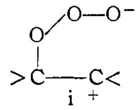
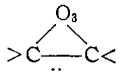
tack, and corrected oxidation–reduction potentials[1,3,4] seems too consistent to be fortuitous.[45] If our conclusion that ozone initially attacks unsubstituted aromatic systems *via* a rate-controlling transition state whose geometry corresponds to the most stable dihydro product[1,3,4] is correct, then in the absence of relevant kinetic data, Criegee[46] with customary foresight has suggested a most appealing alternative: that the formation of (i) (electrophilic) and (ii) (nucleophilic)[47] occurs "nearly simultaneously so the initial ozonide


i


ii

comes together by a kind of four center reaction."[48] This viewpoint suggests that the difference between opposed schools may be more apparent than real.

Acknowledgment.—This research was supported by a grant C-3325 (C2) from the U. S. Public Health Service, National Cancer Institute. Grateful acknowledgment is hereby made to the donor of said funds. We are indebted to Dr. L. T. Capell of the "Chem. Abstracts" Service for the systematic nomenclature used herein. E. J. M. wishes to thank Prof. R. Criegee for his interest, helpful suggestions and many stimulating discussions.

NEW YORK 58, N. Y.

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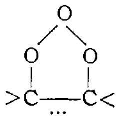
[45] F. T. Wallenberger [*Tetrahedron Letters*, **9**, 5 (1959)] has recently suggested the use of theoretical resonance energy decrease accompanying the reaction to correlate and predict the specificity of the ozonization of polycyclic aromatics. We are indebted to Dr. Wallenberger for providing us with a preprint of his communication.

[46] R. Criegee, *Record Chem. Prog. Kresge–Hooker Sci. Lib.*, **18**, 111 (1957).

[47] Nucleophilic attack on the carbonium ion may occur by the terminal or central oxygen atom to give respectively, iii or iv.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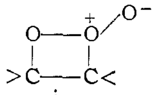
iv

[48] Bailey's π-complex mechanism[40,42b] also shows how this might be accomplished but does not indicate why it should.

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES]

The Reaction of Diborane with Di-*t*-butylethylene and Di-*t*-butylacetylene

BY TED J. LOGAN AND THOMAS J. FLAUTT

RECEIVED SEPTEMBER 14, 1959

The reaction of di-*t*-butylethylene (*trans*-2,2,5,5-tetramethyl-3-hexene) with diborane yields 2,2,5,5-tetramethyl-3-hexylborane, $C_{10}H_{21}BH_2$, a monoalkylborane. Oxidation and hydrolysis of this product lead to the corresponding alcohol, 2,2,5,5-tetramethyl-3-hexanol. Heating of the hydroborated olefin prior to oxidation, however, results in the unexpected formation of a C_{10}-diol, namely, 2,2,5,5-tetramethyl-1,4-hexanediol, as the end product. Nuclear magnetic resonance spectra enabled this structural assignment to be made. The same product is obtained in a 20% yield from the hydroboration, thermal isomerization and oxidation of di-*t*-butylacetylene (2,2,5,5-tetramethyl-3-hexyne). An explanation of the unexpected results is offered.

Hennion[1] discovered that secondary and tertiary alkyl groups attached to boron may be thermally isomerized to the corresponding primary alkyl groups. Brown[2] found that trialkylboranes, formed by the reaction of B_2H_6 with non-terminal olefins, undergo a similar thermal isomerization to the corresponding 1-alkylboranes. The over-all conversion of internal olefins to primary alcohols is then completed by oxidation and hydrolysis.

Brown[2] suggested that the isomerization of internal boranes to the terminal derivatives could proceed through a thermally induced equilibrium of the trialkylborane with olefin and dialkylborane, and that conversion to the more stable terminal derivative is achieved by a series of addition and elimination reactions. According to this mechanism boron atom migration past a quaternary carbon atom could not occur. Hennion's proposed mechanism,[1] on the other hand, would permit such a migration.

The present study was undertaken to establish whether or not this boron migration could occur and to learn more about the migration mechanism in general. This object was not fully realized because it was found that the isomerization of hydroborated di-*t*-butylethylene proceeds abnormally. A product is obtained which can be oxidized to a C_{10}-diol, instead of the expected monoalcohol. Di-*t*-butylethylene was chosen for study because it is well described in the literature[3-6] and because the boron atom in its hydroborated product must pass a quaternary carbon atom in order that the 1-alkylborane and, ultimately, a primary alcohol can be produced.

trans-Di-*t*-butylethylene reacts with B_2H_6 to form 2,2,5,5-tetramethyl-3-hexylborane, $C_{10}H_{21}BH_2$,[7] identified by its infrared spectrum and elemental

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[1] G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, A.C.S. Abstracts of Papers, 130th Meeting, Atlantic City, N. J., September, 1956, p. 53-O; also, THIS JOURNAL, **79**, 5190 (1957).

[2] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957).

[3] G. F. Hennion and T. F. Banigan, Jr., THIS JOURNAL, **68**, 1202 (1946).

[4] F. L. Howard, T. W. Mears, A. Fookson and P. Pomerantz, *ibid.*, **68**, 2121 (1946).

[5] F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz and D. B. Brooks, *J. Research Natl. Bur. Standards*, **38**, 365 (1947).

[6] W. H. Puterbaugh and M. S. Newman, THIS JOURNAL, **81**, 1611 (1959).

[7] This is the first reported example of the preparation of a monoalkylborane by hydroboration of an olefin. Brown has previously reported the preparation of dialkylboranes from the reaction of B_2H_6 with substituted olefins (ref. 9 and A.C.S. Abstracts of Papers, 135th Meeting, Boston, Mass., April, 1959, p. 39-O); unsubstituted olefins invariably lead to the trialkylboranes. NOTE ADDED IN PROOF.—Brown has recently reported that "reaction with tetrasubstituted olefins appears to halt at the monoalkylborane, RBH_2, stage," THIS JOURNAL, **81**, 6428 (1959).

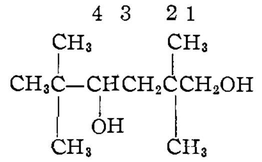
analyses, and by oxidation and hydrolysis to 2,2,5,5-tetramethyl-3-hexanol. This hexanol was identical with an authentic sample (IV) prepared by the reaction of methyl *t*-butylacetate with *t*-butylmagnesium chloride, as evidenced by identical infrared spectra, no mixture melting point depression of the alcohols or their phenylurethan derivatives, and identity of the X-ray powder patterns.

Since Puterbaugh and Newman[6] reported that chlorination of *trans*-di-*t*-butylethylene gave a rearranged dichloride, the product obtained from the hydroboration, oxidation and hydrolysis of the same olefin was examined for the presence of rearranged alcohol. By establishing that the product was identical with the authentic sample of 2,2,5,5-tetramethyl-3-hexanol, it was shown that rearrangement had not occurred.

To determine whether or not the boron atom could migrate past a quaternary carbon atom, 2,2,5,5-tetramethyl-3-hexylborane was heated in diglyme (dimethyl ether of diethylene glycol) for 20 hr. at 160–165°. Oxidation and hydrolysis of the isomerized product gave, unexpectedly, a C_{10}-diol in 60% yield. Elemental analysis of the product and its bis-(phenylurethan) derivative, and hydroxyl value determinations established that the product was a C_{10}-diol. When 2,2,5,5-tetramethyl-3-hexanol and the diol are acetylated under the usual conditions, the hydroxyl values are too low. Under more vigorous conditions, the hydroxyl values for both the known C_{10}-monoalcohol and the C_{10}-diol increase and eventually reach approximately 90% of theory. The results suggest that the diol possesses one unhindered alcohol group and one with a degree of hindrance comparable to that in 2,2,5,5-tetramethyl-3-hexanol. The infrared spectrum of the diol (in CS_2 solution) shows primary (9.5μ) but not tertiary alcohol absorption. The region in which secondary alcohol absorption should occur (9.4μ) as determined by examination of the spectrum of the monoalcohol, is masked by the primary alcohol absorption (see Fig. 1).

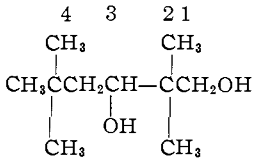
The structure of the diol was assigned on the basis of (1) infrared spectra, (2) hydroxyl value determinations and (3) examination of the nuclear magnetic resonance spectra.

According to chemical and infrared evidence, several structures for the diol are possible



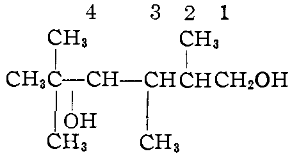
$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2OH}$$

I



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}CH_2OH}$$

II



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}-\underset{CH_3}{CH}\overset{CH_3}{CH}CH_2OH}$$

III

Methyl migration is necessary for the formation of III. Other structures involving similar migrations may be written which are in accord with the chemical and infrared evidence. All these structures may be considered with structure III in the discussion of structure assignment based on n.m.r. data.

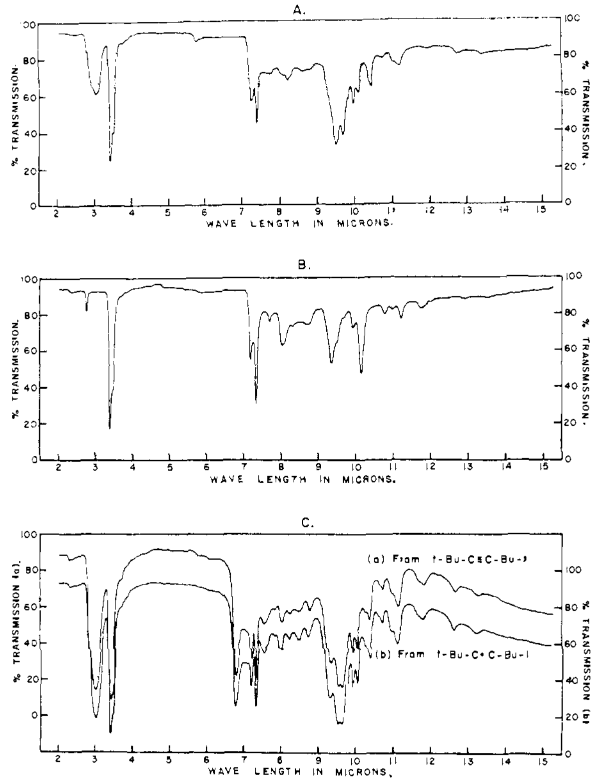


Fig. 1.—Infrared spectra in CS_2 (1%): A, 2,2,5,5-tetramethyl-1,4-hexanediol (I); B, 2,2,5,5-tetramethyl-3-hexanol (IV). C, a and b, diols from di-*t*-butylacetylene and di-*t*-butylethylene, resp.

The n.m.r. spectrum of the diol is given in Fig. 2B. The peak at 5.06 p.p.m. arises from hydroxyl protons, the peak at 6.61 p.p.m. from protons on the hydroxylated carbons, the doublet at 8.65 p.p.m. from protons on a carbon adjacent to the hydroxylated carbon, and the sharp peak at 9.14 p.p.m. from methyl protons. A detailed discussion of these assignments is found under N.m.r. Peak Assignment in the Experimental section.

Structure III for the diol may be eliminated by examination of the spin coupling pattern exhibited by the peaks at 6.61 p.p.m. and at 8.65 p.p.m. (Fig. 2B).

For structures I and II the doublet at 8.65 p.p.m. is assigned to the protons on the internal methylene group of either I or II. This peak is a doublet because these two equivalent protons are spin coupled by the single proton on the adjacent hydroxylated carbon atom. If the structure were III, the pattern at 8.65 p.p.m. should be more complex, a doublet superimposed on a triplet. The doublet would arise from coupling of the 3-carbon proton with the 4-carbon proton. Spin coupling of the two 1-carbon protons by the 2-carbon proton should lead to a triplet. In addition, if the structure were III, the pattern of the 6.61 p.p.m. peak should be a superposition of two doublets, one from coupling of the 3- with the 4-carbon proton and the other

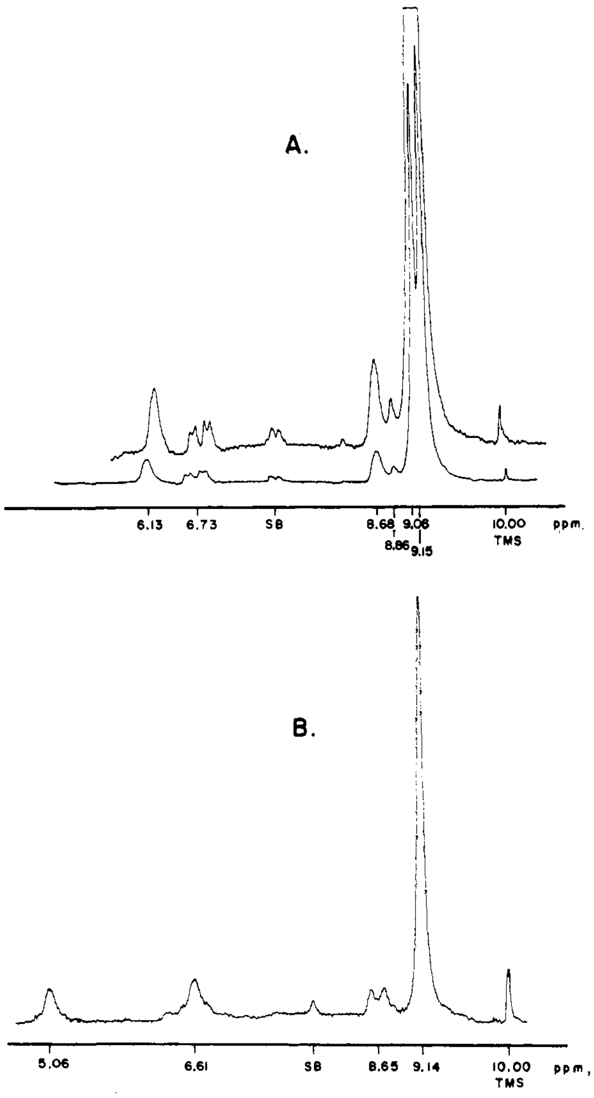
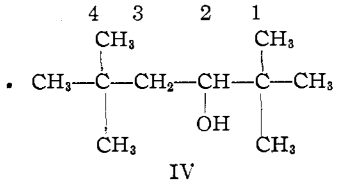


Fig. 2.—Proton n.m.r. spectra: A, 2,2,5,5-tetramethyl-3-hexanol (IV) in CCl_4 (50%); B, 2,2,5,5-tetramethyl-1,4-hexanediol (I) in CCl_4 (25%); tetramethylsilane (TMS) internal reference; SB refers to a spinning sideband of the methyl peak; magnetic field increases from left to right.

from the coupling of the two equivalent 1-carbon protons by the 2-carbon proton. Such a pattern at the 6.61 p.p.m. peak is not found in the spectrum of the diol (Fig. 2B). Instead, the pattern expected from I or II is seen, a singlet superimposed on a triplet. The two 1-carbon protons give a singlet because the 2-carbon has no protons to spin couple. Coupling of the 4-carbon proton by the two 3-carbon protons in I, or the 3-carbon proton by the two 4-carbon protons in II, gives rise to the triplet. Both the patterns at 8.65 and 6.61 p.p.m. therefore indicate that the carbon skeleton is that of I and II, not III.

The spectrum of 2,2,5,5-tetramethyl-3-hexanol[8] (IV) may be used to serve as a model compound to distinguish between the 1,4- and 1,3-diols (I and II, respectively). The splitting of the methyl resonances (Fig. 2A) shows that there are two chemi-



$$\mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\underset{OH}{CH}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3}$$

IV

cally different types of methyl protons, those attached to the carbon beta to the hydroxylated carbon and those attached to the carbon gamma to the hydroxylated carbon (peaks at 9.06 and 9.15 p.p.m.). The chemical shift of the methyl group beta to the hydroxyl is slightly changed by the presence of the hydroxyl group further down the chain. However, it is not expected that the gamma protons would be affected. In the spectrum of the diol (Fig. 2B) there is only one type of methyl resonance peak (at 9.14 p.p.m.). If the diol were II, there should be two types of methyl groups, those beta to a hydroxyl group and those gamma to a hydroxyl group. If the diol is I, then there should be only methyl groups attached to carbons beta to hydroxylated carbons. Two of these methyl groups are also gamma to the internal hydroxyl group. However, as noted above, the gamma substituent is too far removed to be expected to have an effect on the n.m.r. spectrum. Since there is only one peak in the spectrum of the diol, the n.m.r. data indicate that it possesses the 1,4-structure of I. Attempts to synthesize II by a different route were unsuccessful.

It is clear from the results obtained that hydroboration of di-*t*-butylethylene proceeds normally (although it does stop at the RBH_2 stage) and that the precursor of the diol is formed in the isomerization step. The precursor must possess either two C–B bonds or must be a boron heterocycle in order that a diol be produced on oxidation and hydrolysis. Acetylenic bonds are known to add two B–H linkages,[9] and the resulting product should lead to a glycol on oxidation. In order to compare the products obtained from di-*t*-butylethylene and di-*t*-butylacetylene, the latter was hydroborated, thermally isomerized, oxidized and hydrolyzed. As one of the products there was obtained a 20% yield of a C_{10}-diol, which was shown by infrared (see Fig. 1) and by mixture melting point of the bis-(phenylurethan) derivatives to be identical with the C_{10}-diol from di-*t*-butylethylene.

Hydroboration, oxidation and hydrolysis of di-*t*-butylacetylene gave several products, including 2,2,5,5-tetramethyl-3,4-hexanediol and 2,2,5,5-tetramethyl-3-hexanol, the latter identified by its phenylurethan derivative. The monoalcohol presumably arises from the addition of a single B–H linkage to the acetylene bond. This product yields, after a

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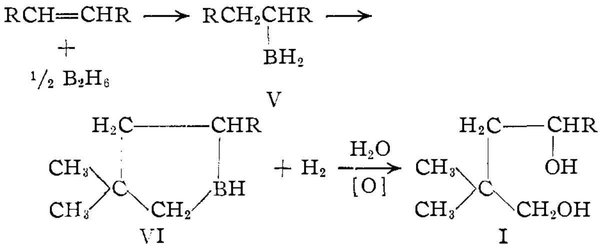
(8) The existence of the doublet (Fig. 2B, 8.65 p.p.m.) arising from the protons of the internal methylene group of I indicates that the spin coupling is identical for each of the two protons. This is not the case for the monoalcohol IV. The spin coupling pattern for IV (Fig. 2A, 8.68 and 8.86 p.p.m.) is of the ABX variety [H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957)], two inequivalent protons whose chemical shift is small compared with their mutual spin coupling, each coupled unequally to a third proton. With this assignment the spin coupling constants are: J_{AX} = 6.7 c.p.s., J_{BX} = 2.6 c.p.s., and J_{AB} = 13.5 c.p.s. Hindered rotation is the probable explanation for unequal coupling of the two protons of the methylene group.

(9) H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 1512 (1959).

portion of it has been oxidized and hydrolyzed, an unsaturated alcohol which rearranges to the ketone. It is assumed that this ketone is then reduced to the saturated alcohol by unoxidized B–H bonds.

Since it was entirely unexpected that a diol would be obtained by the hydroboration, isomerization and oxidation of an olefin, the intermediate boron compounds in each of the above steps were examined in order to gain further information concerning their role in diol formation. 2,2,5,5-Tetramethyl-3-hexylborane begins to undergo change at its melting point (84–86°) so that attempts to duplicate the melting point with the same sample gave lower values with ever-increasing ranges. Isomerization at 160° for 20 hr. in the absence of solvent gave a yellow oil which still possessed B–H bonds. Gas evolution (presumably H_2) during the heating process was evident. It is believed that heating causes dehydrogenation, with subsequent formation of a boron heterocycle. The following sequence of reactions is suggested as one possibility for C_{10}-diol formation (R = *t*-Bu)[10]



At room temperature, V is stable and may be oxidized to the corresponding alcohol, but at elevated temperatures, an intramolecular alkylation reaction yields VI and H_2. Other workers have reported that the alkylation of diborane and its derivatives yields alkylboranes and H_2. Hurd[11] found that diborane could be alkylated with saturated hydrocarbons under vigorous conditions to give low yields of trialkylboranes and H_2. Recently, Winternitz[12] reported that heating tri-*n*-amylborane or tri-*n*-hexylborane under reflux resulted in the formation of the corresponding olefin, H_2 and a boron heterocycle, probably formed by the intramolecular alkylation of the boron atom in the dialkylborane.[12] The heterocycle formed from tri-*n*-amylborane is 5-membered, apparently because the strain involved in a similar 4-membered ring prevents its formation. Similarly, the intramolecular alkylation of the boron atom in V proceeds to yield a 5- rather than a 4-membered ring, leading ultimately to a 1,4- rather than a 1,3-diol.

The final formation of a diol from di-*t*-butylethylene is probably a direct consequence of the sterically hindered double bond. Because of this hindrance, hydroboration proceeds only to the monoalkylborane, a stronger Lewis acid than the corresponding dialkylborane. The crowding in the borane places the boron atom in close proximity to the δ-carbon atom, facilitating reaction at this site.

Since the isomerization of 2,2,5,5-tetramethyl-3-hexylborane proceeds abnormally, the present study neither substantiates nor disproves Brown's proposed isomerization mechanism.

Experimental

General.—All manipulations with boron compounds described below were carried out in a nitrogen atmosphere. Diborane generation and the procedures for hydroboration and oxidation were those previously described by Brown.[2] Diglyme (dimethyl ether of diethylene glycol) was distilled from $LiAlH_4$ and BF_3 etherate was distilled in a nitrogen atmosphere at reduced pressure. Diborane was generated by the slow addition of a diglyme solution of $NaBH_4$ to the BF_3 etherate and carried into the olefin solution by a slow stream of N_2. The exhaust gases were passed through an acetone wash bottle which trapped any unreacted B_2H_6.

All melting points are uncorrected.

Preparation of *trans*-2,2,5,5-Tetramethyl-3-hexene (VII).—The reported[6] pyrolysis of 2,2,5,5-tetramethyl-3-hexyl acetate at 390° gave good yields of VII. Combined products from several runs were distilled at atmospheric pressure to give the olefin, b.p. 125.0–126.4°, $n^{25}D$ 1.4089. Reported[5] values are b.p. 125.013° and $n^{25}D$ 1.40890.

Preparation of 2,2,5,5-Tetramethyl-3-Hexylborane (V).—A 14.0-g. quantity (0.1 mole) of the olefin VII was dissolved in 250 ml. of anhydrous ether in a 3-necked flask equipped with a water-cooled reflux condenser, thermometer, B_2H_6 inlet tube and magnetic stirrer. Diborane, generated from 4.82 g. of $NaBH_4$ in 150 ml. of diglyme and 34.2 g. of BF_3 etherate over a 2-hr. period, was carried into the olefin solution with N_2. The hydroboration was slightly exothermic. Stirring was continued for 1 hr. before solvent and excess B_2H_6 were removed with a rapid N_2 stream. The residue of 15.8 g. of a white solid was placed in a box filled with dry N_2. An ether solution of the hexylborane, saturated at room temperature, was prepared, filtered, and then cooled with Dry Ice. Crystals precipitated and were filtered with suction on a sintered glass filter. The temperature was kept below 32° (the maximum temperature reached during hydroboration) to prevent structural changes. The infrared spectrum showed an absorption band at approximately 4.0 μ. This agrees with the B–H stretching frequency assigned by Bellamy.[13]

Anal. Calcd. for $C_{10}H_{21}BH_2$: C, 77.94; H, 15.05; B, 7.02. Found: C, 77.24; H, 14.59; B, 6.46.

A small portion of this solid was oxidized with 30% H_2O_2 to yield an alcohol shown to be identical with IV by its phenylurethan derivative, m.p. 126°.

Another portion, 4.2 g., was heated at 160–165° for 20 hr. under N_2. Gas evolution was evident during the first 6 hr. The infrared spectrum of the resultant viscous yellow oil showed B–H absorption. Without purification, the oil gave the following elemental analyses: C, 74.55; H, 13.26; B, 7.10.

Hydroboration and Direct Oxidation of VII.—In a duplication of the experiment described above, except that the ether solvent was replaced by diglyme (136 ml.), the borane was oxidized *in situ* to the alcohol. To destroy excess B_2H_6, 50 ml. of water was first added dropwise. This gave a very vigorous reaction with much gas evolution and foaming, and the temperature reached 41°. After all water had been added, 14.4 g. of NaOH in 25 ml. of water (foaming and heat evolution again), and, finally, 37.4 g. of 30% H_2O_2 were added dropwise. The solution was stirred in an erlenmeyer flask with 275 ml. of water for 1 hr. After separation, the aqueous layer was extracted with petroleum ether. The combined organic layers were dried with $MgSO_4$ and the solvent was removed by atmospheric distillation. There remained 13.0 g. of alcohol IVa, 82.2% yield, m.p. and mixture m.p. with IV, 52.5–53.0°. For analysis, a sample was purified by sublimation at atmospheric pressure.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 75.68; H, 13.97.

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[10] The authors are grateful to the referees of this paper, Drs. H. C. Brown and G. F. Hennion, for suggesting this reaction sequence, which is similar to that reported by P. F. Winternitz, A.C.S. Abstracts of Papers, 135th Meeting, Boston, Mass., April, 1959, p. 19-M.

[11] D. T. Hurd, THIS JOURNAL, **70**, 2053 (1948).

[12] Rosenblum has previously shown that trialkylboranes may be thermally decomposed to give the olefin and dialkylborane; L. Rosenblum, *ibid.*, **77**, 5016 (1955).

[13] L. J. Bellamy, W. Gerrard, M. F. Lappert and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

TABLE I

X-RAY POWDER DIFFRACTION DATA

A[a]		B[b]		A		B		A		B	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
10.93	vs	11.04	vs	2.92	s	2.94	s	2.05	vvw	2.06	vw
8.25	vs	8.18	vs	2.79	vw	2.79	vw	1.97	w	1.97	ms
5.45	vvs	5.53	vvs	2.71	m	2.73	m	1.91	vw	1.91	m
4.84	s	4.82	s	2.56	w	2.58	m	1.86	vw	1.86	ms
4.49	s	4.53	ms	2.43	m	2.44	ms	1.80	vvw	1.81	vw
4.08	vs	4.11	s	2.31	w	2.30	m	1.78	vvw	1.78	vw
3.83	s	3.83	ms	2.25	vvw	2.25	w	1.75	vvw	1.76	w
3.60	vw	3.59	vw	2.22	w	2.21	m	1.61	vw	1.64	m
3.43	w	3.42	w	2.16	vw	2.17	m	1.59	vw	1.60	mw
3.16	m	3.18	m	2.13	vw	2.13	w				

[a] Authentic sample of 2,2,5,5-tetramethyl-3-hexanol (IV). [b] Alcohol IVa from hydroboration, oxidation and hydrolysis of 2,2,5,5-tetramethyl-3-hexene.

The phenylurethan of IVa was prepared and purified by sublimation.

Anal. Calcd. for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.81. Found: C, 73.68; H, 9.80.

The m.ps. and mixture m.p. of the phenylurethans of IV and IVa were 125–126°. An X-ray powder diffraction pattern and infrared comparison of IV and IVa further confirmed their identity (see Table I for X-ray data).

Hydroboration, Isomerization and Oxidation of VII.—Hydroboration of VII was carried out exactly as described previously. The hydroborated product in diglyme was heated to reflux (160–165°) for 20 hr. When the clear, red-brown liquid had cooled, hydrolysis and oxidation were carried out as before. The addition of water gave no foaming or heat evolution, as had been observed in the preceding example. Isolation of the product as before, followed by vacuum distillation, gave a forerun, 2.06 g., b.p. 27–75° (3.0 mm.), which contained an alcohol, phenylurethan m.p. 118°. There was also obtained 10.41 g., 59.8% yield, of C_{10}-diol (I), b.p. 94–97° (3.0 mm.), m.p. 40.5–42.5°, hydroxyl value 600.5 (see Table II).

TABLE II

HYDROXYL VALUE DETERMINATIONS

Sample	Reagent	Time, min.	Found	H.V. calcd.
$C_{10}H_{22}O$ (IV)	Ac_2O	40	51	354
	Ac_2O	120	113	354
	MeCOCl	40	266	354
	MeCOCl	120	309	354
$C_{10}H_{22}O_2$ (I)	Ac_2O	40	366	644
	Ac_2O	120	401	644
	MeCOCl	80	586	644
	MeCOCl	120	601	644

These values were obtained by heating the alcoholic solution to 60° with the anhydride or chloride, in pyridine, for the periods indicated.

A gas chromatographic analysis of the C_{10}-diol showed that the product was 97.5% pure.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.91; H, 12.72; O, 18.36. Found: C, 68.76; H, 12.38; O, 18.25.

The bis-(phenylurethan) melted sharply at 146° after recrystallization from a 50–50 mixture of CCl_4 and petroleum ether (b.p. 30–60°).

Preparation of Di-*t*-butylacetylene (VIII).—This was prepared according to directions given by Hennion.[3] The most difficult step of this synthesis, the conversion of pinacolone dichloride to mono-*t*-butylacetylene, was greatly facilitated by following the variations suggested by Puterbaugh and Newman.[6] This involves strongly heating a slurry of the dichloride with KOH in mineral oil, instead of the dry distillation originally described by Ivitzky.[14]

Product from several runs was combined and redistilled to give pure VIII, b.p. 111.7–112.5°, n^{25}D 1.4072; literature values[3] are b.p. 111.9° (746) mm.), n^{25}D 1.4026.

Hydroboration and Oxidation of VIII.—Diborane, generated from 6.43 g. of $NaBH_4$ in 200 ml. of diglyme and 45.6 g. of BF_3 etherate, was used to hydroborate 13.8 g. (0.1 mole) of VIII. The temperature reached a maximum of 42°. After standing an additional hour with stirring, 25 ml. of water was added, then 14.4 g. of NaOH in 25 ml. of water. Gas and heat evolution were evident in both steps. Oxidation was accomplished by the dropwise addition of 37.4 g. of 30% H_2O_2 giving a maximum temperature of 41°. The product was mixed with 300 ml. of H_2O, and, after separation of the layers, the aqueous layer was extracted with petroleum ether. Vacuum distillation of the combined organic layers gave the fractions: (1) 1.21 g. of sublimed alcohol, m.p. and mixture m.p. with IV, 52.5–53.0; phenylurethan m.p. 124.5–125.0°; (2) 0.54 g. of solid, m.p. 113.0–113.5°, believed to be 2,2,5,5-tetramethyl-3,4-hexanediol,[15] which showed no primary alcohol absorption in the infrared; (3) 0.23 g. of liquid, b.p. 62–72° (9.0 mm.); (4) 0.66 g. of liquid, b.p. 110–114° (9.0 mm.); (5) 0.75 g. of low melting solid, b.p. 112–114° (9.0 mm.); (6) 2.78 g. of residue. No attempts were made to identify the latter fractions.

Hydroboration, Isomerization and Oxidation of VIII.—The hydroboration was carried out as described above. The reaction products were heated to reflux in diglyme (160–165°) for 20 hr. After cooling, the dark, red-brown liquid was oxidized as before with 30% H_2O_2. Vacuum distillation of the petroleum ether extracted product gave the fractions: (1) 1.60 g. of solid, identified by infrared spectrum, m.p. and m.p. of phenylurethan derivative as 2,2,5,5-tetramethyl-3-hexanol; (2) 3.56 g. of C_{10}-diol, 20.4% yield, b.p. 116–122° (11.0 mm.), infrared spectrum identical (see Fig. 1) with the diol from VII, bis-(phenylurethan) m.p. and mixture m.p. with the same derivative from VII, 146°; (3) 0.85 g. of liquid, b.p. 117° (5.0 mm.), unidentified; (4) 1.74 g. of residue. The bis-(phenylurethan) of fraction 2 was recrystallized from a CCl_4–petroleum ether mixture and was analyzed.

Anal. Calcd. for $C_{24}H_{32}N_2O_4$: C, 69.87; H, 7.82; N, 6.79. Found: C, 70.04; H, 7.62; N, 6.75.

N.m.r. Measurements.—The n.m.r. spectra were obtained with a Varian high-resolution instrument, model V4200B, at a frequency of 40 mc. The samples were dissolved in carbon tetrachloride. Tetramethylsilane (TMS) was added to the solvent to serve as an internal reference. Calibration of the spectrogram abscissa was accomplished by the usual sideband technique. A Hewlett–Packard 524B frequency counter was used to measure sideband frequency to 0.1 c.p.s. The minimum precision for a given peak was 0.10 p.p.m. (4 c.p.s.). Measurements of the methyl resonances were precise to 0.005 p.p.m. The numbers given as peak positions in Fig. 2 represent the average of three measurements. The chemical shift of TMS is taken to be 10.00 p.p.m.[16] Areas of the peaks of the diol I were measured with a planimeter on spectra obtained under non-saturating conditions. Theoretical ratios for peaks

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[14] M. P. Ivitzky, *Bull. soc. chim. France,* [4] **35**, 357 (1924).

[15] This glycol is listed in "Beilstein," Vol. 1, p. 496, 4th edition, reported m.p. 83–84°. It was prepared by the reductive coupling of trimethylacetic acid with the corresponding acid chloride in the presence of Na(Hg). The difference in m.ps. may be due to *erythro–threo* isomerism.

[16] Following the convention proposed by G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(Fig. 1B) at 5.06, 6.61, 8.65 and 9.14 p.p.m. are 2:3:2:15. Ratios found were 1.8 ± 0.1:3.0 (assumed):2.0 ± 0.1:14.9 ± 2.7. It is noted (Fig. 1B) that peaks at 8.65 and 9.14 p.p.m. overlap; therefore a somewhat arbitrary manual separation must be made.

N.m.r. Peak Assignments. 2,2,5,5-Tetramethyl-3-hexanol (Fig. 2A).—The characteristic shift of one peak (6.13 p.p.m.) with dilution of the samples marked it as the hydroxyl group. The other low field multiplet (6.73 p.p.m.) must therefore be the proton attached to the hydroxylated carbon. It is well known that such protons have a peak in this region.[17] The two sharp peaks (9.06 and 9.15 p.p.m.) represent the methyl protons because of their position, intensity and sharpness. This leaves the other multiplet (in the region of 8.68 p.p.m.) to be assigned to the protons attached to the 4-carbon. As noted above, the spin coupling pattern is entirely consistent with this assignment if it is assumed that the two protons on the 4-carbon couple unequally with the proton on the 3-carbon.

2,2,5,5-Tetramethyl-1,4-hexanediol (Fig. 2B).—The hydroxyl peak was identified by the disappearance of the peak at 5.06 p.p.m. after exchange of the diol with D_2O. The other low field peak (6.61 p.p.m.) must therefore be due to the protons attached to the hydroxylated carbon. The methyl groups were assigned to the sharp peak at high field (9.14 p.p.m.) for the same reasons as noted for the monoalcohol. This leaves the doublet at 8.65 p.p.m. to be assigned to the remaining two internal methylene protons. As noted above, area measurements of the peaks are in good agreement with this assignment.

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[17] Correlations of chemical shift with proton type have been published by N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE WILLIAM MARSH RICE AND YALE UNIVERSITIES]

Heats of Hydrogenation. VII. The Cycloheptatrienylium (Tropylium) Ion

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The heat of hydrogenation of tropylium chloride in acetic acid is −86.2 kcal./mole. Its heat of formation in the same solvent is +19.8 kcal./mole and may be compared with estimations of +19.6 and +23.8 kcal./mole for the heat of formation of the covalently bonded isomer. The heat of solvation in water of gaseous tropylium ion is estimated to lie between −50 and −68 kcal./mole. An attempt is made to compare the heat of formation of tropylium ion with that of its isomer, the benzylcarbonium ion.

As the parent of the heptagonal aromatic system, the cycloheptatrienylium ion occupies the same relative position as benzene in the hexagonal system and the cyclopentadienide anion in the pentagonal. Paralleling a perennial concern with the energy content and aromaticity of benzene, today's interest in the experimental and theoretical energy content of tropylium arises from wonder at the very existence of this stable carbonium ion and at the high π-electron delocalization energy of 3.0 β Hückel[1] calculated for it by his molecular orbital treatment. Unlike benzene, where three times the heats of hydrogenation of cyclohexene[2] or of ethylene minus corrections[3] serve as convenient models for comparison with a theoretical π-electron delocalization energy of 2.0 β, tropylium ion has no adequate, localized model.

To obtain a fundamental thermodynamic datum from which heats of formation and solvation may be estimated, the heat of hydrogenation of tropylium ion has been determined. The hydrogenation experiments employ the technique described in the first paper of this series.[4] Tropylium bromide[5] was hydrogenated in stock acetic acid at 25° to cycloheptane and hydrogen bromide. On the basis of hydrogen absorbed, which was about 97% of theory for four molar equivalents of hydrogen calculated from the weight of sample employed, the heat of hydrogenation is −89.06 ± 0.17 kcal./mole (see Table I).

Tropylium chloride has the disadvantage of being more hygroscopic and more unstable than tropylium bromide. Pure samples, obtained by cyrstallization from dilute solution in acetonitrile in the complete absence of air, remain colorless if stored under prepurified nitrogen at −60°. The material rapidly becomes sticky and turns yellow on exposure to air. Carefully prepared samples absorbed 90.2% of the required amount of hydrogen. Calculated on the basis of hydrogen actually absorbed, the heat of hydrogenation is 86.20 ± 0.33 kcal./mole.[6] This absorption is appreciably greater than that obtained with a sample prepared and handled in the usual way.[5] This latter sample, despite absorbing only 74.3% of the required hydrogen, gave a heat of hydrogenation of −86.23 ± 0.77 kcal./mole. The excellent agreement can be rationalized by assuming the impurity in the samples of tropylium chloride to be water.

The difference of 2.9 kcal./mole in the heats of hydrogenation of the chloride and bromide is noteworthy since the reaction observed in both cases is the hydrogenation of tropylium ion to cycloheptane and a proton. Although the discrepancy can be attributed in part to variation in

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[1] (a) E. Hückel, "Grundzüge der Theorie ungesättigter und aromatischer Verbindunge," Verlag Chemie, Berlin, 1938, pp. 71–85; (b) J. D. Roberts and A. Streitwieser, Jr., THIS JOURNAL, **74**, 4579 (1952); (c) J. L. Franklin and F. H. Field, *ibid.*, **75**, 2819 (1953).

[2] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **58**, 146 (1936).

[3] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

[4] R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

[5] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[6] For reasons noted below, the solvent indicated by aq. AcOH consisted of 225 ml. of stock acetic acid to which 0.3 ml. of water was added.