1238. *Reaction of Acetylenic Hydrocarbons with Trialkylboranes*

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Acetylenes react irreversibly with trialkylboranes to give trialkenylboranes, with liberation of olefin from the trialkylborane. Each acetylenic bond becomes linked to only one boron atom. Hydrolysis of the trialkenylborane gives a *cis*-olefin, and oxidation gives a ketone. As a stereospecific partial-reduction method this reaction offers advantages over Lindlar reduction and trisiamylborane reduction, especially of conjugated diacetylenes. The liberation of olefin from primary alkyl boranes occurs without migration, to give exclusively terminal olefins.

IT is well known[1-3] that olefins undergo an exchange or displacement reaction with trialkylboranes whose alkyl groups have more than one carbon atom and carry at least one β-hydrogen atom, for example:

$$\mathrm{RCH{:}CHR} + \mathrm{>B{\cdot}CH_2{\cdot}CH_3} \rightleftharpoons \mathrm{>B{\cdot}CHR{\cdot}CH_2R} + \mathrm{CH_2{:}CH_2}$$

The reaction is reversible and slow, and in order to get complete conversion the liberated olefin has to be removed, for example by distillation, if it is more volatile than the original olefin. Actually, this reversibility is the basis for the use of trialkylboranes as olefin-isomerisation catalysts.

The behaviour of the acetylenic bond on treatment with trialkylboranes does not seem to have been studied before. In fact, a smooth reaction takes place, and an irreversible transfer of boron to the acetylenic bond with liberation of olefin was observed, as in the following example:

$$\mathrm{3RC{\vdots}CR} + \mathrm{B(CH_2{\cdot}CH_3)_3} \longrightarrow \underset{\text{(I)}}{\mathrm{B(CR{:}CHR)_3}} + \mathrm{3H_2C{:}CH_2}$$

Each acetylenic bond becomes linked to only one boron atom, and the obtained trialkenylboranes (I) undergo the known reactions[1,2] of hydrolysis with acetic acid to give *cis* double bonds (the overall result being a stereospecific partial reduction of acetylenic bonds), and oxidation with alkaline hydrogen peroxide to give ketones.

The formation of alkenylborane is very rapid and can be used to regenerate pure terminal olefins. Thus, mixtures of isomeric olefins, obtained for instance by dehydration of an alcohol, give, after treatment with tri-isobutylborane or diborane, under isomerising conditions, only the most stable primary boranes, which can then be treated with a higher-boiling acetylene; the liberated olefin will have exclusively terminal (vinyl) double bonds. The method is particularly attractive in a combined process, because an acetylenic compound can be chosen which it is anyway desired to reduce or to convert into a ketone. Compared with the alternative method of exchange with a high-boiling olefin,[1-3] the reaction with an acetylene is very rapid. An alternative method is the oxidation of the final primary borane to an alcohol with subsequent dehydration, which is less simple and leads to extensive double-bond migration back into the chain.

Reaction Conditions for Trialkenylborane Formation.—Usually a temperature of 160—200° is necessary to achieve a fast and complete reaction between the trialkylborane and the acetylenic compound. The simplest trialkylborane having β-hydrogen, triethylborane, is not interesting on a laboratory scale because of its low boiling point, requiring the use of an autoclave, and because of its inflammability in air. The readily available tri-isobutylborane is very suitable for the reaction. It is most conveniently used in excess, generally three-fold, that is, one mole per acetylenic bond, so as to serve also as the solvent and to increase speed and completeness of the reaction. After the evolution of isobutene has

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[1] H. C. Brown, *Tetrahedron*, 1961, **12**, 117.

[2] H. C. Brown, " Hydroboration," Benjamin Inc., New York, 1962.

[3] R. Köster, *Annalen*, 1958, **618**, 31.

stopped, which usually takes about five minutes, the excess of tri-isobutylborane is recovered by distillation. The reaction can also be carried out in high-boiling inert solvents, such as diglyme, but without improvement of the yield.

The relatively high temperature required is a limitation; sensitive substances polymerise to some extent. The yield when conjugated diynes are used can be somewhat increased by the addition of quinol as a trapping agent for free radicals. Addition of Lewis acids (such as titanium tetrachloride) did not lower the required reaction temperature. Tricyclohexylborane was also tried in the hope that the less stable secondary carbon–boron [1,2] bond would permit the reaction to proceed at a lower temperature, but no difference was observed.

The kind of acetylenic compounds which undergo this reaction smoothly and in good yields seems to be practically limited to disubstituted acetylenes and diacetylenes. Monosubstituted acetylenes give after hydrolysis only a small quantity of vinyl hydrocarbons besides polymeric substances. Compounds having systems of three or more conjugated triple bonds give only polymerisation products.

The overall reaction can be considered formally as a displacement reaction or an " exchange of unsaturation; " the acetylenic bond loses half its unsaturation which goes to the alkyl group in the borane. From a mechanistic point of view the selectivity may be due to the low concentration of reactive $>$BH groups furnished by the equilibrium

$$>B{\cdot}CH_2{\cdot}CHMe_2 \rightleftharpoons >BH + CH_2{:}CMe_2$$

which prevents the triple bond from adding a second time, as this would be a more difficult step requiring a higher concentration of $>$BH groups.

Scope of the Stereospecific Partial Reduction Method.—Acetic acid hydrolysis of the trialkenylboranes can of course give *cis*-olefins only when the original triple bond is disubstituted. The yields for simple acetylenes (Table 1) are about 80—90% of very pure *cis*-olefins, which compares very favourably with other methods such as Lindlar hydrogenation [4] (on poisoned Pd catalyst), reduction with diborane or disiamylborane,[1,2] and reduction with di-isobutylaluminium hydride.[5] The main advantage of the trialkylborane method is that control of the reaction is so easy; no over-reduction takes place, yet there is no starting material present.

TABLE 1

Reduction of acetylenic hydrocarbons with tri-isobutylborane

Acetylenic compound	Isobutene evolved (% of theory)	Product	M. p.	Yield (%)
Dec-5-yne	91	*cis*-Dec-5-ene	liq.	88
Cyclotetradeca-1,8-diyne	100	*cis,cis*-Diene	43—45°	67
		(+ impure crop)	(30—40°)	(+28)
Diphenylacetylene	100	*cis*-Stilbene	liq.	80
Hexa-2,4-diyne	—	*cis,cis*-Diene	liq.	~50
				(Cf. Exp. sect.)
Dodeca-5,7-diyne	99	,,	liq.	42
Hexadeca-7,9-diyne	91	,,	liq.	64—75 *
2,2,7,7-Tetramethylocta-3,5-diyne	—	Mixture of unsat. hydrocarbons	liq.	—
Dicyclohexylbuta-1,3-diyne	120	*cis,cis*-Diene	liq.	50
Diphenylbuta-1,3-diyne	75	,,	63°	36
1,14-Diphenyltetradeca-6,8-diyne	92	,,	liq.	13
Cyclo-octadeca-1,3,10,12-tetrayne	100	all-*cis*-Tetraene	117°	33

* No quinol: 64%. With 1,5,10, and 20% of quinol present the yields were 58, 71, 74, and 75%, respectively.

The yields for compounds containing one conjugated diyne system are lower, but also quite satisfactory (Table 1); when there are two such systems present of course a further lowering is observed. Compared with other methods, the trialkylborane reduction of

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[4] H. Lindlar, *Helv. chim. Acta*, 1952, **35**, 446.

[5] G. Wilke and H. Müller, *Chem. Ber.*, 1956, **89**, 444.

diacetylenes is far superior. Thus, a Lindlar reduction of cyclo-octadeca-1,3,10,12-tetrayne gave no clear break in absorption rate, and only 5% of impure all *cis*-tetraene (m. p. 100—105°) was obtained, while the present method gave 33% yield of the pure compound (m. p. 110—115°). Again, there is no over-reduced product, or starting material, or other geometrical isomer present, the loss being solely due to polymerisation. Diborane or disiamylborane reductions of diacetylenes to dienes have not been reported to be successful; presumably they are difficult to control in the former case and incomplete in the latter. An experiment with disiamylborane and dodeca-5,7-diyne gave a mixture of products and permitted only the conclusion that there was less than 10%, if any, of the *cis,cis*-diene present.

Steric hindrance, such as in 2,2,7,7-tetramethylocta-3,5-diyne, impedes the reaction (Table 1). Also, carbonyl groups, etc., must evidently be absent.

Preparation of Ketones from Acetylenes.—Oxidation of the trialkenylboranes to ketones (through enols) with alkaline hydrogen peroxide [1,2] represents a good method of converting a triple bond into a $CO{\cdot}CH_2$ group (Table 2).

TABLE 2

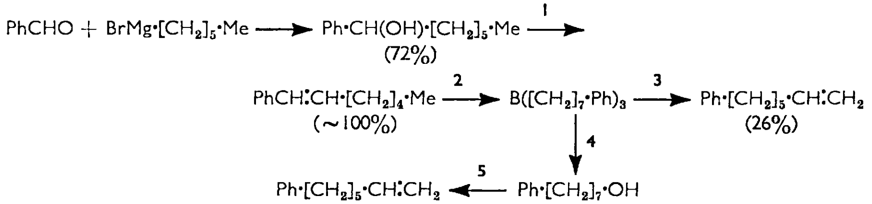
Conversion of acetylenic hydrocarbons into ketones by way of trialkenylboranes

Acetylenic compound	Ketone	M. p.	B. p.	Yield (%)
$PhC{\vdots}CPh$	$PhCO{\cdot}CH_2Ph$	49—52°		50
$C_4H_9{\cdot}C{\vdots}C{\cdot}C_4H_9$	$C_4H_9{\cdot}CO{\cdot}C_5H_{11}$	liq.	200—210°	76

In the case of conjugated diacetylenes there are three (or four in the asymmetrical case) isomeric diketones possible: 1,3 (or 2,4), 1,4, and 2,3. It was examined whether the addition of boron would show any selectivity, for example by the formation of a five-membered ring by linking the 1- and 4-positions. However, in the case of dodeca-5,7-diyne a mixture of three different ketones was obtained, and even the relative yields corresponded to a completely random attack. The steric shielding in dicyclohexylbuta-1,3-diyne did not introduce any further selectivity; again three main products were formed together with several other minor products.

Preparation of Terminal Olefins from Isomer Mixtures.—The preparation of olefins having the double bond exclusively in the terminal position of a chain (vinyl double bond) by dehydration of an alcohol is in general practically impossible. Usually, a mixture is obtained if there is no specially preferred interior position. On the other hand, since a primary carbon–boron bond is more stable than a secondary one, isomerisation of any open-chain olefin isomer with trialkylboranes or diborane leads ultimately to fixation of boron at the end.[1,2] Oxidation to the primary alcohol and dehydration is usually accompanied by extensive migration (~50% by infrared spectroscopy) back into the chain, as shown in the case of 7-phenylheptan-1-ol (Scheme 1). In the simpler one-step operation using a non-volatile disubstituted acetylene (monosubstituted acetylenes give explosions) absolutely no migration of the double bond takes place. The low yield (26%) is due to the difficulty of distilling the olefin from the viscous polymeric trialkenylboranes, and can no doubt be improved by using a high-boiling inert solvent.

Scheme 1

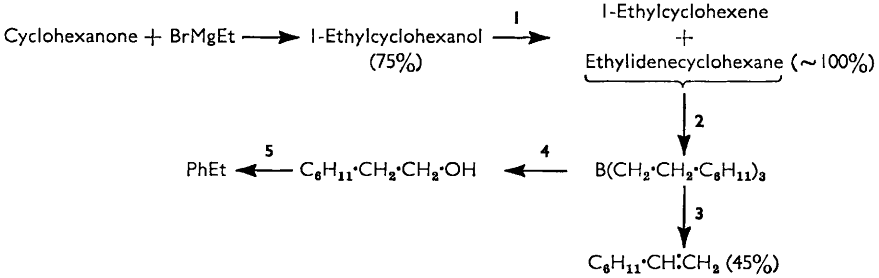


+ as much of isomeric non-terminal olefins (total 44%).

Reagents: 1, Al_2O_3, 300°; 2, BBu^i_3, 200°, 24 hr.; 3, cyclotetradeca-1,8-diyne, 200°; 4, H_2O_2–NaOH; 5, Al_2O_3, 350°.

An even more striking difference is observed in the analogous synthesis of vinylcyclohexane (Scheme 2), where dehydration of 2-cyclohexylethanol over alumina gave simultaneous dehydrogenation to ethylbenzene.

Scheme 2



Reagents: 1, Al_2O_3, 300°; 2, BBu^i_3, 200°; 3, cyclotetradeca-1,8-diyne, 160°; 4, H_2O_2–NaOH; 5, Al_2O_3, 350°.

EXPERIMENTAL

Preparation of Acetylenic Compounds.—Cyclotetradeca-1,8-diyne and cyclo-octadeca-1,3,10,12-tetrayne were prepared as previously described.[6] Dec-5-yne was prepared in a reaction between disodium acetylide (1 mole) and 1-bromobutane (2 moles) in liquid ammonia (1 l.).[7] Hexa-1,4-diyne, dodeca-5,7-diyne, and hexadeca-7,9-diyne were prepared [8] in a reaction of disodium diacetylide (1 mole) in liquid ammonia (2 l.) with 2 moles of methyl bromide, 1-bromobutane, and 1-bromohexane, respectively. 2,2,7,7-Tetramethylocta-3,5-diyne was prepared by oxidative coupling [9] of t-butylacetylene. Diphenylbuta-1,3-diyne was prepared by oxidative coupling [9] of phenylacetylene. 1,14-Diphenyltetradeca-6,8-diyne was prepared from 7-phenylhept-1-ene, whose synthesis is described below. This terminal olefin was treated with bromine in carbon tetrachloride to give the 1,2-dibromide (77%) which was then converted with sodamide into 7-phenylhept-1-yne (25%); it shows an acetylenic CH infrared band at 3·05 μ. Oxidative coupling of this acetylene in acetone [9] gave the diyne in 78% yield; the band at 3·05 μ is now absent. Dicyclohexylbuta-1,3-diyne was prepared from vinylcyclohexane, whose synthesis is described below. Treatment with bromine in carbon tetrachloride, then sodamide, gave cyclohexylacetylene [10] (30%). Oxidative coupling in acetone [9] gave the diyne (m. p. 102°) in 30% yield.

Preparation of Trialkylboranes.—Tri-isobutylborane was prepared [3] from tri-isobutylaluminium and boron trifluoride etherate. Tricyclohexylborane was prepared [3] by exchange between tri-isobutylborane and cyclohexene.

Reduction of Acetylenic Hydrocarbons with Trialkylboranes.—(a) *Cyclotetradeca*-1,8-*diyne.* The diyne (15 g., 0·08 mole) was dissolved in tri-isobutylborane (20 g., 0·11 mole) and heated under nitrogen on an oil-bath. Evolution of isobutene started slowly at 150°, became vigorous at 170°, then stopped sharply after 5 min. By weighing before and after the reaction it was verified that exactly 1 mole of isobutene had escaped. The excess of tri-isobutylborane was recovered by distillation at 0·01 mm. Acetic acid (20 ml.) was then added to the residue, and the mixture heated on a water-bath for 5 min. After addition of water the *cis,cis*-cyclotetradeca-1,8-diene [6] was extracted with hexane. Recrystallisation gave 10·0 g., m. p. 43—45°, and a second crop of 4·3 g., m. p. 30—40°.

When the same diyne was heated with tricyclohexylborane at 100°/14 mm. no weight loss was observed. At normal pressure distillation of cyclohexene took place at 160—180°.

(b) *Dec-5-yne.* This acetylene (10 g., 0·068 mole) was treated as above with tri-isobutylborane (12 g., 0·066 mole) at 170°. Of the expected quantity of isobutane 91% was evolved. In this case it was not easy to separate the excess of tri-isobutylborane by distillation. The whole mixture was therefore hydrolysed with acetic acid, the hydrocarbon extracted, and the last traces of boranes were destroyed with alkaline hydrogen peroxide. Extraction with hexane

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[6] J. Dale, A. J. Hubert, and G. S. D. King, *J.*, 1963, 73.

[7] *Inorg. Synth.*, 1946, **2**, 79.

[8] J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J.*, 1952, 1993; J. B. Armitage, C. L. Cook, E. R. H. Jones, and M. C. Whiting, *J.*, 1952, 2010.

[9] A. S. Hay, *J. Org. Chem.*, 1962, **27**, 3320.

[10] G. Darzens and Rost, *Compt. rend.*, 1909, **149**, 681.

and distillation gave the *cis*-dec-5-ene (8·8 g.) as a liquid, b. p. 50—60°/20 mm. The infrared spectrum showed bands for a *cis*-double bond at 3·34, 6·04, and 14 μ.

(c) *Diphenylacetylene.* The acetylene (2 g., 0·11 mole) was treated as in (a) with tri-isobutylborane (2 g., 0·11 mole). The calculated quantity of isobutene was evolved, and after distillation of the excess of tri-isobutylborane and hydrolysis, the *cis*-stilbene (1·6 g.) was isolated by distillation, b. p. 120°/1 mm. The infrared spectrum showed bands for the *cis*-double bond at 3·27, 6·24, and 14·4 μ. The ultraviolet spectrum had structureless bands at 207, 225, and 278 mμ (ε 22,000, 19,700, 10,600).

(d) *Hexa*-2,4-*diyne.* The reaction of tri-isobutylborane with this compound was incomplete because its high volatility prevented heating to the required temperature in an open vessel. An impure *cis,cis*-hexa-2,4-diene, b. p. 80—90°, was obtained in only 50% yield owing to loss by volatilisation. The low absorption intensity at 230 mμ (ε 8500) indicates at most 40% of conjugated diene.

(e) *Dodeca*-5,7-*diyne.* The diyne (5·2 g., 0·032 mole) was heated at 170° with tri-isobutylborane (10·9 g., 0·065 mole); the weight loss corresponded to 99% of the expected isobutene. After recovery of the excess of the borane by distillation and hydrolysis with acetic acid the cis,cis-*dodeca*-5,7-*diene* (42%) was isolated by distillation, b. p. 120°/3 mm. (Found: C, 86·2; H, 13·4. $C_{12}H_{22}$ requires C, 86·7; H, 13·3%). The infrared spectrum showed bands for conjugated *cis*-double bond at 3·32, 6·20, and 14·0 μ. The ultraviolet spectrum showed a structureless band at 236 mμ (ε 24,000).

(f) *Hexadeca*-7,9-*diyne.* In a reaction as in (e) using 10 g. of diyne (0·046 mole) and 16·7 g. of tri-isobutylborane (0·092 mole), 91% of isobutene was evolved and the *cis,cis*-hexadeca-7,9-diene (64%) was isolated by distillation, b. p. 120°/0·01 mm. The typical infrared bands were at 3·30, 6·22, and 14·0 μ, and the ultraviolet maximum at 236 mμ (ε 23,000). The yield, determined by gas chromatography, could be increased up to 75% by the addition of quinol (see Table 1).

(g) 2,2,7,7-*Tetramethylocta*-3,5-*diyne.* The reaction was very slow with this sterically hindered diyne, and a mixture of unsaturated hydrocarbons was obtained whose ultraviolet absorption intensity (ε 10,700) may correspond to at most 45% of diene.

(h) *Dicyclohexylbuta*-1,3-*diyne.* In a reaction as in (e) 120% of the expected quantity of isobutene was evolved, the only case for which over-reduction is indicated. The cis,cis-*dicyclohexylbuta*-1,3-*diene* (50%) was obtained as a liquid, b. p. ~100°/0·1 mm. (Found: C, 86·85, H, 11·8. $C_{16}H_{26}$ requires C, 88·0; H, 12·0%). Infrared bands for *cis*-double bonds were at 3·30, 3·34, 6·25, and 13·80 μ; the ultraviolet absorption maximum was at 238 mμ (ε 24,900). Ozonolysis and reduction [11] gave only one peak, cyclohexylcarbinol, in the gas-chromatogram; hence no migration had occurred.

(i) *Diphenylbuta*-1,3-*diyne.* The diyne (0·25 mole) reacted with tri-isobutylborane (0·50 mole) as in (e) to liberate 75% of the expected quantity of isobutene. The *cis,cis*-1,4-diphenylbuta-1,3-diene (36%) crystallised, m. p. 63°. The ultraviolet spectrum shows a maximum at 300 mμ (ε 29,800).

(j) 1,14-*Diphenyltetradeca*-6,8-*diyne.* In a reaction as in (e), 92% of the expected isobutene was evolved. The cis,cis-1,14-*diphenyltetradeca*-6,8-*diene* (13%) was isolated as an oil (Found: C, 90·3; H, 9·8. $C_{26}H_{34}$ requires C, 90·1; 9·9%). Infrared bands for *cis*-double bonds were at 3·30, 3·34, 6·22, and 14·4 μ; the ultraviolet maximum was at 236 mμ (ε 25,300).

(k) *Cyclo-octadeca*-1,3,10,12-*tetrayne.* Exactly the expected quantity of isobutene was obtained. The *all*-cis-*cyclo-octadeca*-1,3,10,12-*tetraene* (33%) was isolated by crystallisation from ethanol, m. p. 117° (Found: C, 88·4; H, 11·6. $C_{18}H_{28}$ requires C, 88·45; H, 11·55%). Infrared bands were at 3·33, 6·25, and 13·0 μ; the ultraviolet spectrum showed a structured band with maximum at 228 mμ (ε 55,000).

Conversion of Acetylenes into Ketones with Trialkylboranes.—(a) *Diphenylacetylene.* This compound (2·9 g., 0·016 moles) was treated with tri-isobutylborane as in the reduction method. The resulting trialkenylborane was diluted with hexane and dropped into a mixture of sodium hydroxide (6N) and hydrogen peroxide (30% in water).[1, 2] Extraction gave crystals of deoxybenzoin (1·6 g.), m. p. 49—52°, and an oil (1·3 g.).

(b) *Dec*-5-*yne.* The same procedure as in (a) was used and gave decan-5-one (76%) as a liquid, b. p. 200—210°. The infrared spectrum showed a band at 5·8 μ.

(c) *Conjugated diynes.* Both dodeca-5,7-diyne and dicyclohexylbuta-1,3-diyne were treated

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[11] A. J. Hubert, *J.*, 1963, 4088.

as in (a). Gas chromatography revealed in each case the presence of three major peaks (diketones) together with, especially in the latter case, several other minor peaks.

Preparation of Pure Terminal Olefins by Exchange of Primary Boranes with Acetylenes.—(a) *Vinylcyclohexane.* The olefin mixture obtained by dehydration over alumina of 1-ethylcyclohexanol (Scheme 2) contained no vinylcyclohexane (no infrared band at 11·0 μ). It was heated with 1·15 equiv. (1/3 mole + 15%) of tri-isobutylborane at 200° until refluxing stopped (4 hr.) to give, by isomerisation and finally fixation of boron at the terminal carbon atom,[1,2] tri-(2-cyclohexylethyl)borane. Cyclotetradeca-1,8-diyne in 10% excess was added, and the mixture heated to 160—200° under nitrogen. Very pure vinylcyclohexane (45%) distilled off, b. p. 130—140°. At the end the residue became very viscous; addition of a high-boiling inert solvent might no doubt have permitted the distillation to continue. The infrared spectrum howed the characteristic bands at 3·26, 3·32, 6·10, 10·1, and 11·0 μ for the vinyl group, and no other olefinic bands. [In contrast, a hydrocarbon obtained by oxidation of the borane with alkaline hydrogen peroxide and dehydration of the formed 2-cyclohexylethanol over alumina at 350° showed no olefinic bands, but proved to be mainly ethylbenzene formed by further dehydrogenation.]

(b) 7-*Phenylhept*-1-*ene.* 1-Phenylhept-1-ene (1 mole) (b. p. 74°/0·2 mm., olefinic infrared bands at 6·08 and 10·4 μ) was obtained by dehydration of 1-phenylheptan-1-ol over alumina (Scheme 1). It was heated with tri-isobutylborane (1/3 mole + 15%) at 200° for 24 hr., to give tri-(7-phenylheptyl)borane. Cyclotetradeca-1,8-diyne (0·55 mole) was added, and the mixture heated to 200°. Very pure 7-phenylhept-1-ene (26%) distilled off, b. p. 58—62°/0·2 mm., but again the viscosity of the residue prevented the exhaustive distillation of the olefin. The infrared spectrum showed only the vinyl bands at 10·1 and 11·0 μ, and no trace of *trans*-olefin absorption at 10·4 μ. [In contrast, the olefin obtained (44%) by oxidation of the borane with alkaline hydrogen peroxide and dehydration of the obtained 7-phenylheptan-1-ol over alumina at 350° showed a band at 10·35 μ having the same intensity as the band at 11·0 μ].

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