845. *A Two-step Preparation of Azulene from Naphthalene or Tetralin.*

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The production of up to 0·25% of azulene by dehydrogenation of certain commercial specimens of decalin is shown to be due to the presence of decahydroazulene. The decahydroazulene is derived from naphthalene, *via* tetralin, by rearrangement of the carbon skeleton during reduction at high temperature and pressure over a tungsten or molybdenum sulphide catalyst.

Azulene is most conveniently separated from mixtures by extraction with concentrated hydrochloric acid. The yield (24%) of azulene from decahydro- and other reduced azulenes by vapour-phase dehydrogenation is much higher than previously claimed; this favourable result is due to the large amount of decalin employed as carrier.

Seven years ago Dr. G. O. Aspinall, and later Dr. P. G. Jones, working in this laboratory observed that vapour-phase dehydrogenation of certain specimens of decalin over a palladium–charcoal catalyst gave a product, containing much naphthalene, which was unexpectedly blue.* The substance responsible for the colour behaved as an azulene by dissolving in 85% phosphoric acid giving a brownish solution which regenerated the blue colour on dilution with water.

We have now isolated azulene in up to 0·25% yield from these blue dehydrogenation products, using a new rapid procedure involving extraction with concentrated hydrochloric acid. The fact that azulene dissolves in concentrated hydrochloric acid has not previously been reported, though Plattner, Heilbronner, and Weber (*Helv. Chim. Acta*, 1952, **35**, 1036) record that guaiazulene is soluble in this acid. This preparation of azulene from a cheap, commercial product was most attractive, but it was found that different samples of decalin gave amounts of azulene which varied from 0·0 to 0·25%. The many references to the dehydrogenation of decalin, including the use of palladium–charcoal at 340°, platinum- or palladium–asbestos at 300°, platinum–charcoal at 333°, osmium–asbestos at 228—277°, and nickel–charcoal at 350°, contain no mention of the occurrence of azulene in the product (see Elsevier, " Encyclopædia of Organic Chemistry," Series III, Vol. 12B, pp. 84—85).

Experiments have shown that for the production of azulene : (*a*) the temperatures may vary from 350° to 420° (most of the experiments were conducted at 380—400°/20 mm.); (*b*) a 1% is as active as a 10% palladium–charcoal catalyst, but the latter yields more naphthalene and retains its activity for longer; (*c*) a catalyst which gives almost complete conversion of the decalin into naphthalene gives no more azulene than one which gives insufficient naphthalene to crystallise from the unchanged decalin, and the rate of addition of decalin is conveniently adjusted to give a product containing only a small amount of solid naphthalene.

With regard to the formation of azulene it could clearly not be due to isomerisation of naphthalene, because the reverse change is known to occur under very similar conditions (Heilbronner, Plattner, and K. Wieland, *Experientia*, 1947, **3**, 70; Günthard, Süess, Marti, Fürst, and Plattner, *Helv. Chim. Acta*, 1951, **34**, 959). Indeed, when a 1% solution of azulene in decalin (a specimen which itself yielded no azulene on dehydrogenation) was submitted to the normal dehydrogenation procedure, only 25% of the azulene was recovered. Again, the azulene cannot be derived from decalin by rearrangement of the carbon skeleton before or during dehydrogenation, because all specimens of decalin would then give the same yield of azulene. It was, therefore, assumed that certain commercial

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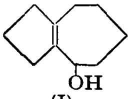
* In a few experiments in which the same specimens of decalin were similarly passed over untreated charcoal, supplied by the British Drug Houses, Limited, traces of azulene were again obtained, but not enough naphthalene to separate in the solid state. This result we attribute to the presence of metals; spectrochemical analysis showed the presence, amongst other metals, of copper in some quantity, smaller amounts of chromium, nickel, and manganese, and traces of vanadium, tin, and titanium. We are grateful to Dr. G. Ludwell and Dr. S. W. K. Morgan of the Imperial Smelting Corporation Limited, Avonmouth, for this analysis.

decalins contained a substance which yielded azulene by dehydrogenation, and the main purpose of this paper is to report the identification of this substance as decahydroazulene and its origin as the naphthalene from which the decalin was originally prepared. The true explanation of these unexpected findings was reached only after exploration of others which seemed at first more likely. In the following account the expressions " active decalin " and " inactive decalin " refer to decalin which did, or did not, yield azulene on dehydrogenation.

Through the kindness of the heads of many chemistry departments of Universities, University Colleges, Technical Colleges, and of industrial organisations, we obtained many specimens of decalin which varied in their ability to yield azulene, but only one gave no azulene at all. There appeared to be some correlation between the age of the decalin and its ability to produce azulene (this is referred to later), and this suggested that the decalin had undergone a change on storage with production of the azulene precursor. *trans*-Decalin combines with oxygen to give the 9-hydroperoxide and this has been converted by several steps into azulene (see Criegee, *Ber.*, 1944, **77**, 22, 722; *Annalen*, 1948, **560**, 127; Cope and Holzmann, *J. Amer. Chem. Soc.*, 1950, **72**, 3062). It was conceivable, therefore, that the hydroperoxide might give an azulene derivative, *e.g.*, *via* 1 : 6-epoxy-1-hydroxy-*cyclo*decane, 6-hydroxy*cyclo*decan-1-one, *cyclo*decane-1 : 6-dione, and *cyclo*pentено*cyclo*heptenone. The following evidence, however, showed that this could not be the case.

All specimens of active decalin contained peroxide, but there was no relation between the peroxide content and the yield of azulene. The yield of azulene was not raised by treatment of the decalin with oxygen at 120° (conditions which give the 9-hydroperoxide; Criegee, *loc. cit.*), even after such decalin had been kept for three months. *trans*-9-Decalyl hydroperoxide, its benzoyl derivative, and 1-tetralyl hydroperoxide gave no azulene when submitted to dehydrogenation in inactive decalin, but *cyclo*decane-1 : 6-dione gave azulene in 7% yield.

Negative evidence as to the nature of the precursor was obtained by the following experiments. Treatment of active decalin with Girard P reagent or with 2 : 4-dinitrophenylhydrazine did not diminish the activity, although small quantities of ketones were removed. Repeated shaking with concentrated sulphuric acid also failed to affect the activity. Four possible precursors (I), (II), (III), (IV), which as 1—2% solutions in inactive decalin gave 22, 19, 22, and 12% yields of azulene respectively when dehydrogenated, were all rapidly removed from decalin by shaking with concentrated sulphuric acid. Moreover, active decalin, purified by treatment with ten portions of sulphuric acid, and then with several portions of 2 : 4-dinitrophenylhydrazine, did not react with bromine in the cold as did substances (I) to (IV), and its infra-red spectrum showed that carbonyl and hydroxyl groups were absent. Active decalin retained its activity after hydrogenation in presence of 10% palladium–charcoal at 200°/300 atm.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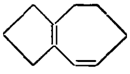
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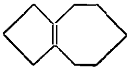
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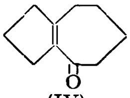
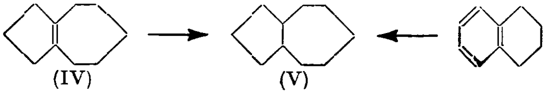

(IV)

This evidence is consistent only with the supposition that the azulene precursor is decahydroazulene (V), a specimen of which (Günthard, Süess, Marti, Fürst, and Plattner, *Helv. Chim. Acta*, 1951, **34**, 959) when dehydrogenated as a 2% solution in inactive decalin gave azulene in 24% yield.

Attempts to isolate decahydroazulene from active decalin have been unsuccessful.


(IV) (V)

A sample (*ca.* 500 g.) of active decalin, purified by treatment with sulphuric acid and then with 2 : 4-dinitrophenylhydrazine, was very slowly fractionated in a Podbielniak column at atmospheric pressure in nitrogen, using a reflux : distillation ratio of 45 : 1; the maximum efficiency of the column was 110 theoretical plates at total reflux. The fractionation yielded approximately 5% of butylbenzenes, 70% of *trans*- and 15% of *cis*-decalin, and 10% of tetralin; no separate decahydroazulene fraction was obtained. Dehydrogenation showed that the azulene precursor occurred partly in the *trans*-decalin (b. p. *ca.* 184—185°, n_D^{20} 1·4695), and in about twice the concentration (giving 0·45% of azulene) in the *cis*-decalin (b. p. *ca.* 194—195°, n_D^{20} 1·4789); the highest concentration (giving 0·60% of azulene) was found in a small fraction collected at 192·8—194·2°/775 mm. (n_D^{20} 1·4766), between the boiling points of *trans*- and *cis*-decalin; this observation is consistent with the conclusion that the precursor is decahydroazulene. This fractionation was carried out in the laboratories of Imperial Chemical Industries Limited, Blackley, Manchester, through the kindness of Dr. M. A. T. Rogers.

No concentration of the decahydroazulene was achieved by chromatography, by freezing, or by complex formation with thiourea which gave crystalline inclusion compounds with *cis*- and *trans*-decalin and with decahydroazulene.

Origin of Decahydroazulene in Certain Technical Decalins.—The decahydroazulene might have been derived *either* from some compound containing the azulene skeleton present in the original naphthalene, *or* from naphthalene by rearrangement of the carbon skeleton during reduction. Through the kindness of Dr. D. McNeil, Director of Research of the Coal Tar Research Association, Gomersal, Leeds, we were able to examine many representative, pooled specimens of naphthalene, but none gave azulene when dehydrogenated in decalin. Decalins obtained from crude and refined naphthalenes by reduction at low temperature and pressure gave no azulene on dehydrogenation.

We were informed by Dr. D. McNeil, and by Dr. W. d'Leny, of Imperial Chemical Industries Limited, Durham, that decalin had been prepared technically either from fairly pure naphthalene by low temperature and pressure hydrogenation, or from crude naphthalenes by hydrogenation at about 370°/250 atm. over a molybdenum trisulphide or tungsten trisulphide catalyst. The latter process was formerly carried out at Billingham, from where one of the most active specimens of decalin had come, and some isomerisation to methylindanes had been observed under these conditions. This isomerisation was also reported by Khadzhinov (*Ukrain. Chem. J.*, 1933, **8**, 333) when reducing naphthalene at 430—440°/120 atm. over a molybdenum sulphide catalyst. It seemed possible, therefore, that during the reduction of naphthalene at high temperature and pressure over such a sulphide catalyst, some rearrangement of the carbon skeleton might occur to give, amongst other products, decahydroazulene. This suggestion, which was independently made to us by Dr. D. McNeil, has been found to be correct. Specimens of pure naphthalene were reduced in presence of Raney nickel at 120—140°/100 atm. and at 400°/200—250 atm.; neither of the resulting decalins gave any azulene on dehydrogenation. When this same naphthalene was reduced in presence of a tungsten trisulphide catalyst at 385—410°/200—230 atm., the resulting decalin, after distillation from Raney nickel to remove traces of sulphur, gave a 0·185% yield of azulene on dehydrogenation over palladium–platinum–charcoal at 380°. A series of further experiments carried out in collaboration with Dr. E. W. Sawyer of Imperial Chemical Industries Limited, Billingham, showed that tungsten trisulphide is slightly more active in giving azulene at 370° than at 405° (0·18 and 0·13% yields respectively), and that a molybdenum trisulphide catalyst is less active at these temperatures (0·1% yield).

The rearrangement takes place at some intermediate stage in the reduction of naphthalene to decalin. When inactive decalin is submitted to the action of hydrogen at *ca.* 400°/200 atm. over a tungsten sulphide catalyst it remains inactive, but when it is mixed with an equal volume of inactive tetralin and reduced under the same conditions, a 0·17% yield of azulene is obtained. The reduction of tetralin is more convenient than the reduction of naphthalene, and is as effective in giving decahydroazulene.

The apparent correlation, previously mentioned, between the age of many specimens of decalin and their ability to yield azulene, is undoubtedly due to the fact that Imperial Chemical Industries Limited, one of the larger manufacturers of decalin, ceased some years ago to prepare it by reduction of naphthalene at high temperature and pressure over metallic sulphide catalysts.

The new azulene synthesis in two steps from naphthalene or tetralin appears to have advantages, particularly for large-scale preparative work, over the recently-described two-step synthesis from indane by ring-enlargement with diazomethane and dehydrogenation (Doering, Mayer, and DePuy, *J. Amer. Chem. Soc.*, 1953, **75**, 2386).

Note on the Use of Decalin as a Carrier in Dehydrogenation Processes.—Although azulenes have always been prepared by a final dehydrogenation process, the yields have seldom been accurately stated, and, if mentioned at all, have been referred to as very small. The following three cases of the preparation of azulene itself give quantitative information. Anderson and Nelson (*J. Amer. Chem. Soc.*, 1951, **73**, 232) dehydrogenated 1 : 2 : 3 : 4 : 5 : 6-hexahydroazulene in the vapour phase over palladium–charcoal at 320—340°/15 mm., and obtained azulene in 3·4% yield, but when allowance was made for 82% of recovered starting material the yield was 18%. Günthard *et al.* (*loc. cit.*) made a detailed study of the dehydrogenation of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 10-octahydroazulene, and obtained as their highest yield 11% of azulene using 5% palladium–charcoal at 328°/1 atm. in nitrogen. Doering, Mayer, and DePuy (*J. Amer. Chem. Soc.*, 1953, **75**, 2386) dehydrogenated a tetrahydroazulene over 5% palladium–charcoal at 340°/20 mm., and obtained azulene in 18·3% yield. With the object of preventing the isomerisation of the azulene to naphthalene, the need for rapid dehydrogenation involving very brief contact of the vapour of the hydroazulene with the catalyst has been stressed (see, *e.g.*, Nunn and Rapson, *J.*, 1949, 825).

The new technique of using a solution (say 2%) of the hydroazulene in decalin under similar conditions is clearly of considerable advantage; in the case of decahydroazulene a 24% yield of azulene is obtained in one operation, and its separation from naphthalene, decalin, and tetralin presents no difficulty. The precise functions of the decalin are not known, but it will undoubtedly diminish the time during which the azulene derivatives and the azulene itself are in contact with the catalyst surface, by itself occupying the surface whilst undergoing dehydrogenation. Another effect is likely to be to sweep the azulene and derivatives rapidly through the tube owing to the large total volume of organic vapour and evolved hydrogen. Other carriers, *e.g.*, tetralin, appear equally effective, and it is likely that a carrier which itself undergoes dehydrogenation may find use in other cases than for the preparation of azulenes, provided that the desired product may be readily separated from the carrier and from its dehydrogenation products.

EXPERIMENTAL

Light petroleum refers to the fraction of b. p. 40—60°, unless otherwise stated.

Palladium–Platinum Charcoal.—Chloroplatinic acid (7·3 g.) and palladium chloride (4·0 g.) were dissolved in concentrated hydrochloric acid (45 c.c.) and water (400 c.c.), granular charcoal (for gas absorption, B.D.H.) (400 g.) was added, and then 35% aqueous formaldehyde (635 c.c.). The mixture was mechanically stirred and cooled to −10°, and a solution of potassium hydroxide (580 g.) in water (580 c.c.) added so that the temperature did not exceed 5°. The mixture was then vigorously stirred at 60° for 15 min., and the catalyst well washed with water by decantation and finally with 1% acetic acid, then collected, washed with distilled water until free from chloride, and dried over calcium chloride.

Tungsten Sulphide.—Tungstic acid (technical, 60 g.) was dissolved in aqueous ammonia (*d* 0·88; 140 c.c.) and water (400 c.c.) at 40—50° with mechanical stirring during 2 hr. and the filtrate boiled until most of the ammonia was removed. Hydrogen sulphide was then passed in during 24 hr. at room temperature and the solution made acid with dilute sulphuric acid. The brown precipitate (65 g.) was collected without suction on large filter-papers, washed, and dried over sulphuric acid.

Dehydrogenation.—A Pyrex tube (75 × 0·6 cm. internal diameter) was filled for a length of 60 cm. with palladium–platinum–charcoal catalyst (17 g.). This tube passed through a vertical iron tube (60 cm. long), electrically heated and lagged so that an internal temperature of *ca.* 380° could be maintained. The decalin solution was admitted dropwise through a fine orifice from a reservoir at the rate of *ca.* 10 c.c. per hr., the whole evacuated with a water-pump, and the product collected at room temperature in a tube fitted with a side-arm. In the presence of the large amounts of naphthalene and decalin no isolable quantity of azulene was lost from the dehydrogenation product. The dehydrogenation of the decalin solutions of the substances

(I), (II), (III), and (IV) was carried out similarly; the optimum rates of addition of the solutions were, in the first three cases, *ca.* 20, 60, and 10 c.c. per hr. respectively.

Isolation of Azulene.—The isolation was carried out as rapidly as possible to the stage of either formation of the complex with 1 : 3 : 5-trinitrobenzene, or chromatography, in order to minimise loss of azulene through (1) its instability in mineral acid solution (2) its high vapour pressure, and (3) the fact that it is stable only when fairly pure, being otherwise slowly converted into a green product, insoluble in light petroleum.

The deep blue dehydrogenation product (50 c.c.) was mixed with enough light petroleum (usually an equal volume) to dissolve any naphthalene and to render the material more fluid, then shaken vigorously with concentrated hydrochloric acid (25 c.c.; *d* 1·18) for 15 seconds. The acid layer was shaken with light petroleum (50 c.c.), and the clear portion of the lower brown layer run into water (100 c.c.) in a separating funnel. The process was repeated twice with 10 c.c. of hydrochloric acid. The precipitated, crystalline azulene was extracted with light petroleum (40 c.c.) and the organic layer washed with water and filtered through anhydrous sodium sulphate into a weighed flask. The solvent was removed by gentle agitation of the flask while it was evacuated at the water-pump. Azulene remained as intensely blue, rhombic plates.

Purification of Azulene.—Sublimation at room temperature under reduced pressure gave pure azulene, but was less convenient than other methods. One crystallisation from light petroleum or alcohol gave a product of m. p. *ca.* 96°. Azulene of high purity was obtained by dissolving the hydrocarbon (1 part) in ethanol (10 c.c. per g.) and adding a boiling, almost saturated, ethanolic solution of 1 : 3 : 5-trinitrobenzene (2 parts). The complex separated in purplish-brown needles which were collected after cooling and washed with a little cold ethanol; it had m. p. 164° (Found, after one recrystallisation from ethanol: C, 56·4; H, 3·4; N, 12·4. Calc. for $C_{10}H_8,C_6H_3O_6N_3$: C, 56·4; H, 3·2; N, 12·3%). Plattner and Pfau (*Helv. Chim. Acta*, 1937, **20**, 224) give the m. p. of azulene as 98·5—99° after purification on an alumina column, and the m. p. of the trinitrobenzene complex as 166·5—167·5°. The complex was readily decomposed on activated Brockman alumina (Plattner and Pfau) to give an almost quantitative yield of azulene, m. p. 99°.

Azulene of only slightly lower purity was obtained by passing the crude hydrocarbon in light petroleum through a column of unactivated Brockman alumina. The column, which had several brown and greenish-brown bands, was developed with 1 : 1 ether–light petroleum and eluted with ether. The recovery of azulene after removal of solvent was 90—93% of material, m. p. 97·5—98·5°; a column 10 × 60 mm. was required to purify 100 mg. of azulene. Azulene did not form a complex with 2 : 4 : 7-trinitrofluorenone.

Estimation of Azulene.—Colorimetric estimations were made with a Hilger Spekker photoelectric absorptiometer, with 1-cm. cells and ruby filters. Pure azulene was dissolved in light petroleum (b. p. 100—120°) and calibration curves were constructed at concentrations between 30 and 200 mg./100 c.c. Below 80 mg./100 c.c. Beer's law could be used, but at higher concentrations the curve was necessary. The addition of various amounts of naphthalene, decalin, and tetralin did not affect the optical density. The blank cell contained light petroleum (b. p. 100—120°). A known volume (usually 5 c.c.) of the decalin to be tested was passed at a uniform rate of 10 c.c./hr. through fresh catalyst which had been previously heated for at least 1½ hr. and through which 10 c.c. of pure decalin had been passed. The column was then similarly treated with 2 c.c. of pure decalin by which time the product, mainly naphthalene, was colourless. The column was kept evacuated during all these operations. The blue mixture of hydrocarbons was then dissolved in light petroleum (b. p. 100—120°) to a volume of 25 c.c., and estimated colorimetrically. Reproducibility was 5—10% for the dehydrogenation and 1—2% for the estimation. The catalyst was changed when its activity began to decline, usually after about five estimations.

Purification of Decalin.—Samples of decalin described as purified were shaken at room temperature with successive portions (⅕ volume) of concentrated sulphuric acid until only a faint colour was observed in the acid layer; this required up to 10 portions of acid. The decalin was washed with water and stirred vigorously for 2 hr. at 60° with an equal volume of a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, and the decalin separated, filtered, and again stirred with dinitrophenylhydrazine solution until no more orange or red solid was formed. The washed decalin was finally dried, and distilled at 20 mm. pressure.

The 2 : 4-dinitrophenylhydrazones obtained were always very small in amount, and only one has been definitely identified as the 2 : 4-dinitrophenylhydrazone of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-4-oxoazulene (IV). Some of the active decalin samples gave a dark red 2 : 4-*dinitro-*

phenylhydrazone (*ca.* 10 mg. from 50 c.c. of the decalin) which formed short needles (from ethyl acetate or methanol), m. p. 250—251° (decomp.). The m. p. was not depressed on admixture with the 2 : 4-*dinitrophenylhydrazone* prepared directly from a synthetical specimen of (IV); this also had m. p. 250—251° (decomp.) (Found: N, 16·6. $C_{16}H_{18}O_4N_4$ requires N, 17·0%). An isomeric 2 : 4-*dinitrophenylhydrazone* (or possibly a polymorph of the preceding 2 : 4-dinitrophenylhydrazone) was formed from one sample of decalin; after purification on an alumina column and crystallisation from ethyl acetate it formed brick-red needles, m. p. 227—228° (Found: C, 58·0; H, 5·2; N, 17·4. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·5; N, 17·0%).

Hydrogenation of Naphthalene.—In all experiments, recrystallised naphthalene, m. p. 80—81°, was used.

(*a*) *With nickel catalyst.* Naphthalene was hydrogenated at 120—140°/100 atm., and at 400°/200—250 atm. After fractionation neither sample of decalin yielded any azulene on dehydrogenation.

(*b*) *With tungsten trisulphide catalyst.* Naphthalene (55 g.) was hydrogenated in presence of tungsten trisulphide (prepared as described above), benzene (40 c.c.), and carbon disulphide (20 c.c.), at 385—410°/200—230 atm. for 6 hr. The product which had a blue fluorescence (50 g.) was distilled from Raney nickel, giving a colourless liquid, 45 g., b. p. 170—200°, n_D^{20} 1·4882, which developed a deep yellow colour with tetranitromethane and yielded 0·185% of azulene on dehydrogenation. When a tungsten trisulphide catalyst supplied by Imperial Chemical Industries Limited was used the yield of azulene was 0·175%. Tetralin, which gave no azulene on dehydrogenation, when mixed with an equal volume of inactive decalin, gave under the same conditions 0·17% of azulene on dehydrogenation.

Decahydroazulene.—1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-Octahydro-4-oxoazulene was reduced by the Clemmensen–Martin procedure, giving 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroazulene (81%), b. p. 70—71°/28 mm. (Found: C, 88·4; H, 11·8. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%) (cf. Günthard *et al.*, *loc. cit.*). This hydrocarbon gave an intense yellow colour with tetranitromethane, formed a liquid, blue addition product with nitrosyl chloride, and with bromine at 0° rapidly evolved hydrogen bromide. The octahydroazulene was hydrogenated (12 hr.) in light petroleum (15 c.c.) at 250°/25 atm. in presence of Raney nickel. The product, which showed only a very faint yellow colour with tetranitromethane, gave, after two distillations, decahydroazulene (86%), b. p. 63—64·5°/7 mm., n_D^{20} 1·4743 (Found: C, 87·1; H, 12·9. Calc. for $C_{10}H_{18}$: C, 86·9; H, 13·1%) (cf. Günthard *et al.*, *loc. cit.*).

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