

302. Phellandrene Nitrosites. Part II. The α - and the β -Nitrosite of *d*- α -Phellandrene.

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The α - and the β -nitrosite of *d*- α -phellandrene have been prepared, and their properties described.

IN Part I (this vol., p. 466) the physical constants and the mutarotation effects of *l*- α -phellandrene α -nitrosite described by Read and his co-workers (Smith, Hurst, and Read, J., 1923, **123**, 1657; Smith, Carter, and Read, J., 1924, **125**, 930) were confirmed; it was shown that preparations of the β -nitrosite could be isolated which had specific rotations in chloroform of -200° ; and the ready transmutation of such samples to the α -nitrosite was described.

The nitrosites of *d*- α -phellandrene (isolated from the terpene fraction of *Elemi* oil kindly supplied by Messrs. Stafford Allen and Sons, Ltd.) have now been examined, and closely similar effects have been observed. The purified α -nitrosite had m. p. 119—120°, and the values of its specific rotation in various solvents, though somewhat lower, are of approximately the same magnitude as those of *l*- α -phellandrene α -nitrosite, but of opposite sign, so the substances may be regarded as optical antipodes. Close agreement was also found between the preparations of the β -nitrosites, which had similar rotations in chloroform; so these may also be regarded as stereoisomeric, although it is doubtful if the highest degree of optical purity has yet been attained. Values of the specific rotations are recorded below for solutions of approximately the same concentration (*c*, 1.25) in various solvents, at 25°.

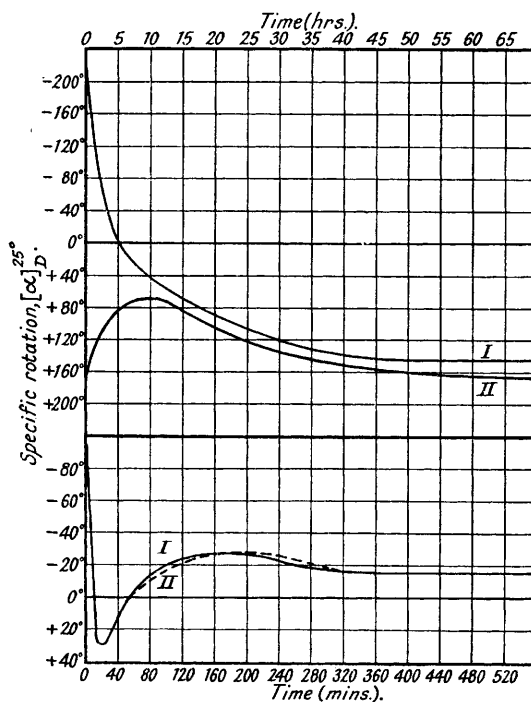
Solvent.	α -Nitrosite of		β -Nitrosite of		"Converted" nitrosite of	
	<i>d</i> - α -	<i>l</i> - α -	<i>d</i> - α -	<i>l</i> - α -	<i>d</i> - α -	<i>l</i> - α -
Acetone	- 168.4°	+ 182°	+ 170°	- 168°	- 163°	+ 175°
Benzene	- 217	+ 227.6	+ 211	- 214	- 209	+ 240
Chloroform	- 134	+ 142	+ 171	- 180	- 131	+ 141

The transmutation of *d*- α -phellandrene β -nitrosite into the α -nitrosite in boiling solution has also been observed; e.g., a sample of the β -nitrosite, m. p. 100°, $[\alpha]_D^{25} + 200^\circ$, gave, after boiling with acetone for a few minutes, a crystalline product, m. p. 118°. The specific

rotations recorded above and the mutarotation curves shown in Figs. 1 and 2 established the identity of the product with *d*- α -phellandrene α -nitrosite. The crude material precipitated from the mother-liquor by addition of methyl alcohol was also levorotatory, having $[\alpha]_D^{25} - 60^\circ$ in chloroform, so complete inversion of sign resulted from the treatment, followed by partial mutarotation of the α -nitrosite.

The mutarotations of the nitrosites in various solvents were examined, but as these closely followed the standard types established by Read and his co-workers (*loc. cit.*) for the corresponding derivatives of *l*- α -phellandrene, being of opposite sign, only a few typical curves are shown in the figures.

FIG. 1.



Upper Curves.

- I. *d*- α -Phellandrene α -nitrosite in benzene.
- II. *d*- α -Phellandrene β -nitrosite in benzene.

Lower Curves.

- I. *d*- α -Phellandrene α -nitrosite in chloroform + N/10-piperidine.
- II. "Converted" nitrosite in chloroform + N/10-piperidine.

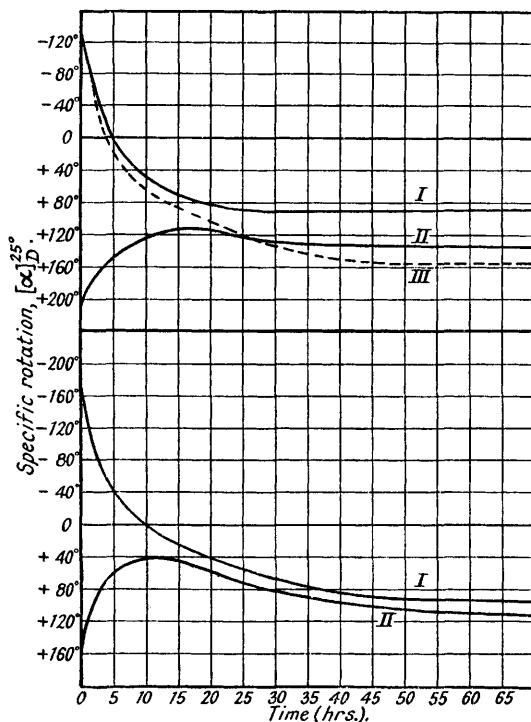
EXPERIMENTAL.

d- α -Phellandrene.—The terpene fraction of *Elemi* oil (500 c.c.), when distilled under reduced pressure through a column packed with aluminium Lessing rings, gave two main fractions: (1) b. p. $53^\circ/11$ mm. (220 c.c.), n_D^{20} 1.4729, d_{20}^{20} 0.8475, $\alpha_D + 72.5^\circ$ (homogeneous), $[\alpha]_D^{20} + 85.5^\circ$; (2) b. p. $53-54^\circ/11$ mm. (172 c.c.), n_D^{20} 1.4734, d_{20}^{20} 0.8473, $\alpha_D + 63.4^\circ$ (homogeneous), $[\alpha]_D^{20} + 74.8^\circ$. These fractions were used in the preparation of the nitrosites, and the flask residue was discarded [90 c.c.; n_D^{20} 1.4802, d_{20}^{20} 0.8781, $\alpha_D + 34.5^\circ$ (homogeneous), $[\alpha]_D^{20} + 39.3^\circ$].

Preparation of α - and β -nitrosites. The method closely followed that described in Part I (*loc. cit.*). In a typical experiment 100 c.c. of one of the *d*- α -phellandrene fractions was converted into the nitrosite in the usual way (Smith, Hurst, and Read, *loc. cit.*) and after an hour the crude nitrosite was filtered off and successively washed with alcohol and water. After being pressed to remove water, the material was stirred to a thin cream (twice) with carbon disulphide (100 c.c.), boiled, and filtered. Crude β -nitrosite was recovered from the filtrate by

dilution with methyl alcohol, the precipitate (1.2 g.) after being washed with methyl alcohol having $[\alpha]_D^{20} + 140.6^\circ$ in chloroform (*c*, 1.23). The original residue (19.4 g.), $[\alpha]_D^{20} + 51.6^\circ$ after being dried on a tile, was stirred into boiling chloroform (50 c.c.) and, after the addition of methyl alcohol (200 c.c.), placed in the refrigerator for a few hours. The residue was filtered off, washed with methyl alcohol (45 c.c.), and used for the preparation of the pure α -nitrosite (see below). *d*- α -Phellandrene β -nitrosite (0.9 g.) separated from the filtrate on standing in the refrigerator for 15 hours after the addition of water (80 c.c.). It had m. p. 100° , $[\alpha]_D^{20} + 198.3^\circ$ in chloroform (*c*, 1.15) (Found: N, 13.4. $C_{10}H_{16}O_3N_2$ requires N, 13.2%). Samples of the β -nitrosite from other preparations had specific rotations in chloroform of $+200.3^\circ$, $+205.7^\circ$, and $+211^\circ$.

FIG. 2.



Upper Curves.

- I. *d*- α -Phellandrene α -nitrosite in chloroform.
- II. *d*- α -Phellandrene β -nitrosite in chloroform.
- III. "Converted" nitrosite in chloroform.

Lower Curves.

- I. *d*- α -Phellandrene α -nitrosite in acetone.
- II. *d*- α -Phellandrene β -nitrosite in acetone.

The residue (above), which was still feebly dextrorotatory, was worked up for α -nitrosite by repeated solution in chloroform and precipitation with methyl alcohol. After two treatments the substance had m. p. 117° , $[\alpha]_D^{20} - 132.9^\circ$, and after five, m. p. 119° , $[\alpha]_D^{20} - 133.8^\circ$ in chloroform (*c*, 1.265). These values were not further improved by two more treatments. *d*- α -Phellandrene α -nitrosite was isolated as fine, white needles, m. p. 119° , $[\alpha]_D^{20} - 133.8^\circ$ in chloroform (*c*, 1.265), -168.4° in acetone (*c*, 1.253), and -217° in benzene (*c*, 1.255) (Found: N, 13.1%).

Transmutation of d- α -Phellandrene β -Nitrosite into the α -Nitrosite.—Ready conversion of the labile β - into the α -nitrosite occurs on boiling solutions for a few minutes; *e.g.*, β -nitrosite of m. p. 100° and $[\alpha]_D^{20} + 200^\circ$ in chloroform, when refluxed for 5 minutes in acetone and cooled, crystallised as fine white needles, m. p. 118° , $[\alpha]_D^{20} - 132.5^\circ$ in chloroform (*c*, 1.26). The specific rotation in other solvents, and the similarity of the mutarotation of this product in various

solvents to those of the pure α -nitrosite, established its identity with the latter. A precipitate of impure α -nitrosite, m. p. 100—102°, $[\alpha]_D^{20} - 59.7^\circ$ (c , 0.99 in chloroform), was recovered from the mother-liquor on standing overnight in the refrigerator after the addition of methyl alcohol. Inversion of sign was therefore complete, the crude substance being apparently contaminated by traces of the mutarotation products of the α -nitrosite. Similar transmutation was also observed on refluxing with other solvents.

Mutarotation Effects.—These were in all cases examined at 25°, the solutions employed being of substantially the same concentration. The complete changes in typical cases are shown in Figs. 1 and 2, and the effects in various solvents are summarised below.

d- α -Phellandrene α -nitrosite: in benzene (c , 1.2552) there was a steady fall from the initial value -217.5° (5 mins.) with inversion of sign occurring after some 6 hours ($+9.6^\circ$), the final value $+145^\circ$ being reached after 48 hours; in acetone (c , 1.253) a somewhat similar series of changes, -168.4° (5 mins.), $+11.2^\circ$ (11 hrs.), $+95^\circ$ (48 hrs.); in chloroform (c , 1.2536), -134° (5 mins.), $+24^\circ$ (7 hrs.), $+86^\circ$ (33 hrs.); in chloroform containing N/10-piperidine, -95.8° (2 mins.), $+7.2^\circ$ (9 mins.), $+29.5^\circ$ (18 and 30 mins.), -2.4° (1 hr.), -24° (2 hrs.), -18° (5 hrs.). The "converted" nitrosite gave very similar values.

d- α -Phellandrene β -nitrosite: in benzene (c , 1.2532), $+171.5^\circ$ (5 mins.), $+70^\circ$ (minimum, 10—12 hrs.), $+155^\circ$ (50 hrs.), $+166^\circ$ (72 hrs.); in acetone (c , 1.2576), $+162^\circ$ (4 mins.), $+31.8^\circ$ (minimum, 11 hrs.), $+102^\circ$ (48 hrs.), $+113^\circ$ (72 hrs.); in chloroform (c , 1.26), $+210^\circ$ (2 mins.), $+166^\circ$ (24 hrs.), $+136^\circ$ (72 hrs.); in acetone containing N/10-piperidine (c , 1.234), $+117.5^\circ$ (3 mins.), $+10^\circ$ (8 mins.), -54° (15 mins.), -74° (20 mins.), -105° (30 mins.), -110° (1.5 hrs.), -92° (60 hrs.).

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