THERMOLYSIS OF SOME THIOUREA DERIVATIVES*

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Thermolysis of N-benzoyl-N',N'-diphenylthiourea (BDTU) (*I*) at 250°C gives NH_3, H_2S, H_2O, benzaldehyde, benzil, benzonitrile, diphenylamine, diphenylcyanamide, 2-phenylbenzimidazole, benzoyl isothiocyanate, carbazole and 2-phenylbenzthiazole, whereas, thermolysis of N-benzoyl-N'-*o*-tolylthiourea (BTTU) (*II*) under the same conditions affords NH_3, H_2S, H_2O, benzaldehyde, benzil, benzonitrile, *o*-toluidine, *o*-tolyl isothiocyanate, *o*-tolylcyanamide, benzoyl isothiocyanate and N,N'-di-*o*-tolylthiourea. The main feature of these thermolyses is homolysis of the amide and thioamide bonds providing free radicals that undergo the common reactions involving H-abstraction, dimerization, coupling, fragmentation, rearrangement and cyclization. A suitable mechanism has been suggested to account for the observed products.

Various thiourea derivatives were reported to have versatile applications in many industrial fields[1-3]. Despite the voluminous literature on the acid catalyzed degradation of thiourea[4], knowledge of the non-catalyzed process is surprisingly meagre. Recently, we have observed that the non-catalyzed thermal and photodegradation of some thiourea derivatives results in products of great significance[5]. This prompted us to carry out more experiments to gain further informations on the behaviour of such a class of organic compounds on thermolysis. Thermolysis of N-benzoyl-N'-arylthiourea (*I*, *II*) by heating under reflux at ~250°C for 15 h gives NH_3, H_2S, H_2O, benzaldehyde, benzil, benzonitrile, *o*-toluidine, diphenylamine, diphenylcyanamide, *o*-tolylcyanamide, benzoyl isothiocyanate, *o*-tolyl isothiocyanate, carbazole, 2-phenylbenzthiazole, 2-phenylbenzimidazole and N,N'-di-*o*-tolylthiourea (Table I).

Formation of these products can be assumed to follow the series of reactions shown in Scheme 1 which implies the preliminary homolysis of the amidyl function (route *a*) forming benzoyl and arylaminothioamidyl radical pairs. The benzoyl radicals may abstract hydrogen from the medium to give benzaldehyde or undergo dimerization into benzil, whereas the arylaminothioamidyl radicals may abstract hydrogen to give arylthiourea which subsequently decomposes into ammonia and

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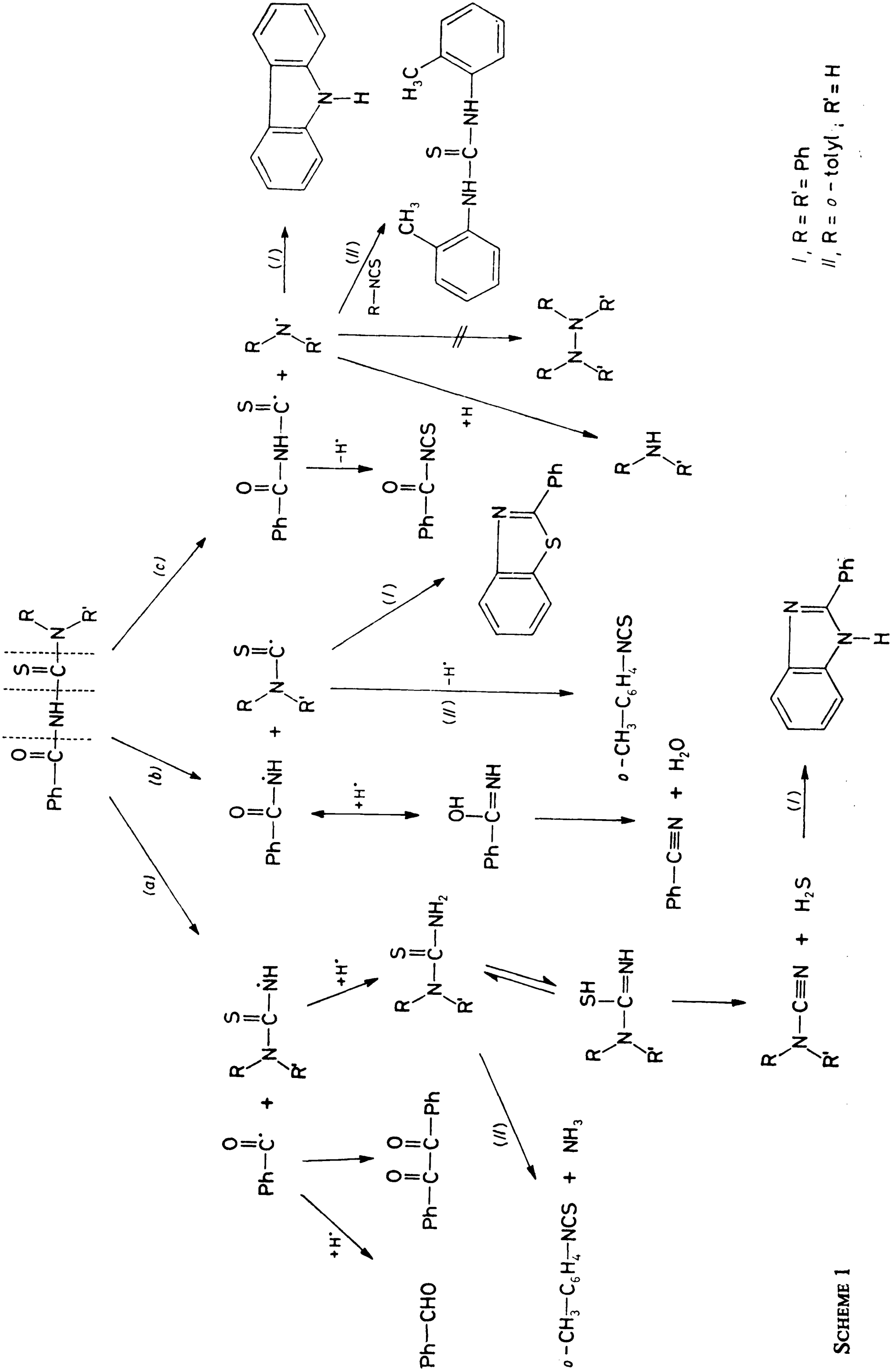
* Part II; Part I: Aly M. M., Fahmy A. M., Gaber A. M.: Phosphorus, Sulfur, Silicon *53*, 253 (1990).



I, R = R' = Ph
II, R = *o*-tolyl; R' = H

SCHEME 1

o-tolyl isothiocyanate[6]. Arylthiourea may undergo rearrangement into arylisothiourea which decomposes on heating into H_2S and arylcyanamide[7]. Moreover, in the case of thermolysis of BDTU, the arylcyanamide gives after N–C phenyl migration followed by cyclization 2-phenylbenzimidazole[8].

Formation of benzonitrile, water, *o*-tolyl isothiocyanate and 2-phenylbenzthiazole can be assumed to proceed through the homolysis of the thioamidyl function (route *b*) to phenylamidyl and arylaminylthione radical pairs which on disproportionation give benzamide and *o*-tolyl isothiocyanate. Benzamide may be considered as the precursor of benzonitrile and water as shown in Scheme 1. Furthermore, diphenylaminylthione may undergo intramolecular cyclization through 1,2-phenyl migration, forming 2-phenylbenzthiazole[8].

TABLE I

Product of thiourea thermolysis (reflux for 15 h). Amounts are given in grammes and %

Thermolysis product	Thiourea derivative	
	BDTU	BTTU
NH_3	evolved	evolved
H_2S	evolved	evolved
H_2O	drops	drops
Benzaldehyde[a]	2·5(16·7)	2·1(14)
Benzil[b]	1·5(10)	1·8(12)
Benzonitrile[c]	0·8(5·3)	0·5(3·3)
o-Tolyl isothiocyanate[d]	—	2·0(13·3)
Amine derivative	2·3[e](15·3)	2·4[f](16)
Cyanamide derivative	1·1[g](7·3)	1·5[h](10)
Benzoyl isothiocyanate[i]	0·7(4·7)	1·0(6·7)
2-Phenylbenzimidazole[j]	1·5(10)	—
2-Phenylbenzthiazole[k]	1·2(8)	—
N,N′-Di-*o*-tolylthiourea[l]	—	1·8(12)
Carbazole[m]	0·9(6)	—
Residue (non-volatile)	1·1(7·3)	1·6(10·7)

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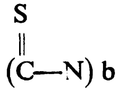
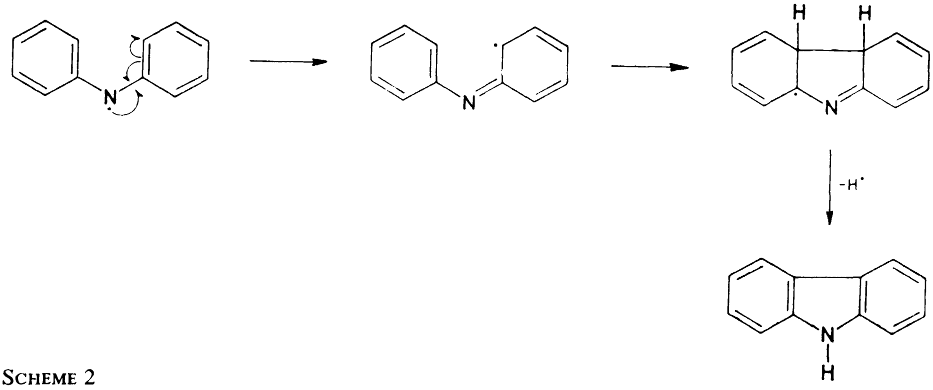
[a] B.p. 75°C/1·3 kPa, estimated in the mixture as dinitrophenylhydrazone derivative m.p. 235°C; [b] mixture m.p. 94°C, dinitrophenyl hydrazone derivative m.p. 185°C; [c] n_D^{20} 1·5270, on hydrolysis gives benzoic acid, m.p. 120°C; [d] b.p. 170—180°C/1·3 kPa, n_D^{20}: 1·6361; [e] diphenylamine, m.p. 54°C, picrate m.p. 182°C; [f] *o*-toluidine, b.p. 150—160°C/1·3 kPa, benzoyl derivative m.p. 145°C; [g] N,N-diphenylcyanamide, m.p. 75°C; [h] *o*-tolylcyanamide, m.p. 80°C; [i] b.p. 125 to 135/1·3 kPa, n_D^{20} 1·6334; [j] mixture m.p. 295°C; [k] mixture m.p. 115°C; [l] b.p. 160—170°C/1·3 kPa, m.p. 160°C; [m] identified by preparative TLC using ether–petroleum ether (40—60°C) (1 : 7 v/v) as eluent, $R_F = 0{\cdot}35$; picrate m.p. 185°C.

Another competing pathway for the thermolysis of N-benzoyl-N'-arylthiourea is homolysis of the  $(\overset{S}{\overset{\|}{C}}\text{—}N)$ bond (route c) leading to the formation of arylamidylthione and arylaminyl radical pairs. The former may lose hydrogen to give benzoyl isothiocyanate, whereas the latter may abstract hydrogen forming arylamine (diphenylamine or *o*-toluidine) or couple with *o*-tolyl isothiocyanate affording N,N'-di-*o*-tolylthiourea especially in case of thermolysis of BTTU. Cyclization of the diphenylaminyl radical[9] (Scheme 2) is a plausible explanation for carbazole formation.



SCHEME 2

It may be noted that tetraphenylhydrazine was not formed as the normal product of dimerization of diphenylaminyl free radicals. Such result may be attributed to the unstability of the N—N bond[10].

EXPERIMENTAL

All melting points are uncorrected. The IR spectroscopic analyses were carried out on a Pye-Unicam IR spectrophotometer, Model Sp. 3-100. Gas chromatography was carried out using Perkin-Elmer Sigma-3B apparatus and the columns used were 1 200 × 4 mm, packed with 30% SE 30 on Chromosorb W (35—80 mesh), or 10% SE 30 on celite (60—80 mesh) at 180°C, using nitrogen as a carrier gas. Thin-layer chromatography was carried out on glass plates covered with silica gel (25—40 mesh) and eluted with acetone–petroleum ether (60—80°C) (1 : 4 v/v). The following compounds were used in this study: N-Benzoyl-N',N'-diphenylthiourea[11], recrystallized from ethanol as white crystals, m.p. 135°C; N-benzoyl-N'-*o*-tolylthiourea[12], recrystallized from ethanol as pale yellow crystals, m.p. 117—120°C; *o*-tolyl cyanamide[13], pale yellow crystals, m.p. 80°C; N,N-diphenyl cyanamide[14], white crystals from ethanol, m.p. 74°C; 2-phenylbenzimidazole[15], white crystals from ethanol, m.p. 295°C; 2-phenylbenzthiazole[16]. recrystallized from ethanol, m.p. 115°C; N,N-di-*o*-tolylthiourea[17], white crystals, m.p. 160°C.

Thermolysis of Thiourea Derivatives

The thioureas (15 g) were heated under reflux at ~250°C for 15 h. The gases evolved were detected by standard procedures (NH_3 by Nessler's reagent and H_2S by lead acetate). The pyrolysate was separated into its constituents, first by fractional distillation under reduced pressure where the following compounds were obtained: benzaldehyde, benzonitrile, *o*-tolyl isothiocyanate, *o*-toluidine, benzoyl isothiocyanate. The remaining residue was separated by column chromatography on silica gel, following the gradient elution technique using the solvents: petroleum ether (40–60°C), petroleum ether (60–80°C), their mixture (1 : 1), (1 : 2), petroleum ether (60–80°C)-benzene (5 : 1), (1 : 1), (1 : 2) and then benzene, in succession. The separated products were identified by physical constants, boiling points, melting points, TLC, GLC, IR and compared with authentic samples. The results are shown in Table I.

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