

$[\alpha]_D = +68.3^\circ$. This is converted by acetic anhydride into the optically inactive N-phenyl-C-methylsydnone described by Earl and Mackney³. Also the rates of racemization and of sydnone formation by acetic anhydride in ethereal solution at the ordinary temperature are parallel. Furthermore, N-phenylsydnone exhibits its relationship to enols in that it undergoes instantaneous bromination in glacial acetic acid solution, yielding a monobromo derivative, m.p. 134° .

The structure (II) of this product follows from the fact that whereas hydrolysis by hydrochloric acid yields phenyl hydrazine hydrochloride, alkaline hydrolysis furnishes sodium benzene diazotate, identified by conversion into benzene-azo- β -naphthol.

This experimental evidence justifies the analogy quoted above, and is in line with the ideas expressed by Prof. Wilson Baker and W. D. Ollis.

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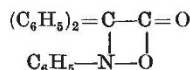
¹ *Nature*, **158**, 703 (1946).

² *Biochem. Z.*, **203**, 280 (1928); compare Du Vigneaud and others, *J. Biol. Chem.*, **96**, 511 (1932); **98**, 295 (1932); **99**, 143 (1932).

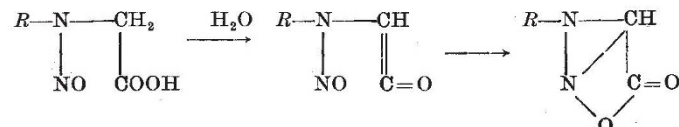
³ *J. Chem. Soc.*, 899 (1935).

THE fused-ring structure for the sydnones is as unacceptable to Prof. Wilson Baker and his colleague¹ as to Mr. Eade and myself. They suggest that since a reasonable structure of the classical type cannot be assigned to these substances, they are probably hybrids of some of the possible extreme dipolar structures, but they give no experimental evidence. The subject having been raised, it might be as well to indicate the lines on which we have done further experimental work.

N-Phenyl-C-phenyl-sydnone can be prepared by the action of acetic anhydride on a benzene solution of N-nitroso- α -anilinophenylacetic acid. If one of the optically active forms of the acid is used, the sydnone is inactive and identical with that prepared from the inactive acid. This was expected, but it is conceivable that racemization might not have occurred in building up the fused-ring structure. Further experimental evidence is available from the ready decomposition of N-phenylsydnone in boiling aqueous solution when a little sodium carbonate or sodium acetate is added. There is a rapid evolution of carbon dioxide and the formation of resinous products. This suggests an analogy with the decomposition of the products obtained when nitroso-compounds condense with ketenes. One of the two products formed from nitrosobenzene and diphenylketene

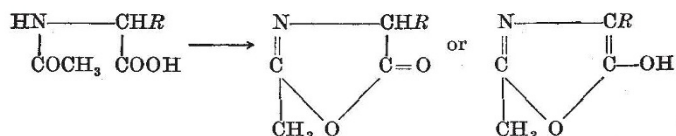


is very unstable and decomposes spontaneously to carbon dioxide and benzophenone anil². It is conceivable that sydnone formation might involve the following steps



again leading to the unlikely bicyclic structure.

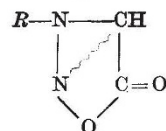
The similarity in behaviour of the carbonyl and nitroso groups suggests an analogy between the sydnones and the compounds formed by the action of excess of acetic anhydride on the α -acetylaminocarboxylic acids³.



In this case there is no need to consider a possible bicyclic structure.

A further fact which must be considered in arriving at a satisfactory structure for the sydnones is the frequent occurrence of phenyl isocyanide among the decomposition products of N-phenyl-sydnone (for example, on its pyrolysis).

Taking all our present knowledge of the sydnones into consideration, I venture to suggest that we have in their structure a partly formed bond. There must always be a stage in the formation of a chemical bond between two reacting atoms in which they can be regarded as neither being uninfluenced by one another, nor in a state of complete and settled combination. It is usually not possible to arrest the process at this stage, but in the sydnones the five-membered ring controls the situation. The sydnones do not show any obvious dipolar characteristics, and if their structure is to be regarded as a hybrid of two dipolar structures, it may be merely one way of saying that there is present an incipient non-polar structure which one might write, *faute de mieux*,



the wavy line indicating an incipient link between the carbon and nitrogen. The same wavy line may have the further symbolism of indicating the doubt which must remain in our minds on this structural question until considerably more experimental evidence is forthcoming.

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¹ *Nature*, **158**, 703 (1946).

² Staudinger, "Die Ketene" (1912).

³ Bergmann and Zervas, *Biochem. Z.*, **203**, 280 (1928).

Colorimetric Estimation of Penicillin II

THE Kapeller-Adler¹ method for the estimation of phenylalanine depends on the nitration of phenylalanine to give 3:4-dinitrophenylalanine; this is then reduced by alkaline hydroxylamine to a coloured nitroso derivative. It appeared probable that, by virtue of its phenylacetic radical, penicillin II (G) might be estimated in the same way and in the presence of penicillin I (F).

Unfortunately, nitrated samples of penicillin II treated with hydroxylamine gave