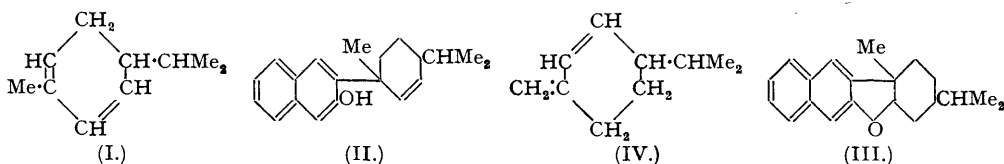


175. Application of the Diene Synthesis to Terpenoid Compounds.
Part III. Reaction between β -Phellandrene and β -Naphthol.

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The addition product formed between (–)- β -phellandrene and β -naphthol is shown to be identical with that obtained from (–)- α -phellandrene (cf. Salfeld, *Ber.*, 1940, **73**, 376). During the reaction more than 50% of the (–)- β -phellandrene is converted into (–)-limonene. It would appear that an unstable intermediate compound may be formed which then decomposes to give the (–)- α -phellandrene adduct and (–)-limonene, but attempts to isolate such an initial product were unsuccessful.

SALFELD (*Ber.*, 1940, **73**, 376) has pointed out that reactions such as the conversion of β -naphthol into β -naphthylamine on treatment with sodium hydrogen sulphite and ammonia are usually explained by postulating an intermediate carbonyl form for the phenol and that such a structure might be expected to behave as a dienophile in the Diels–Alder reaction. On heating β -naphthol with α -phellandrene (I) at 130° for 15 hours, Salfeld did obtain a product containing the reactants in the proportion 1 : 1, but from a consideration of the properties of this adduct he decided that addition had not taken place in a 1 : 4 position to the conjugated system of the terpene and assigned the formulæ (II) and (III) respectively to this compound and to the *iso*-adduct into which it was converted readily on treatment with (among other reagents) a methyl-alcoholic solution of hydrochloric acid. The *iso*-adduct was also obtained directly from β -naphthol and α -phellandrene when the condensation was effected under the conditions specified by Claisen (*Ber.*, 1921, **54**, 200; cf. Smith *et al.*, *J. Org. Chem.*, 1939, **4**, 311) which involve the use of an acid catalyst.



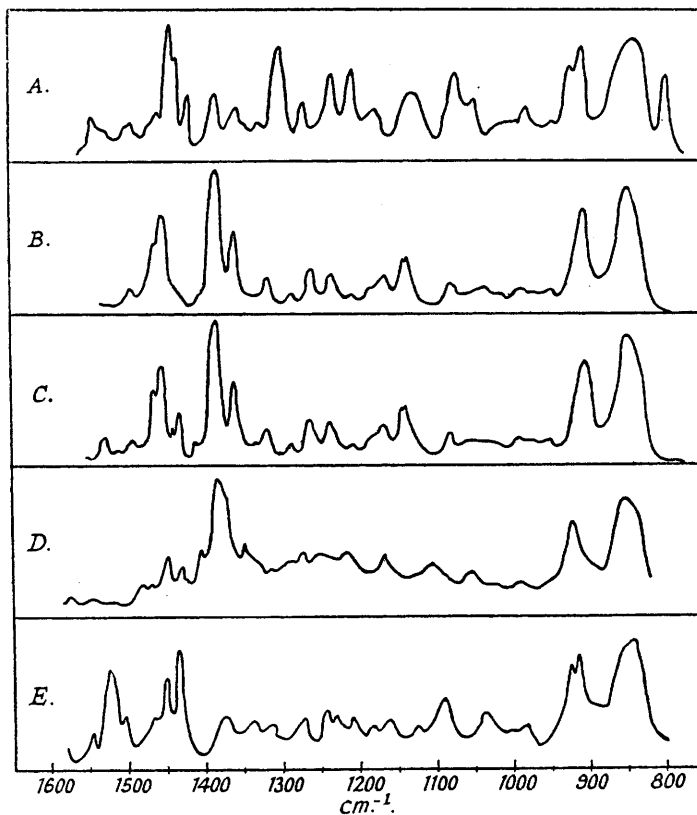
Salfeld reported that, when heated at 275° in the presence of selenium, the adduct was converted partly into its components, α -phellandrene and β -naphthol, but the method of identifying the terpene was not recorded. We have found that on distillation at atmospheric pressure, the adduct is decomposed into β -naphthol and α -terpinene.

In view of the behaviour of β -phellandrene (IV) towards maleic anhydride (Goodway and West, *J.*, 1938, 2028) and recent observations on the co-existence of α - and β -phellandrene in essential oils (*inter alii*, Berry, Macbeth, and Swanson, *J.*, 1937, 1443; Berry and Macbeth, *J.*, 1947, 1039), it appeared of considerable interest to investigate the reaction of this terpene with β -naphthol. (–)- β -Phellandrene can be obtained in a state of high purity from the readily available Canada balsam oil (Macbeth, Smith, and West, *J.*, 1938, 119). The adduct obtained from the (–)- β -phellandrene had m. p. 139–140° after recrystallisation from light petroleum, and $[\alpha]_D +124.8^\circ$ (in alcohol). Now Salfeld recorded a m. p. of 139–140° for the adduct which he obtained from α -phellandrene but unfortunately neither the constants nor the source of his sample of terpene was specified. Accordingly, we prepared a sample of (–)- α -phellandrene by fractional distillation from the terpene fraction of the oil of *Eucalyptus dives* which had previously been rendered free from cineole. The adduct which we obtained therefrom had m. p. 138.5–139.5°, $[\alpha]_D +123.9^\circ$ (in alcohol), and the melting point was not depressed on admixture with the adduct derived from the (–)- β -phellandrene (Acheson and West, *Nature*, 1948, **161**, 976). The identity of the adducts from the two terpenes was confirmed by preparing the *p*-nitrobenzoates and the *iso*-adducts. The infra-red absorption spectrograms of α - and β -phellandrene are distinct and characteristic (see figure) and, by this means, it was possible to detect as little as 5% of the α - in the presence of the β -isomeride in artificial mixtures of the two terpenes. This observation confirmed the conclusion reached by Goodway and West (*loc. cit.*; *J. Soc. Chem. Ind.*, 1937, **56**, 472r; 1938, **57**, 37) on chemical grounds that the (–)- β -phellandrene present in Canada balsam oil is free from the α -isomeride.

The yields of crude adduct from the α - and β -phellandrene were comparable (20–30% of the theoretical) and a method of purifying the adduct was devised so that the bulk of the unreacted terpene was recovered. After reaction of β -phellandrene with β -naphthol it was noticed that the terpene recovered failed to react with β -naphthol to give a further yield of adduct. It was

then observed that the constants had altered markedly and the flat nature of the ultra-violet absorption curve confirmed that β -phellandrene was not present (Booker, Evans, and Gillam, *J.*, 1940, 1453). This terpene was identified by the preparation of a tetrabromide of which the melting point was not depressed on admixture with a sample of authentic (-)-limonene tetrabromide. Furthermore, the infra-red absorption spectrogram of the recovered terpene was identical with that of dipentene (see figure).

Infra-red absorption spectrograms of terpenes.



Curve A— α -Phellandrene.

Curve B— β -Phellandrene.

Curve C—Recovered terpene from β -phellandrene- β -naphthol reaction.

Curve D—Dipentene.

Curve E—Recovered terpene from α -phellandrene- β -naphthol reaction.

The sample of (-)- α -phellandrene utilised in the reaction appeared, from its physical constants, to be in a fairly high state of purity although it was probably considerably less pure than the samples of the β -isomeride derived from Canada balsam oil. After reaction with β -naphthol the failure of the recovered terpene to react with maleic anhydride under mild conditions (Goodway and West, *J. Soc. Chem. Ind.*, 1937, 56, 472T; Birch, *J. Proc. Roy. Soc. N.S.W.*, 1937, 71, 261) and the nature of the ultra-violet absorption curve (Booker *et al.*, *loc. cit.*) proved that a conjugated system was no longer present, so the α -phellandrene had likewise undergone a reaction leading to redistribution of the double bonds. It has not proved possible to obtain crystalline derivatives from this product (probably a mixture owing to impurities in the original α -phellandrene) which remains unidentified, but the infra-red absorption spectrogram indicated that it did not contain limonene (see figure).

The β -phellandrene adduct (= α -adduct) was not decomposed into a terpene when heated at 147° for 15 hours; the oily by-product obtained on washing the crude β -phellandrene adduct with light petroleum was also unaffected by this treatment; the small amount of alkali-soluble material, isolated by acidifying the alkaline washes used to free the reaction product from

β -naphthol and extracting them with light petroleum, was not converted into a terpene on heating at 130° for 15 hours. Thus these three reaction products do not appear to be precursors of the (-)-limonene. (-)- β -Phellandrene was recovered unchanged when steam-distilled in the presence of β -naphthol, and when (-)- β -phellandrene was treated with $\frac{1}{2}$ mol. of β -naphthol the terpene recovered consisted of a mixture of (-)-limonene and unreacted β -phellandrene. The latter observation and the persistence of optical activity suggest that an unstable intermediate is formed which decomposes to give (-)-limonene and the adduct as products. Unfortunately it has not proved possible to isolate such an intermediate compound.

EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford.)

Reaction of (-)- β -Phellandrene with β -Naphthol.—In a typical experiment the β -phellandrene derived, by fractional distillation using a Podbielniak column, from Canada balsam oil (Smith and West, *J. Soc. Chem. Ind.*, 1937, 56, 300r) had b. p. 42–43°/4 mm., n_D^{20} 1.4805, α_D^{25} –43.4°, λ_{max} 2320 Å., ϵ_{max} 8300 (cf. Macbeth, Smith and West, *J.*, 1938, 119; Booker, Evans, and Gillam, *J.*, 1940, 1453). This terpene (40 g.) and β -naphthol (80 g.) were heated in an oil-bath at 128° \pm 2° for 20 hours. The cooled mixture was dissolved in ether (200 ml.) and washed with 2N-sodium hydroxide (300 ml.) three times, then with brine and finally with water. The ethereal solution was steam-distilled and the solution of recovered terpene in ether separated from the distillate (cf. Salfeld, *Ber.*, 1940, 73, 382). Removal of the ether gave 22.6 g. of recovered terpene having n_D^{20} 1.4752, α_D^{25} –74.2°. This oil (17 g.) on fractional distillation gave the following fractions:

Wt. (g.)	2.6	3.5	4.3	5.2	0.5
n_D^{20}	1.4744	1.4746	1.4750	1.4754	Residue
$[\alpha]_D$ (in EtOH)	–71.9°	–77.7°	–81.5°	–88.8°	—

Portions of these fractions were treated with reagents in the following proportions. Bromine (1.1 g.) was added dropwise to a solution of the terpene (0.5 g.) in ethyl alcohol (2 ml.) and ether (1 ml.), kept at 0° to –5°. Under these conditions each fraction gave a crystalline tetrabromide (m. p. approx. 88–91°). A mixed sample recrystallised from ether had m. p. 103–104°, $[\alpha]_D^{20}$ –65.4° (*c.*, 1.07 in chloroform) (Found: Br, 70.7. Calc. for C₁₀H₁₆Br₄: Br, 70.2%). (Oil of *Abies alba* on fractional distillation gave (-)-limonene having b. p. 53–53.5°/7 mm., n_D^{20} 1.4726, α_D^{25} –93.6°. The tetrabromide prepared therefrom had m. p. 103–104°, $[\alpha]_D^{20}$ –72.8° (*c.*, 1.03 in chloroform); mixed with the tetrabromide prepared from the recovered terpene, m. p. 103–104°.) The light brown, waxy residue remaining after steam-distillation was extracted with ether, and the ethereal solution boiled with charcoal to give a crude adduct (23.9 g.) which on trituration with light petroleum (b. p. 30–60°) gave 19.3 g., m. p. 128–134°, raised by five recrystallisations from light petroleum to 139–140°, $[\alpha]_D^{28}$ 124.8° (*c.*, 2.973 in ethyl alcohol) (Found: C, 85.7; H, 8.8. Calc. for C₂₀H₂₄O: C, 85.7; H, 8.6%). In other experiments (working essentially as described above or according to Salfeld, *loc. cit.*), using β -phellandrene having n_D^{20} 1.4796–1.4810, α_D –43° to –46°, the terpene recovered (56–70% of the weight taken) had n_D^{20} 1.4734–1.4755, $[\alpha]_D$ –61.4° to –82.6° (in ethyl alcohol) and the yield of crude adduct was 20–31% of the theoretical. The following is typical of experiments to utilise a neutral solvent in the reaction. β -Phellandrene (10 g.) having n_D^{20} 1.4803, α_D^{25} –41.2°, β -naphthol (20 g.), and benzene (30 g.), heated under reflux for 15 hours and worked up essentially as described above, gave recovered terpene (5.8 g.) having b. p. 56–58°/12 mm., n_D^{20} 1.4795, α_D^{25} –47.75°, and an oily adduct (2.1 g.) which on trituration with light petroleum gave a product (0.8 g.) which after recrystallisation from light petroleum had m. p. 136–137° not depressed on admixture with the adduct, m. p. 139–140°. In spite of the higher reflux temperatures, the yields of adduct were not increased when the reaction was carried out in toluene or xylene solution. Two other typical experiments were conducted as follows: (a) (-)- β -Phellandrene (20 g.) having n_D^{20} 1.4810, α_D^{25} –43.8°, and β -naphthol (10.6 g.), heated at 130° for 15 hours, gave a crude adduct (6.5 g.) which was recrystallised to m. p. 139–140°. The recovered terpene (12.5 g.) had b. p. 72–74°/21 mm., n_D^{20} 1.4780, α_D^{25} –58.4°, displayed a strong nitrosite reaction for phellandrene, and gave, in low yield, (-)-limonene tetrabromide, m. p. 101–102° after recrystallisation from ether, not depressed on admixture with authentic (-)-limonene tetrabromide. The sodium hydroxide washings on acidification gave 7.6 g. of product, m. p. 119–120° not depressed on admixture with β -naphthol. (b) (-)- β -Phellandrene (20 g.), treated as above with β -naphthol (21.2 g.), gave 9.9 g. of crude adduct which after two recrystallisations had m. p. 139–140°, and recovered terpene (14.1 g.) having b. p. 68–69°/15 mm., n_D^{20} 1.4751, α_D^{25} –69.65°, from which (-)-limonene tetrabromide, m. p. (and mixed m. p.) 103–104°, was prepared.

A sample of recovered terpene (8.5 g.), having b. p. 77–78°/30 mm., n_D^{20} 1.4750, $[\alpha]_D^{20}$ –85.8° (*c.*, 1.05 in ethyl alcohol) (Found: C, 88.0; H, 11.6. Calc. for C₁₀H₁₆: C, 88.2; H, 11.8%), and β -naphthol (17 g.) were heated in an oil-bath at 130° for 15 hours, and the reaction mixture treated as before. The recovered terpene (7.1 g.) had b. p. 75–77°/30 mm., n_D^{20} 1.4750, $[\alpha]_D^{25}$ –74.9° (*c.*, 1.15 in ethyl alcohol), and only 0.96 g. of dark, oily adduct was obtained, which deposited a small amount of solid material on standing. After twice recrystallising from light petroleum, this product (30 mg.) had m. p. 135–137°, and mixed with β -phellandrene adduct, m. p. 135–138.5°.

Derivatives of the β -Naphthol Adduct Derived from β -Phellandrene.—By proceeding essentially as described by Salfeld (*loc. cit.*), the following were prepared: *iso*-adduct, m. p. 105–106° (Found: C, 86.0; H, 8.8. Calc. for C₂₀H₂₄O: C, 85.7; H, 8.6%); *p*-nitrobenzoate of the adduct, m. p. 164.5–165.5° (Found: C, 74.9; H, 6.4. Calc. for C₂₂H₂₂O₄N: C, 75.5; H, 6.3%).

Preparation of the Adduct from (-)- α -Phellandrene.—In a typical experiment (-)- α -phellandrene, prepared by fractional distillation from a terpene fraction of the oil of *E. dives*, previously rendered free

from cineole by repeated shaking with a 50% aqueous solution of resorcinol, had b. p. 49.5—50°/10 mm., n_D^{20} 1.4735, α_D^{25} -102.5°, λ_{\max} . 2640 Å., ϵ_{\max} . 2260 (cf. Booker *et al.*, *loc. cit.*). This sample (40 g.) and β -naphthol (80 g.) were heated together during 15 hours at 130°, and the product worked up as described above. The crude adduct (23.1 g.), m. p. 128—133°, on trituration with light petroleum, gave 14.9 g., m. p. 133.5—134°, raised by two recrystallisations to 138.5—139.5°, [α_D^{28} 123.9° (c. 4.947 in ethyl alcohol)]. The terpene recovered (20.8 g.) during the steam-distillation had b. p. 58—58.5°/13 mm., n_D^{20} 1.4775, α_D^{25} -32.6°. The *iso*-adduct and the *p*-nitrobenzoate of the adduct (Salfeld, *loc. cit.*) had m. p. 106° and m. p. 164.5—165°, respectively. This adduct and these derivatives did not depress the m. p.s when admixed with the corresponding compounds derived from (-)- β -phellandrene.

Thermal Decomposition of the Adduct.—The adduct (8 g.) was distilled at atmospheric pressure with decomposition. The distillate was dissolved in ether, and washed three times with 2*N*-sodium hydroxide solution (40 ml.), with brine, and finally with water. The ethereal solution on steam-distillation gave a terpene (1.7 g.), b. p. 68—69°/22 mm., n_D^{20} 1.4779, α_D^{24} 5.0°, λ_{\max} . 2650 Å., ϵ_{\max} . 2320. The infra-red absorption spectrogram corresponded with that of an authentic sample of α -terpinene, and the presence of this terpene was confirmed by the preparation (Gascoigne, *J. Proc. Roy. Soc. N.S.W.*, 1941, **74**, 353), in low yield, of the adduct with *p*-benzoquinone, m. p. 86—87°, not depressed on admixture with a sample, m. p. 86—87°, prepared from authentic α -terpinene having b. p. 52.5—53°/12 mm., n_D^{20} 1.4782, $\alpha_D^{25} \pm 0^\circ$, λ_{\max} . 2655 Å., ϵ_{\max} . 5000 (cf. Booker *et al.*, *loc. cit.*). On acidification the alkaline washings gave a product (1.9 g.), m. p. 120—121°, not depressed on admixture with β -naphthol.

Determinations of absorption spectra in the ultra-violet were made in alcoholic solution by means of a Beckman quartz spectrometer, and in the infra-red on the undiluted substances using a Perkin-Elmer infra-red spectrometer (Model 12B); standard procedures were employed.

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