The Photoisomerisation of Some Chloronitroso-terpenes.

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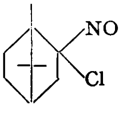
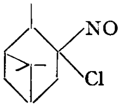
On exposure to light of suitable wave-length, the 2-chloro-2-nitroso-derivatives of pinocamphane, carane, and *p*-menthane all show a small bathochromic displacement of the nitroso absorption band. In this respect they resemble 2-chloro-2-nitrosocamphane (*J.*, 1953, 3483) but differ from it in that their rotatory dispersion curves are not inverted on irradiation. From these results and from kinetic measurements it is concluded that an isomerisation of the normal→*iso* type is involved in each case. Spatial configurations are suggested for the isomeric forms.

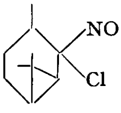
As an extension of work on the photochemistry and optical properties of chloronitroso-compounds, the terpene derivatives (II), (III), and (IV) have now been prepared and examined. Some data are also included for the structurally related material (V).



(I)



(II)



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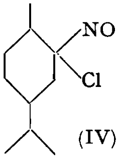

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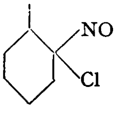


(V)

While studying the rotatory dispersion of (—)-2-chloro-2-nitrosocamphane (I), Mitchell, Watson, and Dunlop (*J.*, 1950, 3440) found that both mutarotation and photolysis result from irradiation. Hope and Mitchell later (*J.*, 1953, 3483) showed that exposure to red light produced a slight bathochromic displacement of the absorption and rotatory dispersion curves, in addition to the inversion of the latter previously observed. The product of photomutarotation was isolated and proved to be isomeric with the starting material. It was also shown how a photo-electric estimation of concentration would allow for photolysis and permit the calculation of specific rotations which give the true course of mutarotation. This procedure renders unnecessary the isolation of pure rearranged product, and has now been applied to compounds (I)—(III) which have been irradiated in alcoholic solution with mercury yellow light (Table 1).

For (I) the specific rotation falls to a final value of opposite sign, but for (II) and (III) it decreases to a limiting value of the same sign. Attainment of this final value $[\alpha]_\infty$ gives the time at which rearrangement is complete. When log $\{[\alpha]_t - [\alpha]_\infty\}$ is plotted against time a straight line is obtained in each case (Fig. 1), indicating a reaction of the first order.

TABLE 1. *Effect of irradiation on the specific rotation of* (I), (II), *and* (III).

Time (hr.)	0	0·25	0·50	1·00	1·25	1·50	2·00	4·00	6·00	12·00	18·00
(I) $[\alpha]_{6025}$	+ 947°	+ 804°	+ 652°	+ 374°	+ 280°	+ 181°	+ 18°	−341°	−455°	−510°	−510°
(II) $[\alpha]_{5800}$	− 390°	− 351°	− 320°	− 281°	− 263°	− 248°	−221°	−182°	−167°	−167°	−165°
(III) $[\alpha]_{5950}$	+1790°	+1452°	+1338°	+1271°	+1250°	+1250°	—	—	—	—	—

FIG. 1.

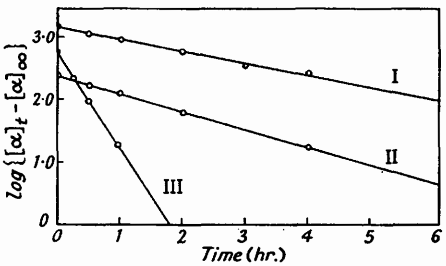


FIG. 2.

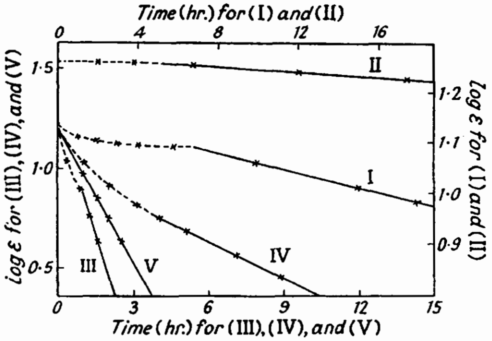


TABLE 2. *Rotations and absorptions for compounds* (II)—(V).

		Before irradiation	After isomerisation	Displacement
2-Chloro-2-nitrosopinane (II)	λ at ε_{max}	6350 Å	6450 Å	100 Å
	$[\alpha]_{max.}$	+390° at 6600 Å	+210° at 6700 Å	—
	λ at [α] = 0°	6300 Å	6400 Å	100 Å
	$[\alpha]_{min.}$	−390° at 5750 Å	−180° at 5850 Å	—
2-Chloro-2-nitrosocarane (III)	λ at $\varepsilon_{max.}$	6675 Å	6750 Å	75 Å
	$[\alpha]_{max.}$	+1800° at 5900 Å	+1126° at 5975 Å	—
	λ at [α] = 0°	6620 Å	6680 Å	60 Å
	$[\alpha]_{min.}$	−1600° at 6850 Å	−1265° at 6925 Å	—
2-Chloro-2-nitroso-*p*-menthane (IV)	λ at $\varepsilon_{max.}$	6870 Å	6885 Å	15 Å
	$[\alpha]_{max.}$	+353° at 7100 Å	+353° at 7100 Å	—
	λ at [α] = 0°	6570 Å	6570 Å	Undetectable
	$[\alpha]_{min.}$	−247° at 5900 Å	−247° at 5900 Å	—
2-Chloro-1-methyl-2-nitroso*cyclo*hexane (V)	λ at $\varepsilon_{max.}$	6850 Å	6850 Å	None
		Inactive	Inactive	—

Table 2 contains optical data for compounds (II)—(V) which show considerable differences in individual behaviour. The displacements of rotatory dispersion and absorption curves are all bathochromic, and are most pronounced for (II). The largest values of specific rotation are given by (III). During irradiation there is no change in the specific rotation of (IV), but the expected bathochromic shift of the absorption band is just detectable. Compound (V) has not been resolved into its enantiomorphic forms, and no displacement of the absorption curve was observed on irradiation.

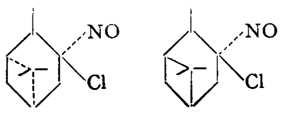
A study of the kinetics of photolysis for (V) led to the development of a new method of detecting photoisomerisation, which has found particular application in the case of (IV). The plot of log ε against time shows a linear relation only with (V) (Fig. 2), where *cis–trans* skeletal rearrangement is impossible. In all other cases there is an initial curved part which later simplifies into a straight line. The inflection gives the time at which a complex process, consisting of (*a*) photolysis of the original molecule, (*b*) rearrangement of the original molecule, and (*c*) photolysis of the rearranged molecule, resolves into (*c*) alone, which conforms to kinetics of the first order. The times for complete isomerisation found from the points of inflection of curves (I), (II), and (III) in Fig. 2 agree well with those required for the specific rotation to reach the limiting values recorded in Table 1. Finally, we have calculated velocity constants for the photolysis of the rearranged molecules from the straight parts of the graphs in Fig. 2. These are given in Table 3 along with the velocity constants for photoisomerisation obtained from the slopes of the lines in Fig. 1.

TABLE 3. *Velocity constants for photoisomerisation and photolysis.*

Compound	(I)	(II)	(III)	(IV)	(V)
Photoisomerisation k_1 (hr.$^{-1}$)	0·56	0·66	3·40	—	—
Photolysis k_2 (hr.$^{-1}$)	0·020	0·005	0·74	0·107	0·41

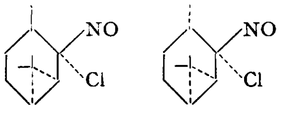
DISCUSSION

The interchange of the NO and Cl groups on $C_{(2)}$ in these compounds requires inversion of their Cotton effects. This has been shown to take place with (I) (Hope and Mitchell, *loc. cit.*), but with the others the rotatory dispersion curves do not invert on irradiation and we interpret the isomerisation as being of the type pinocamphone ⟶ *iso*pinocamphone, carone ⟶ *iso*carone, carvomenthone ⟶ *iso*carvomenthone for (II), (III), and (IV), respectively, as the ketones used for starting materials are predominantly of the normal form. Such isomerisation is impossible in (I) because of the locking effect of the 1 : 4-bridge on the stereochemistry of $C_{(1)}$, and rearrangement proceeds by interchange of the NO and Cl groups in such a way as to accommodate the excited chromophore in the more stable *endo*-position relative to the bridge (cf. Shoppee, *Chem. and Ind.*, 1952, 86; Barton, *J.*, 1953, 1040). In each of the other three structures, however, rearrangement of the molecular skeleton appears to take place more readily than inversion of the groups on $C_{(2)}$, and the excited nitroso-group again becomes *endo* to the bridge in (II) and to the methyl group in (III) and (IV). Since, in addition, the sign of the Cotton effect gives the spatial arrangement of the groups on $C_{(2)}$ in each case, the following configurations may be assigned to the isomeric forms.



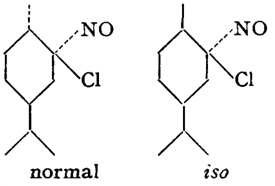
normal *iso*

2-Chloro-2-nitrosopinane



normal *iso*

2-Chloro-2-nitrosocarane



normal *iso*

2-Chloro-2-nitroso-*p*-menthane

EXPERIMENTAL

All the chloronitroso-compounds were prepared in subdued light.

Materials.—(−)-*Pinocamphone.* Distillation of oil of hyssop gave a fraction, b. p. 212—214°/741 mm. This crude pinocamphone was purified through the semicarbazone which after recrystallisation from a large volume of methanol had m. p. 228—230°. The ketone was regenerated by steam-distillation with oxalic acid, and then redistilled (b. p. 208—209°/745 mm., n_D^{17} 1·4743, α_D −19·7°).

(+)-2-*Chloro*-2-*nitrosopinane*. Oximation of the above ketone by Cook and Bachmann's method (*J.*, 1936, 79) gave a product which after distillation had b. p. 83°/0·4 mm., α_D −18·9°. This oxime (4 g.) was dissolved in dry ether (100 ml.), and chlorine passed in for 1½ hr. Removal of the solvent and excess of chlorine under reduced pressure left the *chloronitroso*-compound as a blue oil which distilled under a vacuum (b. p. 47°/0·4 mm.) (Found : Cl, 17·5. $C_{10}H_{16}ONCl$ requires Cl, 17·6%).

(+)-*Carone*. Commercial (+)-carvone had b. p. 231—233°/755 mm., n_D^{18} 1·4980, α_D +56·5°. Reduction by Wallach's method (*Annalen*, 1894, **279**, 377) resulted in saturation of the double bond conjugated with the carbonyl group, and purification of the product through the bisulphite compound gave dihydrocarvone, b. p. 88·5°/11·2 mm., n_D^{20} 1·4703, α_D −15·93°. Dry hydrogen chloride was passed into the ketone at 0°, until an increase in weight corresponding to 120% of the theoretical amount had occurred (Klotz, *J. Amer. Chem. Soc.*, 1944, **66**, 88). The resulting material still contained unchanged (−)-dihydrocarvone, but further treatment with hydrogen chloride gave the required hydrochloride, b. p. 68—70°/0·25 mm., n_D^{20} 1·4800, α_D −13·07°. Ring closure was effected in alcoholic potassium hydroxide, essentially as described by Richter, Wolff, and Presting (*Ber.*, 1931, **64**, 877), but modified according to Klotz (*loc. cit.*). The product had b. p. 86—87°/12·2 mm., n_D^{20} 1·4781, α_D +131°. Removal of unsaturated impurities by washing with neutral permanganate solution raised the rotation to +145·6°, the other properties remaining unchanged.

(−)-2-*Chloro*-2-*nitrosocarane*. Carone oxime prepared from the above ketone by Cook and Bachmann's method (*loc. cit.*) had b. p. 123—125°/14 mm., α_D +283°. Dry chlorine was passed through a solution of the oxime (1·2 g.) in dry ether (10 ml.) at −10° for 1 hr. Removal of the solvent and excess of chlorine under reduced pressure gave the *chloronitroso*-compound as a blue viscous oil, b. p. 56—57°/0·25 mm. (Found : Cl, 17·7. $C_{10}H_{16}ONCl$ requires Cl, 17·6%).

(−)-*Carvomenthone*. Redistilled commercial (+)-carvone was hydrogenated as described by Read and Johnston (*J.*, 1934, 229) with a palladium hydroxide–calcium carbonate catalyst. After 3¼ hr., 97·8% of the theoretical amount of hydrogen had been absorbed.

(+)-2-*Chloro*-2-*nitroso*-p-*menthane*. The crude (−)-carvomenthone contained some carvacrol and was oximated in the usual way. The resulting mixture was poured into ice-water, and the precipitated oxime was dried on a porous plate and then *in vacuo*. On recrystallisation from low-boiling petroleum, it had m. p. 95—97°, $[\alpha]_D$ −30·9° (*c*, 1·10 in EtOH). This oxime (2·5 g.) in dry ether (100 ml.) was chlorinated for 0·5 hr. at 0°. Removal of the solvent and excess of chlorine under reduced pressure left the blue non-viscous *chloronitroso*-compound, b. p. 53·5°/0·5 mm. (Found : Cl, 17·3. $C_{10}H_{18}ONCl$ requires Cl, 17·4%).

2-*Chloro*-1-*methyl*-2-*nitroso*cyclo*hexane*. The oxime of 2-methyl*cyclo*hexanone prepared by Cook and Bachmann's method (*loc. cit.*) had b. p. 114—115°/16 mm. Chlorination of the oxime (1 g.) in dry ether (250 ml.) at 0° for 2 hr. yielded an emerald-green solution. Removal of the solvent and excess of chlorine under reduced pressure gave the required *compound* as a viscous blue oil, b. p. 67—68°/14 mm. (Found : Cl, 22·0. $C_7H_{12}ONCl$ requires Cl, 22·0%).

Apparatus and Procedure.—All measurements were made with solutions ($c \simeq 1·5$) of the chloronitroso-compounds in ethanol (previously freed from dissolved oxygen by distillation in nitrogen). The solutions, in sealed 1-cm. cells, were irradiated with a high-pressure mercury arc, the yellow doublet being isolated by means of an Ilford filter. Rotation and absorption readings were taken at room temperature with the apparatus prevously described (Hope and Mitchell, *loc. cit.*). The spectrophotometric estimations of concentration were made for each material in the same way as for 2-chloro-2-nitrosocamphane, specific rotations being calculated during the reaction, and the corrected absorption curves were constructed for the isomerised products after irradiation.

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