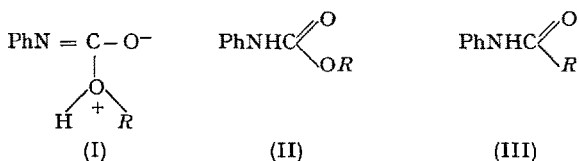


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The Structure of Phenylurethanes

Phenylurethanes are formed by the interaction of phenols (or alcohols) with phenylisocyanate and it has long been known¹ that this reaction can be reversed by heating the urethane. Recently ILLARI and MARENGHI and co-workers² have studied the thermal decomposition of various phenylurethanes and they concluded that in general the products obtained by interaction of phenols and phenylisocyanate are *not* phenylurethanes but "molecular complexes", probably of type (I). (BAKER and GAUNT³ have shown that the uncatalysed reaction between phenylisocyanate and alcohols proceeds via an intermediate complex of this type.) On the other hand the products obtained from β -naphthol and eugenol were considered to have the authentic urethane structure (II) since they gave rise, on pyrolysis, to carbanilide and a diaryl carbonate along with some phenylisocyanate and the original phenol. The basis on which ILLARI *et al.* assign structures (I) or (II) to phenylisocyanate-phenol reaction products is very inadequate and their formation in pyridine solution⁴ appears to exclude structure (I) (cf. BAKER and GAUNT⁵).



We have now examined the infra-red spectra of a number of the compounds prepared by ILLARI *et al.* Anilides (III) show their carbonyl stretching band in the region 1660-1680 cm^{-1} (THOMPSON and RICHARDS⁶). Comparison of the carbonyl frequencies of simple ketones and esters indicates that an oxygen atom adjacent to the C=O group raises its frequency about 30-40 cm^{-1} . Therefore if phenylurethanes have structure (II) a carbonyl frequency of 1690-1720 cm^{-1} would be anticipated. On the contrary structure (I) would not be expected to give any band in this region except a C=N band probably between 1630 and 1670 cm^{-1} . The following values were found.

In addition all the spectra showed a band near 1530 cm^{-1} which is characteristic of the -CO-NH- group. These figures agree with those of THOMPSON, NICHOLSON, and

Phenylurethane (solid)	cm^{-1}
Menthol	1697
tert. Butyl alcohol	1690
Phenol	1715
β -Naphthol	1720
o-Nitrophenol	1705
	1728
p-Nitrophenol	1715

SHORT¹ and provide clear evidence for the accepted structure (II) of phenylurethanes.

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Zusammenfassung

Die Infrarotspektren verschiedener Phenylurethane zeigen, dass diese die angenommene Struktur (II) besitzen und nicht molekulare Komplexe darstellen, wie ILLARI *et al.*¹ annehmen.

¹ H. W. THOMPSON, D. L. NICHOLSON, and L. N. SHORT, *Farad. Soc. Discussions* 9, 229 (1950) (The senior author has confirmed that the figure 7000 in Table II is an error and should be 1700.).

A New Synthetic Sulfur-Containing Amino Acid: S-Aminoethylcysteine

The mechanism by which the organism acquires the mercaptoethylamine for the synthesis of CoA is still completely unknown. While we know that pantothenic acid, necessary for such a synthesis, must be brought to the organism from outside, we have no information indicating that mercaptoethylamine too must be obtained from the diet.

It is highly probable therefore that mercaptoethylamine is synthesized by the animal in one of the following ways:

(1) decarboxylation of cystine or cysteine; (2) dismutation of cystamine disulfoxide; (3) transulfuration from cysteine or homocysteine to ethanolamine. The last mechanism might be of real interest after the discovery of biological transulfuration reactions from homocysteine to serine with the production of cysteine¹.

¹ V. DU VIGNEAUD, G. B. BROWN, and J. P. CHANDLER, *J. Biol. Chem.* 143, 59 (1942). - F. BINKLEY, W. P. ANSLOW, and V. DU VIGNEAUD, *J. Biol. Chem.* 143, 559 (1942). - F. BINKLEY, *J. Biol. Chem.* 155, 39 (1944).

¹ R. LEUCKART and M. SCHMIDT, *Ber. dtsch. chem. Ges.* 18, 2339 (1885).

² G. ILLARI, I. MARENGHI, and E. TARANTELLI, *Ann. Chim. Appl. Roma* 43, 55 (1953). - G. ILLARI, I. MARENGHI, and A. STUANI, *Ann. Chim. Appl. Roma* 43, 744 (1953).

³ J. W. BAKER and J. GAUNT, *J. Chem. Soc.* 1949, 19.

⁴ G. ILLARI, I. MARENGHI, and A. STUANI, *Ann. Chim. Appl. Roma* 43, p. 744. (1953).

⁵ J. W. BAKER and J. GAUNT, *J. Chem. Soc.* 1949, 9.

⁶ H. W. THOMPSON and R. E. RICHARDS, *J. Chem. Soc.* 1947, 1252.