

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE GOVERNMENT COLLEGE OF LAHORE.]

STUDIES ON PHOTOTROPISM IN SOLUTION. PART I.

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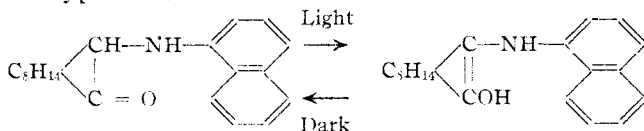
In the series of investigations, of which this is a preliminary note, it is intended to examine substances which exhibit phototropy *in solution*. With one possible exception, namely, di-9-hydroxy-phenyl-anthryl-10-amine,¹ phototropy has not hitherto been observed except in the case of solids. The reddening of solutions of benzaldehyde phenylhydrazone in alcohol and in alcohol acidified with acetic acid is not due to the transposition of hydrazone as has been pointed out by Baly and Tuck but to oxidation under the catalytic influence of light. The color change which slowly takes place in the dark is greatly accelerated in light. The solution of α -naphthylamino-camphor in chloroform is colorless and it remains so if it is kept in the dark, but on exposure to direct sunlight, the color becomes deep bottle-green within a minute. Similarly a chloroform solution of *m*-phenylene-bisamino-camphor is colorless in the dark but on exposure to direct sunlight for about 5 minutes a deep green color is developed. Again the solution of ar. tetrahydro- α -naphthylamino-camphor is slightly reddish when dissolved in chloroform, and it remains so if the solution is not exposed to light, but when presented to direct sunlight, the color develops to green within about 2 minutes. In the above cases the green color completely vanishes when the green solutions are placed in the dark for about 24 hours. The time which is required for the transformation of the colorless to the colored solution varies considerably with the intensity of light. The brighter the sunshine the quicker the change. Even diffused light can bring about the change but in that case the time required may be some hours or even days. The electric light and the light of a sodium flame have no effect on the colorless solution. The slightly green tinge which is developed in a few seconds can be made to vanish by placing the solution in the dark for even less than an hour. The change can be repeated half a dozen times or even more, each repeated change producing less and less sharp color, owing to decomposition of the substance.

This investigation thus opens up a new chapter, in the study of the phototropic transformation; and Senier and Shepheard's² suggestion that the change is not due to intramolecular but to extramolecular rearrangement into molecular aggregates, therefore needs revision in the light of the present investigation. It may be noted here, that Senier and Shepheard's explanation may be quite applicable to the solid substance but in the case

¹ Foresti, *Atti accad. Lincei*, [V] 23, 270 (1914).

² Senier and Shepheard, *J. Chem. Soc.*, 95, 1944 (1909).

of solutions it is untenable. The change in this case is very probably due to a change in the chemical structure of the molecule. For instance, in the case of α -naphthylamino-camphor the change may be represented as the keto-enol type thus,



The colorless solution probably contains the keto compound, whereas the green solution is due to the change of the keto to the enol form. The imino-derivatives in each of the above 3 cases do not show this phototropic behavior. The effect is produced only when the imino compound is transformed into the amino derivative, in which case alone the tautomeric change is possible. This may be regarded as a proof for the view put forward as to the mechanism of the change, but in the preliminary survey of a new field which is now presented, it is not possible to prove definitely the occurrence of dynamic isomerism of the above type. The true explanation of the change must, however, wait until the experiments, which have been instituted with this end in view have been completed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ROCHESTER.]

THE CONDENSATION OF ACETYLENE WITH BENZENE AND ITS DERIVATIVES IN THE PRESENCE OF ALUMINUM CHLORIDE.

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The first and most important work on this condensation was that of Varet and Vienne.¹ They passed acetylene through a mixture of benzene and aluminum chloride, and reported the formation of a product containing 80% phenyl ethylene (styrene), 15% *unsym.* diphenylethane and 5% *sym.* diphenylethane (dibenzyl). Neither the actual amounts obtained, referred to the reacting materials, nor the conditions under which the runs were made, were stated.

Since the results of some work in this laboratory tended to throw considerable doubt on the correctness of these conclusions, this investigation was begun to ascertain, if possible, the general conditions governing the action of acetylene on benzene and benzene derivatives, and to determine the products formed by these reactions.

Work of a somewhat similar nature, but under entirely different con-

¹ Varet and Vienne, *Compt. rend.*, **164**, 1375 (1886).