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Manganese Dioxide Oxidation of Thioureas

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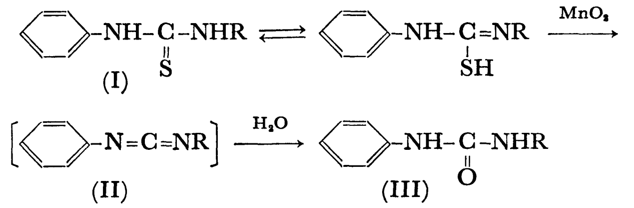
Synopsis. Manganese dioxide oxidation of thioureas in chloroform at room temperature gave the corresponding ureas.

The oxidation of thiourea and its derivatives has received wide attention due to its potential importance in the biological activity of these compounds. The oxidation of these compounds is reported to give rise to a variety of products, depending upon the nature of the oxidant and the reaction conditions. Thus, thiourea and its alkyl and aryl derivatives have been oxidized to the corresponding disulfide with potassium bromate in sulfuric acid medium,[1] whereas *N,N'*-dialkylthioureas are readily oxidized to the corresponding carbodiimides by alkaline hypochlorites.[2] Carbodiimides have also been prepared by the desulfurization of *N,N'*-disubstituted thioureas with various metal oxides such as mercury(II) oxide,[3] lead oxide,[4,5] and arsenic oxide.[6] However, thiourea, when oxidized with potassium permanganate, gave urea.[7] In the oxidation of thioureas with bromine or thionyl chloride, bis(*N*-substituted amidino) disulfides were isolated as hydrobromide salts.[8–13]

In this laboratory we have oxidized thioureas to ureas by manganese dioxide, a very mild and selective reagent. The reactions have been completed at room temperature by shaking a mixture of the oxidant and the substrate in chloroform. In every case, the corresponding urea has been obtained as the end product, identified by its melting point, elemental analysis, and IR spectrum. The IR spectra of these compounds showed intense absorption in the 1655—1670 cm^{-1} region due to carbonyl stretching.



(a) R=H (b) R=C_6H_5
(c) R=$C_6H_4CH_3(p\text{-})$ (d) R=$C_6H_4Cl(p\text{-})$
(e) R=$C_6H_4OCH_3(p\text{-})$ (f) R=$C_6H_4Cl(m\text{-})$

A probable mechanism for this reaction may involve the initial formation of carbodiimide(II) which reacts with water, under the experimental conditions, to afford the corresponding urea (III).

Experimental

Starting Materials. Active manganese dioxide was prepard from manganese sulfate dihydrate and potassium permanganate according to the literature method.[14] All thioureas were prepared by mixing phenyl isothiocyanate and corresponding anilines in molecular ratio in ethanol and heating the mixture.

Oxidation of Phenylthiourea. A mixture of phenylthiourea (2 g), manganese dioxide (10 g) and chloroform (150 ml) was shaken at room temperature for 5 h. The mixture was filtered and the oxide was washed with chloroform. The combined filtrate and washings were evaporated to afford a residue (1.1 g), which on crystallization from benzene gave colorless crystals of phenylurea (IIIa), mp 148 °C (lit,[15] mp 147 °C). (Found: C, 61.7; H, 5.8; N, 20.4%. Calcd for $C_7H_8N_2O$: C, 61.8; H, 5.9; N, 20.6%). λ_{max} (KBr); 3435, 3315, 1670, 1625, 1605, 1565, 1507, 1460, 1365, 1295, 1265, 755, and 705 cm^{-1}.

The other products of this series obtained similarly are listed in Table 1. These compounds have been crystallized from benzene.

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References

1) B. Singh, B. Chand, and M. S. Saran, *Bull. Chem. Soc. Jpn.*, **38**, 43 (1965).
2) E. Schmidt, M. Seefelder, R. S. Jennen, W. Striewsky, and M. Von Martius, *Ann.*, **571**, 83 (1951).
3) W. Weith, *Ber.*, **6**, 1389 (1873).
4) I. W. Herzog, *Z. Angew. Chem.*, **33**, 140 (1940).

Table 1. Various ureas obtained

Compound No	Mp °C	Yield %	Formula		C%	H%	N%
IIIb	236 (lit,[16] mp 237—237.5)	65	$C_{13}H_{12}N_2O$	Calcd	73.6	5.6	13.2
				Found	73.4	5.6	13.1
IIIc	217 (lit,[17] mp 218)	62	$C_{14}H_{14}N_2O$	Calcd	74.3	6.2	12.4
				Found	74.2	6.0	12.2
IIId	237 (lit,[18] mp 237—238)	64	$C_{13}H_{11}N_2OCl$	Calcd	63.5	4.4	11.3
				Found	63.3	4.4	11.1
IIIe	190 (lit,[19] mp 186—190)	70	$C_{14}H_{14}N_2O_2$	Calcd	69.4	5.8	11.6
				Found	69.3	5.6	11.3
IIIf	184 (lit,[20] mp 183—184)	68	$C_{13}H_{11}N_2OCl$	Calcd	—	—	11.3
				Found	—	—	11.0

5) E. Schmidt, W. Striewsky, and F. Hitzler, *Ann.*, **560**, 222 (1948).

6) R. F. Coles, *Chem. Abstr.*, **54**, 24464 (1960).

7) E. A. Werner, *J. Chem. Soc.*, **115**, 1168 (1919).

8) P. K. Srivastava and Y. R. Rao, *J. Indian Chem. Soc.*, **40**, 803 (1963).

9) P. K. Srivastava, *Indian J. Chem.*, **1**, 434 (1963); **2**, 154 (1964).

10) P. Klatsmanyi-Gabor, T. Meisel, and L. Erdey, *Acta Chim. Acad. Sci. Hung.*, **40**, 99 (1964).

11) F. Kurzer and P. M. Sanderson, *J. Chem. Soc.*, **1957**, 4461; **1959**, 1058; **1963**, 3336.

12) G. Barnikow and J. Bodeker, *Chem. Ber.*, **100**, 1394 (1967).

13) P. K. Srivastava and M. Saleem, *Tetrahedron Lett.*, **1968**, 2725.

14) E. F. Pratt and T. P. McGovern, *J. Org. Chem.*, **29**, 1540 (1964).

15) T. L. Davis and K. C. Blanchard, *J. Am. Chem. Soc.*, **45**, 1816 (1923).

16) J. R. Scott and J. B. Cohen, *J. Chem. Soc.*, **121**, 2034 (1922).

17) C. K. Ingold, *J. Chem. Soc.*, **125**, 87 (1924).

18) C.-H. Kao, H.-Y. Fang, and Peter P. T. Sah, *J. Chinese Chem. Soc.*, **3**, 137 (1935); *Chem. Abstr.*, **29**, 6173 (1935).

19) C. Naegeli, A. Tyabji, and L. Conrad, *Helv. Chim. Acta*, **21**, 1127 (1938); *Chem. Abstr.*, **33**, 541 (1939).

20) R. P. Lastovskiĭ, *Zh. Obshch. Khim.*, **18**, 921 (1948); *Chem. Abstr.*, **43**, 170 (1949).