CCXXXVI.—*The Asymmetric Photochemical Decomposition of Humulene Nitrosite by Circularly Polarised Light.*

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VAN 'T HOFF ("Die Lagerung der Atome im Raume," 1894, p. 30) appears to have been the first to suggest that optically active substances might be produced under the asymmetric influence of circularly polarised light, and several investigators have subsequently endeavoured to realise this idea experimentally.

Cotton (*Ann. Chim. Phys.*, 1896, **8**, 347) discovered that alkaline solutions of copper tartrate exhibit unequal absorption for right- and left-handed circularly polarised light from the red end of the spectrum. Since, in addition, these solutions are decomposed by sunlight, Cotton considered them particularly suitable for asymmetric photochemical experiments. During the summer of 1897 (see *J. Chim. physique*, 1909, **7**, 81) he worked with an alkaline solution of copper racemate contained in two glass cells. One was exposed to right-handed and the other to left-handed circularly polarised light, and it was hoped that rotations of opposite sign would be developed. After considerable decomposition had taken place the two solutions were transferred to polarimeter tubes, but no rotation could be detected in either.

Byk (*Z. physikal. Chem.*, 1904, **49**, 641) carried out some experiments with optically active photographic preparations (silver tartrate paper and silver bromide plates sensitised with chlorophyll); each was exposed simultaneously in a spectrograph to right- and left-handed circularly polarised light of the same intensity, but no difference could be observed in the effects produced.

Freundler (*Bull. Soc. chim.*, 1907, **1**, 657) exposed a solution of the racemic diamyl acetal of *o*-nitrobenzaldehyde in *r*-amyl alcohol to right-handed circularly polarised light; amyl *o*-nitrosobenzoate was formed, but neither this substance nor the amyl alcohol recovered from the experiment showed any rotation.

Henle and Haakh (*Ber.*, 1908, **41**, 4261) studied the photochemical transformation of methylethylcyanoacetic acid into methylethylacetonitrile, and of dichlorodimethylsuccinic acid into dichlorodimethylpropionic acid, but although circularly polarised light was used in both cases, only inactive products resulted.

Bredig (*Z. angew. Chem.*, 1923, **36**, 456) also made unsuccessful attempts, in which diazocamphor, lactic acid, and asymmetric cobaltammine salts were exposed to circularly polarised ultra-violet light.

Of these fruitless attempts, that of Cotton alone merits further consideration. Byk (*loc. cit.*) has shown that an alkaline solution of copper tartrate is not acted on by light from the red end of the spectrum, as Cotton had thought, the decomposition being caused by ultra-violet rays (λ = 4000—3500 Å.U.) just beyond the visible violet. It is important, therefore, to ascertain if alkaline solutions of copper tartrate show circular dichroïsm for these ultra-violet rays. Cotton did not continue his measurements beyond 4370 Å.U., so the present work included observations made down to 3500 Å.U. in order to settle the question.

Extension of Cotton's Experiment.—The apparatus employed was that described by the author (J., 1928, 3258).* The solution consisted of 1 g. of copper tartrate, 0·5 g. of potassium hydroxide, and 0·5 g. of sodium hydroxide made up to 100 c.c. with distilled water. A 10-cm. layer was first used and it was decreased in stages down to 3 mm., photographs being taken at each stage. The absorption extended at the ultra-violet end to about 4000 Å.U. with the thickest layer and gradually receded to about 3500 Å.U. with the thinnest layer, but no difference could be detected between the absorption for right- and left-handed circularly polarised light in this region. It would appear, therefore, that asymmetric photochemical decomposition of alkaline solutions of copper racemate cannot be expected.

Whilst the additional work now described was in progress, two positive results were published. Kuhn and Braun (*Naturwiss.*, 1929, **17**, 227) exposed alcoholic solutions of racemic ethyl α-bromopropionate in quartz flasks to circularly polarised ultra-violet light (λ = 2800 Å.U.), whereupon the solution acted on by the right-handed light developed dextrorotation and *vice versa* : the greatest effect obtained in each case was 0·05°. Later, Kuhn and Knopf (*ibid.*, 1930, **18**, 183; *Z. physikal. Chem.*, 1930, *B*, **7**, 292) exposed the racemic dimethylamide of α-azidopropionic acid in hexane solution to circularly polarised ultra-violet light (λ 3200—2800). After 37% decomposition by left-handed circularly polarised light, the liquid dimethylamide was recovered and showed a rotation of —1·04° in a 1 dm. tube. A corresponding experiment with right-handed circularly polarised light gave a reading of + 0·78°.

Experiments with Caryophyllene Nitrosite.—Kremers and Schreiner (*Pharm. Arch.*, 1892, **2**, 287) studied the action of light on caryophyllene nitrosite, and found that in benzene solution nitrogen was evolved and crystals of the decomposition product separated. From experiments with coloured solutions as light filters, they concluded

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* In this earlier paper the terms right- and left-handed circularly polarised light were used in the sense originally employed by Cotton, which is opposite to that in general use.

that the reaction was caused by the red and yellow rays of sunlight. This conclusion was confirmed by placing a row of tubes containing the blue nitrosite solution in the spectrum obtained from an electric arc. The solution in the tubes exposed to red and yellow light turned green, whilst that in the others remained unchanged.

Mitchell (*loc. cit.*) has already investigated the rotation dispersion and circular dichroïsm of this substance in alcoholic solution. The rotation reaches a high maximum positive value about 6250 Å.U., becomes zero at 6800 Å.U., and is thereafter negative. Absorption spectra revealed a band in the red region with its head about 6800 Å.U. When the absorption was examined with circularly polarised light, it was found that the right-handed light was more strongly absorbed than the left-handed. This substance was considered, therefore, to be very promising for asymmetric photochemical work.

The selection of a suitable solvent presented some difficulty. Ethyl butyrate was used finally because it dissolved both the nitrosite and the decomposition product readily and was not too volatile. A 5% solution showed $\alpha_{5461} + 36^\circ$ in a 6-cm. tube. On exposure to sunlight, nitrogen was evolved, the blue solution gradually became colourless, and the rotation decreased to a small negative value. The decomposition could, therefore, be followed conveniently with the polarimeter.

For the experiments with circularly polarised light, a 4·6% solution was put in a specially constructed double cell (see Fig. 2). One side was exposed to right-handed and the other to left-handed circularly polarised red light. Polarimeter readings were taken at intervals of four hours, but as the difference between the rotations for the two sides of the cell was small and erratic, no definite conclusions could be drawn. The apparatus proved to be successful, however, in the following experiments.

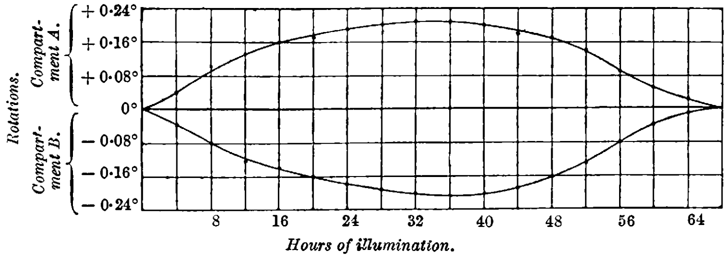
Experiments with Humulene Nitrosite.—Unfortunately, the racemic form of caryophyllene is not known, but the inactive sesquiterpene humulene is very closely related to it and forms a blue nitrosite which is so similar to that of caryophyllene that it was thought advisable to submit the humulene derivative to the action of circularly polarised light. Both hydrocarbons contain the grouping $CMe_2{:}C<$, which absorbs nitrous anhydride to give $CMe_2(ONO){\cdot}C(NO)<$; and, since the other two groups attached to the second carbon atom are different, the addition renders this atom asymmetric. The existing optical activity in the case of caryophyllene seems to be sufficient to cause the exclusive formation of the dextrorotatory nitrosite. In the case of inactive humulene, however, there is no such directing influence so that a racemic mixture of dextro- and lævo-forms is obtained.

In a preliminary experiment, the double cell was filled with a

3·5% solution of humulene nitrosite in ethyl butyrate. On polarimetric examination no rotation was observed in either compartment. As in the earlier experiment with caryophyllene nitrosite, one side was then illuminated with right-handed and the other with left-handed circularly polarised red light. After 4 hours the solutions were again examined in the polarimeter, and it was found that the side which had been exposed to left-handed light had developed a slight dextrorotation, whilst the other side had developed a small lævorotation. On further illumination the difference between these values increased until after 12 hours one side showed a rotation of + 0·11° and the other − 0·09° ($\lambda = 5461$). On still further illumination, however, the difference between these values decreased.

The results of a further experiment with a 7% solution of the nitrosite are given in Table I, in which the rotations denoted by A and B refer to the compartments illuminated by left-handed and right-handed light, respectively. Remarkable symmetry is revealed when these results are represented graphically (Fig. 1). A maximum rotation of 0·21° ($\lambda = 5461$) on each side of the zero was developed after 36 hours of illumination. Additional readings taken at this stage with mercury yellow light gave rotations of + 0·30° and − 0·30°. During the earlier part of the experiment, observations with yellow light were impossible because it was too strongly absorbed by the solution, but this difficulty diminished as the decomposition proceeded.

FIG. 1.

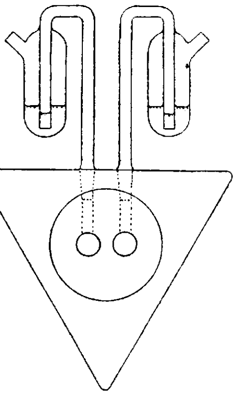


EXPERIMENTAL.

The humulene was obtained by distillation of hop oil, the fraction of b. p. 115—122°/10 mm. being sufficiently pure for the present purpose. The nitrosite was prepared as described by Chapman (J., 1895, **67**, 780); after crystallisation from a cold mixture of alcohol and chloroform it melted at 113°.

Apparatus.—All parts of the apparatus were rigidly mounted on an optical bench. An automatic electric arc served as source of illumination. Cored carbons, 7 mm. positive and 5 mm. negative, were used with a current of 12 amps. In front of the arc was placed a circulating water filter 3″ thick, followed by a red gelatin filter transmitting light of 6000—7800 Å.U. The light was rendered parallel by a convex lens and was plane polarised by passage through a Nicol prism. Half of the field was then covered with a mica λ/4 plate suitably oriented and of the correct thickness to give right-handed circularly polarised light of about 7000 Å.U. The other half was covered with a λ/4 plate cut from the same piece of mica and oriented to give left-handed circularly polarised light. Finally came a double cell containing the solutions under examination. This was held in a V-shaped trough which could be raised, lowered, tilted, or moved laterally so that all necessary adjustments could be made to ensure that the light passed straight through the cell and that the two compartments were illuminated by different kinds of circularly polarised light. An end elevation of the double cell is shown in Fig. 2. Two holes, of 0·2″ diameter, were drilled through a 60° glass prism 2·5″ long, and inlet holes were drilled from the top. The latter were slightly tapered and bubblers of the type shown were ground into them. During the experiments the bubblers were partly filled with solvent. The two horizontal holes were carefully polished until both held exactly the same volume of liquid. The end pieces were made of the best quality optical glass, and cemented in position. A thin brass plate with two holes of equal diameter, just smaller than those through the prism, covered the end of the cell next the light source, and so protected the solutions from stray light. This device also facilitated the taking of polarimeter readings. A Hilger polarimeter was used, the adjustable V-shaped trough provided with the instrument being particularly convenient for comparative measurements with the double cell. After each period of illumination, the cell was transferred to the polarimeter, where the solutions were allowed to settle for about ½ hour before the rotations were read. Throughout the experiment the room was maintained at a temperature of 21°.

FIG. 2.



It is interesting that these effects have been produced by visible light and that it has been possible to take polarimeter readings during the course of the reaction. The experimental procedure described is simpler and more direct than that employed by Kuhn and his collaborators (*locc. cit.*). Indeed, humulene nitrosite has proved to be an almost ideal substance for demonstrating the asymmetric photochemical action of circularly polarised light.

TABLE I.

Time of illumination, hours.	Rotations.		Diff.	Time of illumination, hours.	Rotations.		Diff.
	A.	B.			A.	B.	
4	+0·04°	−0·04°	0·08°	36	+0·21°	−0·21°	0·42°
8	+0·10	−0·08	0·18	40	+0·20	−0·20	0·40
12	+0·13	−0·12	0·25	44	+0·18	−0·19	0·37
16	+0·16	−0·14	0·30	48	+0·17	−0·16	0·33
20	+0·17	−0·16	0·33	52	+0·14	−0·13	0·27
24	+0·19	−0·18	0·37	56	+0·09	−0·08	0·17
28	+0·20	−0·19	0·39	60	+0·05	−0·04	0·09
32	+0·21	−0·20	0·41	64	+0·02	−0·01	0·03

In conclusion, I desire to acknowledge a grant from Imperial Chemical Industries, Ltd., which defrayed part of the cost of the investigation. I have also pleasure in thanking Mr. Stanley B. Cormack, M.A., B.Sc., for assistance with the expermental work.

UNIVERSITY OF GLASGOW. [*Received, May* 19*th*, 1930.]