

Brèves communications – Kurze Mitteilungen – Brevi comunicazioni – Brief Reports

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The Zinc Reduction of Benzoin

One of the standard preparations of stilbene involves the reduction of benzoin by means of a modified Clemmensen procedure^{1,2}. This reaction, even though it has been extensively employed in this capacity, is still not clearly understood^{3,4}. An investigation of the reaction was initiated in an attempt to clarify the reaction mechanism. In an attempt to isolate intermediates, a chromatographic analysis of the benzoin reduction products was undertaken. This analysis disclosed the presence of trans-stilbene (70%), cis-stilbene (5%), benzoin 5(%) and deoxybenzoin pinacol (2%). The expected intermediates, benzyl phenyl carbinol, hydrobenzoin or deoxybenzoin, were not isolated. The reduction of these compounds was also attempted. Under reductive conditions¹, the carbinol and hydrobenzoin did not react; the ketone afforded deoxybenzoin pinacol (75%).

Since the α -substituent to the carbonyl group appears to be a prerequisite for the reaction, it was suggested that information on the reaction may be obtained by varying this substituent. Therefore the reduction of benzoin methyl ether, benzoin acetate and benzoate, and desyl chloride were attempted. In each case, the major product

was trans-stilbene; the yields of olefin were 83, 72, 80, and 71%, respectively. Thus the reaction appears to be a general reduction for benzoin derivatives.

Our explanation for the absence of intermediates in the reduction is that a zinc complex⁵ is reduced directly to the olefin.

Zusammenfassung. Es wird die Reduktionsarbeit des Benzoin beschrieben.

G. E. RISINGER, E. E. MACH, and J. H. GARRETT

Department of Chemistry, Louisiana Polytechnic Institute, Ruston (Louisiana, U.S.A.), January 16, 1963.

¹ D. A. BALLARD and W. H. DEHN, J. Amer. chem. Soc. **54**, 3969 (1932).

² R. L. SHRINER and A. BERGER, in *Organic Syntheses*, Coll. vol. 3 (John Wiley and Sons, Inc., New York 1955), p. 786.

³ L. F. FIESER, *Experiments in Organic Chemistry* (D. C. Heath and Co., Boston 1951), p. 179.

⁴ J. H. BREWSTER, J. Amer. chem. Soc. **76**, 6364 (1954).

⁵ J. H. BREWSTER, J. Amer. chem. Soc. **76**, 6361 (1954).

Free Amino Acids in *Limnaea* II

It has already been found¹ that the amount of free amino acids in the *Limnaea* eggs (fertilized) increases greatly just before hatching. We could not, however, determine the number of amino acids at this stage, for there was absolutely no chromatographic resolution either on Whatman paper no. 1 or on Whatman no. 4. But it would be interesting to ascertain this point, for it might help us to determine exactly when the adult tissues assume their characteristic pattern of free amino acids.

We have therefore tried a slightly different approach, which, though still imperfect, enables us to assert that the number of free amino acids in the mature egg is not more than two. In order to attain this improved result we have carefully separated the individual eggs from the jelly-like substance in which they are embedded. This can easily be accomplished by cutting and scraping with razor blades. These separated eggs, crushed one after another on Whatman paper no. 1, were chromatographed with the solvent system *n*-Butanol:acetic acid:water = 4:1:1. The

result was better and comparable with the chromatogram of recently hatched snails. There was a spot of slight intensity just above the origin, apparently starting from the origin itself followed by two more recognizable spots with a very marked trailing or streaky effect. This pattern has been noted in young snails¹ up to 45 days after hatching².

The densitometric curve corresponding to the egg chromatogram was obtained from a recording densitometer (Figure 1). Because of the excessive trailing effect one should be cautious in evaluating the result; but we may safely say that there are not more than two free amino acids in any remarkable quantity. In case of eggs 1–2 days before hatching, the *R_f* values corresponding to amino acids were 0.33 and 0.22 (serine) approximately, in a room of constant temperature of about 26°C.

In our earlier work we were surprised to find such a small number of free amino acids, because, according to

¹ R. L. BRAHMACHARY and A. BHATTACHARYA, *Exper.* **19**, 143 (1963).

² R. L. BRAHMACHARY, unpublished data.