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THERMAL SYNTHESIS AND CHARACTERISATION OF *N*,*N'*-DI(CHLOROBENZYL) UREAS

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ABSTRACT

The thermal stability of the Schiff base ethylacetoacetate-*o*-chlorobenzylamine (**II**), *N*-*o*-chlorobenzyl-*C*-benzoyl acetamide (**III**), and *N*-*p*-chlorobenzyl-*C*-benzoyl acetamide (**IV**) were studied by thermogravimetric analysis. **II** Gave *N*,*N'*-di(*o*-chlorobenzyl) urea (**Ia**) at 60°C, whereas the thermogravimetric curves of **III** and **IV** indicate that reactions other than formation of **I** may occur. The urea derivatives (**I**) have also been prepared from benzylamines and the corresponding β-ketoester and identified.

INTRODUCTION

Previously, ureas were prepared by the procedure of Wöhler or his modified method. Symmetrical tetra-substituted ureas have been obtained from the action of secondary amines on carbon monoxide in the presence of selenium in tetrahydrofuran [1]. Symmetrical diaryl ureas have usually been prepared from heating an aqueous solution of urea and the arylamine hydrochloride, or from the condensation of *N*-substituted anilines with thiophosgene and oxidation of the corresponding thioureas [2].

We now report a new and very simple preparation of *N*,*N'*-di(chlorobenzyl) ureas (**I**). The products were identified by elemental analysis, IR, UV and mass spectra, and some of the reactions were followed thermally.

EXPERIMENTAL

Measurements of the elemental analyses, IR, UV and mass spectra were discussed elsewhere [3,4]. The thermogravimetric (TG and DTG) analyses were carried out using a MOM derivatograph thermoanalyser which has been described in detail elsewhere [5,6].

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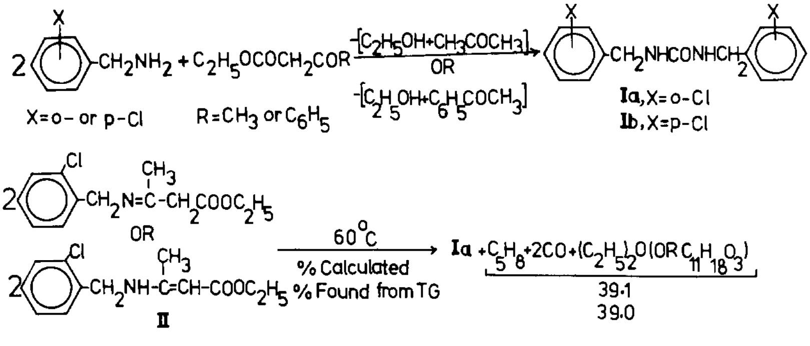

Scheme 1.

Compounds **II** (m.p., 62°C), **III** (m.p., 119°C) and **IV** (m.p., 96°C) were prepared by condensation of 1 : 1 (w/w) of chlorobenzylamines and the corresponding β-ketoester. They were purified and characterised according to ref. 7.

Compound **I** (Scheme 1) was prepared by gently boiling of 2 : 1 (w/w) of chlorobenzylamines and the corresponding β-ketoester for 5–10 min. On cooling, a crystalline solid separated out and was collected and washed repeatedly with hot ethanol. Acetone, ethanol and acetophenone have been identified as by-products. Compound **I** was also prepared by direct fusion of **II**, just above the melting point, for 15–20 min. The product has exactly the same physical and spectral properties, indicated in Tables 1 and 2.

RESULTS AND DISCUSSION

Spectral identification

Direct boiling of chlorobenzylamines with the corresponding β-ketoester, and fusion of the Schiff base **II** just above its melting point gave the same

TABLE 1

The melting points, elemental analysis, IR and UV spectral data of **I**

Compound No.	M.p. (°C)	% Calcd. (found)				IR bands in Nujol mull (cm^{-1})	UV bands in CH_2Cl_2: λ_{max} (nm) (ϵ(m^2 mol^{-1}))
		C	H	N	Cl		
Ia	229–231	58.25 (58.24)	4.53 (4.66)	9.06 (8.95)	22.98 (22.91)	3300 (N–H), 1615 (C=O)	264 (60), 224 (110)
Ib	241–243	58.25 (58.26)	4.53 (4.57)	9.06 (9.00)	22.98 (22.90)	3300 (N–H), 1605 (C=O)	268 (60), 227 (330)

TABLE 2

Mass spectral data of **I**

m/z (% relative abundance) [a]		Suggested fragment ion
Ia [b]	**Ib** [c]	
	311 (5) [d]	$M^+ + 2$
310 (2) [d]	310 (21) [d]	$M^+ + 1$
	309 (6)	M^+
308 (3)	308 (34)	$M^+ - H$
276 (10)		
275 (37) [d]		
274 (20) [d]		
273 (100)	273 (2)	$^+C_6H_4CH_2NHCONHCH_2C_6H_4Cl$
	185 (15) [d]	
184 (3) [d]	184 (4) [d]	
183 (9)	183 (36)	$ClC_6H_4CH_2NHCONH^+$
142 (13) [d]	142 (34) [d]	
141 (5) [d]	141 (10) [d]	
140 (63)	140 (100)	$ClC_6H_4CH_2NH^+$
127 (5) [d]	127 (19) [d]	
126 (7) [d]	126 (5) [d]	
125 (56)	125 (53)	$ClC_6H_4CH_2^+$
	113 (6)	
107 (6) [d]	107 (3) [d]	
106 (29)	106 (15)	$C_6H_5CH_2NH^+$
89 (16)	89 (16)	
77 (25)	77 (16)	$C_6H_5^+$

[a] Peaks less than 4% are not included unless they are significant.

[b] Sample temperature 155°C.

[c] Sample temperature 165°C.

[d] Isotopic peaks.

product, namely, *N,N'*-di(chlorobenzyl) urea (**I**; Scheme 1). Typical melting points, elemental analyses, IR, UV and mass spectral data of **I** are summarised in Tables 1 and 2. The mass spectral fragmentation of **I** is quoted as an almost copy-book example of simple fragmentation of alkyl and aryl ureas [8,9], because the predominant part of the fragment ions corresponds to the α cleavage of the carbonyl group, i.e., fragment ions at *m/z* 183, 140, 125 and 106 (see Table 2).

Thermogravimetric analyses

Direct condensation of chlorobenzylamines with the corresponding β-ketoester proceeded via elimination of ethanol + acetophenone or ethanol + acetone molecules (see Experimental Section; Scheme 1). The thermogravimetric curve for compound **II** (Fig. 1) shows that it loses 39.0% of its weight at 60°C, i.e., at this temperature **I** is formed from **II**, probably by elimination

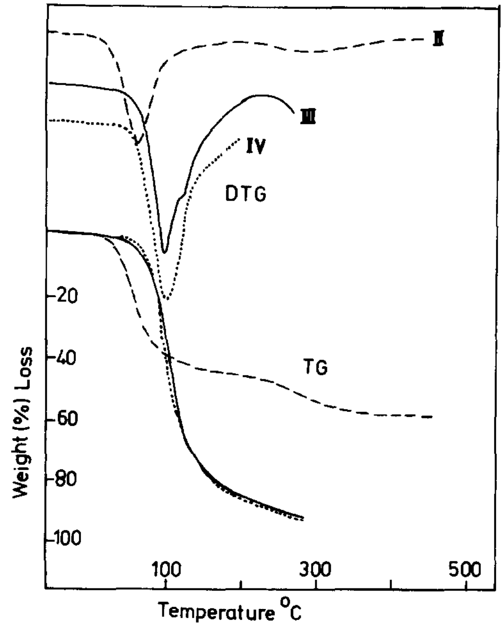

Fig. 1. Thermogravimetric curves (DTG and TG) for: (— — —) compound **II**; (———) compound **III**; (· · · · · ·) compound **IV**.

of $C_5H_8 + 2CO + (C_2H_5)_2O$ molecules (or $C_{11}H_{18}O_3$). On the other hand, the thermogravimetric curves for compounds **III** and **IV** (Fig. 1) show that both compounds lose 78.9% of their weight at 96°C and 100°C, respectively, which indicates that reactions other than the formation of **I** may occur. Therefore, we were unable to isolate **I** from **III** or **IV**.

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