

shift the equilibrium of reaction (1) completely to the right-hand side. On addition of oxygen, the spectrum of (II) is fundamentally altered. The various ϵ -values depend, *inter alia*, on the time of exposure to oxygen and on its partial pressure. The spectrum of oxidized (II), for specified experimental conditions, is shown by curve (b). The molar light absorption coefficient, ϵ , is defined by optical density/optical path-length $\times c$, where c , the polymer concentration, is calculated from the initial concentration of cyclopentadiene and the number average degree of polymerization specified before¹.

Spectrophotometric tests, in the range 4500–6500 Å., were carried out continuously during the conversion of the monomer and it was possible, therefore, to study by an optical method the gradual building up of this coloured polymer. The results of these experiments will be discussed elsewhere.

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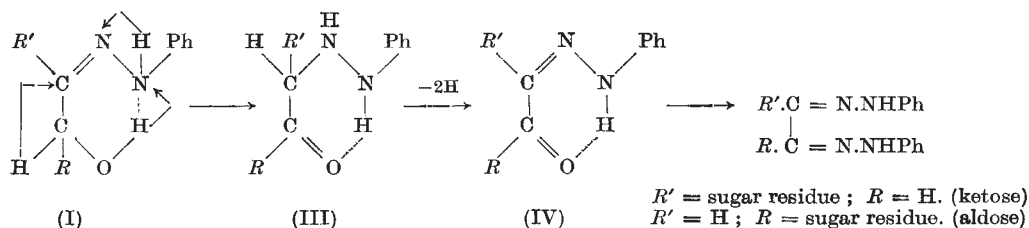
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¹ *Nature*, **168**, 459 (1951).

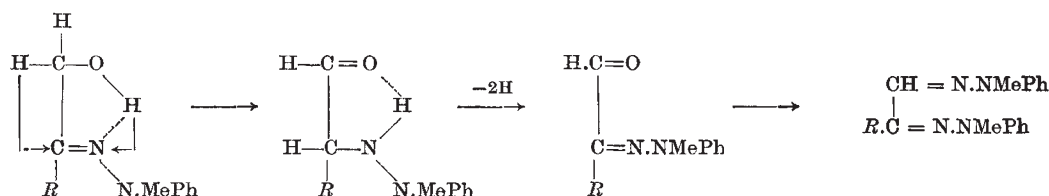
² *Nature*, **172**, 73 (1953).

Mechanism of Osazone Formation

A FACT which seems to have escaped attention in formulating a mechanism for osazone formation is



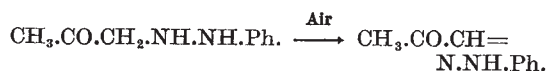
or,



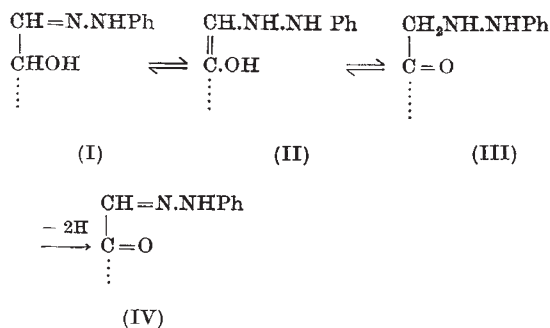
that β -alkyl substituted phenylhydrazines are oxidized very readily in air to form phenylhydrazones¹:



Further, it has been found recently² that β -acetyl phenylhydrazine is also oxidized by air at room temperature extremely readily:



Here, it seems, is an important clue for detecting the mechanism of osazone formation, since if, as Weygand suggested³, an Amadori rearrangement (I \rightarrow III) is assumed:



then it is no longer necessary to search for an oxidizing agent to convert (III) into (IV). All that is required is a hydrogen acceptor such as oxygen, or the phenylhydrazonium cation⁴, which is reductively cleaved to aniline and ammonia.

This mechanism will accommodate all the known facts on osazone formation, including the observation of Orning and Stempel⁵ that the reaction is inhibited at 30° C. in the absence of air. Since oxygen and the phenylhydrazonium cation are competing hydrogen acceptors, one would expect to find a correlation between the yield of aniline (and ammonia) and the quantity of oxygen present.

The formation of osazones and methylphenyl-osazones may proceed through the hydrogen bonded structures shown below:

Two suggestions have been put forward⁶ to explain why the reaction is not continued to C₃ of the sugar residue, but a choice between these must await further experimental evidence.

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¹ Gramatacakis, *C.R. Acad. Sci., Paris*, **204**, 1262 (1937); **210**, 303 (1940).

² Mitchell (in the press).

³ Weygand, *Ber.*, **73**, 1259 (1940).

⁴ Kenner and Knight, *Ber.*, **69**, 341 (1936). Braude and Forbes, *J. Chem. Soc.*, 1763 (1951). Bloink and Pausacker, *J. Chem. Soc.*, 661 (1952).

⁵ Orning and Stempel, *J. Org. Chem.*, **4**, 410 (1939).

⁶ Percival, "Adv. Carbohydrate Chem.", **3**, 43 (1948). Fieser and Fieser, "Organic Chemistry", 351 (D. C. Heath and Co., Boston, 1944).