121. *The Asymmetric Photolysis of* β-*Chloro*-β-*nitroso*-αδ-*diphenylbutane with Circularly Polarised Light.*

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Some years ago, the successful asymmetric photolysis of humulene nitrosite was described (Mitchell, J., 1930, 1829), but attempts to extend this work to simpler nitrosites and ψ-nitroles did not lead to positive results. Recently, however, chloronitroso-compounds were found to be more suitable, and experiments have now been carried out with β-chloro-β-nitroso-αδ-diphenylbutane. This compound (in methyl alcohol) was irradiated with right-handed circularly polarised red light until about 90% of it had been decomposed. The unattacked portion was recovered and showed $\alpha^{20°}_{5300} = -0{\cdot}10°$ ($l = 1$, $c = 4\%$ in methyl alcohol). A corresponding experiment with left-handed light gave the value $+0{\cdot}11°$.

In 1896, Cotton found that certain optically active substances absorb right- and left-handed circularly polarised light to different extents and he called the phenomenon " circular dichroism." He suggested that, if a substance possessed this property when in the dextro- or lævo-form and was susceptible to photochemical decomposition, it might be possible to effect a partial resolution of the racemic form by irradiating it with one type of circularly polarised light. This problem of asymmetric photolysis is of interest in connection with the question of the origin of optically active compounds in Nature, but its experimental realisation is extremely difficult (see Mitchell, " The Cotton Effect," London, 1933; Mathieu, " La Synthèse Asymétrique," Paris, 1935). In the first place, although many substances have been found to exhibit circular dichroism, the relative difference in absorption of the two kinds of circularly polarised light is usually only a few units %. It is expressed as the "anisotropy factor," $(\varepsilon_l - \varepsilon_r)/\varepsilon$, where ε_r, ε_l, and ε are the molecular extinction coefficients for right- and left-handed and ordinary light, respectively. In addition, there are three photochemical requirements: (*a*) destruction of the molecular dissymmetry by the light, (*b*) a quantum efficiency of 1, and (*c*) absence of dark reactions. Of these (*a*) is essential, and (*b*) and (*c*) should be fulfilled as strictly as possible.

Despite many attempts at asymmetric photolysis by a number of workers, conclusive results were not obtained till 1930, when Kuhn and Knopf (*Z. physikal. Chem.*, *B*, **7**, 292) decomposed the dimethylamide of α-azidopropionic acid with circularly polarised ultra-violet light, and Mitchell (J., 1930, 1829) acted on humulene nitrosite with circularly polarised red light. It was thought desirable to extend the work to simpler nitroso-compounds, although it was realised that they might not yield such striking results.

The nitrosites of bornylene, phellandrene, and zingiberene were first studied by Mitchell and Cormack (J., 1932, 415). They were white solids which gave colourless solutions in organic solvents at room temperature. A solution of bornylene nitrosite (in toluene) turned blue on warming (due to dissociation of double molecules) but lost its colour again on cooling. The blue solution showed circular dichroism and at 70° had an anisotropy factor of about 0·04. Unfortunately, considerable decomposition was caused by the prolonged heating which would have been necessary for photochemical experiments, and, as the phellandrene and zingiberene compounds were even less stable, work upon these three nitrosites was abandoned.

Some ψ-nitroles, $CR(NO_2)NO{\cdot}R'$, were next examined. Although usually white in the solid state, they dissolve in organic solvents to give blue solutions at room temperature, which absorb oxygen in red light to afford the corresponding dinitro-compounds. Hammick and Lister (J., 1937, 489) found the quantum efficiency of this reaction for dimethyl-ψ-nitrole in benzene solution to be 0·89. When R and R′ are different, the molecule has an asymmetric carbon atom which is destroyed by the photo-oxidation. An attempt was made (with Roy R. Gordon) to prepare the active form of methylethyl-ψ-nitrole from *d*-β-nitrobutane (cf. Kuhn and Albrecht, *Ber.*, 1927, **60**, 1297), but our product had no rotation. We also studied the photo-oxidation of methylethyl-ψ-nitrole, but found that it was accompanied by an appreciable dark reaction. With ψ-nitroles of higher molecular weight the dark reaction became more rapid, so work on these compounds was abandoned.

An investigation of the photochemical action of nitrosyl chloride on *n*-hexane (Mitchell and Carson, J., 1936, 1005) directed attention to chloronitroso-compounds, and the photolysis of β-chloro-β-nitrosobutane was carried out by Mitchell and Cameron (J., 1938, 1964). It appeared from this work that chloronitroso-compounds would be suitable for asymmetric photochemical experiments, but this one was rather volatile. Before proceeding further, however, it was desirable to find if the chlorine atom interferes with the Cotton effect of the nitroso-group in this type of compound. Satisfactory evidence on this point was obtained by Mitchell and Simpson (J., 1940, 784) from a study of *l*-menthyl *d*-chloro-β-nitrosobutyrate. It had an anisotropy factor of about 0·04 (in ethyl alcohol) and analysis of the rotatory dispersion curve showed that the contribution due to the nitroso-group was not affected by the presence of the chlorine atom.

β-Chloro-β-nitroso-αδ-diphenylbutane, $CH_2Ph{\cdot}CCl(NO){\cdot}CH_2{\cdot}CH_2Ph$, was selected for further work from a number of compounds examined by Mitchell, Schwarzwald, and Simpson (J., 1941, 602). It fulfilled the three photochemical requirements outlined above: (*a*) The main product of photolysis (in methyl alcohol) was the hydrochloride of αδ-diphenylbutan-β-oneoxime, so the asymmetry of the carbon atom was destroyed by the light. (*b*) The quantum efficiencies for λ 6100 and 6580 A. were 1·10 and 0·78, respectively, giving an average value of 0·94. (*c*) There was no dark reaction.

Preliminary asymmetric photochemical experiments, in which the compound was decomposed to the extent of 75%, showed conclusively that irradiation with right-handed light produced negative rotation for λ 5300 A., a wave-length on the short-wave side of the absorption band ($\varepsilon_{\text{max.}} = 6580$ A.), and positive rotation (for the same wave-length) was developed with left-handed light. The rotations observed were rather small, however, and in order to obtain larger values we decided to continue the irradiation till about 90% of the chloronitroso-compound had been decomposed. As it was difficult to isolate the unchanged substance in a pure condition if the decomposition had gone too far, we carried out the asymmetric photolysis in four stages (one of 50% and three of 40%), recovering the unattacked compound after each stage. This procedure also saved a considerable amount of light. Polarimetric examination of the final specimens which had been exposed to right- and left-handed light, respectively, gave the values $\alpha_{5300}^{20^\circ} = -0{\cdot}10^\circ$ and $+0{\cdot}11^\circ$ ($l = 1$, $c = 4\%$, in methyl alcohol), or $[\alpha]_{5300}^{20^\circ} = -2{\cdot}50^\circ$ and $+2{\cdot}75^\circ$.

EXPERIMENTAL.

αδ-Diphenylbutan-β-one.—This was prepared at first by oxidation of β-hydroxy-αδ-diphenylbutane (from β-phenylethylmagnesium chloride and phenylacetaldehyde; cf. Tiffeneau, Orékhoff, and Lévy, *Bull. Soc. chim.*, 1931, **49**, 1846), but owing to difficulty in obtaining phenylacetaldehyde, the method described by Haworth, Mavin, and Sheldrick (J., 1934, 1424) was also used. Phenylacetonitrile was condensed with methyl β-phenylpropionate (cf. Beckh, *Ber.*, 1898, **31**, 3160) to give α-cyano-αδ-diphenylbutan-β-one, which was converted into the corresponding amide and then into the required ketone (m. p. 43°).

αδ-Diphenylbutan-β-oneoxime.—When αδ-diphenylbutan-β-one is treated with hydroxylamine hydrochloride and potassium acetate in aqueous alcohol and only slight heat is applied, a mixture of the two forms of the oxime is obtained in which the high-melting form (m. p. 121°) predominates. Prolonged heating (over 3 hours) favours the production of the low-melting form (m. p. 80°). For the present purpose it was not necessary to separate the two forms.

β-Chloro-β-nitroso-αδ-diphenylbutane.—This is best prepared by passing chlorine into a solution of αδ-diphenylbutan-β-oneoxime in dry ether until the oxime hydrochloride, which is precipitated at first, has disappeared and the solution is green. The ether is then distilled off, and the product crystallised from methyl alcohol; m. p. 47°. It can also be prepared directly from the oxime hydrochloride (recovered from photolysis) but it is more satisfactory to use the oxime (which crystallises out when the hydrochloride is boiled with methyl alcohol and the solution allowed to cool).

Apparatus.—The light source was an automatic carbon arc run from a D.C. generator with a current of 10 amps. A condensing lens ($f = 3''$) formed an enlarged image of the positive pole on a projection lens ($f = 12''$) about 2 feet away. Immediately behind the condenser was a diaphragm with a square aperture of 2 in. side. Following this was a 3-inch circulating water filter and a red glass filter for cutting off infra-red rays and light below 6000 A., respectively. In front of the projection lens a large double-image prism and a $\lambda/4$ plate (for red light) were fixed. Two images of the square aperture were thus produced side by side, and each was received on a glass cell ($5 \times 5 \times 2$ cm.), the $\lambda/4$ plate being oriented so that one cell was illuminated with right-handed and the other with left-handed circularly polarised light.

Procedure.—5 G. of β-chloro-β-nitroso-αδ-diphenylbutane were weighed into each cell, and a piece of plate glass through which a small hole had been drilled was cemented on top of each. When the cement had set, the cells were filled with methyl alcohol (freed as far as possible from dissolved oxygen) and the holes were closed with ground stoppers made from pieces of capillary tubing fitted with stopcocks. Some of the blue solid did not dissolve at first, but it gradually passed into solution as the experiment progressed. The cells were placed in position and irradiated until 50% decomposition had taken place (12 hours). This was determined by means of a photoelectric colorimeter. The contents of each cell were then evaporated to dryness under reduced pressure, and the blue compound was extracted from the oxime hydrochloride with dry ether. After removal of the ether, the residue was crystallised from methyl alcohol. The experiment was repeated four times, and the recovered chloronitroso-compound was used for the second stage of the asymmetric photolysis (40%) which was carried out twice. Only one experiment was necessary at the third and the fourth stage (each 40%). The average amount of chloronitroso-compound recovered from each cell in the four stages was 2·2, 2·1, 1·9, and 0·8 g., respectively. Approximately the same weights of oxime hydrochloride were also obtained. The total time of irradiation was 80 hours. The rotation measurements were made visually with a Hilger polarimeter (Lippich half-shadow angle = 5°) used in conjunction with a Zeiss–Winkel monochromator, the light source being a 100-c.p. Pointolite lamp.

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