

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Ethynylation of 4-*t*-Butylcyclohexanone and Kinetics of Saponification of the Ethynylcarbinol Esters¹

BY G. F. HENNION AND FRANCIS X. O'SHEA²

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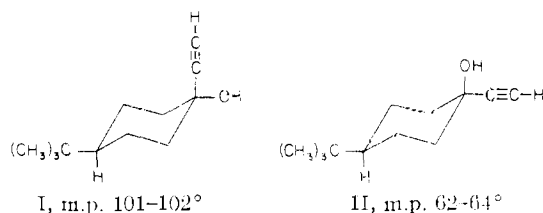
The ethynylation of 4-*t*-butylcyclohexanone with sodium acetylide in liquid ammonia produces chiefly 1-ethynyl-*trans*-4-*t*-butylcyclohexanol (*t*-butyl and hydroxyl equatorial). The corresponding *cis* isomer (*t*-butyl and ethynyl equatorial) is formed simultaneously but in much smaller amount (*trans/cis* ratio approximately 8:1). Both isomers have been characterized and configurations assigned based mainly on the kinetics of the saponification of the *p*-nitrobenzoate esters of the ethynylcarbinols and other related alcohols.

Discussion

It was mentioned in a previous paper³ in this series that the *p*-nitrobenzoate esters of 1-ethynylcyclohexanol and one of the isomers of 4-*t*-butyl-1-ethynylcyclohexanol⁴ saponify at nearly the same rate.

Since Winstein and Holness⁵ have already shown, in an excellent recent paper, that a 4-*t*-butyl group constrains the cyclohexyl ring to one chair conformation with *t*-butyl equatorial, it was suspected that the sample of 4-*t*-butyl-1-ethynylcyclohexanol on hand⁴ had equatorial hydroxyl and was therefore 1-ethynyl-*trans*-4-*t*-butylcyclohexanol (I). It thus became of interest to examine the ethynylation of 4-*t*-butylcyclohexanone and to characterize and identify the two possible isomers.

4-*t*-Butylcyclohexanone presents a straightforward instance for determining the stereochemical course of ethynylation of substituted cyclohexanones in view of the *t*-butyl group influence.⁵ Since the *t*-butyl preference for the equatorial position is very great (about 5.6 kcal./mole⁵), it is clear that each of the isomers of 1-ethynyl-, 1-vinyl- and 1-ethylcyclohexanol having a 4-*t*-butyl group must be conformationally homogeneous. Thus the ethynyl compounds, for example, must be formulated only as I and II, respectively.



It has now been determined that the ethynylation of 4-*t*-butylcyclohexanone with sodium acetylide in liquid ammonia produces chiefly I. The crude reaction product, obtained in good yield, is contaminated with a small amount of unreacted ketone and with a little II. Fortunately II can be recovered from crystallization residues by chromatography on alumina. The isomers I and II are formed in approximately an 8 to 1 ratio which appears to result from kinetic control since treatment of I and II separately with sodium acet-

ylide in liquid ammonia effects no detectable isomerization in either case. The configurations I and II are assigned on the basis of studies on the kinetics of the saponification of esters.

The *p*-nitrobenzoates of I and II were prepared and each was semihydrogenated to the corresponding vinyl compound. Compound I was hydrogenated fully to the ethyl compound. 4-*t*-Butylcyclohexanone was then allowed to react with ethylmagnesium bromide in ether; fortunately, this gave the two 4-*t*-butyl-1-ethylcyclohexanols (III and IV) in a 1:2.7 ratio, readily separable by chromatography. The higher melting ethyl compound (III) so obtained was identical with the ethyl compound made by hydrogenation of I. Both of the ethyl compounds were transformed to *p*-nitrobenzoates. The six esters (the two ethynyls, V and VI; two vinyls, VII and VIII; and two ethyls, IX and X) were saponified in 80% aqueous acetone at 25° and the second-order rate constants determined (Table I). It is already well established^{5,6} that cyclohexyl esters with equatorially disposed ester groups saponify more rapidly than do the corresponding axial esters. It has not been established previously, however, that this principle applies to esters derived from *t*-alcohols. That it does indeed apply appears well justified from the consistency of the data in Tables I and II.

TABLE I
SAPONIFICATION RATES OF *p*-NITROBENZOATE ESTERS OF 4-*t*-BUTYLCYCLOHEXANOLS IN 80% AQUEOUS ACETONE AT 25°

Cpd.	Conformation I-eqtl.	I-axial	Initial concn., mole/ liter	k_2 , l. ² /mole-sec. × 10 ⁴	
				Exptl.	Mean
V	-OPNB ^a	C≡CCH	0.00996	329	
			0.00806	321	325
VI	C≡CCH	OPNB	0.00996	248	
			0.00996	243	246
VII	-OPNB	-CH=CH ₂	0.01015	32	
			0.01050	30	30
VIII	-CH=CH ₂	-OPNB	0.01050	15.3	
			0.01050	15.7	15.5
IX	-OPNB	-CH ₂ CH ₃	0.00994	5.5 ^b	
			0.00994	6.0 ^b	5.8 ^b
X	-CH ₂ CH ₃	-OPNB	0.00994	0.8	
			0.00994	0.9	0.9
XI	-OPNB	-H	0.00996	574	
			0.00996	585	580
XII	H	OPNB	0.01030	235	
			0.01050	230	233

^a -OPNB represents *p*-nitrobenzoate. ^b Approximate; see Experimental.

(1) Paper LXXVII on substituted acetylenes; previous paper, ref. 3.
(2) Dow Chemical Co. Fellow, 1956-1957. Abstracted from a portion of the Ph.D. Dissertation of F. X. O'S.

(3) G. F. Hennion and S. Olivia Barrett, *THIS JOURNAL*, **79**, 2148 (1957).

(4) Supplied by Air Reduction Chemical Co., New York, N. Y.

(5) S. Winstein and N. Holness, *THIS JOURNAL*, **77**, 5592 (1955).

(6) D. H. R. Barton, *Experientia*, **6**, 319 (1950); *J. Chem. Soc.*, 1027 (1953).

TABLE II
SAPONIFICATION RATES OF *p*-NITROBENZOATE ESTERS, RR'CR''OCOC₆H₄NO₂, IN 80% AQUEOUS ACETONE AT 25°

Cpd.	R	R'	R''	Initial concn., mole/liter	<i>k</i> ₂ , l./mole-sec. × 10 ⁴ Exptl.	Mean
XIII	—CH ₂ (CH ₂) ₃ CH ₂ —		—C≡CH	0.00996 .00996	297 297	297
XIV	—CH ₂ (CH ₂) ₃ CH ₂ —		—CH=CH ₂	.01015 .01050	16.1 16.2	16.2
XV	—CH ₂ (CH ₂) ₃ CH ₂ —		—CH ₂ CH ₃	.01015 .00996	1.4 1.2	1.3
XVI	—CH ₂ (CH ₂) ₃ CH ₂ —		—H	.00996 .00996	521 526	524
XVII	—CH ₂ CH ₃	—CH ₂ CH ₃	—C≡CH	.00996 .00986	203 208	206
XVIII	—CH ₂ CH ₃	—CH ₂ CH ₃	—CH=CH ₂	.01050 .01050	12.0 12.4	12.2
XIX	—CH ₂ CH ₃	—CH ₂ CH ₃	—CH ₂ CH ₃	.00996 .01050	1.1 1.3	1.2

The 1-ethynyl-, 1-vinyl- and 1-ethyl-4-*t*-butylcyclohexyl *p*-nitrobenzoates, (V), (VII) and (IX), respectively, shown to have the same configuration by hydrogenation and designated as having equatorial ester groups, in each case were saponified more rapidly than their isomers. As can be seen from the data in Table I, the difference in rates between a given pair of *cis-trans* isomers varies according to the structure of the alcohol moiety. The *trans/cis* rate ratios for the two 1-vinyl- and the two 1-ethyl-substituted esters are reasonably comparable to the factor of about 3 observed for the relative saponification rates of *trans-* and *cis-*4-*t*-butylcyclohexyl *p*-nitrobenzoates (XI and XII). However, the difference in rates between the pair of ethynyl compounds (*ca.* 30%) was not as great as anticipated. The anomaly appears to lie in the saponification rate of 1-ethynyl-*cis*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (VI). It was previously demonstrated³ that substitution of —C≡CH for —H in alcohol *p*-nitrobenzoates leads to a decrease of about 25–50% in the rate of saponification. A comparison of the rate constants cited for VI and XII indicates, therefore, that VI saponifies faster than expected. This may possibly be due to an exaggeration of the polar effect of the ethynyl group when it is confined in the equatorial position.

Further evidence for configurational assignments was furnished by chromatography of mixtures of isomeric alcohols. Winstein⁵ has stated that isomers having equatorial hydroxyl groups can be expected to be adsorbed more strongly on chromatography and therefore would be more difficultly eluted than the isomers having the more hindered axial hydroxyls. This was demonstrated by the chromatography of a mixture of *cis-* and *trans*-4-*t*-butylcyclohexanol.⁵ In the present work, the isomers assigned axial hydroxyl groups were eluted first in each instance.

It is interesting to make other comparisons of the rate data listed in Tables I and II. From the values obtained for the saponification of *trans-* and *cis-*4-*t*-butylcyclohexyl *p*-nitrobenzoates (XI and XII) and for cyclohexyl *p*-nitrobenzoate (XVI), it can be calculated^{5,7} that the *p*-nitrobenzoate group is more stable in the equatorial than in the axial position by about 0.98 kcal./mole. The rate values

obtained for the three corresponding 1-ethynyl compounds V, VI and XIII reveal that the ethynyl group has only a very small preference for the equatorial position as opposed to the axial position. Unfortunately, the rate differences are not large enough for accurate calculation of the energy relationships. Qualitatively, the equilibrium between the two possible conformations of 1-ethynylcyclohexyl *p*-nitrobenzoate appears to lie principally in the direction of the conformation with ethynyl axial and *p*-nitrobenzoate equatorial. In 1-vinyl- and 1-ethylcyclohexyl *p*-nitrobenzoates the opposite conformation, bearing *p*-nitrobenzoate axial, appears to be predominant. It should be noted also that the saponification rates for 3-ethyl-1-pentyn-(en and an)-3-yl *p*-nitrobenzoates (XVII, XVIII and XIX) are quite similar to those obtained for the corresponding *cis-*4-*t*-butylcyclohexyl compounds (VI, VIII and X).

Experimental

Materials.—A sample of 4-*t*-butylcyclohexanone was provided by Dow Chemical Co. and was used after one recrystallization from petroleum ether (Skellysolve F). Generous samples of 3-ethyl-1-pentyn-3-ol and 1-ethynylcyclohexanol were supplied by Air Reduction Chemical Co. 1-Vinylcyclohexyl *p*-nitrobenzoate and 3-ethyl-3-pentanol were supplied by Dr. Olivia Barrett. Samples of *cis*-rich 4-*t*-butylcyclohexanol and *trans*-4-*t*-butylcyclohexyl acid phthalate were provided by Dr. Ernest Eliel.

Preparation of *p*-Nitrobenzoates.—The esters were prepared from the alcohols by the procedure described by Hennion and Barrett.⁸ Among the esters prepared in this manner were these several known compounds: *cis*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (XII), 47% yield, m.p. 133–134° (lit.^{9,10} m.p. 130.2–131.0°, 133–134°); 1-ethynylcyclohexyl *p*-nitrobenzoate (XIII), 74% yield, m.p. 65° (lit.⁸ m.p. 66°); 1-ethylcyclohexyl *p*-nitrobenzoate (XV), 76% yield, m.p. 73.5–74.5° (lit.¹¹ m.p. 73–74°); cyclohexyl *p*-nitrobenzoate (XVI), 77% yield, m.p. 50.5–52° (lit.¹² m.p. 51.5–52.5°); and 3-ethyl-1-pentyn-3-yl *p*-nitrobenzoate (XVII), 93% yield, m.p. 76–77° (lit.⁸ m.p. 77°).

***trans*-4-*t*-Butylcyclohexyl *p*-Nitrobenzoate (XI).**—*trans*-4-*t*-Butylcyclohexyl acid phthalate (m.p. 145–147°, lit.⁵ m.p. 146.2–146.7°) was saponified to the alcohol as described by Winstein.⁵ The alcohol (1.56 g., 0.01 mole), m.p. 81–82° (lit.⁵ m.p. 81–82°), yielded 2.43 g. (80%) of the ester, m.p. 123–124° after recrystallization from methanol.

(8) G. F. Hennion and S. Olivia Barrett, *ibid.*, **79**, 2146 (1957).

(9) G. Stork and W. White, *ibid.*, **78**, 4617 (1956).

(10) E. Eliel and R. Ro, *ibid.*, **79**, 5992 (1957).

(11) J. Cook and C. Lawrence, *J. Chem. Soc.*, 58 (1938).

(12) C. Siebenmann and R. Schnitzer, *This Journal*, **65**, 2126 (1943).

(7) E. Eliel and C. Lukach, *This Journal*, **79**, 5986 (1957).

Anal. Calcd. for $C_{17}H_{25}NO_4$: C, 66.86; H, 7.59. Found: C, 66.96; H, 7.57.

Ethynylation of 4-*t*-Butylcyclohexanone.—A single piece of clean sodium (8.3 g., 0.35 mole) was converted to sodium acetylide in 1.5 liters of liquid ammonia. A solution of 30.8 g. (0.2 mole) of 4-*t*-butylcyclohexanone, m.p. 47–49°, in 250 ml. of anhydrous ether then was added with stirring (35 min.). An additional 100 ml. of anhydrous ether was put in immediately and further 100-ml. portions were added after 2, 4, 6 and 7 hours to replace the ammonia lost by evaporation. Mechanical stirring was maintained throughout with continuous admission of acetylene. After 8 hours, 15 g. of ammonium chloride was added in small portions followed by 100 ml. of concentrated ammonium hydroxide and 200 g. of chopped ice. The ethereal layer was separated and the aqueous portion was extracted with 100 ml. of ether. The combined ether extract was washed with 100 ml. of cold water, 100 ml. of dilute hydrochloric acid, 100 ml. of cold water and finally with 100 ml. of brine. The solution was then dried overnight with anhydrous potassium carbonate.

The ether was removed by distillation, the last portion *in vacuo*. The white, crystalline residue (35.6 g., m.p. 87–97°) was dissolved in 240 ml. of hot petroleum ether (Skellysolve F) and the solution was allowed to crystallize at room temperature. After 6 hours 13.7 g. of product, m.p. 100–102°, was removed by filtration. The filtrate was allowed to crystallize further in the refrigerator overnight and thus yielded an additional 5.0 g., m.p. 100–102°. Since further crystallization could not be induced, the filtrate was evaporated to dryness at room temperature (3 days) leaving 14.0 g. of oily solid. This material was dissolved in 50 ml. of petroleum ether and chromatographed on 200 g. of alumina wetted with petroleum ether. The column was eluted with 500 ml. of petroleum ether, 500 ml. of 10% ether–petroleum ether, 500 ml. of 20% ether–petroleum ether, 250 ml. of 50% ether–petroleum ether and finally with 500 ml. of ether. The eluate was collected in 50-ml. portions (42 fractions).

Fractions 7–18 yielded 4.0 g. of 4-*t*-butylcyclohexanone, m.p. 46–49°; fractions 24–31 gave 2.2 g. of nearly pure 1-ethynyl-*cis*-4-*t*-butylcyclohexanol (II), m.p. 62–64°, while fractions 35–42 provided 3.6 g. of 1-ethynyl-*trans*-4-*t*-butylcyclohexanol (I), m.p. 101–102.5°, not depressed by mixture with material obtained from the original crystallization. The intermediate fractions 19–23 gave 1.7 g. of oil identified as a mixture of ketone and *cis*-alcohol; and fractions 32–34 (1.3 g., m.p. 52–92°) proved to be a mixture of the two alcohols.

The total recovery of 1-ethynyl-*trans*-4-*t*-butylcyclohexanol (I) was 22.3 g. or 62% of the theoretical based on starting ketone.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.02; H, 11.28.

The yield of 1-ethynyl-*cis*-4-*t*-butylcyclohexanol (II) was 2.2 g. (6%). After two recrystallizations from petroleum ether the m.p. was 62–64°.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.15; H, 11.29.

Based on pure products isolated the ratio of *trans*- to *cis*-alcohol was 10:1. If it is assumed that eluates 19–23 consisted of ketone and *cis*-alcohol in equal amounts, and that eluates 32–34 contained the *cis*- and *trans*-alcohols in equal quantities, the ratio becomes 6:1.

Infrared spectra of the alcohols (10% in $CHCl_3$) were similar in many respects; each showed OH bands near 2.8 and 2.9 μ and the typical ethynyl hydrogen at 3 μ . The ethynyl group was revealed feebly at 4.7 μ . The spectrum of the *cis*-alcohol exhibited a strong band at 12.1 μ which was not observed for the *trans* isomer. This band appears also in the spectra of *cis*-4-*t*-butylcyclohexanol and 1-ethyl-*cis*-4-*t*-butylcyclohexanol but not in the spectra of the corresponding *trans* isomers.

1-Ethynyl-*trans*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (V) was prepared from the alcohol; m.p. after three recrystallizations from aqueous ethanol, 106–106.5° (lit.⁸ m.p. 107–109°).

1-Ethynyl-*cis*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (VI) was obtained in a similar manner (66% yield). The m.p. after three recrystallizations from methanol was 148–149°.

Anal. Calcd. for $C_{19}H_{25}NO_4$: C, 69.28; H, 7.04. Found: C, 69.44; H, 7.13.

1-Vinyl-*trans*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (VII) was prepared by semi-hydrogenation of V. The ester (3.29 g., 0.01 mole) was dissolved in 30 ml. of petroleum ether (Skellysolve B) and 15 ml. of ethyl acetate and 0.120 g. of 5% Pd/BaCO₃ was added. The reduction was carried out at room temperature (1.75 hr.) at an initial pressure of 48 p.s.i.g. The solution was filtered and the filtrate allowed to evaporate at room temperature. The product was recrystallized from aqueous ethanol, yielding 2.7 g. (81%) of 1-vinyl-*trans*-4-*t*-butylcyclohexyl *p*-nitrobenzoate, m.p. 115–116.5°.

Anal. Calcd. for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60. Found: C, 68.94; H, 7.67.

1-Vinyl-*cis*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (VIII) was prepared in a similar manner from 1.0 g. (0.003 mole) of VI and 0.03 g. of 5% Pd/BaCO₃ in 30 ml. of petroleum ether and 30 ml. of ethyl acetate. The product (0.91 g., 90%) melted at 116–117° after recrystallization from methanol (mixed m.p. with *trans* isomer VII, 89–109°).

Anal. Calcd. for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60. Found: C, 68.29; H, 7.66.

3-Ethyl-1-penten-3-yl *p*-nitrobenzoate (XVIII) was prepared in a similar manner from 5.2 g. (0.02 mole) of XVII and 0.06 g. of 5% Pd/BaCO₃ in 50 ml. of ethyl acetate. The product was recrystallized from methanol yielding 3.67 g. (70%) of 3-ethyl-1-penten-3-yl *p*-nitrobenzoate, m.p. 85–86°.

Anal. Calcd. for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51. Found: C, 63.73; H, 6.45.

1-Ethyl-*trans*-4-*t*-butylcyclohexanol (III) was prepared by hydrogenation of I. The alcohol (5.0 g., 0.028 mole) was dissolved in 30 ml. of absolute ethanol and 0.6 g. of wet Raney nickel was added. The reduction was carried out at room temperature for 45 min. at an initial pressure of 41 p.s.i.g. The solution was filtered and the solvent removed by distillation *in vacuo*. The product was recrystallized from petroleum ether (Skellysolve F) yielding 4.13 g. (80%) of 1-ethyl-*trans*-4-*t*-butylcyclohexanol, m.p. 84–85°.

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.37; H, 13.37.

Reaction of Ethylmagnesium Bromide with 4-*t*-Butylcyclohexanone.—4-*t*-Butylcyclohexanone (7.71 g., 0.05 mole), m.p. 47–49°, was treated with ethylmagnesium bromide (prepared from 1.82 g. (0.075 mole) of magnesium turnings and 14 g. (0.13 mole) of ethyl bromide in 160 ml. of anhydrous ether) in the usual manner. The product, isolated as a viscous liquid weighing 9.2 g., was dissolved in 50 ml. of pentane and chromatographed on 250 g. of alumina wetted with pentane. The column was eluted with 500 ml. of pentane, 500 ml. of 10% ether–pentane, 500 ml. of 20% ether–pentane, 250 ml. of 50% ether–pentane and finally with 500 ml. of ether. The eluate was collected in 50-ml. portions (37 fractions).

Fractions 5–20 yielded 5.7 g. of 1-ethyl-*cis*-4-*t*-butylcyclohexanol (IV), n_D^{25} 1.4638,¹³ while fractions 25–30 provided 2.11 g. of 1-ethyl-*trans*-4-*t*-butylcyclohexanol (III), m.p. 82–84°, not depressed by mixture with material obtained from hydrogenation of 1-ethynyl-*trans*-4-*t*-butylcyclohexanol. The intermediate fractions 21–24 gave 0.24 g. of an oil identified as a mixture of the two alcohols, while fractions 31–34 (0.47 g., m.p. 45–70°) proved to be a mixture of III and *trans*-4-*t*-butylcyclohexanol. The presence of the latter (in fractions 31–34) was shown by the infrared spectrum and by preparation of the *p*-nitrobenzoate ester (m.p. 122–123°, not depressed by mixture with an authentic sample).

The recovery of 1-ethyl-*trans*-4-*t*-butylcyclohexanol was 2.11 g. or 23% of the theoretical based on starting ketone.

The yield of 1-ethyl-*cis*-4-*t*-butylcyclohexanol was 5.7 g. (62%), and the compound was analyzed only in the form of its *p*-nitrobenzoate ester (see below). Based on pure materials isolated, the ratio of *cis*- to *trans*-alcohol was 2.7:1.

Infrared spectra of each alcohol (10% in $CHCl_3$) showed OH bands near 2.8 and 2.9 μ . The spectrum of the *cis*-alcohol exhibited a strong band at 12.1 μ which was not observed for the *trans* isomer.

1-Ethyl-*trans*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (IX) was prepared from the alcohol in 73% yield, m.p. after three recrystallizations from methanol, 117–117.5°.

(13) A sample obtained later from the saponification of the *p*-nitrobenzoate ester had n_D^{25} 1.4642.

Anal. Calcd. for $C_{13}H_{27}NO_4$: C, 68.44; H, 8.16. Found: C, 68.18; H, 8.22.

1-Ethyl-*cis*-4-*t*-butylcyclohexyl *p*-nitrobenzoate (X) was obtained in a similar manner (50% yield). The m.p. after three recrystallizations from methanol was 82–83°.

Anal. Calcd. for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16. Found: C, 68.59; H, 8.13.

3-Ethylpentan-3-yl *p*-nitrobenzoate (XIX) was prepared from the alcohol in 59% yield, m.p. 42.5–43.5° after three recrystallizations from methanol.

Anal. Calcd. for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22. Found: C, 63.64; H, 7.45.

General Kinetic Procedure.—The rates of saponification were determined as previously described³ with the exceptions that 80% acetone was used as the solvent and brom cresol purple as the indicator.

In cases where the saponification proceeded very slowly

(*i.e.*, for esters IX, X, XV and XIX) drift in the rate constants toward progressively greater consumption of alkali was observed. This was not due to solvolysis since solutions of the esters in the solvent remained neutral after five days at room temperature. An alkaline solution of 80% acetone, however, very slowly lost basic strength through some side reaction with the solvent. Corrections were therefore applied in those cases where drift was observed, to account for this side reaction. The corrections were satisfactory in all cases except for IX where the rate values then drifted in the opposite direction. This value is therefore approximate.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. IX. Preparation and Properties of Diisobutyl-*t*-butylborane¹

BY G. F. HENNION, P. A. MCCUSKER AND A. J. RUTKOWSKI²

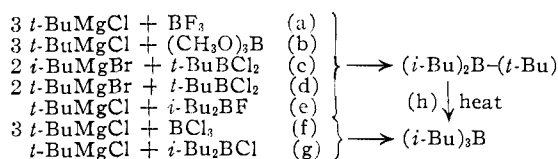
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Diisobutyl-*t*-butylborane, $((CH_3)_2CHCH_2)_2B-C(CH_3)_3$, stable to disproportionation and to rearrangement when distilled *in vacuo* (below *ca.* 60°), has been prepared in five ways. Distillation at atmospheric pressure causes rearrangement to triisobutylborane. All attempts to prepare tri-*t*-butylborane failed.

Discussion

It was reported in a previous paper³ in this series that tri-*t*-butylborane was not obtainable from the reaction of *t*-butylmagnesium chloride with boron chloride or with boron fluoride and that distillation of all such reaction products at atmospheric pressure gave triisobutylborane in good yield. Since it has been demonstrated conclusively that one *t*-butyl group can be attached to boron to form *t*-butylboron oxide and *t*-butylboron dichloride,⁴ attempts have been made to prepare mixed *t*-butyl-alkylboranes and hence to determine, *inter alia*, whether tri-*t*-butylborane can be made by disproportionation.

We wish to report now concerning the preparation and properties of diisobutyl-*t*-butylborane, $((CH_3)_2CHCH_2)_2B-C(CH_3)_3$. As shown below this compound has been prepared in five ways, (a) to (e). Reactions f and g gave only triisobutylborane.



The properties of triisobutylborane and diisobutyl-*t*-butylborane are compared in Table I.

The authenticity of the product from the reactions a to e is indicated not only from these various

(1) Previous paper, *THIS JOURNAL*, **79**, 5190 (1957).

(2) Abstracted in part from the Ph.D. Dissertation of A. J. R. Presented at the New York Meeting of the American Chemical Society, September, 1957.

(3) G. F. Hennion, P. A. McCusker, *et al.*, *THIS JOURNAL*, **79**, 5190 (1957).

(4) P. A. McCusker, *et al.*, *ibid.*, **79**, 5180, 5183 (1957).

TABLE I

	B.p. °C.	Mm.	n_D^{25}	d_4^{25}	$M_{R\text{Dobs}}$
(<i>i</i> -C ₄ H ₉) ₃ B	52–53	4	1.4203	0.7352	62.73
(<i>i</i> -C ₄ H ₉) ₂ B- <i>t</i> -C ₄ H ₉	48–49	2.7	1.4244	0.7428	62.62

modes of formation, but also from the fact that oxidation with alkaline hydrogen peroxide^{5,6} gave isobutyl and *t*-butyl alcohols in exactly a 2:1 ratio. Surprisingly, diisobutyl-*t*-butylborane may be redistilled repeatedly *in vacuo*, if the boiling point does not exceed about 60°, without disproportionation or rearrangement.⁶ At higher temperatures, as obtain during distillation at atmospheric pressure, rearrangement to triisobutylborane occurs smoothly. Disproportionation to tri-*t*-butyl- and triisobutylboranes has not been achieved. Furthermore, all attempts to prepare tri-*t*-butylborane *via* Grignard reactions (methods a, b, d and f) have met with failure under various experimental conditions, as have attempts to prepare di-*t*-butyl-iso-butylborane.

Since the alkylation of a boron halide or ester with a Grignard reagent must proceed in a stepwise manner, *i.e.*, $\text{BX}_3 \rightarrow \text{RBX}_2 \rightarrow \text{R}_2\text{BX} \rightarrow \text{R}_3\text{B}$, it is not possible to determine unequivocally at what stage or how rearrangement occurs. It is believed that the reaction of *t*-BuMgX with boron fluoride (method a) produces initially *t*-BuBF₂ and that the subsequent alkylations proceed only with rearrangement. On the other hand, when boron chloride is used (method f), even the first butyl group attaches only with rearrangement.

(5) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 5694 (1956).

(6) To our knowledge this is the first recorded instance of a mixed trialkylborane completely stable to disproportionation at so high a temperature. This suggests that disproportionation of mixed boranes is subject to steric hindrance. Further work in this connection is under way.