700. *The Photomutarotation of* (−)-*2-Chloro-2-nitrosocamphane.*

By A. J. N. HOPE and STOTHERD MITCHELL.

When (−)-2-chloro-2-nitrosocamphane is exposed to either red or ultra-violet light, the rotatory-dispersion curve is modified and shifted slightly towards longer wave-lengths. The absorption curve is displaced in a similar manner. These effects are due to a simple isomeric change, and probable configurations are assigned to the two forms of the compound.

IN a previous paper (Mitchell, Watson, and Dunlop, *J.*, 1950, 3440) it was shown that irradiation of an alcoholic solution of (—)-2-chloro-2-nitrosocamphane with red light produced a gradual inversion of the Cotton effect. From further work we now conclude that under the influence of light the positions of the chlorine and nitroso-groups on $C_{(2)}$ are interchanged. When photoisomerisation is accompanied by a change in optical rotation, as in the present case, the process may be called " photomutarotation."

Specimens of 2-chloro-2-nitrosocamphane, prepared by the action of chlorine on camphor oxime hydrochloride, have $[\alpha]_{6000} \approx +700°$. This value is not raised appreciably by chromatography on a number of adsorbants (which are effective for the purpose of purification), but passage through activated alumina gives a product with $[\alpha]_{6000} = +964°$. This increase in rotation can be explained by postulating two isomeric forms one of which is converted into the other (of higher rotation) during adsorption on alumina.* The rotatory dispersion curve (Mitchell *et al.*, *loc. cit.*) shows that (—)-2-chloro-2-nitrosocamphane has been produced.

An alcoholic solution of this material was irradiated with red light in the hope of isolating the mutarotated product, but on removal of the solvent an intractable gum remained. When a thin layer of the solid was irradiated *in vacuo*, however, the product could be purified by chromatography on sugar-charcoal. After further irradiation and purification $[\alpha]_{6060}$ became constant at −508°. Analysis confirmed that the materials before and after irradiation were indeed isomeric. Rotatory-dispersion data are given in Table 1, and from these it is apparent that the rotatory dispersion curve is an inverted form of the original. The new isomer may therefore be called (+)-2-chloro-2-nitrosocamphane.

TABLE 1. *Rotatory dispersion of* (+)-*2-chloro-2-nitrosocamphane in alcohol.*

$c = 1{\cdot}408$ g./100 ml.; $l = 2{\cdot}5$ cm.; $t = 18°$.

λ, Å	5200	5400	5500	5600	5700	5800	5900	6000	6100	6200	6300
α, °	−1·01	−1·18	−1·27	−1·38	−1·50	−1·59	−1·68	−1·74	−1·78	−1·70	−1·60
[α], °	−287	−335	−361	−392	−426	−452	−477	−494	−506	−483	−454

λ, Å	6400	6500	6600	6700	6800	6900	7000	7100	7200	7300	7400
α, °	−1·45	−1·26	−1·04	−0·46	+0·26	+0·79	+1·16	+1·39	+1·50	+1·44	+1·33
[α], °	−412	−358	−295	−131	+ 74	+224	+330	+395	+426	+409	+378

---

* Several other examples of isomerisation on polar adsorbants are known (cf. Gillam and El Ridi, *Biochem. J.*, 1936, **30**, 1735; Gallaway and Murray, *J. Amer. Chem. Soc.*, 1948, **70**, 2584).

The anomalies in rotatory dispersion for the two forms can now be compared :

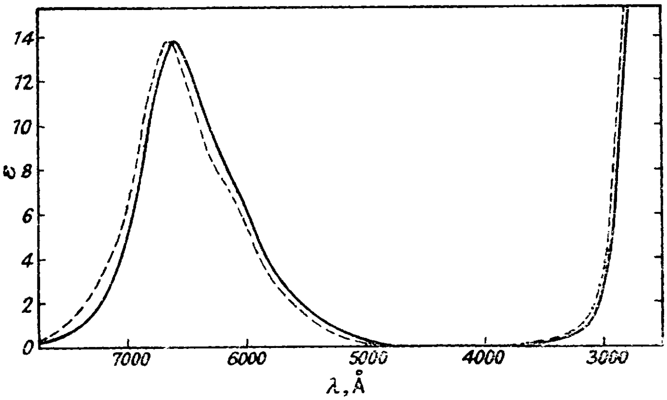
	Short-wave maxima	Reversal	Long-wave maxima
(−)-form	$[\alpha] = +964°$ at 6000 Å	6700 Å	$[\alpha] = -946°$ at 7100 Å
(+)-form	$[\alpha] = -508°$ at 6060 Å	6760 Å	$[\alpha] = +430°$ at 7160 Å

Thus, besides being inverted, the rotatory-dispersion curve for the (+)-form is displaced about 60 Å towards longer wave-lengths.

Absorption spectra for alcoholic solutions of the two forms are shown in Fig. 1. The curves are very similar but are separated by some 50—60 Å. In each case two regions of absorption are apparent; the band in the red is due to the nitroso-group, and the ultra-violet absorption to the presence of chlorine.

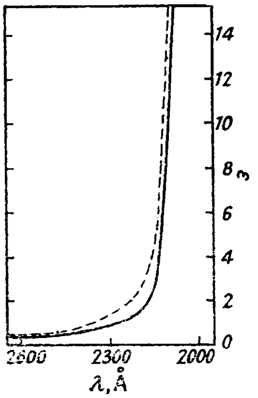
Since red light causes photomutarotation it appeared likely that the same effect might be produced by ultra-violet light, and this was tested experimentally by using a mercury lamp (with a Chance OX 7 filter to eliminate the green and yellow lines). The results are set out in Table 2, which shows the fall in rotation with time. In this case, the rate of photolysis is greater than that of photomutarotation so that the rotation does not pass through a minimum value as when red light was employed. We have corrected for photolysis by making a photoelectric estimation of concentration at 6625 Å (for which both the absorption curves in Fig. 1 have the same value of ε). This enabled us to calculate specific rotations which show the true course of mutarotation.

FIG. 1.



——— (—)-2-Chloro-2-nitrosocamphane.
– – – – (+)-2-Chloro-2-nitrosocamphane.

FIG. 2.



——— Bornyl chloride.
– – – – *iso*Bornyl chloride.

TABLE 2. *Irradiation of an alcoholic solution of* (—)-2-*chloro*-2-*nitrosocamphane with ultra-violet light.*

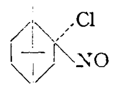
Concn. (c_0) = 1·888 g./100 ml. in a 1-cm. cell.
$k = \log I_0/I$ at 6625 Å, and $[\alpha] = 1000\alpha/c$ where $c = c_0 \times k/k_0$.

Min.	0	5	15	30	45	60	90	135	180	210
α_{6030}, °	1·80	1·68	1·51	1·25	1·04	0·85	0·56	0·33	0·17	0·11
k	1·27	1·22	1·16	1·05	0·95	0·86	0·71	0·54	0·40	0·32
$[\alpha]_{6030}$, °	953	926	876	801	736	665	531	411	286	231

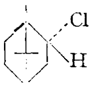
We also constructed an absorption curve after 135 min. of irradiation with ultra-violet light and found on comparing it with the original that the shift characteristic of photomutarotation had taken place.

When 2-chloro-2-nitrosocamphane prepared from (±)-camphor was exposed to red light no observable rotation developed at any stage in the reaction, but the absorption curve of the final material was found to be displaced 50—60 Å to longer wave-lengths, showing that both enantiomorphic forms had mutarotated, but in opposite directions and at exactly the same rate.

Having shown that (—)-2-chloro-2-nitrosocamphane isomerises under the influence of light, it remained to assign configurations to the two isomeric forms.* The compounds of known configuration most closely related to them are bornyl chloride and *iso*bornyl chloride. We have examined the absorption spectra of these two compounds (in hexane) as far into the ultra-violet as our instrument would permit, and they are given in Fig. 2. The difference in position of the absorption curves here is closely analogous to that shown in Fig. 1 for the two chloro-nitroso-isomers under investigation. Accordingly we suggest that the following pairs have similar configurations. The usual steric conventions are employed.

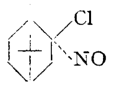


(—)-2-Chloro-2-nitrosocamphane

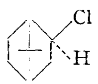


Bornyl chloride

endo



(+)-2-Chloro-2-nitrosocamphane



*iso*Bornyl chloride

exo

EXPERIMENTAL

(—)-2-*Chloro*-2-*nitrosocamphane*.—Camphor oxime hydrochloride in dry ether was chlorinated according to Mitchell *et al.* (*loc. cit.*) but with the following modifications. After removal of the ether, the blue solid was dissolved in the minimum volume of light petroleum, and the unchanged oxime hydrochloride filtered off. The filtrate was transferred to a column of sugar charcoal (50 × 2·5 cm.), and the blue band eluted with the same solvent. This treatment yielded a product with $[\alpha]_{6000} = +707°$; $\varepsilon_{\text{max.}} = 13·6$; m. p. 145—146° (decomp.). Passage of this material through a column (50 × 2·5 cm.) of Light's alumina (activated at 200° for 4 hr.) gave a product with $[\alpha]_{6000} = +803°$; $\varepsilon_{\text{max.}} = 13·7$ (for $\lambda = 6600$ Å); m. p. 145—146° (decomp.). Re-adsorption on alumina raised $[\alpha]_{6000}$ to +964° while the absorption maximum and m. p. remained unchanged. All operations were carried out in diffuse light.

(+)-2-*Chloro*-2-*nitrosocamphane*.—A cylindrical 200-ml. cell, containing (—)-2-chloro-2-nitrosocamphane (0·25 g.), was placed vertically on one end and evacuated to 0·1 mm. The bottom surface was kept at 30—40° on a warm plate and the upper end cooled to —180° by contact with a brass vessel containing liquid air. The material sublimed on the cold upper surface in the course of 30 min., forming a thin 15-sq. cm. film. The cell was irradiated with light from a carbon arc, the condensed beam first passing through a circulating water filter and a piece of infra-red glass (Chance ON 20). Irradiation was continued for 30 min., during which time the cell was reversed frequently. Thereafter, the vacuum was released and the solution of material in light petroleum chromatographed on sugar-charcoal (25 × 1 cm.). The product had $[\alpha]_{6060} = -438°$; $\varepsilon_{\text{max.}} = 13·7$ (for $\lambda = 6650$ Å); m. p. 140—141° (decomp.). This procedure was repeated several times and the products were combined and used as starting material for the second stage, which consisted of irradiation and purification as before. This gave (+)-2-*chloro*-2-*nitrosocamphane* with $[\alpha]_{6060} = -508°$; $\varepsilon_{\text{max.}} = 13·8$; m. p. 140—141° (decomp.). Continued processing by these methods did not change the rotation further (Found: C, 59·8; H, 7·6; N, 6·7. $C_{10}H_{16}ONCl$ requires C, 59·7; H, 7·9; N, 6·9%).

Ultra-violet Irradiation of (—)-2-*chloro*-2-*nitrosocamphane*.—A solution of (—)-2-chloro-2-nitrosocamphane (1·888 g./100 ml.) in oxygen-free alcohol was contained in a stoppered Vitreosil cell (1 cm.) with strain-free end-pieces. This was irradiated with a Kromayer water-cooled mercury lamp, a Chance OX 7 filter being used.

Polarimetric and absorption measurements were made at various times. For the latter a special carrier was constructed enabling the cell to be fitted directly into the spectrophotometer.

Inactive 2-*Chloro*-2-*nitrosocamphane*.—The preparation and purification were similar to those for (—)-2-chloro-2-nitrosocamphane. After chromatography on sugar-charcoal, the product was found to have absorption maximum and m. p. identical with the above compound. All operations were carried out in diffuse light.

Bornyl Chloride.—Commercial "pinene hydrochloride" (22·5 g.) was crystallised twice from "AnalaR" amyl alcohol (18·5 g.). The crystals were washed with methyl alcohol (2 ml.), and

---

* It should be noted that we have no means of establishing that our separation of the two isomeric forms is complete. We can say, however, that the (—)-form has the highest maximum rotation obtainable by adsorption on alumina, and the (+)-form has the lowest minimum rotation that irradiation with red light can produce.

trituration with this solvent removed the remaining traces of amyl alcohol. The product, dried *in vacuo* over sodium hydroxide, had m. p. 132—133°, $[\alpha]_D = +25{\cdot}9°$ (*c*, 1·004 in EtOH).

iso*Bornyl Chloride*.—This is best prepared by the rearrangement of camphene hydrochloride under carefully controlled conditions according to Meerwein and van Emster (*Ber.*, 1922, **55**, 2526), who claim 99·6% purity. Our product had m. p. 159—160°.

Optical Measurements.—Rotation readings were taken with a Hilger (triple-field) polarimeter in conjunction with a Winkel–Zeiss monochromator and a 12-v projection lamp. Absorption measurements were made on a Unicam SP. 500 spectrophotometer.

The microanalyses were carried out by Mr. J. M. L. Cameron and Miss M. W. Christie.

UNIVERSITY OF GLASGOW.

[*Received, July* 1*st*, 1953.]