222. *The Action of Nitrosyl Chloride on* n-*Hexane in Presence of Light.*

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Lynn (*J. Amer. Chem. Soc.*, 1919, **41**, 368) found that when a solution of nitrosyl chloride in *n*-heptane was exposed to sunlight it developed a transient blue colour, evolved hydrogen chloride, and deposited a brown oil which on steam distillation gave di-*n*-propyl ketone and smaller quantities of isomeric ketones. Later, Lynn and Hilton (*ibid.*, 1922, **44**, 645) showed that the oil contained oximes. The solution from which the oil had separated was not examined, but it was concluded that the blue colour was due to the formation of secondary nitrosoparaffins, which in presence of light were transformed into the corresponding oximes :

$$C_7H_{16} + NOCl \xrightarrow{-HCl} C_7H_{15}\cdot NO \text{ (blue)} \longrightarrow C_7H_{14}:N\cdot OH \text{ (oil)}$$

We became interested in the latter reaction, as it appeared to be promising for asymmetric photochemical work (cf. Mitchell, J., 1930, 1829). By using *n*-hexane instead of *n*-heptane, we expected to obtain secondary nitrosoparaffins with asymmetric carbon atoms whose asymmetry would be destroyed by the oxime transformation, and we hoped that it might be possible to isolate them from the blue solution. Michael and Turner (*Ber.*, 1906, **39**, 2153) have shown that *n*-hexane is readily chlorinated in sunlight, giving products which boil over a considerable temperature range, so it was desirable to use pure nitrosyl chloride in our experiments. Lynn had been content with the mixture of gases obtained by heating aqua regia. Owing to photochemical decomposition of the nitrosyl chloride (cf. Kistiakowsky, *J. Amer. Chem. Soc.*, 1930, **52**, 102), however, a certain amount of chlorination was to be expected even with pure nitrosyl chloride.

We prepared our nitrosyl chloride by heating a mixture of dry sodium chloride and pure nitrosylsulphuric acid, the latter having been obtained by the action of sulphur dioxide on cold fuming nitric acid. The gaseous nitrosyl chloride was passed into *n*-hexane (b. p. 67—69°) until it was saturated. Our first experiments with this solution were carried out in open boiling-tubes, and with bright sunlight the reaction proceeded exactly as described by Lynn for *n*-heptane. During a period when the available sunlight was not very bright, we were surprised to find that, although the blue colour developed slowly and then gradually disappeared, scarcely any oil was obtained. Photo-oxidation of the nitroso-compounds had evidently been taking place, for when air was excluded a brown oil separated as before, and a quantity was collected.

Examination of the Brown Oil.—Some of the oil was dissolved in water, neutralised with barium carbonate, and steam distilled. A colourless liquid was obtained, b. p. 79—82°/10 mm., $n_D^{20°}$ 1·4494 (Found : C, 62·3; H, 11·0. Calc. for $C_6H_{13}ON$: C, 62·6; H, 11·3%). Trapesonzjanz (*Ber.*, 1893, **26**, 1433) gave $n_D^{20°}$ 1·4464 for methyl *n*-butyl ketoxime.

A second portion of the oil was submitted to steam distillation without being neutralised, and yielded a colourless liquid, b. p. 120—130°, $n_D^{19°}$ 1·4055. Some of the latter was treated with chromic acid in the cold (cf. Michael and Turner, *loc. cit.*), but no hexoic acid resulted, so no aldehyde had been present. Another quantity of the liquid was allowed to react with semicarbazide hydrochloride, and the semicarbazone which separated was crystallised from alcohol (Found : C, 53·3; H, 9·5; N, 27·1. Calc. for $C_7H_{15}ON_3$: C, 53·5; H, 9·55; N, 26·8%). Following the procedure of Michael (*Ber.*, 1906, **39**, 2146), we found that the liquid consisted of about equal amounts of methyl *n*-butyl ketone and ethyl *n*-propyl ketone, and we concluded that the brown oil contained the oxime hydrochlorides of these ketones.

Absorption Spectra.—The absorption spectrum of a solution of nitrosyl chloride in *n*-hexane was next examined. The violet and ultra-violet rays were strongly absorbed and bands were located in the orange and blue with their heads at about 6000 and 4780 A., respectively. Using a carbon arc lamp in conjunction with suitable filters, we showed that the absorbed light in each of these regions was capable of turning the nitrosyl chloride solution blue, but the violet and ultra-violet rays were much more effective than the others.

We removed the hydrogen chloride and unchanged nitrosyl chloride from one of the blue solutions by blowing nitrogen through it, and examined its absorption spectrum. We found a band in the red with its head at about 6600 A.

Examination of the Blue Solution.—For preparing a quantity of the blue solution the red rays were filtered off from sunlight * by means of a solution of copper sulphate, and air was excluded from the nitrosyl chloride solution. The latter was contained in long tubes which were immersed in cylinders containing the copper sulphate solution. Under these conditions the reaction was arrested at the blue stage and only a little oil separated. When the evolution of hydrogen chloride ceased, the solutions were resaturated with nitrosyl chloride and again exposed to light. The process was then repeated so that in all each solution had three saturations. The resulting blue solutions were thoroughly washed with dilute sodium bicarbonate solution, dried, and fractionated under reduced pressure. A blue liquid, b. p. 39—42°/13 mm., was collected. From 1 l. of hexane, only a few c.c. of this liquid were obtained, so its preparation was somewhat tedious. The blue liquid could be kept in the dark for several weeks without any apparent decomposition (Found : N, 5·8; Cl, 25·0%; *M*, in benzene, 136).

We were at first surprised that the molecular weight and the chlorine content were so high. From the boiling point it was expected that monochlorohexanes would be present, but as these could account for only part of the chlorine it was evident that the compounds containing the nitroso-group must also contain chlorine. Further, the stability of the blue liquid led us to believe that the nitroso-groups were attached to tertiary carbon atoms (cf. Ipatieff, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 426). The conditions are satisfied by ββ- and γγ-chloronitrosohexanes, and it seemed likely that the blue liquid was a mixture of these compounds together with some monochlorohexanes. Rheinboldt and Dewald (*Annalen*, 1927, **455**, 300) prepared both ββ- and γγ-chloronitrosohexanes by the action of nitrosyl chloride on the corresponding oximes and showed that they were readily oxidised by nitric acid to chloronitro-compounds. We therefore oxidised some of our blue liquid by this method and on fractionating the product obtained a lower fraction, b. p. 45—55°/15 mm., which did not contain nitrogen, and a higher one, b. p. 79—80°/17 mm., which did. The former gave Cl, 29·7 (Calc. for $C_6H_{13}Cl$: Cl, 29·4%) and the latter Cl, 21·7 (Calc. for $C_6H_{12}O_2NCl$: Cl, 21·4%), so our conclusions are confirmed.

Rheinboldt and Dewald (*loc. cit.*) also showed that chloronitroso-compounds are oxidised by light and air in the same way as by nitric acid, but they did not carry out any photochemical experiments in the absence of oxygen. We felt, therefore, that it was desirable to submit our blue liquid to the action of red light in absence of oxygen. When this was done in hexane solution,† oxime hydrochlorides separated along with a quantity of tar as in our earlier experiments. We can conclude therefore that the oxime hydrochlorides which we obtained previously were produced (in part at least) from the blue chloronitroso-compounds. Further, since the ketone mixture obtained from the original brown oil consisted of about equal amounts of methyl *n*-butyl ketone and ethyl *n*-propyl ketone, it seems likely that the ββ- and γγ-chloronitrosohexanes are present in much the same proportion.

CONCLUSIONS.

When a solution of nitrosyl chloride in *n*-hexane is exposed to light from the violet end of the spectrum it rapidly turns blue. We have shown that the blue colour is due to the formation of ββ- and γγ-chloronitrosohexanes and not to secondary nitrosohexanes as the work of Lynn had led us to suppose. Probably secondary nitroso-compounds are first formed, but pass over immediately to the corresponding oximes, which (without the help of light) are converted into the chloronitroso-compounds by more nitrosyl chloride. Oxime hydrochlorides are produced from the chloronitroso-compounds with red light in absence of oxygen, but photo-oxidation takes place in presence of oxygen.

We thank the Carnegie Trust for the Universities of Scotland for a scholarship which enabled one of us (S. C. C.) to take part in this work.

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* In some experiments a mercury vapour lamp was used instead of sunlight.

† When methyl alcohol was used as solvent, the solution remained homogeneous and became only faintly brown. After the methyl alcohol had been distilled off, the remaining acid oil was extracted with hexane and the residue was dissolved in water. The solution was neutralised and the precipitated oil was extracted with chloroform and distilled. A liquid, b. p. 80—83°/11 mm., was obtained with $n_D^{20°}$ 1·4494 (Found : C, 62·1; H, 11·0%). These values are in agreement with those recorded for our original oxime mixture.