

# Notes

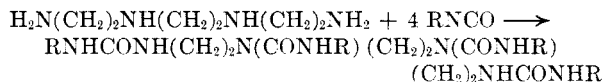
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## Tetracarbamyl Derivatives of 1,2-Bis(2-aminoethyl)ethylenediamine

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The reaction of phenyl isocyanate with 1,2-bis-(aminoethyl)ethylenediamine, the "triethylenetetramine" of Hofmann,<sup>1,2</sup> to form 1,2-bis{3'-phenyl-1'-[2''-(3'''-phenylureido)ethyl]ureido}ethane was first reported by van Alphen.<sup>3</sup> Phenyl isothiocyanate reacts to produce the corresponding thioureido derivative. Although other derivatives of this tetrafunctional amine have been described,<sup>4-6</sup> the prod-



As anticipated, attempts to react di- and tri-isocyanates, for example toluene-2,4-diisocyanate or toluene-2,4,6-triisocyanate, resulted in the formation of viscous polymers.<sup>7</sup> Using smaller amine:isocyanate ratios it was not found possible to isolate mono-, di-, or tri-substituted derivatives.

Products ranged from white crystalline solids, soluble with difficulty in isopropyl alcohol, in the case of short-chain compounds, to waxy solids, easily soluble in alcohol, in the case of long-chain derivatives.

TABLE I  
TETRACARBAMYL DERIVATIVES OF 1,2-BIS(2-AMINOETHYL)ETHYLENEDIAMINE  
[CH<sub>2</sub>N(CONHR)(CH<sub>2</sub>)<sub>2</sub>NHCONHR]<sub>2</sub>

R	Formula	Yield, %	M.P., °C. <sup>9</sup>	% N	
				Calcd.	Found
Allyl	C <sub>22</sub> H <sub>38</sub> N <sub>8</sub> O <sub>4</sub>	97	211	23.4	23.3
Isopropyl	C <sub>22</sub> H <sub>46</sub> N <sub>8</sub> O <sub>4</sub>	96	245-247 dec.	23.0	22.8
n-Butyl	C <sub>26</sub> H <sub>54</sub> N <sub>8</sub> O <sub>4</sub>	98	216-217	20.7	20.7
Cyclohexyl	C <sub>34</sub> H <sub>62</sub> N <sub>8</sub> O <sub>4</sub>	100	246-247 dec.	17.3	17.1
Phenyl	C <sub>34</sub> H <sub>38</sub> N <sub>8</sub> O <sub>4</sub>	100	237-238	18.0	18.1
n-Octyl	C <sub>42</sub> H <sub>86</sub> N <sub>8</sub> O <sub>4</sub>	98	97-98	14.6	14.5
n-Dodecyl	C <sub>58</sub> H <sub>118</sub> N <sub>8</sub> O <sub>4</sub>	96	170-171	11.3	11.1
n-Octadecyl	C <sub>82</sub> H <sub>166</sub> N <sub>8</sub> O <sub>4</sub>	95	162	8.4	8.3
1-Naphthyl	C <sub>50</sub> H <sub>46</sub> N <sub>8</sub> O <sub>4</sub>	98	182	13.6	13.7
2-Biphenyl	C <sub>58</sub> H <sub>54</sub> N <sub>8</sub> O <sub>4</sub>	92	222	12.1	11.9

ucts of reaction of other monoisocyanates have not been reported.

During a study of the reaction of mono- and polyisocyanates with various polyamines the work of van Alphen was confirmed and a series of new derivatives of 1,2-bis(2-aminoethyl)ethylenediamine has been synthesized. Using a 1:4 molar ratio of tetramine:isocyanate in chloroform solution the following strongly exothermic reaction occurred in almost theoretical yield:

## EXPERIMENTAL

Technical grade triethylenetetramine<sup>8</sup> and reagent grade isocyanates were obtained from Distillation Products Industries, Rochester, N. Y. Di- and tri-isocyanates were supplied by the Mobay Chemical Company, New Martinsville, W. Va.

The triethylenetetramine was fractionally distilled under reduced pressure, the liquid of b.p. 157°/20 mm. being collected and stored under nitrogen in dark bottles.

*General preparative procedure.* Four one-hundredths of a mole of isocyanate was added cautiously to a mechanically stirred mixture of 1.46 g. (0.01 mole) of triethylenetetramine dissolved in 10-20 ml. of ice cold chloroform. The reaction was strongly exothermic and care was taken not to allow the temperature to exceed about 30°. On cooling, the finely crystalline derivative was filtered, washed with chloroform followed by isopropyl alcohol, then dried *in vacuo*. Recrystallization was effected from isopropyl alcohol in which the lower members were very sparingly soluble. The products are listed in Table I.

(1) A. W. Hofmann, *Proc. Roy. Soc.*, **10**, 224, 619 (1860); **11**, 413, 424 (1862); *Ber.*, **3**, 762 (1870); **4**, 666 (1871); **23**, 3297, 3711 (1890).

(2) F. G. Mann, *J. Chem. Soc.*, 461 (1934); *Chem. Abstr.*, **28**, 4379 (1934).

(3) J. van Alphen, *Rec. trav. chim.*, **55**, 412 (1936).

(4) D. H. Peacock, *J. Chem. Soc.*, 1518 (1936).

(5) R. G. Fargher, *J. Chem. Soc.*, 117, 1351 (1920).

(6) I. Heilbron and H. M. Bunbury, *Dictionary of Organic Compounds*, Oxford University Press, New York, 1953, volume 4, p. 571.

(7) British Patent, **706,717** (April 7, 1954).

(8) Contaminated with small amounts of diethylenetriamine, tetraethylenepentamine, and pentaethylenhexamine.  
(9) Melting points are uncorrected.

When 1:2 or 3:4 molar ratios of triethylenetetramine and toluene-2,4-diisocyanate or toluene-2,4,6-triisocyanate were reacted the products were viscous polymers.

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### Carbonyl Derivatives of $\gamma$ -Cyano and $\gamma$ -Carboxy- $\alpha,\alpha$ -dimethylpentanal

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Although  $\gamma$ -cyano- $\alpha,\alpha$ -dimethylpentanal, also called Ibanitrile, and  $\gamma$ -carboxy- $\alpha,\alpha$ -dimethylpentanal, also called Iba-acid, have been known for some time,<sup>1,2</sup> several of the simple carbonyl derivatives of these compounds have not been previously described. The availability of Ibanitrile from the

reaction of isobutyraldehyde with acrylonitrile suggests that the data for these compounds be made available. We have prepared several of these derivatives whose properties are recorded in the table. All were prepared by standard methods. The unusual formation of the hydrazone, rather than the azine, from equimolar quantities of Ibanitrile and hydrazine is noteworthy. Usually the azine is the exclusive product from the reaction of an aliphatic aldehyde with hydrazine. Only the azine was obtained from hydrazine and Iba-acid.

#### EXPERIMENTAL<sup>3</sup>

*$\gamma$ -Carboxy- $\alpha,\alpha$ -dimethylpentanal.* This acid was obtained in 75% yield by hydrolysis of the nitrile with 25% aqueous hydrochloric acid; b.p. 130–132°/3 mm.;  $n_D^{25}$ , 1.4450.

*Derivatives of  $\gamma$ -cyano- $\alpha,\alpha$ -dimethylpentanal.* **Hydrazone.** The nitrile (12.5 g.) was added dropwise to a solution of 10 g. of hydrazine in 50 ml. of benzene. The mixture was refluxed for 1 hr. with azeotropic removal of the water formed in the reaction. The benzene solution was dried and evaporated to leave a residue which was fractionated to give 8.3 g. (60%) of the hydrazone, b.p. 101–103/1.5 mm.;  $n_D^{25}$ , 1.4805. Attempted refractionation partially converted this material to the azine. **Azine.** A solution of 4.0 g. of hydrazine and 2.5 g. of nitrile in 100 ml. of benzene was refluxed for 1 hr. with azeotropic removal of the water formed in the reaction. Evaporation of the solvent left a solid residue, 2.9 g. (75%), which was recrystallized from ethanol-water, m.p. 76–78°. The infrared absorption spectrum for this azine shows strong absorption bands at 2250  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$  stretching frequency); 1630  $\text{cm}^{-1}$  ( $\text{C}=\text{H}$  stretching frequency); 1450  $\text{cm}^{-1}$  ( $\text{C}-\text{H}$  deformation frequency in  $\text{CH}_2$ ); 1380  $\text{cm}^{-1}$  and 1358  $\text{cm}^{-1}$  [ $\text{C}-\text{H}$  deformation frequency in  $(\text{CH}_2)_2\text{C}$ ]; and 1195  $\text{cm}^{-1}$  and 770  $\text{cm}^{-1}$  [ $(\text{CH}_2)_3\text{C}$  skeletal vibration]. **Methylhydrazone and dimethylhydrazone.** These compounds were prepared by refluxing the aldehyde with methyl- and dimethylhydrazine. Properties are given in the table. **Dinitrophenylhydrazone.** This compound was prepared as previously described,<sup>4</sup> m.p. 139–140°. **Semicarbazone.** This compound precipitated from a solution of the aldehyde, semicarbazide hydrochloride, and sodium acetate in water. **Thiosemicarbazone.** A solution of 12.5 g. of the nitrile and 9.0 g. of thiosemicarbazide in 40 ml. of ethanol was refluxed for 2 hr. The precipitated solid left on evaporation of the ethanol was recrystallized from methanol-water to give 12.4 g. (62%) of the product, m.p. 95–96°. **Aminoguanidine sulfate.** A mixture of 26.5 g. of aminoguanidine sulfate, 25 g. of the aldehyde, and 2 drops of concd. sulfuric acid were agitated to homogeneity. After standing at room temperature for 24 hr., the solvent was evaporated under vacuum at room temperature. The viscous residue solidified on standing and was recrystallized by dissolving in methanol at 45° and cooling to  $-20^\circ$ .

*Derivatives of  $\gamma$ -carboxy- $\alpha,\alpha$ -dimethylpentanal.* **Azine.** The white solid product separated from a benzene solution of the aldehyde and an equivalent amount of hydrazine. **Dimethylhydrazone, semicarbazone, thiosemicarbazone.** These derivatives were prepared using the procedures given above for the derivatives of the nitrile. **2,4-Dinitrophenylhydrazone.** This compound precipitated from an acidic aqueous solution of the hydrazine and the aldehyde.

Both aldehydes react with phenylhydrazine to give products which could not be recrystallized.

TABLE I  
DERIVATIVES OF IBANITRILE AND IBA-ACID

	M.P. or B.P. <sup>a</sup>	Yield, %	Analysis <sup>b</sup>	
			Calcd.	Found
Ibanitrile Derivatives				
Hydrazone	b103/1.5 <sup>c</sup>	60	30.19N	29.92N
Azine	m76-78EW	75	68.25C 9.00H	68.52C 9.07H
Methyl- hydrazone	b104/4 <sup>d</sup>	87	27.43N	27.51N
Dimethyl- hydrazone	b90/3 <sup>e</sup>	76	25.13N	25.13N
Semi- carbazone	m154W	84	30.75N	30.53N
Thiosemicar- bazone	m95MW	62	28.25N	28.36N
Aminoguani- dine sulfate	m166M	43	29.81N	29.92N
Iba-acid Derivatives				
Azine	m165MW	95	9.99N 140.1NE	10.07N 143.0NE
Dimethyl- hydrazone	m73PC	55	15.04N 186.2NE	15.01N 185.4NE
Semi- carbazone	m175W	98	20.88N 201.2NE	20.95N 201.9NE
Thiosemicar- bazone	m160W	99	19.33N 217.3NE	19.51N 218.4NE
2,4-Dinitro- phenyl- hydrazone	m147E	99	17.27N	17.22N

<sup>a</sup> Solvents for recrystallization: B, benzene; M, methanol; W, water; C, carbon tetrachloride; P, petroleum ether; E, ethanol. <sup>b</sup> C, carbon; H, hydrogen; N, nitrogen; NE, neut. equiv. <sup>c</sup>  $n_D^{25}$  1.4805. <sup>d</sup>  $n_D^{24}$  1.4770. <sup>e</sup>  $n_D^{24}$  1.4660.

(1) N. E. Thiele and W. Franke, Publication Board Reports **35**, 102; **35**, 103 (1944).

(2) W. Retter and W. Franke, Publication Board Report **35**, 112 (1944).

(3) Analyses by Micro Tech Laboratories, Skokie, Ill.

(4) G. Tschudi and S. Schinz, *Helv. Chim. Acta*, **33**, 1870 (1950).