saturated hydrocarbon. This problem arose from the unknown extreme difficulty in separating the two compounds by GLC. NMR spectroscopy confirmed the predominance of the latter. Presumably, 3,5-dimethyl-2-cyclohexen-1-one tosylhydrazone also furnishes the corresponding saturated hydrocarbon in major amount instead of the reported 3,5-dimethylcyclohexene. 4-Cholesten-3-one tosylhydrazone afforded a complex mixture of hydrocarbons and alkenes. Anyway, the procedure does not appear very synthetically useful with cyclohexenones.

(4) Borch and coworkers (ref 5) obtained cyclopentanol upon cyanoborohydride reduction of 2-cyclopentenone. However, a more thorough investigation of the reduction of cholestenone-type systems (ref 6) indicated the major products usually to be the allylic alcohols, leaving the double bonds unmolested.

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(7) See, for example, H. C. Brown and H. M. Hess, *J. Org. Chem.*, **38**, 2206 (1969).

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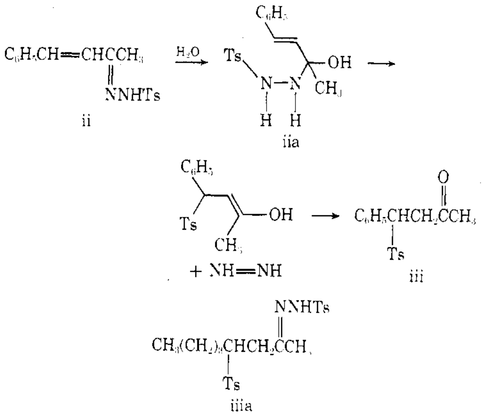
(9) T. Sato and I. Homma, *Bull. Chem. Soc. Jpn.*, **44**, 1885 (1971).

(10) This general type of sigmatropic migration has also been suggested (ref 9) to account for the transformation of certain α,β-unsaturated tosylhydrazone intermediates (i.e., ii) to β-tosyl ketones (i.e., iii) by thermolysis in aqueous acetic acid as indicated. We also observed a similar occurrence upon attempted preparation of (*E*)-3-octen-2-one tosylhydrazone. The only isolatable product was the corresponding β-ketotosylhydrazone iiia. Evidently, rearrangement of the intermediate analogous to iia is very facile for this example; further reaction of the β-tosyl ketone with *p*-toluenesulfonylhydrazine would produce the observed product. The reason this example chose to rearrange while all other α,β-unsaturated ketones gave the normal tosylhydrazones is not obvious.



(11) Sato and Homma (ref 9) also noted the failure of 3-methyl-2-cyclohexenone tosylhydrazone to rearrange to the corresponding β-tosyl ketone and offered a similar explanation.

(12) Analogous sigmatropic rearrangements of intermediate diazenes may also account for the production of rearranged alkenes often encountered in Wolff-Kishner reductions of α,β-unsaturated aldehydes and ketones. See, for example, R. Fischer, G. Lardelli, and O. Jegar, *Helv. Chim. Acta*, **34**, 1577 (1951).

(13) An authentic sample of the *Z* isomer was prepared from the epoxide via the procedure of Vedejs; cf. E. Vedejs and P. Fuchs, *J. Am. Chem. Soc.*, **93**, 4070 (1971).

Reaction of Lithium Aluminum Hydride with Hindered Phenols. New Stereoselective Reducing Agents

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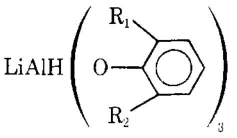
A study involving the reaction of lithium aluminum hydride ($LiAlH_4$) with hindered phenols and alcohols is described. This has resulted in the preparation of a new series of stereoselective reagents for the reduction of substituted cyclohexanones. The most highly selective reagent was formed by the reaction of $LiAlH_4$ with 2 molar equiv of 2,6-di-*tert*-butylphenol followed by 1 molar equiv of neopentyl alcohol. Several experiments involved the reaction of lithium borohydride with hindered phenols in which different results were obtained.

Lithium aluminum alkoxyhydrides have proven to be useful selective reagents in the reduction of organic compounds.[1] The preparation of these reagents by the reaction of lithium aluminum hydride ($LiAlH_4$) with alcohols has been found to be a generally useful and convenient procedure.[1,2] These reagents are of interest not only because of their ease of preparation and useful applications,[1] but also because of their possible role as intermediate species in the reduction of carbonyl compounds with $LiAlH_4$.[3] The stereoselective reducing properties of lithium aluminum alkoxyhydrides and the stabilities of these species (to disproportionation) have recently been discussed.[4] It was also found that the hindered reagent formed from the reaction of 3 mol of di-*tert*-butyl ketone with 1 mol of $LiAlH_4$ reduced 3,3,5-trimethylcyclohexanone to 98% of the trans-axial alcohol.[4] However, this moderately hindered ketone is quite sensitive to stereoselective reduction by bulky reagents,[3,5,6] and a better test substrate for a selective reducing agent is an unhindered ketone such as 4-*tert*-butylcyclohexanone (**1**). Reduction of **1** with the above reagent (in 92 vol % THF, 8% ether) gave 76% of axial *cis*-4-*tert*-butylcyclohexanol (*cis*-**2**). This reagent is thus seen to be more highly stereoselective than other aluminum alkoxyhydrides previously used. For example, reduction of **1** with lithium aluminum tri-*tert*-butoxyhydride gave only 10% of *cis*-**2**.[5a,b,8] Lithium aluminum trimethoxyhydride is generally more highly stereoselective than the tri-*tert*-butoxyhydride owing to its relatively high degree of association;[5c] but it affords only 41% of *cis*-**2** on reduction of **1**.[5a]

In view of the apparent relationship between steric bulk and stereoselectivity of the reagent[3,4] it was thought to be of interest to prepare highly sterically hindered lithium aluminum triaryloxyhydrides by the reaction of $LiAlH_4$ with phenols. It would be of considerable interest to have highly stereoselective reagents easily prepared from relatively inexpensive starting materials. It should be noted that other procedures, most of which do not involve aluminum compounds, have been reported for the synthesis of axial alcohols, in particular the use of lithium tri-*sec*-butylborohydride,[9] potassium triisopropoxyborohydride,[10] iridium tetrachloride–trimethyl phosphite,[11] isobornyloxyaluminum dichloride,[12] and lithium dimesitylborohydride bis(dimethoxyethane).[13]

A study of the stereoselectivities of lithium aluminum triaryloxyhydrides in the reduction of the ketone **1** was undertaken. The general procedure (see Experimental Section for details) involved the addition of a solution of the phenol in tetrahydrofuran (THF) to a standardized solution of $LiAlH_4$ (commercially available in THF or diethyl ether) with measurement of hydrogen evolution. This was followed by addition of **1**. After hydrolysis of the reaction mixture, the concentrated product mixture was analyzed

Table I
Reduction[a] of 4-*tert*-Butylcyclohexanone with A



A

Entry	Reagent: R_1	Reagent: R_2	Reagent: Registry no.	Solvent[b]	% yield[c] of alcohols: Cis (axial)	% yield[c] of alcohols: Trans	% yield[c] ketone[d]	Stereoselectivity, % cis isomer[e]
1	CH_3	CH_3	54081-36-6	THF–ether	11	50	26	21
2	$(CH_3)_2CH$	$(CH_3)_2CH$	54003-97-3	THF	58	42	~0	58
3	$(CH_3)_2CH$	$(CH_3)_2CH$		THF[f]–ether	70	28	0	72
4	$(CH_3)_3C$	H	54003-98-4	THF	9	82	4	10
5	$(CH_3)_3C$[g]	$(CH_3)_3C$[g]	54004-00-1	THF–ether	*h*	*h*	~0	58
6[i]	$(CH_3)_3C$	$(CH_3)_3C$	54003-99-5	THF–ether	49[j]	9[j]	31	85

[a] Reaction times varied, 3–21 hr, reaction temperature ca. 25°. [b] 65–75 vol % tetrahydrofuran (THF) in ether, or 100% THF. [c] Yields determined by GLC analysis using 3,3,5,5-tetramethylcyclohexanone as internal standard. [d] Yield of recovered 4-*tert*-butylcyclohexanone. [e] Cis and trans alcohols normalized to 100%. Best values based on two or more analyses. [f] In 57 vol % THF in ether. [g] The reagent is lithium diaryloxyhydride. [h] Not measured with an internal standard. [i] Reaction mixture heated. [j] Some of the crude reaction product was removed before GLC analysis.

Table II
Reduction[a] of 4-*tert*-Butylcyclohexanone with $LiAlH(OAr)_2(OR)$[b]

Entry	Reagent, R	Registry no.	Solvent[c]	% yield[d] of alcohols: Cis (axial)	% yield[d] of alcohols: Trans	% yield[e] ketone	Stereoselectivity, % cis (axial) isomer[f]
1	$(CH_3)_2CHCH_2$	54004-01-2	THF–ether	*g*	*g*	26[h]	84
2	$(CH_3)_2CH$	54004-02-3	THF–ether	70	18	12	80
3	$(CH_3)_3C\text{-}CH_2$	54004-03-4	THF–ether	64	5	27	93
4	$(CH_3)_3C\text{-}CH_2$		THF–ether	*g*	*g*	31[h]	89
5	$(CH_3)_3C\text{-}CH_2$		THF	54	34	10	61
6	$(CH_3)_3C\text{-}CH_2$		THF	56	36	9	61

[a] Reaction times varied, reaction temperature ca. 25°. [b] Ar = 2,6-di-*tert*-butylphenyl. [c] 65–75 vol % THF in ether or pure THF. [d] Yields determined by GC analysis using 3,3,5,5-tetramethylcyclohexanone as internal standard. [e] Yield of recovered 4-*tert*-butylcyclohexanone. [f] Cis and trans alcohols normalized to 100%. [g] Not measured. [h] Area percent of ketone and alcohol isomers.

by gas chromatography, generally before and after the addition of a suitable internal standard.

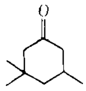
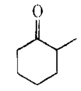
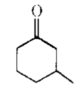
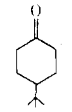
Preparation and Stereoselectivities of Lithium Aluminum Triaryloxyhydride Reagents. Table I summarizes the results of the reaction of $LiAlH_4$ with hindered phenols, and the reduction of 1 with the resulting lithium aluminum triaryloxyhydrides. The 2,6-dimethyl, 2,6-diisopropyl, and 2-*tert*-butylphenols (entries 1–4, Table I) react readily with $LiAlH_4$ in a 3:1 molar ratio at room temperature (ca. 25°) as evidenced by the liberation of 3 molar equiv of hydrogen.

Presumably the reducing species formed is lithium aluminum triaryloxyhydride. In the reaction of 2,6-di-*tert*-butylphenol with $LiAlH_4$ in a 3:1 molar ratio at room temperature (entry 5, Table I) hydrogen evolution ceased before addition of the phenol was complete. After addition of 1 mol of **1**, hydrolysis of the reaction mixture led to the evolution of 1 mol of hydrogen. Therefore only 2 molar equiv of hydride was used in the reaction of $LiAlH_4$ with this highly hindered phenol, since at room temperature the placement of the third aryloxy group about the aluminum atom is slow owing to steric hindrance.[14] It is possible to react $LiAlH_4$ with 3 molar equiv of 2,6-di-*tert*-butylphenol on heating. The resulting reagent (entry 6, Table I) is seen to be quite highly stereoselective. The degree of stereoselectivity is measured by the proportion of axial alcohol.

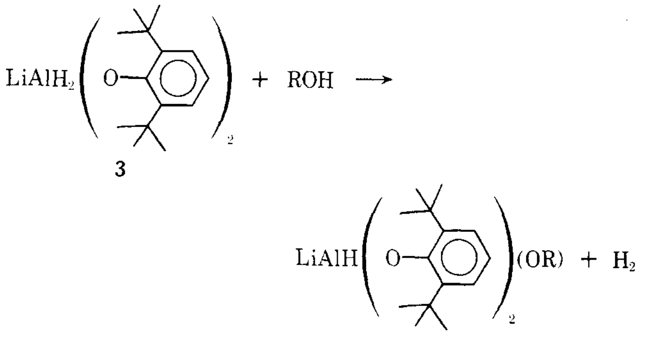
There appears to be a correlation between the size of the ortho substituents in the phenol with the steric requirements of the reducing agent, as long as the solvent remains constant. In THF–ether, stereoselectivity decreases with decreasing size of ortho substituent: $(CH_3)_3C > (CH_3)_2CH > CH_3$ (entries 6, 3, and 1, respectively). There is an interesting solvent effect, in that these reagents prepared from $LiAlH_4$ in ether are consistently more selective than when prepared fron $LiAlH_4$ in THF (compare entries 2 and 3, Table I). This same effect was observed again (vide infra) and was reproducible, although its cause is unknown. With one ortho *tert*-butyl substituent, the aluminum triaryloxyhydride reagent (entry 4, Table I) shows the same selectivity as lithium aluminum tri-*tert*-butoxyhydride, giving predominantly the more stable *trans*-**2** alcohol isomer.

Preparation and Stereoselectivities of Lithium Aluminum Diaryloxyalkoxyhydride Reagents. Since 2,6-di-*tert*-butylphenol reacted with $LiAlH_4$ in only a 2:1 molar ratio at room temperature, a series of experiments was carried out in which the third hydride was replaced with an alkoxy group by reaction with an alcohol. The resulting reagents, assumed to be lithium aluminum diaryloxyalkoxyhydrides, were then used to reduce 1 in order to test their stereoselective reducing properties. This approach has led to a number of new, highly selective reagents, as shown in Table II.

Table III
Reduction[a] of Ketones with $LiAlH(OAr)_2(OR)$[b]

Entry	Ketone	Registry no.	Reaction time, hr	% yield[c] of alcohols Cis	% yield[c] of alcohols Trans	% yield of ketone[d]	Stereoselectivity, % axial isomer[e]
1		873-94-9	16.5	<1	44	37	>99 (trans)
2		583-60-8	22.5	*f*	*f*	31[g]	89 (cis)
3		591-24-2	17	12	69	17	85 (trans)
4[h]			5	64	5	27	93 (cis)

[a] Reaction temperature ca. 25°, solvent 58-75 vol % THF in ether. [b] Ar = 2,6-di-*tert*-butylphenyl, R = neopentyl. [c] Yields determined by GLC analysis using the following internal standards: 3-methylcyclohexanone for entry 1; cyclohexanone for entry 3; 3,3,5,5-tetramethylcyclohexanone for entry 4. [d] Yield of recovered ketone. [e] Alcohols normalized to 100%. [f] Not measured. [g] Area percent of ketone and isomeric alcohols. [h] See entry 3, Table II.



3

4

The reaction of the diaryloxyhydride species **3** with isobutyl and isopropyl alcohols giving the respective species **4** occurred smoothly, with the reagents **4** showing quite high stereoselectivities (entries 1 and 2, Table II). The greatest stereoselectivity was found with the reagent **4** formed by reaction of **3** with neopentyl alcohol in THF–ether (entry 3, Table II). In all cases, the measured hydrogen evolution corresponded closely with that expected for the conversion of **3** to **4**. The satisfactory reproducibility in stereoselectivities is demonstrated for two cases in Table II (entries 3 and 4, and entries 5 and 6). Again, the same solvent effect on stereoselectivity as noted above was encountered (cf. entries 3 and 5, Table II).

In order to evaluate the scope of these new reagents, the best system was selected (entry 3, Table II) and used to reduce several additional ketones. The results of these reductions are shown in Table III. The reagent shows extremely high stereoselectivity in the reduction of the relatively highly hindered 3,3,5-trimethylcyclohexanone (entry 1, Table III), giving the trans–axial epimer almost exclusively. The reduction of 2-methylcyclohexanone also is highly stereoselective, giving 89% of the cis-axial epimeric alcohol (entry 2, Table III). In contrast $LiAlH_4$ itself affords only 24% of the cis epimer,[7] and lithium aluminum trimethoxyhydride gives 69% of the same epimer. Lithium aluminum tri-*tert*-butoxyhydride gives 27% of the cis epimer.[15] A similar high selectivity (85% trans–axial epimer) is seen for the reduction of 3-methylcyclohexanone (entry 3, Table III). In contrast, $LiAlH_4$ reduction affords only 16% of the trans alcohol epimer[16] while only 10% of the same epimer is formed with lithium aluminum tri-*tert*-butoxyhydride (at −23°).[15] Thus the new reagent is seen to be highly stereoselective in the reduction of these various ketones.

Several further observations should be made regarding the data in Tables I–III. In many of the reductions a considerable amount of ketone was found in the product. This appears to be a problem with the most selective highly hindered reagents. A possible explanation is reduced reactivity of the highly hindered reagents. An alternative explanation is enolization of the ketones. Several attempts to measure the infrared spectra of crude reaction mixtures (prior to hydrolysis) have not been conclusive. Further work will be directed toward improving the actual yields of the axial epimers. Analyses using internal standards (as shown in Tables I–III) have indicated that in almost all cases these are no significant products other than the alcohols and recovered starting ketones. Finally, although the reaction times employed in the reductions varied, equilibration of alcohol epimers did not occur, as was shown by control experiments involving the removal and analysis of aliquots during reaction.

Reaction of Lithium Borohydride with Hindered Phenols. Several experiments were carried out in which lithium borohydride was treated with 2,6-di-*tert*-butylphenol and with 2-*tert*-butylphenol. It was found that lithium borohydride did not react at room temperature (*ca.* 25°) with 2,6-di-*tert*-butylphenol in diethyl ether. On heating in THF, lithium borohydride reacted with 3 molar equiv of either of the above phenols (hydrogen evolution measured). The reduction of **1** in both cases afforded 20–22% of the cis–axial alcohol. It is possible that in these experiments reduction was effected by lithium borohydride itself. The reduction of **1** with lithium borohydride in diglyme at 20° is reported to give 15% of the cis–axial alcohol.[17] It is known that trialkoxyborohydrides are more reactive reducing agents than borohydride itself,[18–21] and the reaction of borohydride with the phenol may produce the tetraaryloxyborohydride species and unreacted lithium borohydride which is available for reduction.

Experimental Section

Solvents and Reagents. Tetrahydrofuran was refluxed over potassium hydroxide, then distilled from $LiAlH_4$ through an 18-in. helix-packed column. 4-*tert*-Butylcyclohexanone was distilled. The phenols were obtained from Aldrich Chemical Co. 2-6-Di-*tert*-butylphenol was distilled and kept refrigerated. Isopropyl and isobutyl alcohols were chromatoquality grade obtained from Matheson Coleman and Bell, and neopentyl alcohol (99%) was obtained from Aldrich. Lithium aluminum hydride was obtained from Ventron Corp. as solutions in diethyl ether or THF. The solutions were standardized by reaction with iodine according to the method of Felkin,[22] or by measurement of hydrogen on methanolysis.

Gas chromatographic analyses were done on a Hewlett-Packard Model 5750 instrument using the following columns: 12 ft × 0.125 in. 5% Carbowax 20M at 145° for the separation of *cis*- and *trans*-4-*tert*-butylcyclohexanols; 10 ft × 0.25 in. 10% Carbowax 20M (acid washed, silanized) at 140° for *cis*- and *trans*-3,3,5-trimethylcyclohexanols; 16 ft × 0.25 in. ethylene glycol succinate (acid washed, silanized) at 105° for *cis*- and *trans*-2-methylcyclohexanols; 12 ft × 0.25 in. diethylene glycol succinate (acid washed, silanized) for *cis*- and *trans*-3-methylcyclohexanols.

Apparatus and General Procedure. The reactions were carried out in a 250-ml glass reactor (Ace Glass Co.) stirred magnetically and equipped with a condenser and equilibrated dropping funnel. The apparatus was baked and flushed with dry nitrogen. The general procedure is described in detail for the following two reactions.

Reaction of $LiAlH_4$ with 2,6-Dimethylphenol. Reduction of 1. Fifteen milliliters of 0.90 *M* $LiAlH_4$ in ether was transferred by pipet to the reaction flask. Ten milliliters of THF (distilled freshly from $LiAlH_4$) was added dropwise with the apparatus attached to a wet test meter. No hydrogen evolution occurred. A solution of 2,6-dimethylphenol (4.96 g, 0.0406 mol) in 10 ml of THF was added dropwise over 6 min. The volume of hydrogen was recorded (0.045 mol) by means of a wet test meter. The reaction mixture was clear and colorless. The ketone 1 (1.994 g, 0.0129 mol) was added dropwise as a solution in 10 ml of THF over 4 min. The clear, colorless reaction mixture was stirred overnight under a nitrogen atmosphere. After 23 hr, the reaction mixture was hydrolyzed with 10% sulfuric acid, and hydrogen evolution measured. After washing (saturated sodium bicarbonate and salt solution) and drying over anhydrous $MgSO_4$, the product was concentrated by distillation through a 17-in. helix-packed column, using an oil bath. The concentrated product, 29 g, was clear and colorless, and analyzed by GLC before and after the addition of 3,3,5,5-dimethylcyclohexanone as an internal standard.

Reaction of $LiAlH_4$ with 2,6-di-*tert*-Butylphenol and with Neopentyl Alcohol. Reduction of 1. Twenty milliliters of 1.2 *M* $LiAlH_4$ in ether was transferred by pipet to the reaction flask. Fifteen milliliters of THF was added dropwise with no hydrogen evolution. Distilled 2,6-di-*tert*-butylphenol (9.9155 g, 0.048 mol) in 10 ml of THF was added over 20 min, during which hydrogen evolution (0.045 mol) was measured with a wet test meter. The clear, colorless reaction mixture was then stirred under nitrogen for 35 min, and a solution of neopentyl alcohol (2.1279 g, 0.024 mol) in 15 ml of THF was added over 8 min, again measuring hydrogen evolution (0.021 mol). Hydrogen evolution continued after the addition was complete, indicating a rather slow reaction. After 32 min, a solution of 1 (3.0863 g, 0.020 mol) in 15 ml of THF was added dropwise under nitrogen over 8 min. The reaction mixture was clear and pale yellow. It was stirred under nitrogen for 5 hr, cooled, and hydrolyzed with 10% sulfuric acid, with hydrogen evolution measured with the wet test meter. The aqueous layer was extracted with three portions of ether, and combined organic solution washed twice with saturated sodium bicarbonate, twice with saturated salt solution, and dried over anhydrous magnesium sulfate. The filtered solution was concentrated by distillation through a 17-in. helix-packed column using an oil bath (bath temperature to ~90°, bp ~35°). The concentrated product was clear and colorless and was analyzed by GLC before and after the addition of the internal standard, 3,3,5,5-tetramethylcyclohexanone.

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Registry No.—1, 98-53-3.

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Observations on the Steric Requirement of Wittig Reactions with Trialkylphosphonoacetates

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Investigation of the Wittig reaction of trialkylphosphonoacetate anions with several C-2 substituted cyclohexanones has demonstrated the presence of a previously unrecognized steric constraint for this reaction. Cyclohexanones with a C-2 alkyl group constrained to the equatorial orientation proved unreactive to normal treatment with trialkylphosphonoacetate anions. Cyclohexanones which can undergo facile conformational inversion to give an axial C-2 substituent react normally. Conformationally rigid cyclohexanones in which configurational inversion to give an axial C-2 substituent is not energetically prohibitive react slowly and give a mixture of ester products with the alkyl group predominantly axial.

We wish to report some previously unrecognized steric requirements of the Wittig reaction using trialkylphosphonoacetate anions. The observations reported herein further delineate the range of synthetic utility of reactions involving phosphonate anions and substituted cyclohexanones. In the course of another synthetic problem[1] we attempted to convert ketone 2 into the corresponding α,β-unsaturated ester 3 by treatment with anion 1. Attempts to conduct this