

Organic Reactions at Alumina Surfaces. 6.

Isopropyl Alcohol and Diisopropylcarbinol on Dehydrated Alumina as Reagents for Very Selective Carbonyl Reductions¹

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2-Propanol on dried Woelm alumina at room temperature reduces structurally diverse aldehydes cleanly and rapidly (<2 h) into the corresponding alcohols which are isolated easily in pure form in 65–88% yields. α,β -Ethylene aldehydes are reduced to allylic alcohols, and the following functional groups are stable to the reaction conditions: nitro, ester, amide, nitrile, primary and secondary iodide, benzylic bromide, and olefinic. Chromones 1 and 2 are selectively reduced to the corresponding allylic alcohols. $(\text{CH}_3)_2\text{CDOH}$ on dried alumina reduces $\text{C}_6\text{H}_5\text{CHO}$ to $\text{C}_6\text{H}_5\text{CH(D)OH}$ in 80% yield with high deuterium incorporation. 10-Oxoundecanal, a keto aldehyde, is transformed selectively into 10-oxoundecanol, a keto alcohol, and steroidal keto aldehyde 3 is reduced to ketol 4. 2,4-Dimethyl-3-pentanol (diisopropylcarbinol) on alumina is the first reagent to reduce an aliphatic aldehyde in the presence of an unhindered cyclohexanone. 2-Propanol on alumina reduces steroidal 3,6-, 3,17-, and 3,20-diones selectively at the 3 position. The effectiveness of these secondary alcohol–alumina reagents is compared with that of standard reducing agents, and the role of the alumina is mentioned.

Reduction of carbonyl groups is one of the most fundamental operations in organic chemistry. Catalytic hydrogenation, metal–amine solutions, and complex metal hydrides often allow very clean and selective reduction of one carbonyl group in the presence of another or in the presence of other functional groups.³ New methods and new reagents which offer even greater selectivity are constantly being sought. We report here the scope and limitations of two new reagents, isopropyl alcohol and diisopropylcarbinol on dried chromatographic alumina, which are weaker reducing agents than sodium borohydride⁴ and which are at least as selective as sodium cyanoborohydride⁵ and 9-borabicyclo[3.3.1]nonane⁶ for conversion of α,β -ethylene aldehydes into the corresponding allylic (i.e., not saturated) alcohols, even in the presence of nitro, ester, amide, nitrile, primary or secondary iodide, benzylic bromide, and olefinic functional groups. Furthermore, conditions have been developed under which 2-propanol and 2,4-dimethyl-3-pentanol on dried alumina reduce aldehydes but not ketones, and other conditions have been found for selective reduction of some diones into ketols. The very mild reducing power of these secondary alcohols on dried alumina matches that of the most sophisticated and selective complex hydride reducing agents.^{3d} This mildness and the compatibility of these alumina-supported reagents with a very wide variety of normally reducible functional groups make them useful new reagents for selective reductions especially of polyfunctional compounds.

Reduction of Aldehydes. The general procedure involves drying commercial alumina by heating it in a quartz vessel⁷ at 400 °C, adding 2-propanol in an inert solvent, adding the aldehyde reactant, and stirring the slurry for 2 h. The reaction is quenched by addition of methanol. Vacuum filtration through Celite, washing the Celite with methanol, and rotary evaporation of solvent gives crude alcohols which are either distilled or recrystallized. The results of this mild⁸ procedure using aldehydes of various structural types and 2-propanol-doped Woelm W-200, neutral, dehydrated (W-200-N-D)⁹ alumina are shown in Table I; yields are of isolated, purified products.

Several aspects of reductions 1–8 (Table I) merit discussion. Infrared analysis of the crude alcohol products (before purification) indicates a very small amount of conjugated carbonyl absorption due presumably to aldol condensations; the Meerwein–Ponndorf–Verley reduction of aldehydes using aluminum isopropoxide often gives significant amounts of aldol, Tishchenko, and Cannizzaro condensation products,

and often special precautions must be taken to minimize these side reactions.¹⁰ Because transformations 1–8 are heterogeneous reactions which take place at the alumina–solvent phase boundary, they were each repeated several times to establish their reproducibility; in all cases, reproducible results were obtained to within $\pm 5\%$, even when different batches of commercial Woelm W-200-N alumina were used over the course of a 2-year period. 2-Propanol on dried Woelm W-200 basic and acidic and Alcoa F-20 alumina was found to reduce *n*-decanal about as effectively as 2-propanol on Woelm W-200-N-D alumina. Dehydrating the alumina under vacuum at 300 °C rather than 400 °C lowered the yield of alcohol products by 5–10%, and using activity I (or “super I”) rather than dried alumina gave very poor yields of alcohol products along with many aldol condensation products. Increasing the percentage of 2-propanol above 10% of the amount of alumina did not increase the yields of alcohol products, whereas lowering the 2-propanol percentage to 5% of the alumina also caused no big change in yield; less than 2% (1.7 mmol) of isopropyl alcohol on 5 g of alumina per 1 mmol of substrate, however, gave unsatisfactory reductions with formation of many aldol condensation products as has been observed when aldehydes are placed on “undoped” alumina.¹¹ Adding 2-propanol neat to the dried alumina and storing this reagent in a sealed vial for at least 3.5 months does not decrease its effectiveness as a reducing agent.

Transformation 1 (see Table I) was performed also on a ~ 10 -mmol (~ 2 g) scale to illustrate application of this method to preparation of gram quantities of alcohols; the yield of pure 1-decanol after distillation was 81%. Conversions 2 and 3 demonstrate the effectiveness of the 2-propanol-doped alumina reduction procedure even for aldehydes having especially acidic α protons, and reactions 5 and 6 indicate that nitro and amide functional groups survive under the reaction conditions. From control experiments run under the same conditions, we have recovered the following substrates (% recovered): *p*-nitroacetamide (79%), dimethyl 1,10-decanedioate (96%), 3-hydroxypropionitrile (83%), 1-iodooctane (80%), 2-iodooctane (69%), benzyl bromide (59%), and 1,2-bis(chloromethyl)benzene (84%). Thus 2-propanol on W-200-N-D alumina is highly selective for reduction of aldehyde carbonyl groups. But so is sodium borohydride! Transformations 7 and 8, however, show that 2-propanol on W-200-N-D alumina is more selective than sodium borohydride, which produces saturated alcohols as significant side products in reduction of α,β -ethylene aldehydes (enals).¹²

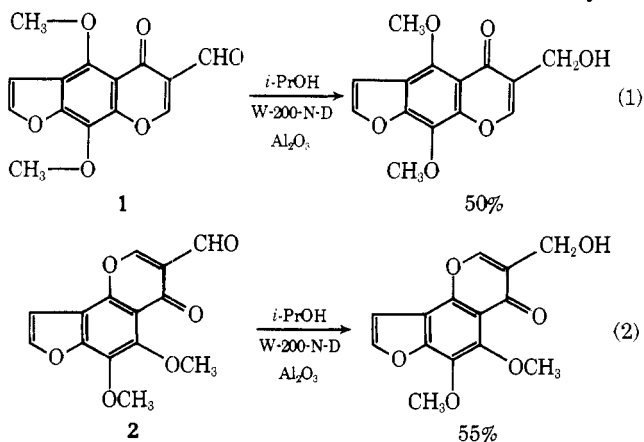
Table I. Reduction of Aldehydes (RCHO) to Alcohols (RCH₂OH) by 10% 2-Propanol on 5 g of W-200-N-D Alumina at 25 °C for 2 h with CCl₄ Solvent

Reaction	RCH ₂ OH	% yield	Comments ^a
1	<i>n</i> -C ₉ H ₁₉ CH ₂ OH	84	<i>n</i> ²² D 1.4366 (lit. ^b <i>n</i> ²⁰ D 1.4368)
2	C ₆ H ₅ CH ₂ CH ₂ OH	65	
3	C ₆ H ₅ CH(CH ₃)CH ₂ OH	77	<i>n</i> ²⁵ D 1.5220 (lit. ^c <i>n</i> ²⁵ D 1.5221)
4	C ₆ H ₅ CH ₂ OH	77	
5	<i>p</i> -O ₂ NC ₆ H ₄ CH ₂ OH	84	mp 95 °C (lit. ^b mp 93 °C)
6	<i>p</i> -CH ₃ CONHC ₆ H ₄ CH ₂ OH	76	mp 120–122 °C (lit. ^d mp 120–121 °C)
7	C ₆ H ₅ CH=CHCH ₂ OH	82	
8	(CH ₃) ₂ C=CH(CH ₂) ₂ CH=CHCH ₂ OH	88	

^a Products were identified by comparing their physical and spectral properties with those reported in the literature or those of authentic samples. ^b "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, 1961. ^c B. Elpern, L. N. Gardner, and L. Grumbach, *J. Am. Chem. Soc.*, **79**, 1951 (1957). ^d R. Grice and L. N. Owen, *J. Chem. Soc.*, 1947 (1963).

Conversions 7 and 8 proceed cleanly, giving no trace of over-reduction (i.e., saturated rather than allylic alcohol) and no substrate isomerization; citral (33:67 neral:geranial) is converted to a 33:67 mixture of nerol:geraniol in 88% yield. Using aluminum isopropoxide under homogeneous Meerwein-Ponndorf-Verley conditions, we find the same citral reduced also to a 33:67 mixture of nerol:geraniol in 89% yield. Although both aluminum hydride¹³ and diisobutylaluminum hydride (DIBAL-H)¹⁴ are effective for reduction of enals to allylic alcohols, both hydride reagents are powerful reducing agents which would not tolerate the presence of many other functional groups. For example, DIBAL-H easily reduces most common groups including esters, amides, and nitriles,^{3d} whereas 2-propanol on W-200-N-D alumina does not consume these types of compounds. And aluminum hydride is similar in reducing power to lithium aluminum hydride, which also reduces esters, amides, and nitriles.^{3d} Because of the difficulty in obtaining clean reduction of α,β -ethylenic aldehydes using various hydride reagents, three new reagents have recently been investigated. Excess sodium and tetrabutylammonium cyanoborohydrides⁵ in acidic hexamethylphosphoramide lead to allylic alcohols in yields comparable to those in conversions 7 and 8, and these new reagents are also compatible with many acid-stable functional groups. 9-Borabicyclo[3.3.1]nonane also is very useful and selective for conversion of enals to allylic alcohols.⁶

The synthetic utility of 2-propanol on dried alumina is further illustrated with polyfunctional α,β -ethylenic aldehydes 1 and 2. Chromones 1 and 2 suffer reduction of both aldehyde carbonyl and α,β -ethylenic groups with the following reagents: sodium borohydride, sodium borohydride-aluminum chloride, DIBAL-H in tetrahydrofuran, and sodium cyanoborohydride in the presence of acid.¹⁵ Although chromones 1 and 2 are inert to Meerwein-Ponndorf-Verley ho-



mogeneous conditions using aluminum isopropoxide,¹⁵ selective and effective aldehyde reduction occurs heterogeneously with 2-propanol on dried alumina, as shown in eq 1 and 2.

That the hydride ion which reduces the aldehyde substrates arises from the carbinol carbon atom of 2-propanol (and not from the methanol used to quench the reaction, for example¹⁶) is unambiguously shown by two experiments. First, when 5-nonanol (instead of 2-propanol) is placed on W-200-N-D alumina and an aldehyde is added, 5-nonanol is isolated in about the same yield as the alcohol derived from reduction of the aldehyde. Second, doping W-200-N-D alumina with (CH₃)₂CDOH and adding benzaldehyde leads in 80% distilled yield to C₆H₅CH(D)OH having the same spectral properties as those of the product of LiAlD₄ reduction of benzaldehyde.¹⁷ Thus the deuterium in (CH₃)₂CDOH is not washed out or diluted by exposure to solid W-200-N-D aluminum oxide, and this procedure therefore has potential for highly selective introduction of deuterium via carbonyl reduction.^{3b}

Selective Reduction of Aldehydes in the Presence of Ketones. Control experiments also showed that under the standard reaction conditions most types of ketones are not so easily reduced by 2-propanol on W-200-N-D alumina as are aldehydes. Table II shows that these heterogeneous reductions are subject to some extraordinarily delicate (presumably steric) effects. Whereas 2-octanone is reduced to the extent of 20%, 5-nonanol is inert, and whereas unhindered cyclohexanones are completely reduced, 2-methylcyclohexanone and 2-isopropyl-5-methylcyclohexanone are reduced only to the extent of 56 and <5%. Noteworthy also is the relative stability of 2-cyclohexenone compared with the high reactivity of the cyclohexanones; 9-BBN is reported to react with 2-cyclohexenone at about the same rate as with cyclohexanone.⁶ Whereas steroidal enal enone 3 reacts with 9-BBN at both

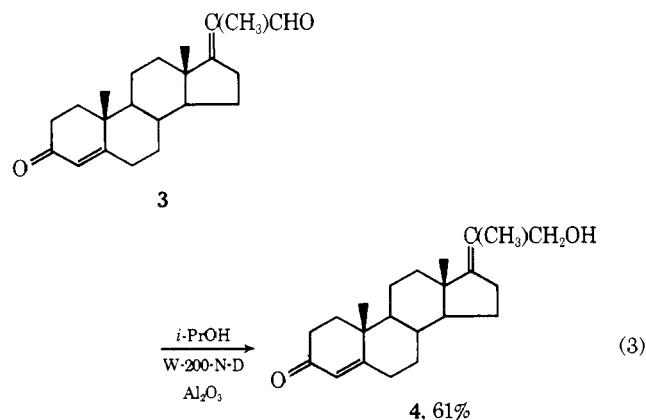
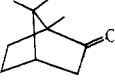
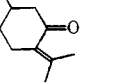

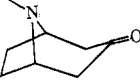

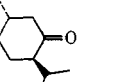





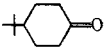


Table II. Amounts of Ketone (1 mmol) Reduction by 10% 2-Propanol on 2.5 g of W-200-n-D Alumina at 25 °C, for 2 h, with CCl₄ Solvent

Ketone substrate	% redn ^a	Registry no.	Ketone substrate	% redn ^a	Registry no.
	0	76-22-2	C ₆ H ₅ COCH ₃	16	98-86-2
	0	15932-80-6		18	502-42-1
	0	532-24-1	<i>n</i> -C ₆ H ₁₃ COOH ₃	20	111-13-7
(<i>n</i> -C ₄ H ₉) ₂ CO	0	502-56-7		~30	120-92-3
	< 5	89-80-5		44	1191-95-3
	8	830-13-7		56	583-60-8
	10	930-68-7		> 90 ^b	98-53-3
			3-Cholestanone	> 90 ^c	15600-08-5

^a % reduction was determined by GLC using calibrated internal standards. ^b 95:5 *trans*:-*cis*-4-*tert*-butylcyclohexanol. ^c Mainly 3 β -cholestanol is formed.

Table III. Amount of Carbonyl Reduction by Various "Selective" Reducing Agents

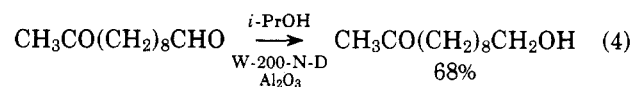
Reducing agent	% redn ^a of	
	RCH ₂ CHO	
Bu ₄ NBH ₃ CN ^b	90 ^b	88 ^b
NaBH(OAc) ₃ ^c	95 ^d	65 ^d
LiAlH(OBu- <i>t</i>) ₃ ^e	High ^e	High ^e
LiBu ₂ -BBN ^f	50-72 ^f	63-77 ^f
9-BBN	63 ^d	64 ^{d,g}
<i>i</i> -PrOH/Al ₂ O ₃	80-90	90
<i>i</i> -Pr ₂ CHOH/Al ₂ O ₃	84	13

^a Determined by GLC using calibrated internal standards; R = C₈H₁₇-*n*. ^b See ref 5. ^c G. W. Gribble and D. C. Ferguson, *J. Chem. Soc., Chem. Commun.*, 535 (1975); N. Umino, T. Iwakuma, and N. Itoh, *Tetrahedron Lett.*, 763 (1976). ^d Determined in our laboratory. ^e C. S. Sell, *Aust. J. Chem.*, 28, 1383 (1975). ^f Y. Yamamoto, H. Toi, A. Sonoda, and S. I. Murohashi, *J. Am. Chem. Soc.*, 98, 1965 (1976). ^g 40:60 *cis*:-*trans*-4-*tert*-butylcyclohexanol.

carbonyl centers, it reacts with 2-propanol on alumina selectively at the enal carbonyl group to give allylic alcohol 4 in 61% yield after preparative TLC.

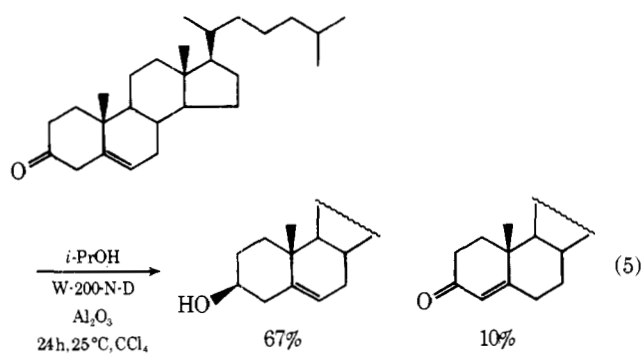
Competition between 1 mmol of *n*-decanal and 1 mmol of 2-octanone for 2 mmol of 2-propanol on 2.5 g of W-200-N-D alumina led to almost complete aldehyde reduction and ketone recovery.¹⁸ It appeared possible in this type of heterogeneous reaction, however, that a difunctional aliphatic keto aldehyde, once adsorbed to the alumina surface, might suffer reduction of both aldehyde and ketone carbonyl groups; we therefore prepared 10-oxoundecanal, a keto aldehyde, and found it to be reduced *selectively* to 10-oxoundecanol, a keto alcohol, in 68% recrystallized yield (eq 4). But within the past 3 years, five different reducing agents have been reported for reduction of an aldehyde (RCH₂CHO) in the presence of the corresponding *methyl* ketone (RCH₂COCH₃), with selectivity of reduction and compatibility toward various functional

groups comparable to those we observe with 2-propanol on W-200-N-D alumina. Not one of these five new reagents, however, can distinguish effectively between an aldehyde and an *unhindered cyclohexanone*. Although 2-propanol on W-200-N-D alumina also fails to distinguish between these two readily reduced units, diisopropylcarbinol on W-200-N-D alumina reduces *n*-decanal but not 4-*tert*-butylcyclohexanone (see Table III)!

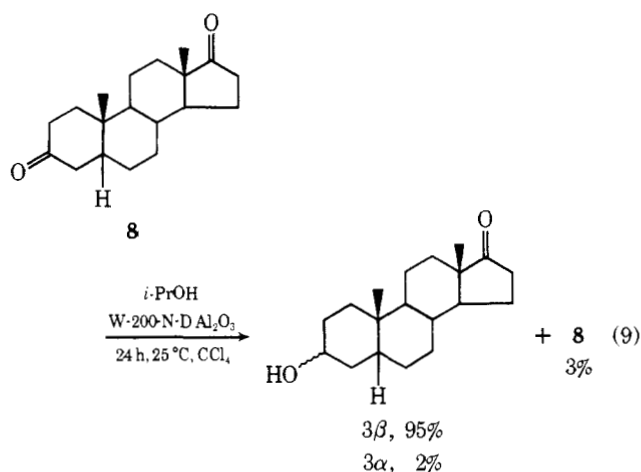
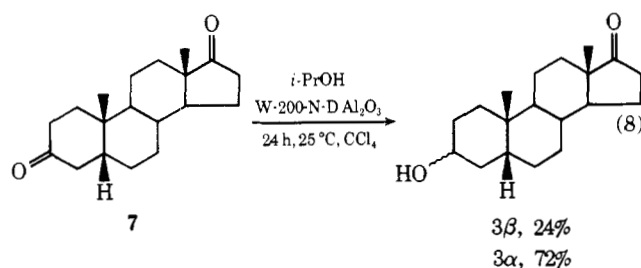
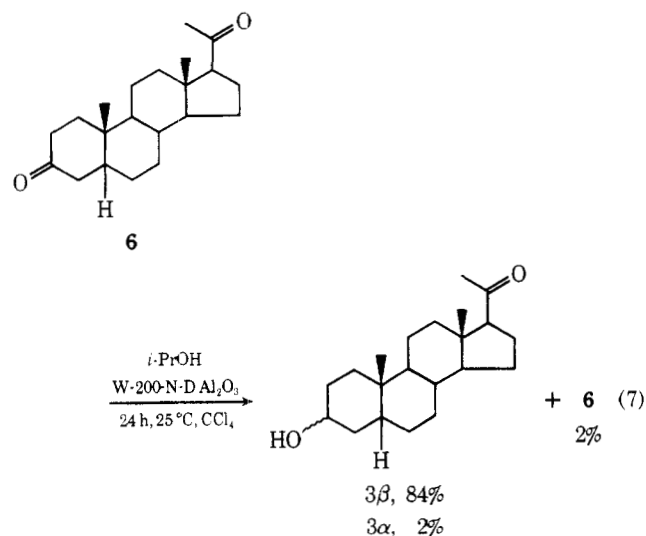
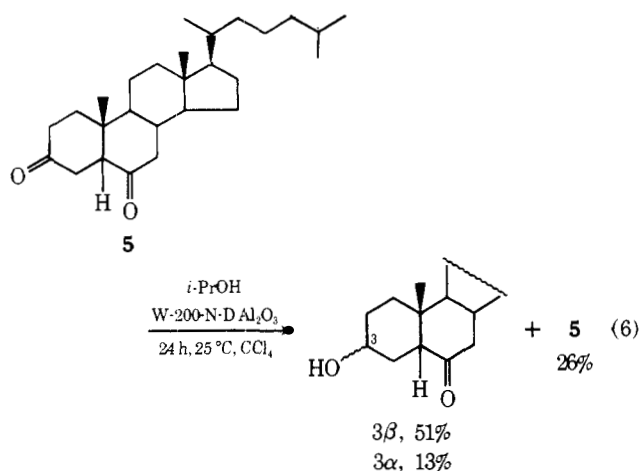


Diisopropylcarbinol on W-200-N-D alumina, therefore, is the first reagent which allows reduction of an unhindered aldehyde in the presence of an unhindered cyclohexanone. One disadvantage, however, of using 2,4-dimethyl-3-pentanol as the reducing agent on alumina is the possible difficulty in separating 2,4-dimethyl-3-pentanol (and any excess 2,4-dimethyl-3-pentanol) from the primary alcohol produced in the reaction. This disadvantage obviously becomes less important as the difference in molecular weight between diisopropylcarbinol and the aldehyde reactant increases and as the aldehyde becomes more complex (e.g., containing heteroatoms) making chromatographic separation practical.

Selective Reduction of Diones. Examination of the large differences in relative rate of ketone reductions (Table II) by 2-propanol on W-200-N-D alumina suggested also that selective dione reductions might be possible. To test whether steroidal ketones containing long alkyl side chains, despite their large molecular size, could enter the pores of the alumina and could be reduced, we determined that Δ^5 -cholesten-3-one is reduced to cholesterol as shown in eq 5. This example illustrates the very mild basicity of W-200-N-D alumina carrying 2-propanol;¹⁹ the rate of ketone reduction is substantially faster than ketone enolization. Note also that conjugated ketone Δ^4 -cholesten-3-one is not reduced even after 24 h under these conditions, as is observed also with Δ^4 -androsterone-3,17-dione.²⁰



Four different steroidal diones were added (separately) to W-200-N-D alumina carrying 2-propanol and were stirred at 25 °C for 24 h, with results as shown in eq 6–9; yields are of purified products. The 24-h instead of 2-h period was chosen to maximize reduction; in no case was any diol (i.e., reduction of *both* carbonyls) observed. The selectivity of 2-propanol on W-200-N-D alumina for reduction at the 3 position in competition with positions 6, 20, and 17 parallels the selectivity shown by many of the complex metal hydride reducing ag-



ents.^{3b,21} For example, in our hands lithium tri(*tert*-butoxy)-aluminumhydride gives roughly the same results as shown in eq 7 and 9.²¹ To demonstrate application of this alumina promoted reduction to preparation of several gram quantities of material, reaction 9 was done on a larger scale, producing ~6 g (84% yield) of pure 5 α -androstan-3 β -ol-17-one.

Although 2-propanol on W-200-N-D alumina may offer no significant advantage over many of the readily available complex metal hydrides in terms of *selectivity* of dione reductions, the *compatibility* of the alcohol-alumina reagent with many types of functional groups may allow it to be used for selective reduction of some multifunctional substrates.

Discussion of the Role of Alumina.²² Several different solid supports have been used to effect some very specific organic transformations: Collins' reagent²³ and silver carbonate²⁴ on Celite and chromic acid on an anion exchange resin²⁵ and intercalated in graphite²⁶ for alcohol oxidations; ozone on silica gel for oxidation of tertiary alkyl centers²⁷ and for oxidation of arenes;²⁸ thallium trinitrate on K-10 montmorillonite clay for oxythallation reactions;²⁹ alcohols on various zeolites³⁰ for reduction of small carbonyl compounds;³¹ and alcohols, thiols, and acetic acid on alumina for displacement and epoxide ring opening reactions.³² Although the detailed function of the inorganic supports may be different in each of these examples, one common feature of the solid support probably is *bringing together the substrate and the reagent in the proper orientation for chemical reaction*.³³ Another important function of the support probably is to *activate* the substrate and/or the reagent.³⁴

Conclusion

The two most serious drawbacks to general use of these secondary alcohol-alumina reagents are (1) the high temperature (400 °C) required for the alumina activation and (2) the relatively large amount of alumina (3–5 g/mmol of carbonyl substrate) required for effective substrate reduction. Several significant advantages of these alumina supported alcohols are (1) low cost of the secondary alcohol which is used in only slight excess over the substrate; (2) easy product isolation; (3) *selectivity* for carbonyl reduction; and (4) *compatibility* with many different types of functional groups. Although 2-propanol and 2,4-dimethyl-3-pentanol certainly will not replace more common reagents for *standard* carbonyl reductions, these new alcohol-alumina reagents will be useful in special cases requiring selective reduction of one carbonyl group in the presence of another or in the presence of other functional groups.

Experimental Section

Analytical gas-liquid phase chromatography was performed on a Varian Aerograph Model 1200 chromatograph. Spectral data were obtained with a Perkin-Elmer 457-A infrared spectrometer and a

Varian A-60 NMR spectrometer. All chemical shifts in the NMR spectra were measured relative to tetramethylsilane used as an internal standard. All absorptions in the infrared were measured relative to the 6.02- μ peak of polystyrene. Melting points were taken on a Mel-Temp melting point apparatus and are uncorrected.

All solvents were commercial reagent grade. All steroids were obtained from Research Plus Steroids except 5 α -cholestane-3,6-dione, which was obtained from Dr. M. Koreeda, and enal 3, which was purchased from Steraloids, Inc. The LiAlD₄ was from Stohler Isotope Chemicals. The aluminum isopropoxide from Eastman was simply distilled before use. The benzaldehyde from Fisher was washed with Na₂CO₃ and distilled from zinc dust before use. The 2-propanol from Baker was dried by distillation from calcium hydride. The Woelm W-200 alumina was obtained from ICN Pharmaceuticals, Inc. All other chemicals were obtained from Aldrich Chemical Co.

General Procedure for Aldehyde Reduction. Woelm W-200, neutral alumina is heated in a quartz vessel at 400 °C (0.06 Torr) for 24 h. A glass-wool plug is placed at the top of the quartz vessel to prevent the alumina from "bumping" out of the vessel. About 5 g of the dehydrated alumina is transferred inside a nitrogen-filled glove bag to an oven-dried, tared 25-ml round-bottom flask containing a magnetic stirring bar. The flask is stoppered and removed from the glove bag. About 5 ml of inert solvent (e.g., diethyl ether, chloroform, carbon tetrachloride, or hexane) containing ~500 mg (10% of alumina weight) of 2-propanol is added. After stirring for 0.5 h at 25 °C, ~1 mmol of aldehyde in ~1 ml of solvent is added and stirring is continued for 2 h at 25 °C. The reaction is quenched by addition of 5 ml of methanol and stirring for 15 min. Vacuum filtration through Celite, washing the Celite with ~35 ml of methanol, and rotary evaporation of solvent gives crude alcohols which are either distilled or recrystallized.

1-Decanol from Decanal. A. Small Scale. A solution of 138 mg (0.89 mmol) of decanal in 6 ml of carbon tetrachloride was stirred over 4.19 g of dehydrated alumina and 420 mg (7.25 mmol) of 2-propanol at 25 °C for 2 h. Filtration, removal of solvent, and Kugelrohr distillation [bp 100 °C (12 mm)] provided 116 mg (84%) of 1-decanol, n_D^{20} 1.4366 (lit.³⁵ n_D^{20} 1.4366).

B. Large Scale. A solution of 1.85 g (11.9 mmol) of decanal in 75 ml of carbon tetrachloride was stirred over 60 g of dehydrated alumina and 6 g (103 mmol) of 2-propanol at 25 °C for 2 h. Filtration, removal of the solvent, and Kugelrohr distillation [bp 100 °C (12 mm)] gave 1.52 g (81%) of 1-decanol.

Cinnamyl Alcohol from Cinnamaldehyde. A solution of 167 mg (1.27 mmol) of cinnamaldehyde in 6 ml of carbon tetrachloride was stirred over 6.03 g of dehydrated alumina and 600 mg (10.3 mmol) of 2-propanol at 25 °C for 2 h. Filtration, removal of solvent, and Kugelrohr distillation [bp 130 °C (12 mm)] yielded 139 mg (82%) of cinnamyl alcohol having spectral properties identical with those of an authentic sample.

Nerol and Geraniol from Citral Using 10% 2-Propanol on Alumina. A solution of 168 mg (1.11 mmol) of citral (33% nerol, 67% geraniol) in 6 ml of carbon tetrachloride was stirred over 5.07 g of dehydrated alumina and 500 mg (8.62 mmol) of 2-propanol at 25 °C for 2 h. Filtration, removal of solvent, and distillation [bp 115 °C (12 mm)] afforded 150 mg (88%) of a mixture of nerol (33%) and geraniol (67%) as determined by vapor phase chromatography (10 ft \times 0.125 in. 5% SE-30 Chromosorb G 100/140) and identified by comparison with known samples.

2-Propanol on Alumina Reduction of Chromone 1. A solution of 300 mg (1.09 mmol) of chromone 1 in 6 ml of carbon tetrachloride was stirred over 5.70 g of dried alumina and 577 mg (9.5 mmol) of 2-propanol at 25 °C for 2 h. Filtration and solvent evaporation gave 279 mg of a solid. Preparative TLC afforded 151 mg (50%) of the allylic alcohol corresponding to chromone 1: mp 130–132 °C; NMR (CDCl₃) δ 4.6 (broad singlet, -CH₂O-, 2 H), 4.12 and 4.2 (sharp singlets, -OCH₃, 6 H), 3.2–3.5 (broad, -OH, 1 H); IR (mineral oil) 2.96 μ (strong, -OH). An analytical sample was prepared by recrystallization from acetone.

Anal. Calcd for C₁₄H₁₂O₆: C, 60.87; H, 4.38. Found: C, 60.70; H, 4.28.

2-Propanol on Alumina Reduction of Chromone 2. A solution of 290 mg (1.06 mmol) of chromone 2 in 6 ml of carbon tetrachloride was stirred over 5.24 g of dried alumina and 531 mg (8.8 mmol) of 2-propanol at 25 °C for 2 h. Filtration and solvent evaporation gave 249 mg of a solid. Preparative TLC gave 159 mg (55%) of the allylic alcohol corresponding to chromone 2: mp 150–153 °C; NMR (CDCl₃) δ 4.60 (singlets, -CH₂O-, 2 H), 4.02 and 4.18 (sharp singlets, -OCH₃, 6 H), 3.1–3.5 (broad, -OH, 1 H); IR (mineral oil) 2.96 μ (strong, -OH). An analytical sample (mp 157 °C) was prepared by recrystallization from acetone.

Anal. Calcd for C₁₄H₁₂O₆: C, 60.87; H, 4.38. Found: C, 60.76; H, 4.30.

When larger amounts (~700 mg) of chromones 1 and 2 were reduced by 2-propanol on alumina, the corresponding allylic alcohols were formed and recrystallized from acetone in 38–40% yields.

C₆H₅CH(D)OH from C₆H₅CHO and (CH₃)₂CDOH on Alumina. To a solution of 170 mg (5.3 mmol) of LiAlD₄ in 2 ml of Et₂O was added dropwise over a 15-min period 500 mg (8.65 mmol) of acetone. After stirring at room temperature for 1 h, the reaction mixture was cooled to 0 °C and quenched with 0.34 ml of H₂O and 0.26 ml of 10% NaOH. The reaction mixture was allowed to stir for 1 h, anhydrous sodium sulfate was added, and the mixture was filtered using carbon tetrachloride to wash the inorganic salts.

A solution of 113 mg (1.07 mmol) of benzaldehyde and the reagent prepared above in about 10 ml of Et₂O/CCl₄ was stirred over 5.02 g of dehydrated alumina at 25 °C for 2 h. Filtration, removal of the solvent, and Kugelrohr distillation [bp 95 °C (12 mm)] afforded 94 mg (81%) of benzyl alcohol-*d*₁ which was spectroscopically (NMR, IR, and mass spectrum) the same as the product obtained by reduction of benzaldehyde directly with LiAlD₄. NMR (CCl₄) of product from the alumina reaction gave δ 2.80 (s, 1 H, OH), 4.32 (s, 1 H, CHO), and 7.10 ppm (s, 5 H, C₆H₅).

Competition between Decanal and 2-Octanone for a Limited Amount of 2-Propanol on Alumina. A solution of 193 mg (1.23 mmol) of decanal and 157 mg (1.22 mmol) of 2-octanone in 6 ml of carbon tetrachloride was stirred over 3.03 g of dehydrated alumina and 159 mg (2.65 mmol) of 2-propanol at 25 °C for 2 h. The course of the reaction was followed by analytical gas-liquid phase chromatography with aliquots taken every 0.5 h. Gas-liquid phase chromatography (10 ft \times 0.25 in., 10% Carbowax 20M on Chromosorb W 60/80) showed there to be 95% reduction of decanal and only 5% reduction of 2-octanone.

10-Oxoundecanol from 10-Oxoundecanal. A solution of 70.6 mg (0.38 mmol) of 10-oxoundecanal³⁶ in 6 ml of carbon tetrachloride was stirred over 2.14 g of dehydrated alumina and 103 mg (1.72 mmol) of 2-propanol at 25 °C for 2 h. Filtration and removal of the solvent afforded 60.0 mg (85%) of a white, crystalline material. Recrystallization from petroleum ether afforded 48.4 mg (68%) of 10-oxoundecanol: mp 35–36 °C (lit.³⁶ mp 42–43 °C); λ_{\max} (film) 2.95, 3.42, 3.50, 5.88, 6.82, 7.33, and 9.50 μ ; δ (CDCl₃) 1.30–1.80 (14 H, chain), 2.12 (s, 3 H, -COCH₃), 2.40 (t, 2 H, -CH₂CO), and 3.60 ppm (t, 2 H, -OCH₂-).

Reduction of 4,17(20)-Pregnadien-3-one-20-carboxaldehyde (3) with 2-Propanol on Alumina. 4,17(20)-Pregnadien-3-one-20-carboxaldehyde (3, 100 mg, 0.306 mmol) in 6 ml of CCl₄ was stirred over 5.0 g of dehydrated alumina and 503 mg (8.3 mmol) of 2-propanol at 25 °C for 24 h. Filtration and removal of the solvent afforded 96 mg of a light yellow oil. Preparative thin layer chromatography of 67 mg (double development with 3:1 diethyl ether-petroleum ether) gave 8.5 mg (13%) of starting material, mp 148–150 °C, 26.6 mg (40%) of one of the geometric isomers of 4,17(20)-pregnadien-3-on-21-ol (4) [mp 155–156 °C; IR (CHCl₃) 3615 (w), 3570–3220 (b), 3090 (w), 3000 (sh), 2940 (s), 2840 (m), 1660 (s), 1615 (w), 1010 cm⁻¹ (s); NMR (CDCl₃) δ 5.78 (s, 1 H, =CHC=O), 4.9 (d, 2 H, -CH₂OH), 2.6–0.8 (b); mass spectrum (70 eV) m/e 310 (M⁺ - 18) 31%, 295 (M⁺ - 18 - Me) 44%, 83 (base) 100%], and 14 mg (21%) of the other geometric isomer of 4 as an oil [IR (CHCl₃) 3620 (w), 3560–3180 (b), 3090 (w), 3000 (sh), 2990 (s), 2940 (s), 2840 (s), 1660 (s), 1615 (w), 1010 cm⁻¹ (s); NMR (CDCl₃) δ 5.78 (s, 1 H, =CHC=O), 4.2 (d, 2 H, -CH₂OH), 2.6–0.8 (b); mass spectrum (70 eV) m/e 328 (M⁺) 2%, 310 (M⁺ - 18) 30%, 295 (M⁺ - 18 - Me) 42%, 83 (base) 100%]. Anal. Calcd for C₂₂H₃₂O₂: C, 80.43; H, 9.82. Found: C, 80.07; H, 9.74.

Competition between Decanal and 4-tert-Butylcyclohexanone for a Limited Amount of 2,4-Dimethyl-3-pentanol. A solution of 107 mg (0.70 mmol) of 4-tert-butylcyclohexanone and 144 mg (0.73 mmol) of decanal in 6 ml of carbon tetrachloride was stirred over 5.63 g of dehydrated alumina and 563 mg (4.85 mmol) of 2,4-dimethyl-3-pentanol at 25 °C for 24 h. Gas-liquid phase chromatography (10 ft \times 0.25 in., 10% Carbowax 20M on Chromosorb W 60/80) showed there to be 84% reduction of the decanal and only 13% reduction of the 4-tert-butylcyclohexanone. Retention times at 120 °C with a flow rate of 60 ml/min were 9.2 (decanal), 18.0 (4-tert-butylcyclohexanone), 22.7 (*cis*-4-tert-butylcyclohexanol), 28 (*trans*-4-tert-butylcyclohexanol), and 30.5 min (decanol). All products were identified by comparison with authentic samples.

Cholesterol from Δ^5 -Cholesten-3-one. A solution of 441 mg (1.15 mmol) of Δ^5 -cholesten-3-one in 6 ml of carbon tetrachloride was stirred over 3.00 g of dehydrated alumina and 307 mg (5.3 mmol) of 2-propanol at 25 °C for 24 h. Filtration and removal of the solvent afforded 476 mg of a white, crystalline material, mp 128–130 °C. Chromatography on 50 ml of silica gel using Et₂O/petroleum ether

as eluent gave 45 mg (10%) of Δ^4 -cholesten-3-one, mp 77–78 °C (lit.³⁶ mp 81–82 °C), and 290 mg (67%) of cholesterol, mp 146 °C (lit.³⁶ mp 148.5 °C).

Stability of Δ^4 -Androstene-3,17-dione toward 2-Propanol on Alumina. A solution of 308 mg (1.08 mmol) of Δ^4 -androstene-3,17-dione in 6 ml of carbon tetrachloride was stirred over 2.65 g of dehydrated alumina and 275 mg (4.75 mmol) of 2-propanol at 25 °C for 24 h. Filtration and removal of the solvent afforded 337 mg of a white, crystalline material, mp 163–165 °C. Chromatography on 35 ml of silica gel using Et₂O as eluent gave 295 mg (95%) of Δ^4 -androstene-3,17-dione which was identical in all respects (including melting point) with the starting material.

2-Propanol on Alumina Reduction of Steroidal Diones. A. 5 α -Cholestane-3,6-dione (5). A solution of 261 mg (0.65 mmol) of 5 α -cholestane-3,6-dione in 6 ml of carbon tetrachloride was stirred over 1.53 g of dehydrated alumina and 155 mg (2.67 mmol) of 2-propanol at 25 °C for 24 h. Filtration and removal of the solvent afforded 276 mg of a white, crystalline material, mp 100 °C. Chromatography on silica gel using Et₂O/petroleum ether as eluent gave 69 mg (26%) of the starting dione, 34 mg (13%) of 5 α -cholestan-3 α -ol-6-one, mp 154–155 °C (lit.³⁷ mp 157–159 °C), and 134 mg (51%) of 5 α -cholestan-3 β -ol-6-one, mp 147–148 °C (lit.³⁸ mp 142–144 °C). The spectral data were identical with those of authentic material.

B. 5 α -Pregnane-3,20-dione (6). A solution of 155 mg (0.49 mmol) of 5 α -pregnane-3,20-dione in 6 ml of carbon tetrachloride was stirred over 1.20 g of dehydrated alumina and 126 mg (2.17 mmol) of 2-propanol at 25 °C for 24 h. Filtration and removal of the solvent afforded 156 mg of a white crystalline material, mp 184 °C. Chromatography on silica gel using Et₂O/petroleum ether as eluent gave 3 mg (2%) of 5 α -pregnan-3 β -ol-20-one, 3 mg (2%) of the starting dione, and 131 mg (84%) of 5 α -pregnan-3 β -ol-20-one, mp 188–189 °C (lit.³⁹ mp 190–196 °C).

C. 5 β -Androstane-3,17-dione (7). A solution of 320 mg (1.11 mmol) of 5 β -androstane-3,17-dione in 6 ml of carbon tetrachloride was stirred over 2.78 g of dehydrated alumina and 281 mg (4.85 mmol) of 2-propanol at 25 °C for 24 h. Filtration and removal of the solvent afforded 337 mg of a glassy material. Chromatography on silica gel using Et₂O/petroleum ether as eluent gave 76 mg (24%) of 5 β -androstane-3 β -ol-17-one and 231 mg (72%) of 5 β -androstane-3 α -ol-17-one having the same spectral properties as those reported in the literature.⁴⁰

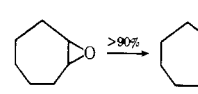
D. 5 α -Androstane-3,17-dione (8). A solution of 252 mg (0.88 mmol) of 5 α -androstane-3,17-dione in 6 ml of carbon tetrachloride was stirred over 2.13 g of dehydrated alumina and 227 mg (3.92 mmol) of 2-propanol at 25 °C for 24 h. Filtration and removal of the solvent afforded 269 mg of a white, crystalline material, mp 152–154 °C. Chromatography on silica gel using Et₂O/petroleum ether as eluent gave 5 mg (2%) of 5 α -androstane-3 α -ol-17-one, 9 mg (4%) of the starting dione, and 240 mg (95%) of 5 α -androstane-3 β -ol-17-one, mp 167–168 °C (lit.⁴¹ mp 173–174 °C). The products were spectroscopically identical with authentic materials.

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Registry No.—RCHO (R = C₉H₁₉), 112-31-2; RCHO (R = C₆H₅CH₂), 122-78-1; RCHO (R = C₆H₅CH(CH₃)), 93-53-8; RCHO (R = C₆H₅), 100-52-7; RCHO (R = *p*-O₂NC₆H₄), 555-16-8; RCHO (R = *p*-CH₃CONHC₆H₄), 122-85-0; RCHO (R = C₆H₅CH=CH), 104-55-2; RCHO (R = (CH₃)₂C=CH(CH₂)₂CH=CH), 54717-64-5; 1, 61268-05-1; 1 allylic alcohol, 61268-06-2; 2, 61268-07-3; 2 allylic alcohol, 61268-08-4; 3, 50323-70-1; E-4, 61268-09-5; Z-4, 61268-10-8; 2-propanol, 67-63-0; 2,4-dimethyl-3-pentanol, 600-36-2; benzyl alcohol-d₁, 4546-45-6; 10-oxoundecanal, 36219-78-0; 10-oxoundecanol, 35345-72-3; C₆H₅COCHO, 1074-12-0; 8-oxabicyclo[5.1.0]octane, 286-45-3.

References and Notes

- For a preliminary account of this work, see G. H. Posner and A. W. Runquist, *Tetrahedron Lett.*, 3801 (1975).
- To whom correspondence should be addressed.
- (a) H. O. House, "Modern Synthetic Reactions", 2d ed, W. A. Benjamin, New York, N.Y., 1972, Chapters 1–3; (b) J. Fried and J. A. Edwards, Ed., "Organic Reactions in Steroid Chemistry", Vol. 1, Von Nostrand-Reinhold, Princeton, N.J., 1972, Chapters 1–4; (c) D. Caine, *Org. React.*, **23**, 1 (1976); (d) E. R. H. Walker, *Chem. Soc. Rev.*, **5**, 23 (1976).
- H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, Chapters 12, 13.
- R. O. Hutchins and D. Kandasamy, *J. Am. Chem. Soc.*, **95**, 6131 (1973); *J. Org. Chem.*, **40**, 2530 (1975); see also D. J. Raber and W. C. Guida, *ibid.*, **41**, 690 (1976).
- S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **40**, 1864 (1975); in press; see also H. C. Brown, S. Krishnamurthy, and N. M. Yoon, *ibid.*, **41**, 1778 (1976).
- By this procedure, Woelm W-200 alumina loses 3–4% of water by weight; for a study of the surface hydration of γ -alumina see J. B. Peri, *J. Phys. Chem.*, **69**, 211 (1965).
- (a) Vapor phase (300 °C) reduction of carbonyl compounds by alcohols over alumina has been reported: D. V. Ramana and C. N. Pillai, *Can. J. Chem.*, **47**, 3705 (1969); *Indian J. Chem.*, **8**, 1106 (1970); L. H. Klemm and D. R. Taylor, *J. Org. Chem.*, **35**, 3216 (1970). (b) For use of ethanol on nondehydrated alumina for carbonyl reduction, see A. Ichihara and T. Matsumoto, *Bull. Chem. Soc. Jpn.*, **47**, 1030 (1974). (c) For redox reactions of ketols on alumina see W. Acklin and V. Prelog, *Helv. Chim. Acta.*, **42**, 1239 (1959); K. Yoshida and T. Kubota, *Tetrahedron Lett.*, 2833 (1976). L. Cotler and G. Descotes, *Bull. Soc. Chim. Fr.*, 1072 (1972). (d) For radiochemical reduction of ketones using 2-propanol see E. Alipour, J. C. Michéau, N. Pallous, J. Mathieu, and A. Lattes, *Tetrahedron Lett.*, 2833 (1976). (e) See also H. Sugimoto and K. Kato, *ibid.*, 4143 (1973).
- "W-200-N-D" stands for "Woelm, activity 200, neutral, dehydrated".
- (a) A. L. Wilds, *Org. React.*, **2**, 178 (1944); (b) S. Patai, Ed., "The Chemistry of the Carbonyl Group", Interscience, New York, N.Y., 1966, Chapter 11, p 532.
- (a) F. A. Lamb, P. N. Cote, B. Slutsky, and B. M. Vittimberga, *J. Org. Chem.*, **39**, 2796 (1974); (b) A. E. T. Kulper, J. Medina, and J. J. G. M. von Bokhoven, *J. Catal.*, **29**, 40 (1973); (c) for a discussion of secondary reactions caused by alumina see E. Lederer and M. Lederer, "Chromatography, a Review of Principles and Applications", Elsevier, Amsterdam, 1957, Chapter 8.
- M. R. Johnson and B. Rickborn, *J. Org. Chem.*, **35**, 1041 (1970).
- M. J. Jorgenson, *Tetrahedron Lett.*, 559 (1962).
- K. E. Wilson, R. T. Seidner, and S. Masamune, *Chem. Commun.*, 213 (1970); see also E. Winterfeldt, *Synthesis*, 617 (1975).
- We thank Dr. Norman Elmore of I.C.I., Pharmaceuticals Division, for a gift of chromones 1 and 2 and for the information on the unsuccessful attempts to reduce these two chromones with standard reducing reagents.
- (a) V. J. Hruby, *Proc. N. Dak. Acad. Sci.*, **16**, 12 (1962); *Chem. Abstr.*, **62**, 1589 (1965); (b) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969); (c) J. Shabtai, L. H. Klemm, and D. R. Taylor, *ibid.*, **35**, 1075 (1970).
- Compare deuteride transfer from 2-deuterio-2-propanol in refluxing aqueous ethanolic potassium hydroxide: R. Caputo, L. Mangoni, P. Monaco, G. Palumbo, and L. Previtera, *Tetrahedron Lett.*, 1041 (1975).
- (a) We have observed only two instances when 2-propanol on W-200-N-D alumina underwent transfer of the entire isopropoxide group:

$$\text{C}_6\text{H}_5\text{COCHO} \xrightarrow{>35\%} \text{C}_6\text{H}_5\text{-C} \begin{array}{l} \text{OH} \\ | \\ \text{CHO} \\ | \\ \text{i-PrO} \end{array} \quad (\text{i})$$


$$\text{Epoxide} \xrightarrow{>90\%} \text{Diol-i-PrO} \quad (\text{ii})$$
- (b) For similar nucleophilic epoxide openings by alcohol-doped alumina see G. H. Posner, D. Z. Rogers, C. M. Kinzig, and G. M. Gurria, *Tetrahedron Lett.*, 3597 (1975).
- In contrast, undoped alumina has been used to effect $\beta, \gamma \rightarrow \alpha, \beta$ -enone isomerization [J. A. Marshall and G. M. Cohen, *J. Org. Chem.*, **36**, 877 (1971)] and ketone enolization [D. H. R. Barton and W. C. Taylor, *J. Chem. Soc.*, 2500 (1958)], and we have found that some undoped W-200-D alumina causes intramolecular aldol condensation of a keto aldehyde to form a 3-hydroxycyclopentanone (unpublished results of C. M. Lentz).
- For overall reduction at C₁₇ of Δ^4 -androstene-3,17-dione see U. Eder, *Chem. Ber.*, **109**, 2954 (1976).
- (a) O. H. Wheeler and J. L. Mateos, *Chem. Ind. (London)*, 395 (1957); *Can. J. Chem.*, **36**, 1049 (1958); (b) J. Fajkos, *Collect. Czech. Chem. Commun.*, **24**, 2284 (1959); (c) for reduction of a β, γ -enone see W. F. Johns, *J. Org. Chem.*, **29**, 1490 (1964); (d) M. H. Boutigue and R. Jacquesy, *C. R. Acad. Sci., Ser. C.*, **276**, 437 (1973).
- For a general discussion see K. Tanabe, "Solid Acids and Bases, Their Catalytic Properties", Academic Press, New York, N.Y., 1970.
- N. H. Andersen and H. Uh, *Synth. Commun.*, **3**, 115 (1975).
- M. Fetizon and M. Gouffier, *C. R. Acad. Sci., Ser. C*, **267**, 900 (1968); F. Kakis, M. Fetizon, N. Douckine, M. Gouffier, P. Morgues, and T. Prange, *J. Org. Chem.*, **39**, 523 (1974).
- G. Cainelli, G. Cardillo, M. Orena, and S. Sundri, *J. Am. Chem. Soc.*, **98**, 6737 (1976).
- J. M. Lalancette, G. Rollin, and P. Cumas, *Can. J. Chem.*, **50**, 3058 (1972).
- Z. Cohen, E. Keinan, Y. Mazur, and T. H. Varkony, *J. Org. Chem.*, **40**, 2141 (1975).
- H. Klein and A. Steinmetz, *Tetrahedron Lett.*, 4249 (1975).
- E. C. Taylor, C.-S. Chiang, A. McKillop, and J. F. White, *J. Am. Chem. Soc.*, **98**, 6750 (1976).
- F. Schwowoch and L. Puppe, *Angew. Chem., Int. Ed. Engl.*, **14**, 620 (1975).
- E. Biran Ph.D. Thesis, Weizmann Institute of Science, Rehovot, Israel, 1975.
- G. H. Posner, D. Z. Rogers, C. M. Kinzig, and G. M. Gurria, *Tetrahedron Lett.*, 3597 (1975).
- See, for example, C. J. Cheer and C. R. Johnson, *J. Am. Chem. Soc.*, **90**, 178 (1968).

- (34) The surface character of alumina is modified by alcohol adsorption: G. C. Bye and G. O. Chigko, *Chem. Ind. (London)*, 31 (1972).
 (35) "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, 1968.
 (36) L. Cotier and G. Descotes, *Bull. Soc. Chim. Fr.*, 4557 (1971).
 (37) J. M. Coxon, M. P. Hurtshorn, and C. N. Muir, *Tetrahedron Lett.*, 3925 (1969).
 (38) D. J. Collins and J. J. Hobbs, *Aust. J. Chem.*, 17, 661 (1964).
 (39) M. Matsui and D. K. Fukushima, *J. Org. Chem.*, 35, 561 (1970).
 (40) (a) K. Dobriner, E. R. Katzenellenbogen, and N. R. Jones, "Infrared Absorption Spectra of Steroids", Vol. 1, Interscience, New York, N.Y., 1953; (b) G. Roberts, B. S. Gallagher, and R. N. Jones, *ibid.*, Vol. 2, 1958.
 (41) G. R. Pettit, A. K. DasGupta, and R. L. Smith, *Can. J. Chem.*, 44, 2023 (1966).

Studies on Friedel-Crafts Chemistry. 2. The $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ Catalyzed Novel Transbenzylation of 4,4'-Dihydroxydiphenylmethanes in Toluene¹

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In the $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ catalyzed transalkylation of 3,5,3',5'-tetra-*tert*-butyl- (9), 3,3'-di-*tert*-butyl- (21), and 3,3'-di-*tert*-butyl-5,5'-dimethyl-4,4'-dihydroxydiphenylmethane (25), it was found that not only *tert*-butyl but also benzyl groups were transferred to toluene used as a solvent and an acceptor of the alkyl group, and that the transbenzylation of 3,3'-dimethyl-4,4'-dihydroxy- (29), 3,3'-dimethyl-4,4'-dimethoxy- (31), and 3,5,3',5'-tetramethyl-4,4'-dihydroxydiphenylmethane (34) took place even under the influence of $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ catalyst which has been known to be inactive in the transbenzylation and isomerization of diphenylmethanes. The mechanism of the $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ catalyzed transbenzylation is discussed.

It has been previously reported that 2,2'-dihydroxydiphenylmethane (2),² 2,2'-dihydroxy- (6),³ and 4,4'-dihydroxydiphenyls³ were easily prepared by the $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ or AlCl_3 catalyzed transalkylation of the corresponding *tert*-butyl derivatives in benzene as shown in Scheme I.

These results suggest that 4,4'-dihydroxydiphenylmethanes as well as 2, 6, and 8 might be prepared by the same manner under the influence of $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ catalyst which is known to be active in the transalkylation of the *tert*-butyl group of

tert-butylbenzenes²⁻⁶ but not in the transalkylation and isomerization of diphenylmethanes.^{2,6-11}

We now wish to report the $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ catalyzed transalkylation of 3,5,3',5'-tetra-*tert*-butyl- (9), 3,3'-di-*tert*-butyl- (21), and 3,3'-di-*tert*-butyl-5,5'-dimethyl-4,4'-dihydroxydiphenylmethane (25) and of the related compounds such as 3,3'-dimethyl-4,4'-dihydroxy- (29), 3,3'-dimethyl-4,4'-dimethoxy- (31), and 3,5,3',5'-tetramethyl-4,4'-dihydroxydiphenylmethane (34) in toluene.

