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Desulfurization of *N,N'*-Diarylthioureas by Lead Tetraacetate Oxidation

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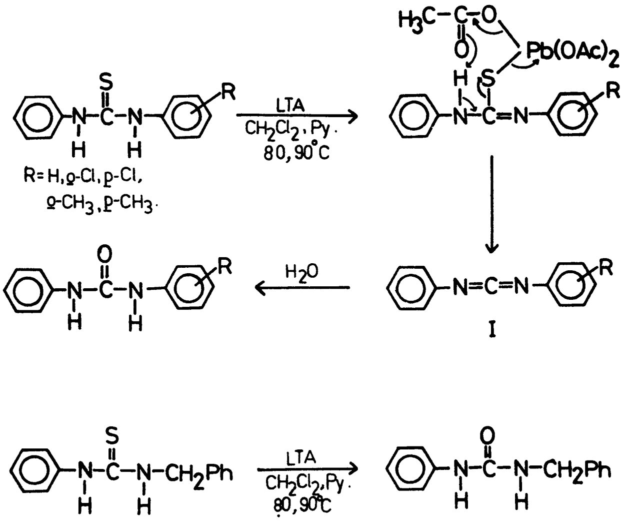
Synopsis. Lead tetraacetate oxidation of *N,N'*-diarylthioureas in refluxing dichloromethane and pyridine gave the corresponding *N,N'*-diarylureas. Sulfur was isolated during each oxidation reaction.

One of the interesting oxidation reactions in organic chemistry is the oxidation of thioureas. Depending on the substitution pattern of thioureas, the oxidizing agent, the polarity of the medium and reaction conditions, a variety of products have been isolated.[1–3]

Suitable synthetic methods are available for the chemical transformation of carbonyl into thiocarbonyl functions. In order to increase the synthetic versatility of this reaction investigation of the proper reagents for carrying out reverse conversion, *i.e.*, thiocarbonyl into carbonyl, is considered to be of great importance. Moreover, because of the discovery of 4-thiouridine in t-RNA of *E. Coli*,[4] it has recently inspired many groups to search for mild reagents for this transformation in order to elucidate the biochemical role of this minor component of t-RNA.[5] Apart from earlier reported reagents, a number of reagents have recently been discovered for conversion of thiocarbonyl compounds to carbonyl analogues. Almost all of them, having different limitations, have been used with varying degrees of success and include, DMSO–acids,[6,7] DMSO–iodine,[8] oxonium tetrafluoroborate,[9] manganese dioxide,[3] mesitylenecarbonitrile oxide,[10] diaryl selenooxides,[11,12] diaryl telluroxide,[13] benzeneseleninic anhydride,[14] thiophosgene,[15] potassium *t*-butoxide/Br_2 or I_2[16,17] and trimethyl phosphite or iron(O) pentacarbonyl.[18]

The oxidation of *N,N'*-diarylthioureas with lead tetraacetate/acetic acid has been reported to give disulfides.[19] Considering the significance of desulfurization reactions, *i.e.*, conversion of thiocarbonyl compounds into their carbonyl analogues, it was thought worthwhile to reinvestigate this reaction with the specific idea of carrying out this transformation. Also, keeping in mind the dependence of oxidation product on reaction conditions it was resolved to achieve this transformation by carrying out the oxidation in aprotic medium.

Thus in our laboratory we have carried out the oxidation of *N,N'*-diarylthioureas with lead tetraacetate in dichloromethane and pyridine at 80—90 °C. In every case, the corresponding urea and sulfur were isolated from the reaction mixture. The products were characterised with the help of IR spectra and melting points. The IR spectra of these compounds showed intense absorption in 1655—1700 cm^{-1} region due to carbonyl stretching. The desulfurization reaction and the formation of ureas is believed to proceed through carbodiimide intermediate(I) as shown in the Scheme 1.



Scheme 1.

Experimental

Starting Materials. Lead tetraacetate was prepared according to literature method.[20] All the *N,N'*-diarylthioureas were prepared by mixing phenyl isothiocyanate and corresponding amines in molecular ratio in ethanol and stirring the mixture at room temperature.

Oxidation of N,N'*-Diphenylthiourea.* To a stirred solution of *N,N'*-diphenylthiourea (2.28 g; 0.01 mol) in dichloromethane (25 cm^3) and pyridine (5 cm^3) was added lead tetraacetate (4.88 g; 0.011 mol) in small portions over a period of 20 min. After complete addition of lead tetraacetate, the reaction mixture was refluxed in an oil bath (80—90 °C) for 1.5 h. The solvent was then removed under reduced pressure and the residue so obtained was chromatographed over a silica-gel column. Elution of the column with hexane gave 0.2 g of sulfur, identified by its undepressed mixed mp. After removal of the sulfur, further elution of the column with a mixture (4 : 1) benzene and ethyl acetate gave 1.8 g (86%) of a solid, identified as *N,N'*-diphenylurea, which was recrystallized from a mixture (1 : 1) of benzene and ethanol, mp 235—236 °C. (Lit,[21] mp 237 °C). IR (Nujol): ν_{max}: 3400 (ν_{N-H}); 3060, 3020, 2970 (ν_{C-H}); 1655 ($\nu_{C=O}$) and 1610, 1580 ($\nu_{C=C}$). These IR bands are common in all the *N*-phenyl-*N'*-arylureas reported here.

Other *N*-phenyl-*N'*-arylureas (Table 1, 2—6) were obtained similarly by lead tetraacetate oxidation of the corresponding *N*-phenyl-*N'*-arylthioureas.

Table 1. *N*-Phenyl-*N'*-arylureas

Sl. No.	Name of the compound	Mp θ_m/°C (Lit)	Yield %
1	*N,N'*-Diphenylurea	235—236 (237)[21]	86
2	*N*-Phenyl-*N'*-(*o*-chlorophenyl)urea	225	65
3	*N*-Phenyl-*N'*-(*p*-chlorophenyl)urea	236 (238)[21]	73
4	*N*-Phenyl-*N'*-benzylurea	166	73
5	*N*-Phenyl-*N'*-(*o*-tolyl)urea	193 (195)[21]	68
6	*N*-Phenyl-*N'*-(*p*-tolyl)urea	220 (219)[3]	73

References

1) C. P. Joshua and K. N. Rajasekharan. *Aust. J. Chem.*, **30**, 1819 (1977) and references therein.

2) C. Christopherson, T. Otterson, K. Seff, and S. Treppendahl, *J. Am. Chem. Soc.*, **97**, 5237 (1975) and references therein.

3) T. C. Sharma, N. S. Sahni, and Ambalal, *Bull. Chem. Soc. Jpn.*, **51**, 1245 (1978) and references therein.

4) M. N. Lipsett, *J. Biol. Chem.*, **240**, 3975 (1965).

5) R. H. Hall, "The Modified Nucleosides in Nucleic Acid," Columbia University Press, New York (1971), p. 347.

6) M. Mikolajezyk and J. Lucazak, *Synthesis*, **1974**, 491.

7) M. Mikolajezyk and J. Lucazak, *Chem. Ind.* (*London*), **1974**, 701.

8) M. Mikolajezyk and J. Lucazak, *Synthesis*, **1975**, 114.

9) R. Mukherji, *Indian. J. Chem.*, *B*, **15**, 502 (1977).

10) R. Grashey, G. Schroll, and M. Weidner, *Chem.-Ztg.*, **100**, 496 (1976).

11) M. Mikolajezyk and J. Lucazak, *J. Org. Chem.*, **43**, 2132 (1978).

12) S. Tamagahi, I. Hatanaka, and S. Kozuka, *Bull. Chem. Soc. Jpn.*, **50**, 3421 (1977).

13) D. H. R. Barton, S. V. Ley, and C. A. Meerholz, *J. Chem. Soc., Chem. Commun.*, **1979**, 755.

14) N. J. Cunam, S. V. Ley, and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 1650.

15) R. Abugar, S. Sharma, and R. N. Iyer, *Indian J. Chem.*, *B*, **19**, 211 (1980).

16) H. Singh, P. Singh, and N. Malhotra, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 2647.

17) H. Singh and P. Singh, *Tetrahedron*, **1981**, 1215.

18) S. A. Kalonstian and W. C. Agorta, *Synth. Commun.*, **1981**, 1011.

19) L. Suchomelova and J. Zyka, *J. Electroanal. Chem.*, **5**, 57 (1963); *Chem. Abstr.*, **59**, 1482b (1963).

20) A. I. Vogel, "A Text Book of Practical Organic Chemistry," English Language Book Society and Longman, London (1978), p. 300.

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