178. *Studies of Compounds related to Natural Perfumes. Part I. Concerning* cis- *and* trans-*Hex-3-en-1-ol.*

By Franz Sondheimer.

A convenient synthesis of hex-3-yn-1-ol (V) has been devised. Partial hydrogenation in the presence of palladium–calcium carbonate at room temperature gives an isomeric mixture of hex-3-en-1-ols, consisting mainly of the *cis*-isomer (" leaf alcohol "). Partial reduction of (V) with sodium in liquid ammonia gives exclusively *trans*-hex-3-en-1-ol (VIII), identical with that prepared by Crombie and Harper (preceding paper) and different from what had previously been considered the *trans*-isomer.

The acetylenic alcohol (V) is converted into the bromide (VI), which on attempted condensation with sodium acetylide in liquid ammonia undergoes dehydrobromination to hex-1-en-3-yne (VII). Similarly the ethylenic bromide (IX) with sodium acetylide gives hexa-1 : 3-diene (X).

In connexion with synthetical studies designed to elucidate the exact stereochemical configuration of the important violet-leaf constituents nona-2 : 6-dienol (I) and nona-2 : 6-dienal (II) (Ruzicka, Schinz, *et al.*, *Helv. Chim. Acta*, 1934, **17**, 1602; 1944, **27**, 1561; Takei *et al.*, *Bull. Agric. Chem. Soc. Japan*, 1938, **14**, 64; *Chem. Zentr.*, 1938, II, 3696; Hunsdiecker,

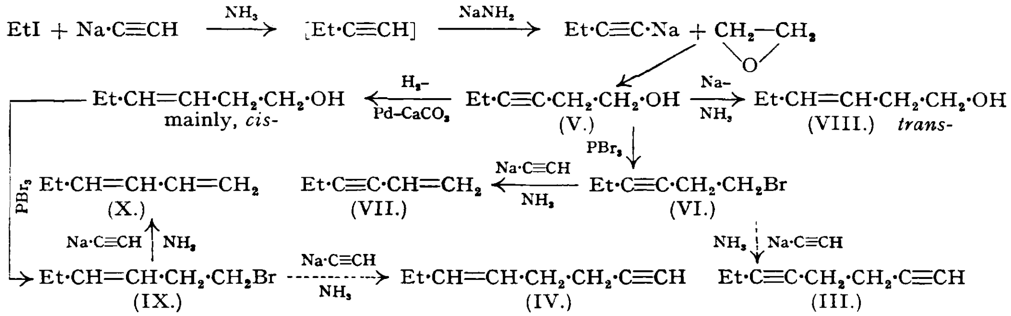
(I.) $CHEt{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH$ $CHEt{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CHO$ (II.)

Chem. Ber., 1947, **80**, 137), octa-1 : 5-diyne (III) and oct-5-en-1-yne (IV) were required. It was hoped to prepare these hydrocarbons from hex-3-yn-1-ol (V) and hex-3-en-1-ol by the action of sodium acetylide in liquid ammonia on the respective bromides (VI) and (IX). In fact it was found that these bromides were very readily dehydrobrominated to the hydrocarbons (VII) and (X) respectively (cf. Vaughn, Hennion, Vogt, and Nieuwland, *J. Org. Chem.*, 1937, **2**, 13), and the required hydrocarbons (III) and (IV) could not be obtained by this route. The diacetylene (III) was subsequently synthesised by a different method, and was successfully converted into nona-2 : 6-dienol (I) and the corresponding aldehyde (II) (Sondheimer, forthcoming publication). However, some interesting results were obtained in the present study concerning the *cis*- and *trans*-isomers of hex-3-en-1-ol and, as there exists some confusion about these compounds in the literature, it seemed desirable to record the results.

Hex-3-yn-1-ol (V) had previously been obtained from but-1-ynylmagnesium bromide and ethylene oxide (Stoll and Rouvé, *Helv. Chim. Acta*, 1938, **21**, 1542; Takei, Ono, and Sinosaki, *Ber.*, 1940, **73**, 950), the overall yield from the starting material, methyl ethyl ketone, being only *ca.* 1—6%. It may also be obtained by the dehydrobromination of the dibromide of hex-3-en-1-ol (Takei, Ono, and Sinosaki, *loc. cit.*; Bohnsack, *Ber.*, 1941, **74**, 1575; Stoll and Commarmont, *Helv. Chim. Acta*, 1949, **32**, 597). When ethyl iodide was treated in liquid ammonia with sodium acetylide (prepared directly from sodium and acetylene; cf. Raphael and Sondheimer, *J.*, 1950, **115**), the highly volatile but-1-yne so formed was not isolated but was converted into the sodio-derivative by the addition of one mole of sodamide. Reaction with ethylene oxide then gave the required hex-3-yn-1-ol (V) (3 : 5-dinitrobenzoate; *α-naphthylurethane*) in 47% yield. After this work had been completed, the reaction between ethylene oxide and the sodio-derivative of 1-butyne (prepared separately) in liquid ammonia solution was reported by Newman and Wotiz (*J. Amer. Chem. Soc.*, 1949, **71**, 1292), who obtained hex-3-yn-1-ol in 48% yield.

The acetylenic carbinol was converted into the *bromide* (VI) by phosphorus tribromide, using various amounts of pyridine, but only in poor yield (cf. Tchao, *Bull. Soc. chim.*, 1933, **53**, 1533; Newman and Wotiz, *loc. cit.*, for the successful bromination of α-acetylenic primary alcohols). The same difficulty in the direct bromination of the β-acetylenic alcohol but-3-yn-1-ol was encountered by Jones and Whiting (private communication), who were however successful in brominating the corresponding toluene-*p*-sulphonate. The acetylenic bromide (VI) was treated with an excess of sodium acetylide in liquid ammonia, whereupon it underwent mainly dehydrobromination; no appreciable amount of the required diacetylene (III) was formed, and hex-1-en-3-yne (VII) could be isolated.

Attention was then turned to the partial reduction of hex-3-yn-1-ol (V). The hex-3-en-1-ol which could thereby be formed is of interest as the starting material for the synthesis of nona-2 : 6-dienol (I) and the corresponding aldehyde (II) (for references see above), and also of the important perfume jasmone (Treff and Werner, *Ber.*, 1935, **68**, 640; Hunsdiecker, *Ber.*, 1942, **75**, 460). The *cis*-isomer is also of importance, as it is found widely distributed in many species of plants. It posesses the characteristic " green " odour of leaves and grass, and is usually termed "leaf alcohol."* Partial hydrogenation of acetylenes in the presence of a colloidal palladium or Raney nickel catalyst is known to give the *cis*-ethylenic compounds (*inter al.*,



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* There exists some controversy in the literature regarding the stereochemical configuration of the natural hex-3-enol (Stoll and Rouvé, *loc. cit.*; *Ber.*, 1940, **73**, 1358; Takei, Ono, and Sinosaki, *loc. cit.*; Ruzicka, Schinz, and Susz, *Helv. Chim. Acta*, 1944, **27**, 1561; Crombie and Harper, *loc. cit.*), but previous evidence together with that presented in this paper clearly points to the *cis*-configuration.

Bourguel, *Bull. Soc. chim.*, 1929, **45**, [iv], 1067; Campbell and Eby, *J. Amer. Chem. Soc.*, **1941**, **63**, 216, 2683; Campbell and Campbell, *Chem. Reviews*, **1942**, **31**, 148), and the catalytic semi-hydrogenation of hex-3-yn-1-ol has already been investigated by Stoll and Rouvé and by Takei, Ono, and Sinosaki (*locc. cit.*). The Swiss workers, using colloidal palladium, obtained a hex-3-enol, which was assigned the *cis*-configuration and shown to be identical with the natural hexenol (" leaf alcohol ") as the 3 : 5-dinitrobenzoate after " five laborious crystallisations " had m. p. 44·5—46°, undepressed on admixture with the natural derivative (m. p. 48—48·5°). The Japanese workers using a palladium–barium sulphate catalyst found that the properties of the hydrogenation product were dependent on the temperature of hydrogenation, the pure natural hex-3-enol being formed at −18°.

On hydrogenation of hex-3-ynol (V) at room temperature in the presence of palladium–calcium carbonate, the uptake of hydrogen practically stopped after 1 mole of gas had been absorbed. The hex-3-enol so obtained was very similar to that reported by Stoll and Rouvé, both in its physical properties and in the fact that the 3 : 5-dinitrobenzoate required seven crystallisations to achieve constant melting point (48—48·5°; undepressed on admixture with the derivative of natural hexenol, m. p. 49—50°). The α-naphthylurethane also needed three crystallisations to reach constant melting point (69—69·5°; undepressed on admixture with the natural derivative, m. p. 70—70·5°). It thus seemed that, although the hex-3-en-1-ol obtained by catalytic hydrogenation consisted predominantly of the *cis*-isomer, it contained an impurity, possibly the *trans*-isomer. This has been confirmed by its infra-red spectrum described below.

A hex-3-en-1-ol has been prepared by the Bouveault–Blanc reduction of ethyl sorbate (Ruzicka and Schinz, *Helv. Chim. Acta*, **1934**, **17**, 1602; Takei, Imaki, and Tada, *Ber.*, 1935, **68**, 953), differing from the natural material by its sharper smell and the lower melting points of its derivatives (3 : 5-dinitrobenzoate, m. p. 28°; α-naphthylurethane, m. p. 61—63°). It was considered to be stereoisomeric with the natural (*cis*-)hexenol, *i.e.*, to have the *trans*-configuration (Ruzicka, Schinz, and Susz, *Helv. Chim. Acta*, **1944**, **27**, 1561; cf. Takei, Imaki, and Tada, *loc. cit.*). Partial reduction of acetylenic hydrocarbons and tertiary carbinols by means of sodium in liquid ammonia has been shown to give the *trans*-ethylenic compounds (Campbell and Eby, and Campbell and Campbell, *locc. cit.*). When the primary alcohol hex-3-yn-1-ol (V) was treated in this way, the trans-*hex-3-en-1-ol* (VIII) so formed in good yield was found to be different from that obtained by the Bouveault–Blanc reduction of ethyl sorbate. Its derivatives (3 : 5-*dinitrobenzoate*, m. p. 46—46·5°; α-*naphthylurethane*, m. p. 68—69°) were considerably higher-melting than those of the Bouveault–Blanc product and, although the melting points of the *trans*-hexenol derivatives were nearly identical with those of the *cis*-isomer, considerable depressions were observed on admixture.

Independently of this work, Crombie and Harper (*loc. cit.*) found that both by the action of lithium aluminium hydride on *trans*-pent-2-ene-1-carboxylic acid, and also by the ring fission of the α-form of 3-chloro-2-ethyltetrahydrofuran, a *trans*-hex-3-enol was obtained, also differing from that described by Ruzicka and Schinz. The melting points of the derivatives of the *trans*-hexenol reported by Crombie and Harper are identical with those of the *trans*-hexenol (VIII) described in the present communication, and identity was established by mixed-melting-point determinations. It is highly probable that the so-called *trans*-isomer of Ruzicka and Schinz was not homogeneous. Nevertheless it must have contained a considerable percentage of the *trans*-hexenol, as the nona-2(*trans*) : 6(*trans*)-dienal prepared from it was shown to be identical with a sample prepared by an independent method (Hunsdiecker, *Chem. Ber.*, 1947, **80**, 137).

The infra-red spectra of the *cis*- and *trans*-hex-3-enols have already been recorded and discussed by Crombie and Harper (*loc. cit.*). The spectrum of the *trans*-isomer (VIII) obtained by the sodium–liquid ammonia reduction of hexynol (Fig. 1) is closely similar to that previously recorded, showing the typical strong " *trans* "-absorption band at 10·3 μ. (Rasmussen, Brattain, and Zucco, *J. Chem. Physics*, **1947**, **15**, 135). The infra-red spectrum of the natural (*cis*-)hex-3-enol has been given by Crombie and Harper (*loc. cit.*), while Fig. 2 shows the spectrum of the hex-3-enol obtained by the catalytic hydrogenation of hexynol. The bands at 11·5 and 13·8 μ. in Fig. 2 are typical for the *cis*-isomer, not being shown by the *trans*-form. On the other hand, the " *trans* "-band at 10·3 μ. is also quite marked. From these data, combined with the fact that on repeated crystallisation the *cis*-derivatives are obtained, it is concluded that catalytic hydrogenation of hexynol (V) under the conditions employed gives a *cis*-*trans*-mixture of hex-3-en-1-ols, consisting predominantly of the *cis*-isomer.

The hex-3-enol (mainly *cis*-) was converted into the bromide (IX), and this was treated with sodium acetylide in liquid ammonia. Again no appreciable amount of the hydrocarbon (IV) could be isolated, dehydrobromination to hexa-1 : 3-diene (X) (determined quantitatively by its ultra-violet light absorption maximum at 2280 A.) being the principal reaction.

FIG. 1.

trans-*Hex-3-enol from* Na *reduction.*

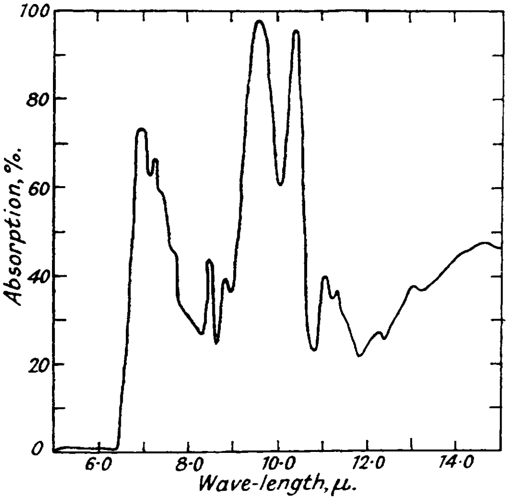
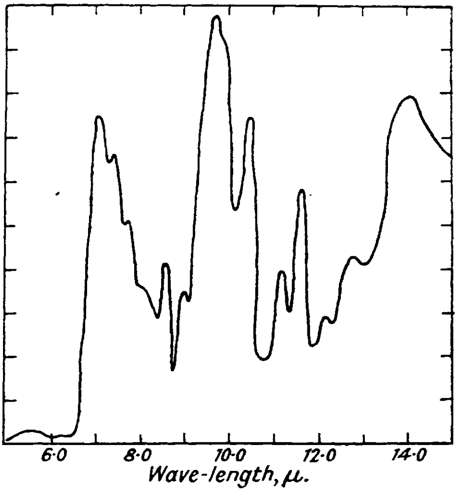


FIG. 2.

Hex-3-enol from catalytic hydrogenation.



EXPERIMENTAL.

Hex-3-yn-1-ol (V).—Sodium (40 g., 1·74 g.-mols.) was added in small pieces to liquid ammonia (1·5 l.) through which acetylene was bubbled, with stirring and cooling (alcohol–carbon dioxde). The acetylene flow was stopped at the exact moment when the blue colour disappeared after the last piece of sodium had been added (to ensure that no excess of acetylene was present in solution), and ethyl iodide (250 g., 1·6 g.-mols.) in dry ether (250 c.c.) was introduced during the course of 45 minutes. The cooled reaction mixture was stirred for 4 hours and the 1-butyne so formed was converted into the sodio-complex by addition, in several portions, of a cooled sodamide suspension in liquid ammonia (1 l.), made from sodium (40 g.), the ferric nitrate catalyst of Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120) being used. After another hour's stirring, ethylene oxide (141 g., 3·2 g.-mols.) was added all at once, and the reaction mixture was stirred for 24 hours, the temperature being held at *ca.* −40°. Ammonium chloride (120 g.) was gradually introduced, and the ammonia evaporated on the steam-bath. Water and ether were added to the residue, and the aqueous layer washed twice with ether. The combined ethereal extracts, after being washed with a small volume of water, were dried ($MgSO_4$) and evaporated. A preliminary distillation, followed by fractionation through a Dufton column, then gave hex-3-yn-1-ol (73·2 g., 47% calc. on ethyl iodide), b. p. 163—164°/772 mm., 73·5—74·5°/23 mm., n_{D}^{17} 1·4579 (Stoll and Rouvé, *Helv. Chim. Acta*, 1938, **21**, 1542, give b. p. 65·5—66°/12 mm., n_{D}^{20} 1·4530). The 3 : 5-dinitrobenzoate after one crystallisation from light petroleum (b. p. 60—80°) had constant m. p. 73—74° (Found : C, 53·6; H, 4·1; N, 9·65. Calc. for $C_{13}H_{12}O_6N_2$: C, 53·4; H, 4·1; N, 9·6%) (Newman and Wotiz, *loc. cit.*, give m. p. 72—73°; Stoll and Commarmont, *loc. cit.*, give m. p. 75—76° and 80—81°). The *a-naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in small needles, m. p. 84—85° (Found : C, 76·45; H, 6·4; N, 5·35. $C_{17}H_{17}O_2N$ requires C, 76·35; H, 6·4; N, 5·25%). In addition a higher-boiling product (13 g.) was obtained, b. p. 116—120°/23 mm., n_{D}^{17} 1·4628, which was not further investigated.

1-*Bromohex-3-yne* (VI).—Phosphorus tribromide (27 g.) in dry ether (15 c.c.) was slowly added to a cooled and stirred solution of hex-3-yn-1-ol (16 g.) in ether (65 c.c.), the temperature being kept at −5°. After being stirred at −5° for a further 90 minutes, the reaction mixture was poured on ice and water. The organic layer was washed with sodium hydrogen carbonate solution and water, and dried. Removal of ether, followed by distillation of the residue, gave 1-*bromohex-3-yne* (3·75 g., 14%) as a colourless liquid, b. p. 63·5—65·5°/18 mm., $n_{\mathrm{D}}^{17.5}$ 1·4890 (Found : Br, 49·1. C_6H_9Br requires Br, 49·6%).

In another experiment, the general conditions of Tchao (*loc. cit.*) were employed. Phosphorus tribromide (14·5 g.) was added dropwise to a cooled mixture of pyridine (0·6 g.) and hex-3-ynol (12·6 g.), with constant stirring during 30 minutes. The reaction mixture was then heated under reflux on the steam-bath for 3 hours, and the product isolated as before. This yielded the bromide (2·4 g., 12%), b. p. 67—68°/25 mm., n_{D}^{27} 1·4931. In addition, a higher-boiling liquid was obtained, b. p. 99—100°/25 mm., n_{D}^{27} 1·5222, giving analytical figures correct for the hydrogen bromide adduct of 1-bromohex-3-yne (Found : Br, 65·55. $C_6H_{10}Br_2$ requires Br, 66·05%).

The conditions of Juvala (*Ber.*, 1930, **63**, 1990) were also employed, using hex-3-ynol (16 g.), pyridine (2·8 g.), and phosphorus tribromide (17·4 g.). This gave a mixed product which could only have contained a very small proportion of the required bromide. Hex-3-en-1-ol can be successfully converted into the bromide under these conditions (see below).

Hex-1-*en*-3-*yne* (VII).—A suspension of sodium acetylide in liquid ammonia (100 c.c.) was prepared by adding sodium (1·2 g.) to the stirred and cooled (alcohol–carbon dioxide) liquid, through which acetylene was being passed. As soon as the colour was discharged, the acetylene flow was reduced, and the acetylenic bromide (3·2 g.) in dry ether (3 c.c.) was added. The cooled reaction mixture was stirred for a further 5 hours, ammonium chloride (4 g.) added, and the solvent removed on the steam-bath. Water and ether were added to the residue, the ethereal layer was washed with sodium hydrogen carbonate solution and water, and dried. The solvent was removed through a short Vigreux column, and the residue distilled. This yielded hex-1-en-3-yne (0·5 g.) as a colourless liquid, b. p. 83—85°/762 mm., n_D^{18} 1·449 (Found: C, 90·45; H, 10·1. Calc. for C_6H_8: C, 89·95; H, 10·05%) (Jacobson and Carothers, *J. Amer. Chem. Soc.*, 1933, **55**, 1622, give b. p. 84·5—85·3°/758 mm., n_D^{20} 1·4522). The distillation residue (0·3 g.) consisted of a viscous brown gum.

Catalytic Partial Hydrogenation of Hex-3-*yn*-1-*ol* (V).—The acetylenic carbinol (14·7 g.) in methyl acetate (30 c.c.) was shaken with Raney nickel for 1 hour to remove the small amount of catalyst poison present. The metal was filtered off and well washed with methyl acetate. The filtrate was shaken in hydrogen in the presence of palladium–calcium carbonate (1·5 g.; 5% of Pd). About 3 l. of gas were rapidly absorbed during 1 hour, whereafter the uptake slowed down. After the absorption of 3590 c.c. of gas (15°/758 mm.; 0·99 mole) the uptake had practically stopped. The catalyst was filtered off, the solvent removed, and the residue distilled. This yielded impure *cis*-hex-3-en-1-ol (13·1 g.), b. p. 156—157°/765 mm., 74—75°/29 mm., n_D^{17} 1·4430, having an odour very similar to that of a sample of natural (*cis*-)hexenol [Stoll and Rouvé, *loc. cit.*, give b. p. 59—61°/12·5 mm., n_D^{24} 1·4373, for the hexenol obtained by catalytic hydrogenation; Ruzicka, Schinz, and Susz, *loc. cit.*, give b. p. 58—58·5°/12 mm., n_D^{20} 1·4380, for pure natural (*cis*-)hexenol regenerated from the crystalline allophanate].

Derivatives of cis-*Hex*-3-*en*-1-*ol*.—The above isomeric mixture was converted into the 3 : 5-dinitrobenzoate in the usual manner. After one crystallisation from light petroleum (b. p. 40—60°) it formed long needles, m. p. 34—35°. After another six crystallisation from this solvent or pentane, the 3 : 5-dinitrobenzoate of *cis*-hexenol was obtained, having constant m. p. 48—48·5° (Found: C, 53·1; H, 4·85; N, 9·65. Calc. for $C_{13}H_{14}O_6N_2$: C, 53·05; H, 4·8; N, 9·5%); this m. p. was not depressed on admixture with a sample (m. p. 49—50°) obtained from the natural hexenol.

The α-naphthylurethane prepared from the isomeric mixture had, after two crystallisations from light petroleum (b. p. 40—60°), m. p. 68°, and after another crystallisation the pure α-naphthylurethane of *cis*-hexenol was obtained as long needles, having constant m. p. 69—69·5° (Found: C, 75·95; H, 7·2; N, 4·9. Calc. for $C_{17}H_{19}O_2N$: C, 75·8; H, 7·1; N, 5·2%); this m. p. was not depressed on admixture with a specimen (m. p. 70—70·5°) obtained from the natural alcohol.

trans-*Hex*-3-*en*-1-*ol* (VIII).—Hex-3-yn-1-ol (4·9 g.), dissolved in dry ether (5 c.c.), was gradually added to a stirred and cooled (alcohol–carbon dioxide) solution of sodium (4·6 g.) in liquid ammonia (200 c.c.). Stirring was continued for a further 2 hours, whereafter the blue reaction mixture was decomposed with ammonium chloride (15 g.). The ammonia was evaporated off on the steam-bath, water and ether were added to the residue, the aqueous layer was once more extracted with ether, and the combined organic extracts were washed with dilute sulphuric acid, sodium hydrogen carbonate solution, and water. The dried solution was evaporated. Distillation of the residue then gave trans-*hex*-3-*en*-1-*ol* (3·7 g., 75%) as a colourless mobile liquid, b. p. 152—153·5°/762 mm., n_D^{18} 1·4406, possessing a characteristic odour distinctly different from the "green" odour of the *cis*-isomer (Found: C, 72·0; H, 12·15. $C_6H_{12}O$ requires C, 71·95; H, 12·1%) (Ruzicka, Schinz and Susz, *loc. cit.*, give b. p. 58·5—60°/12 mm., n_D^{20} 1·4376, for the "*trans*"-isomer obtained by the Bouveault–Blanc reduction of ethyl sorbate).

The 3 : 5-*dinitrobenzoate* was formed in quantitative yield, having m. p. 45—46°; after one crystallisation from light petroleum (b. p. 40—60°) it formed needles having constant m. p. 46—46·5° (Found: C, 53·1; H, 4·9; N, 9·55. $C_{13}H_{14}O_6N_2$ requires C, 53·05; H, 4·8; N, 9·5%). This m. p. was not depressed on admixture with a sample (m. p. 47°) derived from the lithium aluminium hydride reduction of *trans*-pent-2-ene-1-carboxylic acid (Crombie and Harper, *loc. cit.*). On admixture with the *cis*-derivative (m. p. 48—48·5°) described above, the m. p. was 33—35°.

The α-*naphthylurethane* after one crystallisation from light petroleum (b. p. 40—60°) formed needles, m. p. 68—69°, not raised by further crystallisation (Found: C, 75·55; H, 7·1; N, 5·35. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1; N, 5·2%). The m. p. was not depressed on admixture with a sample (m. p. 68·5—69·5°) prepared by Crombie and Harper (*loc. cit.*). On admixture with the "*trans*"-derivative (m. p. 61—63°), prepared from ethyl sorbate (Ruzicka, Schinz, and Susz, *loc. cit.*), the m. p. was 51—53°. On admixture with the *cis*-derivative (m. p. 69—69·5°) described above, the m. p. was 56—60°.

Hexa-1 : 3-*diene* (X).—The hex-3-enol (mainly *cis*-) obtained from the catalytic hydrogenation of the acetylene was converted into the bromide (IX) by the general method of Juvala (*loc. cit.*), as has already been described for the natural (*cis*-)hexenol (Treff and Werner, *loc. cit.*; Hunsdiecker, *Ber.*, 1942, **75**, 460). The 1-bromohex-3-ene so obtained in *ca.* 50% yield had b. p. 49—51°/20 mm., n_D^{20} 1·473.

The ethylenic bromide (3·2 g.) was treated with sodium acetylide (from 1·2 g. of sodium) in liquid ammonia (100 c.c.) as described above for the acetylenic bromide. The reaction was allowed to proceed for 3·5 hours, and the mixture was then carefully poured on ice and *n*-hexane (without evaporating the ammonia, so as not to lose any of the volatile product). The organic layer was washed with dilute sulphuric acid, sodium hydrogen carbonate solution, and water, and dried ($MgSO_4$). The solvent, containing the hexa-1 : 3-diene (Prévost, *Ann. Chim.*, 1928, **10**, 176; *Bull. Soc. chim.*, 1941, **8**, 89) was carefully distilled off through a Dufton column, until the distillation temperature reached 75°. The residue (0·25 g.) was dark and viscous, and could not be distilled. The hexane distllate (180 c.c.) had light absorption: Maximum, 2280 A.; $E^{1\%}_{1\,\text{cm.}} = 14·5$. This corresponds to a *ca.* 0·97-g. content of hexa-1 : 3-diene (60% yield), assuming $\varepsilon = 22{,}000$ for the pure diene.

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