3\,S + 2\,H_2O \longrightarrow C_6H_5CO_2H + 3\,H_2S \quad (1)$$

Yields of about 85% can be obtained with complete

(1) W. G. Toland, Jr., D. L. Hagmann, J. B. Wilkes, and F. J. Brutschy, *J. Am. Chem. Soc.*, **80**, 5423 (1958).

(2) W. G. Toland, *J. Am. Chem. Soc.*, **82**, 1911 (1960).