292. *The Interaction of Acetonephenylhydrazone and Phenyl* iso*Cyanate.*

By W. A. CALDWELL, J. CHAPMAN, H. W. GOODWIN, and F. J. WILSON.

WHYBURN and BAILEY (*J. Amer. Chem. Soc.*, 1928, **50**, 912) heated acetonephenylhydrazone with phenyl *iso*cyanate in a sealed tube at 100° for 2 hours and obtained a substance, m. p. 191°, which they regarded as acetone-2 : 4-diphenylsemicarbazone : $CMe_2{:}N{\cdot}NHPh + PhNCO = CMe_2{:}N{\cdot}NPh{\cdot}CO{\cdot}NHPh$.

It was thought that this substance might be more conveniently prepared from equimol. quantities of these reactants in hot C_6H_6. After 3½ hrs.' boiling, and addition of light petroleum to the solution at 0°, a white solid was slowly deposited, the mother-liquor on concn. yielded tar. From the solid, hot $CHCl_3$ extracted a very sol. component (A), which was recryst. from EtOH (square plates, m. p. 138°), $CHCl_3$–light petroleum (m. p. 140°), and finally $CHCl_3$ (m. p. 141°). The substance (A) was easily sol. in warm $CHCl_3$, EtOH, and C_6H_6, sparingly sol. in Et_2O and light petroleum, and apart from m. p. had the properties mentioned by Whyburn and Bailey. The other component (B) of the solid crystallised from much EtOH or EtOAc as a powder, m. p. 208°, sparingly sol. in most solvents.

The method of Whyburn and Bailey was then followed exactly, and the same mixture as that already described was obtained : it was washed with small quantities of Et_2O to remove a brown resin before being separated into the components as described above.

Repetition of the two experiments under anhydrous conditions with pure freshly distilled reactants gave the same result. The number of recrystallisations necessary make it difficult to state the relative amounts of the two substances formed. The best yield was obtained by keeping the reactants in a pressure flask at 37° for 33 days.

Substance (A) was *acetone-2 : 4-diphenylsemicarbazone* (Found : C, 72·3, 72·2; H, 6·5, 6·5; N, 16·0, 15·7; *M*, ebullioscopic in $CHCl_3$, 267, 242. $C_{16}H_{17}ON_3$ requires C, 71·9; H, 6·4; N, 15·7%; *M*, 267). Hydrolysis with boiling conc. HCl gave Me_2CO, NH_2Ph, and $NHPh{\cdot}NH_2$ in the molecular ratios 1 : 1·09 : 0·9 (calc., 1 : 1 : 1). The $NHPh{\cdot}NH_2$ was estimated by Causse's method (*Compt. rend.*, 1897, **125**, 712), and the NH_2Ph by difference.

Acetone-2 : 4-diphenylsemicarbazone, identical with (A), was formed by boiling 2 : 4-diphenylsemicarbazide in Me_2CO for 1½ hrs.

Substance (B) is regarded by us as *αβ-di(phenylcarbamyl)phenylhydrazine*, $NPh(CO{\cdot}NHPh){\cdot}NH{\cdot}CO{\cdot}NHPh$ (Found : C, 69·0; H, 5·4; N, 16·2; *M*, cryoscopic in camphor, 294, 300. $C_{20}H_{18}O_2N_4$ requires C, 69·4; H, 5·2; N, 16·2%; *M*, 346). It was also formed (*a*) by gradual addition of PhNCO (2 mols.) to $NHPh{\cdot}NH_2$, followed by 5 hrs.' heating on the water-bath, (*b*) as the sole product by boiling PhNCO with 1 : 4- or 2 : 4-diphenylsemicarbazide (mol. quantities) in C_6H_6 for 1½ hrs. and recrystallising the ppt. deposited from the cooled solution. It did not react on long boiling with Ph·CHO in EtOH (absence of $>N{\cdot}NH_2$ group), nor was it affected by $FeCl_3$ in dioxan solution (absence of ·NH·NH· group: 1 : 4-diphenylsemicarbazide under these conditions gave the orange-red phenylazocarbanilide).

Since both 1 : 4- and 2 : 4-diphenylsemicarbazide are produced from phenylhydrazine and phenyl *iso*cyanate, the formation of (B) might proceed in four different ways :

$$\begin{tikzcd}
 & \mathrm{NHPh{\cdot}N(CO{\cdot}NHPh)_2} \quad \mathrm{(III.)} \\
\mathrm{NHPh{\cdot}NH{\cdot}CO{\cdot}NHPh} \arrow[ru, "\mathrm{PhNCO}"] \arrow[r] \arrow[rd] & \mathrm{NHPh{\cdot}NH{\cdot}CO{\cdot}NPh{\cdot}CO{\cdot}NHPh} \quad \mathrm{(II.)} \\
 & \mathrm{NPh(CO{\cdot}NHPh){\cdot}NH{\cdot}CO{\cdot}NHPh} \quad \mathrm{(I.)} \\
\mathrm{NH_2{\cdot}NPh{\cdot}CO{\cdot}NHPh} \arrow[ru, "\mathrm{PhNCO}"] \arrow[r] & \mathrm{NH_2{\cdot}NPh{\cdot}CO{\cdot}NPh{\cdot}CO{\cdot}NHPh} \quad \mathrm{(IV.)}
\end{tikzcd}$$

Of these, (I) only is produced from both 1 : 4- and 2 : 4-diphenylsemicarbazide, so that (I), αβ-di(phenylcarbamyl)phenylhydrazine, should represent (B).

Acetone-*p*-bromophenylhydrazone and PhNCO (mol. quantities) were heated in dry C_6H_6 in a current of dry CO_2 for 3 hrs. The ppt. crystallised from much C_6H_6 or EtOAc as a powder, m. p. 206—207° : it was the only product except tar and a little diphenylurea and was sparingly sol. in the usual solvents. The same substance was produced by heating *p*-bromophenylhydrazine with PhNCO (2 mols.) in C_6H_6 for 2 hrs. We regard it as *αβ-di(phenylcarbamyl)*-p-*bromophenylhydrazine*,

$$C_6H_4Br{\cdot}N(CO{\cdot}NHPh){\cdot}NH{\cdot}CO{\cdot}NHPh$$

(Found: N, 13·2; Br, 18·8. $C_{20}H_{17}O_2N_4Br$ requires N, 13·2; Br, 18·8%).

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THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

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