STEREOCHEMISTRY OF NUCLEOPHILIC ADDITIONS TO THE CARBONYL GROUP

COMMUNICATION 6. REACTIONS OF 3-t-BUTYLCYCLOHEXANONE*

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Over a period of years we have been conducting a study in our laboratory of the stereochemistry of nucleophilic addition to the carbonyl group of cyclic ketones and, in particular, an investigation of steric orientation in the cyanohydrin [1-3], acetylene [1], and organometallic [2-3] syntheses. For the case of 2- and 3-methylcyclohexanones we have shown that in all these reactions the steric orientation is definite, but not always the same. It was shown both by spectroscopic [4-8] and by chemical [1-3] methods that in the case of the cyanohydrin and acetylene syntheses reaction goes with predominant addition of the entering substituent in the axial position. In the case of Grignard synthesis, however, reaction goes with the predominant addition of the substituent in the equatorial position. According to the literature [9-17], the ionic reduction of methylcyclohexanones (with lithium aluminum hydride, sodium borohydride, and sodium in alcohol) also goes with the predominant axial addition of hydrogen. However, in all the cases cited above we were concerned with conformationally labile compounds. Although the methyl group in methylcyclohexanones is predominantly in the equatorial conformation [8], there can be no doubt that the ketone can react not only in this predominant conformation, but also in the conformation with an axial substituent [18-19]. This possibly explains in part the incomplete steric selectivity of the above reactions, which renders their stereochemical treatment difficult [20]. In view of this it was of interest to study the stereochemistry of these reactions for the case of rigid model compounds for which the conformation can be reliably related to configuration. According to Winstein's results [19], the t-butyl group in substituted cyclohexane occupies an equatorial position exclusively and so fixes the conformation of the cyclohexane ring. It would be expected, therefore, that each of the two possible isomers of 1-cyano-, 1-ethynyl-, and 1-ethyl-cyclohexanols would be conformationally homogeneous. For such compounds, only the stereochemistry of the reactions of 4-t-butylcyclohexanone has been described in the literature. Thus, Hennion and coworkers [21] found that in the reaction of 4-t-butylcyclohexanone with sodium acetylide in liquid ammonia trans- and cis-4-t-butyl-1-ethynylcyclohexanols are formed in the proportions of 1 : 8, whereas the reaction of ethylmagnesium bromide with 4-t-butylcyclohexanone in ether leads to trans-4-t-butyl-1-ethylcyclohexanol and cis-4-t-butyl-1-ethylcyclohexanol in the proportions of 2.7 : 1. Houlihan [22] studied the addition of methylmagnesium halides to 4-t-butylcyclohexanone under various conditions and concluded that the relative amounts of cis- and trans-4-t-butyl-1-methylcyclohexanols obtained depends on which methyl halide is used for the preparation of the Grignard reagent, the solvent, and the addition mechanism. The ratio of the amounts of cis and trans products varied with the reaction conditions from 1.02 to 2.26. In the reduction of 4-t-butylcyclohexanone with sodium in alcohol Stork and White [23] found that there is almost exclusive formation of trans-4-t-butylcyclohexanol with an axial hydrogen atom at C_1. According to Eliel and Ro [18] the reduction of the same ketone with lithium aluminum hydride leads to a mixture containing 91-93% of the same alcohol.

We here describe the results of a study of the stereochemistry of acetylene, cyanohydrin, and organomagnesium synthesis and of carbonyl reduction with sodium borohydride for the case of 3-t-butylcyclohexanone (I). For this compound only reduction with lithium aluminum hydride has been described [19], and in this only the cis isomer of the alcohol with an equatorial hydroxy group was isolated.

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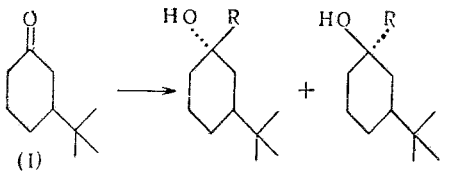
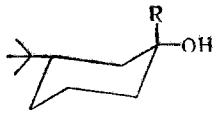
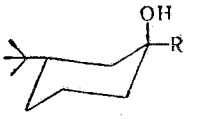


(I)

R = H, CN, C≡CH, C_2H_5

In the condensation of the ketone (I) with acetone cyanohydrin, acetylene, and ethylmagnesium bromide and in the reduction of the ketone (I) with sodium borohydride two stereoisomeric products were obtained in each case: the cyanohydrins (II) and (III), the acetylenic alcohols (IV) and (V), 3-t-butyl-1-ethylcyclohexanols (VI) and (VII), and 3-t-butylcyclohexanols (VIII) and (IX). The relative amounts obtained were: (II):(III) = 19-18:1; (IV) : (V) = 13 : 1; (VI):(VII) = 1 : 6; (VIII):(IX) = 15 : 1.





(II) R = CN, m.p. 46–47°

(III) R = CN, m.p. 72–73°

(IV) R = C≡CH m.p. 81–81.5°

(V) R = C≡CH b.p. 79–80° (6 мм)

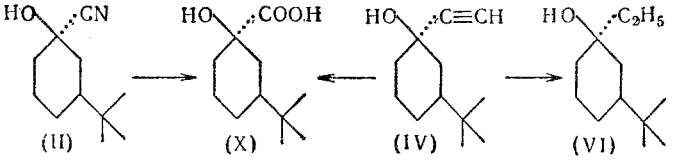
(VI) R = C_2H_5, m.p. 52–52.7°

(VII) R = C_2H_5, b.p. 65–66° (4 мм)

(VIII) R = H m.p. 40–41° *)

(IX) R = H, m.p. 48–49°

In all cases except the first the composition of the products was established by gas-liquid chromatography on a Pye chromatograph and by the preparative separation of the reaction products by continuous chromatography on a thin layer of unbound alumina of Brockmann activity II-III. In their general features the results obtained by thin-layer chromatography agreed with the results of gas-liquid chromatography. We did not succeed in separating the mixture of cyanohydrins (II) and (III) by gas-liquid chromatography, but isolated the individual isomers by continuous chromatography on a thin layer of unbound silica gel freed from traces of iron. The isomers (II), (IV), and (VI) were brought into relation to one another without affecting the asymmetric center by the transformations shown below, and this established that they belong to the same steric series.

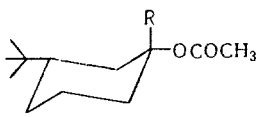


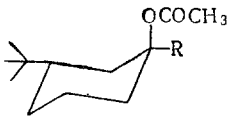
(II) (X) (IV) (VI)

By the hydrolysis of the cyanohydrin (II) with a mixture of hydrochloric and acetic acids saturated with hydrogen chloride we obtained the hydroxy acid (X), which melts without depression in admixtures with the hydroxy acid obtained by the oxidation of the acetylenic alcohol (IV) with potassium permanganate. The catalytic reduction of the isomer (IV) leads to the alcohol (VI), which melts without depression in admixture with the sample isolated by chromatography from the products of Grignard synthesis. Thin-layer chromatography of mixtures of isomeric alcohols showed that the isomers (II), (IV), (VI), and (VIII) have lower R_f values than the corresponding isomers (III), (V), (VII), and (IX). It is known that isomers having an equatorial OH group are characterized by a higher polarity [4], are adsorbed more strongly on a chromatographic column, and are less readily eluted from the adsorbent than the isomers having a less polar, axial OH group [19, 21]. On the basis of these data we supposed that the isomers (II), (IV), (VI), and (VIII) have the trans configuration and the isomers (III), (V), (VII), and (IX) have the cis configuration (with respect to the entering substituent). This was confirmed later by a study of the kinetics of the acetylation of each pair of isomers. It is known from the literature [24-26] that the esterification of compounds with axially disposed hydroxy groups and the hydrolysis of the corresponding esters goes with considerably more difficulty than in the case of compounds with equatorially disposed hydroxy groups.

By the acetylation of the alcohols (II)-(VII) with acetyl chloride, and also with acetic anhydride, we obtained the corresponding acetates (XI)-(XVI).

*According to Winstein's results [19].





(XI) R = CN, b.p. 129–130° (5 mm) (XII) R = CN, b.p. 120–121° (5 mm)

(XIII) R = C≡CH, m.p. 38–38,5° (XIV) R = C≡CH, b.p. 101–101,5° (6 mm)

(XV) R = C_2H_5, b.p. 73–75° (5 mm) (XVI) R = C_2H_5, b.p. 57,5–58° (7 mm)

The isomers (II), (IV), and (VI) (Table 1) are acetylated much more rapidly than their epimers (III), (V), and (VII).

TABLE 1. Rates of Acetylation of Isomeric Alcohols with Acetyl Chloride in Ether at 34-35°

Alcohol	Acetate	Time for complete acetylation, hours	Alcohol	Acetate	Time for complete acetylation, hours
II	XI	7	V	XIV	> 8 *
III	XII	> 15*	VI	XV	2
IV	XIII	2	VII	XVI	4

*Completely acetylated under more severe conditions: by acetic anhydride in presence of p-toluenesulfonic acid.

TABLE 2. Steric Orientation in Nucleophilic Additions to the Carbonyl Groups of 3-t-Butylcyclohexanone and 3-Methylcyclohexanone

Reagent	Entering substituent	For 3-t-butylcyclohexanone content (%) in mixture		For 3-methylcyclohexanone content (%) in mixture		Lit. ref.
		cis form	trans form	cis form	trans form	
$NaBH_4$	−H	6 *	94*	−	−	
$(CH_3)_2C(OH)CN$	−CN	~ 5	~95	24	76	[2, 3]
CH ≡ CH	−C ≡ CH	7 *	93*	−	−	
C_2H_5MgBr	$-C_2H_5$	86 *	14*	−	−	
CH_3MgI	$-CH_3$	−	−	60	40	[2, 3]

*Results of gas-liquid chromatography.

The course of the esterification was followed by means of thin-layer chromatography on alumina or silica gel. The time for complete acetylation was determined from the disappearance of the spot of the original alcohol on the chromatogram. For 3-t-butyl-1-ethylcyclohexanols the configurations of the isomers were proved also by a study of the rates of the dehydration of the alcohols (VI) and (VII). It was found that in the course of a 30-minute heating in hexane in presence of iodine the isomer (VII) is almost completely dehydrated (bromine value of product 94.9; calculated 96.2), whereas the isomer (VI) remains unchanged. In accordance with the rule of more ready trans-diaxial elimination, the isomer (VII) should have the cis, and the isomer (VI) the trans, configuration.

We may thus maintain that the compounds (II), (IV), (VI), and (VIII) have a trans arrangement of the t-butyl group and the entering substituent, whereas the compounds (III), (V), (VII), and (IX) have the opposite configuration.

On comparing the data given in Table 2 we see that, as would be expected, all nucleophilic additions to 3-t-butylcyclohexanone go with higher steric selectivity than in the case of 3-methylcyclohexanone, but the stereochemical orientation in the reaction remains the same. It may be supposed that the axial entry of substituents is determined by the factor of the polar orientation of the nucleophilic addition reaction itself, while equatorial entry depends on steric hindrance arising from the axial hydrogen atoms and the bulk of the entering substituent.

EXPERIMENTAL

Thin-layer chromatography was carried out on commercial alumina of Brockmann activity II-III and KSK silica gel, 100-290 mesh, freed from traces of iron by stirring it for four hours with boiling nitric acid [27]. Gas-liquid

chromatography was carried out with a Pye instrument at the Institute for the Chemistry of Natural Products of the Academy of Sciences of the USSR. For the separation of the isomers continuous chromatography was used [28].

Synthesis of 1,3-Cyclohexanediol. 500 g of pure resorcinol was hydrogenated as a solution in 400 ml of methanol over 50 cc of active nickel catalysts in a rotating autoclave at 150-160° and 120-150 atm until 380 liters of hydrogen had been absorbed. Solvent was driven off, and the residue was vacuum-distilled. We obtained 412 g (80%) of 1,3-cyclohexanediol; b.p. 130-137° for 9-10 mm; n^{20}_D 1.4950. The literature [29] gives: b.p. 133.7-134° for 13 mm; n_D^{20} 1.4922-1.4940.

Synthesis of 1,3-Cyclohexanediol Monoacetic Ester. A solution of 283 g of acetyl chloride in 700 ml of dry chloroform was added with stirring to a solution of 412 g of 1,3-cyclohexanediol in 700 ml of dry chloroform. The mixture was heated in a water bath until no more hydrogen chloride came off. Solvent was driven off, and the residue was treated with water and petroleum ether. The aqueous solution was evaporated, and the residue was vacuum-distilled. We obtained 487 g (85.5%) of the monoacetic ester, b.p. 118-125° for 9-10 mm. The literature [29] gives b.p. 131-132.5° for 13 mm.

Synthesis of 2-Cyclohexen-1-one. A cooled oxidizing mixture consisting of 430 g of $Na_2Cr_2O_7 \cdot 2H_2O$, 1850 ml of water, and 530 ml of sulfuric acid was added with stirring and cooling to a solution of 431 g of 1,3-cyclohexanediol monoacetic ester in 310 ml of ether. When the addition was complete, the reaction mixture was stirred for four hours at −1°, after which the upper layer was separated and the lower layer was extracted with ether several times. The ether extracts were dried over calcium chloride. Ether was distilled off, and the residue was vacuum-distilled with collection of a fraction having b.p. 61-118° at 18 mm and n^{20}_D 1.4720-1.4750. By refractionation of this fraction we isolated 91 g (35%) of 2-cyclohexen-1-one; b.p. 65-70° for 18 mm; n^{20}_D 1.4840. The literature [30] gives: b.p. 61-63° for 14 mm; 67° for 25 mm, 169-171°; n_D^{20} 1.4879; n_D^{18} 1.4842.

Synthesis of 3-t-Butylcyclohexanone (I). A Grignard reagent prepared from 25 g of Mg and 92 g of t-butyl chloride in 200 ml of dry ether was cooled to 0°, 0.5 g of cuprous chloride was added, and then a solution of 48 g of 2-cyclohexen-1-one in 100 ml of ether was added with stirring in the course of 2.5 hours. The mixture was left overnight and then poured into a mixture of 1 kg of ice and 250 g of ammonium chloride. The ether layer was separated and the aqueous layer was extracted with ether several times. The ether extract was dried over sodium sulfate and evaporated. The residue was shaken with 350 ml of saturated sodium bisulfite solution, and the bisulfite compound formed was filtered off. By the steam distillation of the latter in presence of 100 g of sodium bicarbonate in 300 ml of water we obtained 46 g (60%) of the ketone (I); b.p. 80-90° for 8 mm; n_D^{20} 1.4660. The literature [19, 31] gives: b.p. 92-95° for 10 mm, 96-98° for 20 mm; n_D^{20} 1.4615.

Synthesis of 3-t-Butyl-1-ethynylcyclohexanols (IV) and (V). A 2-liter steel reactor was charged with 15 g of potassium hydroxide powder, 350 ml of dry ether, and 1 ml of ethanol, and with good cooling and stirring the reactor was filled with acetylene at a pressure of 6 atm in the course of 20 minutes. A solution of 20 g of the ketone (I) in 100 ml of dry ether was then added with stirring in the course of three hours. After the removal of acetylene the product was treated with stirring with water and neutralized with carbon dioxide. The ether layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate. Ether was driven off, and we obtained 22 g (94%) of a light-yellow product, which crystallized after a short time in a refrigerator. Vacuum distillation of this mixture of isomers gave 19.9 g of product, b.p. 85-105° (5 mm) and n_D^{20} 1.4780.

a) By the repeated crystallization of this mixture of acetylenic alcohols from petroleum ether we isolated trans-3-t-butyl-1-ethynylcyclohexanol (IV), m.p. 81-81.5° (from petroleum ether). At a bath temperature of 60-70° the product sublimes at a residual pressure of 4 mm. Found: C 79.84; 79.67; H 11.25; 11.12%. $C_{12}H_{20}O$. Calculated: C 79.93; H 11.13%.

b) cis-3-t-Butyl-1-ethynylcyclohexanol (V) was isolated by chromatography on an alumina column (benzene-ether, 2:3) as a liquid of b.p. 79-80° (6 mm); n_D^{20} 1.4795. Found: C 79.94; 79.84; H 11.20; 11.15%. $C_{12}H_{20}O$. Calculated: C 79.93; H 11.13%.

The proportion of isomers in the mixture of acetylenic alcohols obtained was assessed by gas-liquid chromatography at 125° on silicone oil. It was then shown that the reaction mixture obtained consisted of three substances: (I), 7.8%; (IV), 85%; (V), 7.2%.

Hydrogenation of trans-3-t-Butyl-1-ethynylcyclohexanol. 4 g of the trans acetylenic alcohol (IV) (m.p. 81-81.5°) was hydrogenated in 35 ml of ethanol over 0.025 g of platinum dioxide. In the course of 75 minutes 1 liter of

hydrogen was absorbed. Fractional distillation gave 4 g (about 100%) of trans-3-t-butyl-1-ethylcyclohexanol, b.p. 99.5° (4 mm and n_D^{20} 1.4700; it solidified on standing; m.p. 52-52.7° (from petroleum ether). Found: C 77.86; 77.92; H 13.00; 13.07%. $C_{12}H_{24}O$. Calculated: C 78.18; H 13.05%. A mixture of this alcohol with a sample prepared in another way melted without depression.

Oxidation of trans-3-t-Butyl-1-ethynylcyclohexanol. A solution of 5 g of potassium permanganate in 100 ml of water was added in the course of four hours with vigorous stirring to a solution of 2.9 g of the trans acetylenic alcohol (IV) in 30 ml of acetone with maintenance of the temperature at not above 20° The mixture was stirred further for one hour at room temperature and was then heated for one hour in a boiling water bath. The precipitate was filtered off and washed with acetone and hot water. Acetone was vacuum-evaporated off. The aqueous layer was extracted with ether. Ether was evaporated, and we then isolated 1.6 g of unchanged original alcohol, m.p. 79-80°. The aqueous layer was vacuum-evaporated to dryness. The residue was acidified with dilute hydrochloric acid and extracted with ether. The ether extract was dried with magnesium sulfate, ether was driven off, and we obtained 0.8 g of trans-3-t-butyl-1-hydroxycyclohexanecarboxylic acid (X), m.p. 145-145.7° (from benzene-hexane), undepressed by admixture of a sample of the trans hydroxy acid prepared in another way. Found: C 65.92; 65.83; H 9.93; 10.06%. $C_{11}H_{20}O_3$. Calculated: C 65.94; H 10.07%.

Synthesis of 3-t-Butyl-1-hydroxycyclohexanecarbonitriles (II) and (III). A mixture of 15.4 g of the ketone (I), 21.3 g of acetone cyanohydrin, and 10 ml of a saturated solution of potassium carbonate in methanol was left overnight at room temperature and was then acidified with concentrated sulfuric acid. The precipitate formed was filtered off. Acetone and methanol were vacuum-evaporated off at 30-35°. Excess of acetone cyanohydrin was vacuum-distilled off. We obtained 17.0 g (92%) of crude product. By vacuum distillation we obtained 12.5 g (68%) of product, b.p. 130-130.5° at 6 mm. By continuous chromatography in a thin unbound layer of silica gel we isolated two isomers. trans-3-t-Butyl-1-hydroxycyclohexanecarbonitrile (II) had m.p. 46-47° (from petroleum ether). Found: Found: C 72.75; 72.55; H 10.34; 10.33%. $C_{11}H_{20}ON$. Calculated: C 72.87; H 10.56%. cis-3-t-Buytl-1-hydroxycyclohexanecarbonitrile (III) had m.p. 72-73° (from hexane). Found: C 72.64; 72.73; H 10.38; 10.42%. $C_{11}H_{20}ON$. Calculated: C 72.87; H 10.56%.

Hydrolysis of trans-3-t-Butyl-1-hydroxycyclohexanecarbonitrile. A solution of 0.9 g of trans-3-t-Butyl-1-hydroxycyclohexanecarbonitrile in 3.6 ml of glacial acetic acid and 5.7 ml of concentrated hydrochloric acid was saturated with hydrogen chloride over a period of one hour, left for four days at room temperature, refluxed for 3.5 hours, and then vacuum-evaporated. The crystalline residue was dissolved in 20 ml of saturated sodium carbonate solution and 80 ml of water, and the solution was heated for one hour in a boiling water bath. The cooled alkaline solution was washed with ether and made strongly acid with dilute hydrochloric acid. The whole mass was extracted several times with ether. The combined ether extracts were dried over magnesium sulfate, ether was driven off, and we obtained 0.98 g of the hydroxy acid, m.p. 145-146° (from benzene-hexane), undepressed by admixture of the hydroxy acid obtained by oxidizing the acetylenic alcohol.

Reduction of 3-t-Butylcyclohexanone with Sodium Borohydride. 0.4 g of 87% sodium borohydride was dissolved in 8 ml of methanol to which a little aqueous sodium hydroxide solution had been first added. In the course of 15 minutes 1.54 g of 3-t-butylcyclohexanone was added with stirring at room temperature, and the mixture was then stirred at the boil for one hour. The course of the reaction was followed by running thin-layer chromatograms at 15-minute intervals. The mixture was made weakly acid by the addition of dilute acetic acid. Most of the methanol was vacuum-evaporated, and the residue was extracted with ether. The ether extract was washed with water, dried over magnesium sulfate, and evaporated. The yield of crude product was 1.41 g (90.5%). Separation of the mixture by continuous chromatography on alumina showed that it consisted of three substances: (I), 14.0%; (VIII), 80%; (IX), 6%. cis-3-t-Butylcyclohexanol was characterized as its phthalate, m.p. 131-132° (from hexane + ethyl acetate). The literature [19] gives m.p. 136-136.8°. Found: 70.95; 70.99; H 7.92; 7.88%. $C_{18}H_{24}O_4$. Calculated: C 71.00; H 7.95%.

Synthesis of 3-t-Butyl-1-ethylcyclohexanols (VI) and (VII). A solution of 7.7 g of 3-t-butylcyclohexanone in 50 ml of dry ether was added in the course of one hour to a Grignard reagent prepared from 1.8 g of magnesium and 10 g of ethyl bromide in 150 ml of dry ether. When the addition was complete, the reaction mixture was boiled for four hours and poured into a mixture of ammonium chloride and ice. The ether layer was separated, and the aqueous layer was extracted with ether several times. The ethereal solution was dried with magnesium sulfate, ether was driven off, and we obtained 8.3 g (90%) of reaction product; b.p. 83-95° for 4 mm; n_D^{20} 1.4720. By continuous thin-layer chromatography on alumina (solvent system: ether-hexane 50:50) we isolated two isomers. cis-3-t-Butyl-1-ethylcyclohexanol (VII) had b.p. 65-66° for 6 mm; n_D^{20} 1.4750. Found C 77.98; 77.95; H 12.77; 12.78%. $C_{12}H_{24}O$. Calculated: C 78.18; H 13.05%. trans-3-t-Butyl-1-ethylcyclohexanol (VI) had m.p. 52-52.7° and n_D^{20} 1.4700. Found: C 77.86, 77.92; H 13.00, 13.07%. $C_{12}H_{24}O$. Calculated: C 78.18; H 13.05%.

By gas-liquid chromatography at 131° (10% silicone oil on celite) it was shown that the mixture contained: (I), 43%; (VI), 8%; (VII), 49%.

Acetylation of cis- and trans-3-t-Butyl-1-ethynylcyclohexanols. a) 0.2 g of acetyl chloride was added to a solution of 0.1 g of trans-3-t-butyl-1-ethynylcyclohexanol (IV) in 1 ml of ether, and the mixture was boiled. The course of the reaction was followed by thin-layer chromatography (alumina of activity II-III; solvent system ether-hexane 50:50). The time for complete aceylation was two hours. trans-3-t-butyl-1-ethynylcyclohexanol acetic ester was obtained in quantitative yield; m.p. 38-38.5° (from petroleum ether); b.p. 95-95.5° for 5 mm; n_D^{20} 1.4680. Found: C 75.33; 75.38; H 10.07; 10.01%. $C_{14}H_{22}O_2$. Calculated: C 75.61; H 9.98%.

b) 0.2 g of acetyl chloride was added to a solution of 0.1 g of cis-3-t-butyl-1-ethynylcyclohexanol (V) in 1 ml of ether. The mixture was boiled for eight hours, but reaction was not complete in this time. To prepare the acetic ester of the cis alcohol (V) a mixture of 2 g of the cis alcohol, 4 g of acetic anhydride, and 0.05 g of p-toluenesulfonic acid was left overnight at room temperature. Acetic acid and acetic anhydride was vacuum-evaporated at 50°. The residue was dissolved in ether, and the solution was washed with aqueous sodium carbonate solution and water and was dried with magnesium sulfate. Distillation gave a quantitative yield of cis-3-t-butyl-1-ethynylcyclohexanol acetic ester: b.p. 101-101.5° for 6 mm; n_D^{20} 1.4669. Found C 75.94; 75.75; H 10.08; 10.08%. $C_{14}H_{22}O_2$. Calculated: C 75.61; H 9.98%.

Acetylation of cis- and trans-3-t-Butyl-1-hydroxycyclohexanecarbonitriles (II) and (III). The alcohols (II) and (III) were acetylated under conditions similar to those used in the acetylation of the alcohols (IV) and (V). The trans alcohol (II) was acetylated completely in seven hours, but more than 15 hours was required for the acetylation of the cis alcohol (III). We then obtained the isomeric acetic esters. trans-1-Acetoxy-3-t-butylcyclohexanecarbonitrile had b.p. 129-130° (5 mm) and n_D^{20} 1.4672. Found: C 69.60, 69.69; H 9.21, 9.26%. $C_{13}H_{21}O_2N$. Calculated: C 69.92; H 9.48%. cis-1-Acetoxy-3-t-butylcyclohexanecarbonitrile had b.p. 120-121° (5 mm) and n_D^{20} 1.4640.*

Acetylation of cis- and trans-3-t-Butyl-1-ethylcyclohexanols (VI) and (VII). The alcohols (VI) and (VII) were acetylated under conditions similar to those used for the acetylation of the alcohols (IV) and (V). The trans alcohol (VI) was acetylated completely in two hours, and the cis alcohol (VII)—in four hours. We then obtained the isomeric acetic esters. trans-3-t-Butyl-1-ethylcyclohexanol acetic ester; b.p. 78.5-80° for 7 mm; n_D^{20} 1.4681. Found: C 73.98, 74.02; H 11.40, 11.45%. $C_{14}H_{26}O_2$. Calculated: C 74.22; H 11.58%. cis-3-t-Butyl-1-ethylcyclohexanol acetic ester; b.p. 57.5-58° for 7 mm; n_D^{20} 1.4680. Found: C 74.11, 74.05; H 11.52, 11.49%. $C_{16}H_{26}O_2$. Calculated: C 74.22; H 11.58%.

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SUMMARY

1. An investigation was made of the stereochemistry of the addition of hydrogen cyanide, acetylene, and ethylmagnesium bromide to 3-t-butylcyclohexanone and of the reduction of 3-t-butylcyclohexanone with sodium borohydride. The configurations were proved to the then formed 3-t-butyl-1-hydroxycyclohexanecarbonitriles, 3-t-butyl-1-ethynylcyclohexanols, 3-t-butyl-1-ethylcyclohexanols, and their derivatives (hydroxy acids, acetic esters).

2. The reactions investigated go more selectively in the case of 3-t-butylcyclohexanone than in the case of 3-methylcyclohexanone.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.