References and Notes

(1) F.F. and A.T. are indebted to NATO and the Italian National Research Council (CNR) for support of this work.
(2) (a) Università di Perugia; (b) Rice University.
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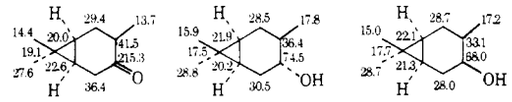

62930-42-1 62930-43-2 62961-15-3

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Organic Reactions at Alumina Surfaces. A Mechanistic and Synthetic Study of Sulfonate Ester Elimination Reactions Effected by Chromatographic Alumina[1,2]

Gary H. Posner,* George M. Gurria, and Kevin A. Babiak

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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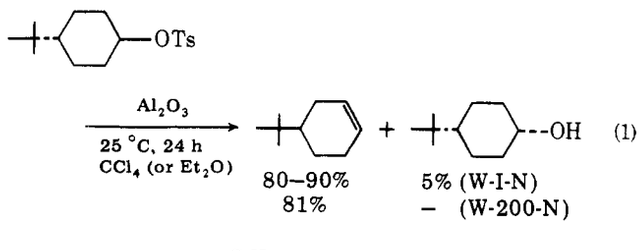
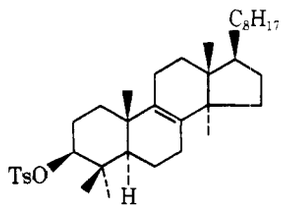
Chromatographic, neutral, highly active Woelm alumina has been used at room temperature for high-yield dehydrosulfonation of some secondary cyclic and acyclic and some primary sulfonate esters. Evidence is presented for the concertedness of these olefin-forming elimination reactions, and application is made to gram-scale chemospecific elimination of sulfonic acids from some highly functionalized esters. The scope and limitations of this heterogeneous procedure are presented, and the practical advantages and disadvantages are noted. Some practical guidelines are suggested for which activity of alumina is needed for optimal elimination reactions, and some generalizations are made concerning the structural types of sulfonate esters which would be most suitable for this alumina promoted dehydrosulfonation reaction.

The very large number of olefin-forming elimination reactions indicates the importance of alkenes as synthetic intermediates and as ultimate target molecules.[3] Because of this importance, new reagents and new synthetic methods are constantly being sought which offer some advantages over known procedures for alkene formation.[4] Recently we have developed a very mild, convenient, and high-yield method for converting some sulfonate esters into the corresponding olefins even in the presence of normally base and acid labile (e.g., carboxylic ester) groups; even some neopentylic tosylates undergo elimination *without skeletal rearrangement*, and in all cases product isolation is easy. These concerted, heterogeneous elimination reactions are effected simply by stirring solutions of the sulfonate esters over untreated[5a] or vacuum-dehydrated[5b] commercial Woelm chromatographic alumina at room temperature. This procedure has some practical advantages over other methods for overall dehydration of alcohols, and it has been chosen recently by other laboratories to prepare some cycloalkenes.[6] We now conclude our study of this alumina procedure by illustrating its application to preparative scale (several grams) reactions, by demonstrating its chemoselectivity in converting a steroidal tetraester into the corresponding olefinic triester, and by extending its scope to conversion of primary cyclohexylmethyl tosylate esters into methylenecyclohexanes. The mechanistic and synthetic aspects of the discussion are organized according to the type of organic reactant: (1) secondary cyclic systems; (2) secondary acyclic systems; and (3) primary systems.

Results and Discussion

Secondary Cyclic Systems. Sulfonate esters are known to undergo concurrent elimination and hydrolysis reactions when exposed to chromatographic alumina.[7,8] We have studied the effect of alumina activity (i.e., dryness) on the ratio of dehydrosulfonation to hydrolysis using Woelm neutral activity I,[5a] activity super-I (W-200-N), and activity super-I-dehydrated (W-200-N-Dehydrated)[5b] alumina.[9] Of these three types of alumina, W-200-N-Dehydrated alumina converts sulfonates into the corresponding olefins with the least amount of alcohol (i.e., hydrolysis) side products; however, W-200-N-Dehydrated alumina has the operational disadvantages of having to be prepared by 400 °C vacuum dehydration of commercially available W-200-N alumina and having to be used immediately after preparation. For convenience and operational simplicity, we have therefore recently examined commercially available W-200-N alumina itself; we now report that *untreated W-200-N alumina used directly from the commercial can* is sufficiently dry to convert substituted *cyclohexyl* tosylates into the corresponding olefins with very little (<2%) or, in some cases, with no alcohol side





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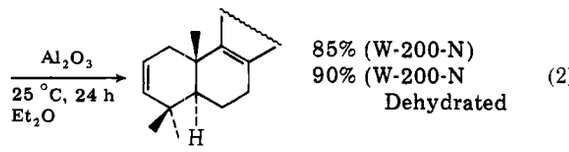


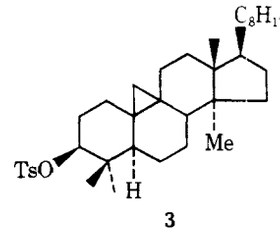
2

products. Equations 1 and 2 illustrate that activity I alumina leads to a small amount of hydrolysis, whereas W-200-N and W-200-N-Dehydrated alumina produce olefins as the only detectable products.

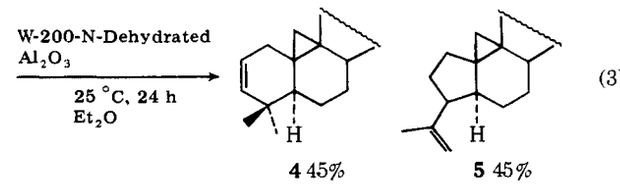
To illustrate the effectiveness of this synthetic method on a preparative scale, 4.2 g of 4-*tert*-butylcyclohexyl tosylate was converted over W-200-N alumina into 4-*tert*-butylcyclohexene reproducibly in 68–81% yield (eq 1). We have recently reported 2-propanol/alumina high-yield and selective reductions of 6–8 g of some steroidal ketones.[2] Thus multigram scale organic reactions at alumina surfaces are practical, convenient, and economical. With our usual ratio of 5 g of alumina/mmol of substrate and at the current price of W-200-N alumina (approximately $25/500 g), the cost for alumina is roughly 25 cents for conversion of 1 mmol of sulfonate into olefin.

In contrast to the effectiveness of activated Woelm alumina in causing dehydrosulfonation of lanosteryl tosylate **1**, Baker reagent-grade aluminum oxide powder activated at 400 °C under vacuum did not consume any of tosylate **1**!

An *unexpected benefit* was associated with the use of W-200-N (or W-200-N-Dehydrated) alumina rather than some less active forms of alumina: neopentylic tosylate **1** underwent elimination *without skeletal rearrangement*![5b] Previously, lanosteryl tosylate **1** had been observed to react on alumina to yield unrearranged diene **2** (43% yield) as well as some rearranged diene(s) (52% yield),[10] and Stevenson had reported a similar mixture of Δ^2-olefin and a 4 → 3 methyl shift product



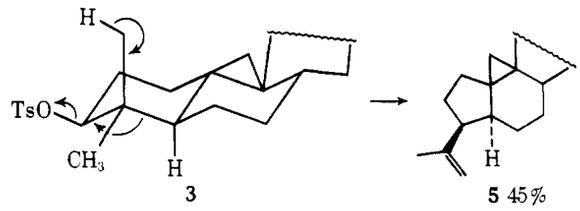
3



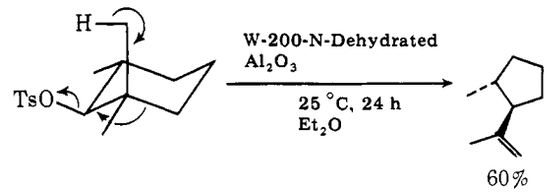
4 45% 5 45%

when some 4,4-dimethyl-3-tosyloxy steroids in the amyrin series were filtered through a column of Woelm W-I-N alumina.[11] Using Merck alumina and refluxing toluene, Barbier had observed the conversion of cycloartanyl tosylate **3** into cyclohexene **4** (1%) and isopropenylcyclopentane **5** (70% yield); our results, shown in eq 3, illustrate the use of W-200-N-Dehydrated alumina in promoting neopentylic tosylate dehydrotosylation to form equal amounts of rearranged and unrearranged olefins even in this especially rearrangement-prone system. These heterogeneous elimination reactions of neopentylic tosylates **1** and **3** are synthetically useful especially because even mild homogeneous conditions (e.g., PCl_5, 0 °C, 1 h;[13] NaOAc, H_2O, acetone[14]) and basic conditions (e.g., $CaCO_3$[13b]) produce rearranged products *exclusively*.

The absence (eq 2) or equal amount (eq 3) of rearranged products suggested that these elimination reactions occurring at the alumina surfaces may be, in part, *concerted* rather than ionic processes.[15] We have shown previously that optically active menthyl tosylate undergoes a concerted syn 1,2 elimination on alumina to the extent of at least 37%, and that optically active neomenthyl tosylate undergoes a concerted syn 1,3 elimination to the extent of about 11%.[5b] Indeed, rearranged steroidal isopropenylcyclopentane **5** could have arisen via a *concerted* 1,3 elimination, as shown in eq 4. The 1,3-elimination pathway may become predominant in some cases, as illustrated in eq 5.

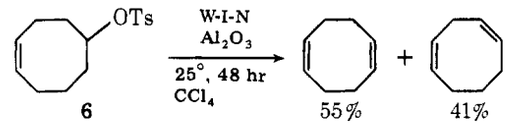


3 5 45%



60%

Another mechanistic probe for ionic (or radical[16]) intermediates involves transannular interactions in medium sized rings. We have found that cyclooctenyl tosylate **6** reacted even on unactivated W-I-N alumina to give only monocyclic diene and no bicyclic products (eq 6). In contrast, homogeneous



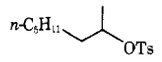
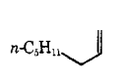
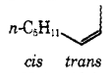
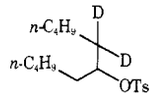
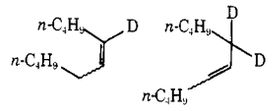
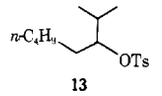
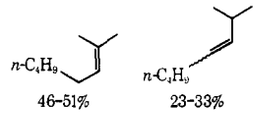
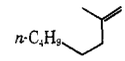
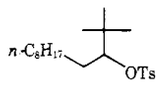
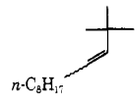
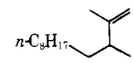
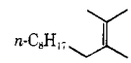
6 55% 41%

solvolysis of tosylate **6** under various conditions gave mainly bicyclic products via carbonium ion intermediates.[17]

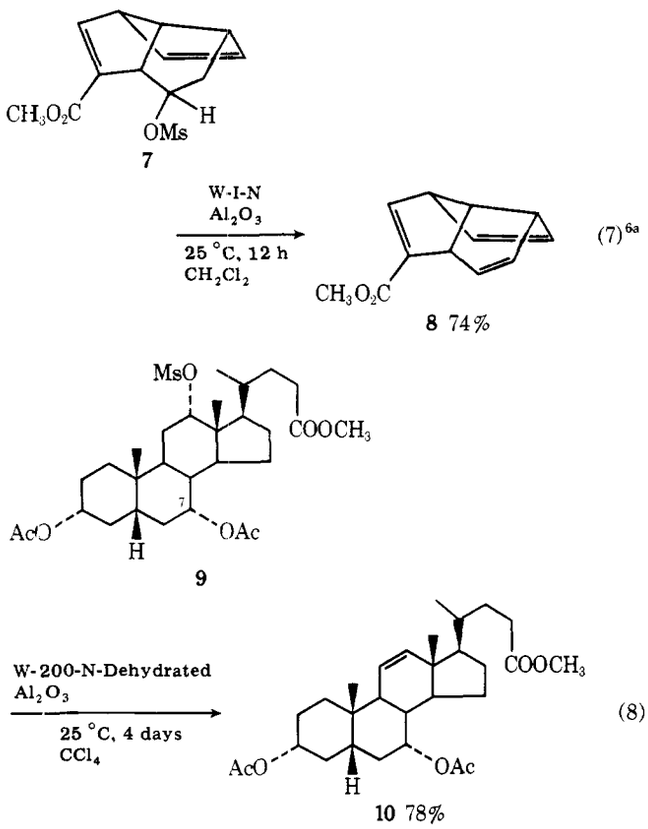
Many olefin-forming elimination reactions involve strongly acidic or strongly basic media and in some cases temperatures in excess of 200 °C.[3,4] Under such conditions many organic functional groups are unstable. We have found that W-200-N-Dehydrated alumina is highly selective for dehydrosulfonation of sulfonate esters even in the presence of such normally labile units as ketone, *carboxylic* ester, and primary and secondary iodides![5] Equations 7 and 8 illustrate the survival of *carboxylic* esters under the heterogeneous alumina reaction conditions.

Paquette has noted that preparation of triene **8** is achieved more *conveniently*, as shown in eq 7, using alumina and mesylate **7** than by direct dehydration of the corresponding alcohol using ethyl(carboxysulfamoyl)triethylammonium hydroxide inner salt.[6a] Chen has reported that transformation

Table I. Secondary Acyclic Tosylate Esters Stirred in Et_2O over W-200-N-D Alumina at 25 °C for 24 h[a,b]

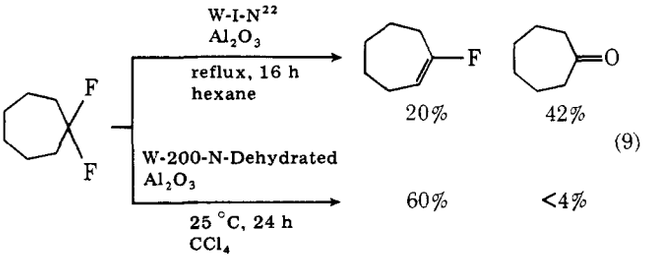
Substrate[c]	1,2-Elimination products	1,3-Elimination products	Other elimination products
 11	 22%	 cis 33% trans 12%	
 12	 1:1.9		
 13	 46-51% 23-33%	 20-26%	
 14	 cis 7% trans 13-16%	 15 59-60%	 16 10-12%

[a] Virtually no alcohol products were detected in any of these reactions using W-200-N-Dehydrated alumina. [b] No olefin isomerization took place under these reaction conditions, as shown by appropriate control experiments. [c] Registry no.: 11, 27770-99-6; 12, 62862-05-9; 13, 62862-06-0; 14, 62862-07-1.



of highly functionalized steroidal mesylate **9** into pharmacologically important cholenate **10** is very difficult using known procedures; he has therefore developed a new method to achieve specifically this conversion, which involves stirring a heterogeneous mixture of mesylate **9** in hexamethylphosphoric triamide (HMPT) containing an excess of potassium (or sodium) acetate at exactly 100 °C for 2 days; the temperature was critical and the yield of cholenate **10** was 80–85% with a small amount of concurrent elimination of the labile axial 7α-acetoxy group.[18] VPC analysis[19] indicated that the cholenate **10**, formed using our alumina procedure (eq 8), was at least as clean as that formed using Chen's procedure and that no skeletal rearrangement (13 → 12 methyl shift) had occurred during the alumina-promoted reaction of neopentylic mesylate **9**.[20,21] The chemospecificity of the alumina-promoted dehydromesylation of steroidal tetraester **9** convincingly illustrates the usefulness of this heterogeneous synthetic method for conversion of complex and polyfunctional sulfonates selectively into the corresponding olefins.

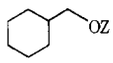
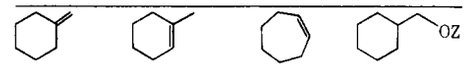
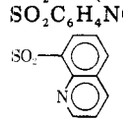
In contrast to most alkyl iodides, bromides, and chlorides, which are relatively stable to W-200-N-Dehydrated alumina at room temperature, *gem*-difluorides undergo a particularly facile dehydrofluorination to produce fluoroolefins. Boswell was the first to recognize the effectiveness of chromatographic alumina for such dehydrofluorinations, but with some particularly unreactive *gem*-difluorides he obtained mainly hydrolysis (i.e., ketone) rather than elimination products.[22] Again, using Woelm alumina dried at 400 °C, we have been able to minimize hydrolysis and to maximize dehydrofluorination, as shown with 1,1-difluorocycloheptane (eq 9).



Secondary Acyclic Systems. Whereas using either W-200-N or W-200-N-Dehydrated alumina made only a small difference in the hydrolysis/elimination ratio for most *cyclic* secondary tosylates, the ratio of hydrolysis/elimination in *acyclic* secondary tosylates was more sensitive to the water content of the alumina; 2-octyl tosylate, for example, was hydrolyzed to 2-octanol in ~30, 10–15, and 0–7% yield on W-I-N, W-200-N, and W-200-N-Dehydrated alumina, respectively.[23] Therefore, if the main objective is to obtain the *highest possible yield* of olefin from an acyclic secondary sulfonate ester, then W-200-N-Dehydrated alumina should be used; if, however, the yield of olefin is not critical, but rather a sample of the olefin is desired and it can be separated easily from ~10–15% of the corresponding alcohol, then W-200-N alumina should be used directly from the commercial can.

The results summarized in Table I show that dehydrotos-

Table II. Cyclohexanemethyl Esters Stirred over W-200-N-D Alumina at 25 °C

Registry no.	 Z=	Solvent	Time, h	Products, % yield[a]  18			
3725-11-9	SO_2Tol (17)	CCl_4[b]	24	61	8	0	27
62862-09-3	$SO_2C_6H_4NO_2$-*p*	Et_2O	44	43	18	tr	23
62862-08-2		CCl_4[b]	24	72	23	1–2	0
57346-53-9	SO_2NMe_2	CCl_4[b]	1	58	20	0	10
	SO_2NMe_2	CH_3CN (50 °C)	1	44	3	0	42
62862-10-6	SOTol	CCl_4[b]	24	2	0	0	67
62862-11-7	$CSSCH_3$	CCl_4	24	1	19	2	49
62862-12-8	$COOCH_3$	CCl_4	24	tr	4	tr	89
33026-78-7	$PO(OPh)_2$	CCl_4	24	tr	17	tr	70
62862-13-9	$PS(OMe)_2$	CCl_4	24	1	13	4	70

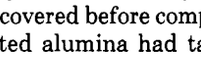
[a] VPC yields using a calibrated internal standard. [b] Alumina doped with 4% (w/w) acetonitrile.

ylation of unsymmetrical tosylates **11** and **12** over alumina proceeded preferentially, but not exclusively, in the direction of the more highly substituted β-carbon atom: methylene in preference to methyl and methine in preference to methylene. This regioselectivity represents a Saytzeff-type elimination.[3] When flanked by $-CH_2$ and $-CD_2$ as in dideuteriotosylate **12**, tosylate elimination occurred selectively in the direction of the $-CH_2$ group; k_H/k_D was about 1.88–1.94. This result is consistent with a stepwise carbonium ion mechanism or with a concerted mechanism involving little *or* much carbon–hydrogen bond heterolysis in the transitions state.[15,24] Although the carbonium ion mechanism cannot be ruled out in this case, it seems unlikely because *l*-2-octyl tosylate was not racemized when it was recovered before complete elimination over W-200-N-Dehydrated alumina had taken place. Furthermore, methanol-doped alumina converted *l*-2-octyl tosylate into *d*-2-methoxyoctane with 90–95% net inversion of configuration;[25] the high stereoselectivity of this heterogeneous displacement reaction on alumina argues against carbonium ion intermediates and argues in favor of a synchronous delivery of $-OCH_3$ and loss of $-OTs$.[26]

The stereochemistry of the olefins produced depended on the structural environment of the parent tosylate and the developing double bond: 2-octyl tosylate (**11**) yielded 2-octene in ~3:1 cis/trans ratio, whereas neopentylic tosylate **14** yielded the corresponding *tert*-butylalkenes in ~1:2 cis/trans ratio.

Encumbered tosylates **13** and **14** yielded not only 1,2-but also 1,3-elimination products; indeed the major olefinic product **15** from neopentylic tosylate **14** was a product derived from overall 1,3 elimination. Distinction between a concerted or stepwise 1,3 elimination is not possible with our data on this system. At least some carbonium ion pathway, however, must be occurring because formation of tetrasubstituted olefin **16** cannot be rationalized via any concerted elimination process;[27] a control experiment showed that tetrasubstituted alkene **16** was not formed via isomerization on alumina of terminal olefin **15**.

Primary Systems. Even with W-200-N-Dehydrated alumina, *n*-alkyl tosylates gave olefins in only very poor yields; hydrolysis was predominant. Primary tosylates having methine β-hydrogen atoms,

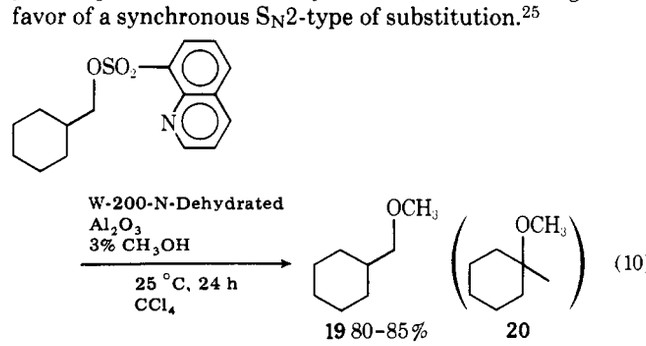


however, did undergo dehydrotosylation on W-200-N-Dehydrated alumina with virtually no accompanying hydrolysis. In this isobutylic-type of tosylate the choice of alumina activity was critical: W-I-N alumina gave 2:1 hydrolysis/elimination, whereas W-200-N-Dehydrated alumina gave olefin cleanly. Table II summarizes our results with some cyclohexanemethyl esters.

The major product in most cases in Table II was methylenecyclohexane (**18**), which is thermodynamically less stable than its double bond isomer 1-methylcyclohexene.[28] Selective formation of exocyclic alkene **18** suggested a concerted 1,2-elimination pathway rather than a stepwise ionic process which would have led mainly to 1-methylcyclohexene via a primary and then a tertiary carbonium ion. Choice of solvent was critical; under the reaction conditions, double bond isomerization from the exocyclic to the endocyclic position did not occur with diethyl ether or with CCl_4/4% CH_3CN, but such isomerization did occur with CCl_4 as solvent. Apparently Et_2O and CCl_4/4% CH_3CN were able to block the acid sites on the alumina, thus preventing double bond migration.[29]

Choice of leaving group was also important. While all sulfonate esters and even a dimethylsulfamate ester gave terminal olefin **18** in good yields, even the slight change to a *p*-tolylsulfinate ester drastically reduced the rate of ester reaction on alumina. Likewise, xanthate, carbonate, phosphate, and thiophosphate esters were found to be unreactive. We have no good explanation for the unusual difference in reactivity between the sulfonate and the other esters, especially for the large reactivity difference between sulfonate and sulfinate esters on alumina.

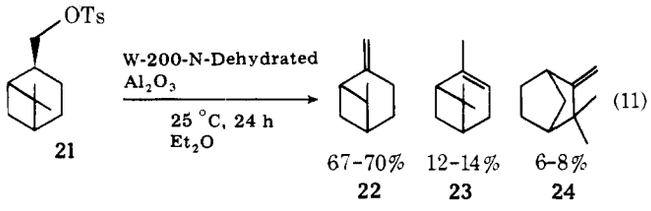
If 3% by weight of methanol was added to W-200-N-Dehydrated alumina and then cyclohexanemethyl 8-quinolinesulfonate was introduced in CCl_4 solution, a displacement reaction occurred cleanly to form methyl ether **19** in 80–85% yield (eq 10). That no tertiary ether **20** was formed argues in favor of a synchronous S_N2-type of substitution.[25]



19 80–85% **20** (10)

The synthetic utility of this conversion of primary cyclohexylmethyl tosylates into the corresponding exocyclic olefins was illustrated further with 10-pinanyl tosylate **21**, a system which is known to undergo skeletal rearrangement at the slightest provocation.[30–32] As shown in eq 11, with Et_2O (or with CCl_4/4% CH_3CN) as solvent, primary tosylate **21** reacted

at room temperature on alumina to give predominantly unrearranged β-pinene (**22**), the product of a concerted 1,2 elimination, and some α-pinene (**23**), the product of a 1,3 elimination. Camphene (**24**) probably arose via a competing ionic process; when the reaction was done in CCl_4 solvent, camphene was the major observed product. Indeed both β- and α-pinenes (**22** and **23**) isomerized to a mixture rich in camphene when they were stirred at 25 °C in CCl_4 solution over alumina, but the pinenes **22** and **23** did not isomerize over alumina with Et_2O as solvent.



(11)

Conclusions

Sulfonate ester dehydrosulfonation effected by Woelm chromatographic alumina is synthetically useful especially in the following instances: (1) when stereoelectronic factors strongly favor elimination in one of two possible directions (e.g., 3β-cholestanyl tosylate giving only 2-cholestene[5b]); (2) when elimination of a methine β-hydrogen atom does not occur because it would lead to a bridgehead double bond (e.g., sulfonate **7**); (3) when the sulfonate ester is symmetrical and elimination in either direction produces the same olefin (e.g., 4-benzoyloxycyclohexyl tosylate);[5b] (4) when a β elimination is possible in only one direction because there are no β′ hydrogen atoms (e.g., cyclic neopentylic sulfonates **1**, **3**, and **9** and cyclohexanementhyl tosylates **17** and **21**).

The major disadvantages of this heterogeneous olefin-forming procedure are as follows: (1) poor regiochemical control of olefin formation when two double bond positional isomers are possible; (2) poor stereochemical control when cis and trans alkenes are possible; (3) indirectness (i.e., alcohol → sulfonate → olefin); (4) large amount of alumina required for complete reaction (5–7 g Al_2O_3 mmol of sulfonate); and (5) the inconvenience of having to dehydrate commercial alumina in order to suppress *completely* hydrolysis of primary and acyclic secondary tosylates.

The major advantages of this sulfonate elimination procedure are as follows: (1) inertness of many acid- and base-sensitive organic functional groups; (2) concerted elimination without skeletal rearrangement of some highly rearrangement-prone tosylates; (3) convenience of using commercially available W-200-N alumina for elimination without any significant amount of hydrolysis, particularly of cyclic secondary sulfonates; and (4) ease of product isolation (i.e., filtration of alumina and evaporation of solvent).

The practical advantages of Woelm chromatographic alumina for introducing double bonds into polyfunctional and complex compounds will make this heterogeneous "reagent" useful to organic chemists.

Experimental Section

Analytical vapor-phase chromatography (VPC) was performed on a Varian Aerograph Model 1200, and preparative vapor-phase chromatography was done on a Varian Aerograph Model 90-P3.

Spectral data were obtained with a Perkin-Elmer 457-A or 337 infrared spectrometer and a Varian A-60 or Jeol MH-100 NMR spectrometer. Mass spectra (70 eV) were measured on a Hitachi RMU-6 mass spectrometer. Optical rotations were measured on solutions in a 10-cm micro cell with a Perkin-Elmer Model 141 polarimeter. Elemental analyses were done by Chemalytics, Inc. (Tempe, Ariz.), or by Micro-Tech Laboratories, Inc. (Skokie, Ill.).

All substrates and standards were best commercially available reagent grades or were prepared from such. Purity was tested before use. All solvents and doping agents were reagent grade and were dried before use (except carbon tetrachloride and freshly opened anhydrous ether, as received). Woelm aluminum oxide, W-200 neutral (activity grade super I), was obtained from ICN Pharmaceuticals, Inc. (Cleveland, Ohio).

***trans*-4-*tert*-Butylcyclohexyl Tosylate.** According to the general procedure described previously,[5b] a solution of 4.15 g (3.4 mmol) of 4-*tert*-butylcyclohexyl tosylate[33] in 120 mL of anhydrous diethyl ether was stirred over 70 g of W-200-N alumina at 25 °C for 24 h. Analytical VPC (10 ft × ⅛ in., 5% SE-30) analysis using a calibrated standard indicated the presence of 4-*tert*-butylcyclohexene (81%) and no *cis*-4-*tert*-butylcyclohexanol. Filtration through Celite, washing with 150 mL of 1:1 Et_2O/CH_2Cl_2, and evaporation of most of the solvent and bulb-to-bulb distillation (15–20 mm, 60 °C) gave 1.26 g (68%) of a clear oil: $n^{20}D$ 1.458 (lit.[34] $n^{20}D$ 1.459); NMR (CCl_4) δ 5.5 (M, 2 H, vinylic H), 0.84 (s, 9 H, *tert*-butyl), identical with that of an authentic sample.[33]

Cycloartanyl Tosylate (3). A solution of 128.3 mg (0.22 mmol) of cycloartanyl tosylate (**3**) (mp 143–146 °C; lit.[12] 144–147 °C) in 8 mL of dry ether was stirred over 7.45 g of W-200-N-Dehydrated alumina at 25 °C for 1 day. Rotary evaporation of the methylene chloride/ether (1:1) extract gave 81.5 mg (90%) of a clear colorless oil, shown by NMR to be a 1:1 mixture of olefin **4** (9,19-cyclo-9-lanost-2-ene) and olefin **5** (3β-isopropenyl-14α-methyl-9,19-cyclo-*A*-nor-5α,9β-cholestane): NMR (CCl_4) δ 5.4 (m, 2 H, Δ2 olefin **4**), 4.61 (m, 2 H, isopropenyl olefin **5**), 2.6–0.6 (m, steroid nucleus), 0.65 (d, unresolved from nucleus band; H_B of 9,19-cyclopropane[12]), 0.35 (d, 1 H, H_A of 9,19-cyclopropane[12] in Δ2 olefin **4**), −0.18 (d, 1 H, H_A of 9,19-cyclopropane[12] in isopropenyl olefin **5**).

***trans*-2,2,6-Trimethylcyclohexyl Tosylate.** A solution of 265 mg (0.89 mmol) of *trans*-2,2,6-trimethylcyclohexyl tosylate (mp 69 °C, NMR δ 4.02, 4.20 (d, >CHOTs), separated by recrystallization from some *cis* isomer, NMR δ 4.4 >CHOTs][35] in 8 mL of dry ether was stirred over 6.3 g of W-200-N-Dehydrated alumina at 25 °C for 1 day. Filtration through Celite, washing with 30 mL of 1:1 Et_2O/CH_2Cl_2, and analytical VPC (10 ft × ⅛ in., 5% SE-30) analysis using *n*-decane as a calibrated internal standard indicated the presence of one major component (60% yield) along with several minor components (~25% yield). Preparative VPC (10 ft × ¼ in., 20% SE-30) gave a clear oil, *trans*-2-isopropenyl-1-methylcyclopentane;[36] IR (CCl_4) 885 cm^{-1} (=CH_2); NMR (CCl_4) δ 0.9 (d, CH_3), 1.65 (br s, allylic CH_3), 4.7 (s, =CH_2); mass spectrum (*m/e*) 124; $n^{23}D$ 1.4423 (lit.[36] $n^{25}D$ 1.4430).

4-Cyclooctenyl Tosylate (6). A solution of 280 mg (1.0 mmol) of 4-cyclooctenyl tosylate (**6**) (mp 47 °C, lit.[17b] mp 47–48 °C) in 3 mL of carbon tetrachloride was stirred over 4.0 g of W-I-N alumina at 25 °C for 48 h. Analytical VPC (10 ft × ⅛ in. FFAP) using 1-tetradecene as a calibrated internal standard showed 1,5-cyclooctadiene (55%) and 1,4-cyclooctadiene (41%). Careful distillation removed most of the CCl_4 solvent and preparative VPC gave pure 1,5-cyclooctadiene [NMR (CCl_4) δ 2.33 (m, 8 H, allylic H), 5.5 (m, 4 H, vinylic); IR (CCl_4) 3000, 2930, 2880 cm^{-1}, identical with that of an authentic sample] and 1,4-cyclooctadiene [NMR (CCl_4) δ 1.2–1.7 (m, 2 H), 2.0–3.0 (m, 6 H, allylic), 5.0–5.9 (m, 4 H, vinylic).

Methyl 3α,7α-Diacetoxy-12α-mesyloxy-5β-cholanate (9). A solution of 201.9 mg (0.34 mmol) of cholanate (**9**) (mp 83–86 °C; lit.[18] mp 85–86 °C) in 4.5 mL of carbon tetrachloride was stirred over 3.91 g of W-200-N-Dehydrated alumina at 25 °C for 3 days. Filtering and rinsing the alumina with 30 mL of ether/methylene chloride (1:1) and with 70 mL of acetonitrile in a Hirsch funnel, followed by removal of solvent by rotary evaporation, gave 158.3 mg of a slightly yellow oil, shown by NMR to contain 77% methyl 3α,7α-diacetoxy-5β-chol-11-enate (**10**) and 23% starting ester (**9**). Further reaction of the material in carbon tetrachloride over 4.82 g of fresh dehydrated alumina for 1.5 days, followed by the same product isolation, gave 141 mg of oil shown by NMR and GLC to be a 94:6 mixture of Δ^{11}-olefin **10** (78% yield) and starting ester **9** (5% recovery), with no observable diene product. Methyl 3α,7α-diacetoxy-5β-chol-11-enate (**10**): NMR[37] ($CDCl_3$) δ 6.15 and 5.44 (AB, q, 2 H, Δ^{11}-olefin), 5.00 (m, 1 H, 7β-H), 4.58 (m, 1 H, 3β-H), 3.65 (s, 3 H, methyl ester), 2.00 and 2.04 (pair of s, 6 H, acetates); mp 140–140.5 °C (lit.[18] 139–141 °C) after preparative thin-layer chromatography and recrystallization from methanol.

1,1-Difluorocycloheptane. A solution of 74.8 mg (0.55 mmol) of 1,1-difluorocycloheptane and 56.5 mg of nonane (calibrated internal standard) in 4 mL of carbon tetrachloride was stirred over 3.45 g of W-200-N-Dehydrated alumina at 25 °C for 1 day. Analysis by VPC (10 ft × ⅛ in., 5% SE-30 on Chromosorb W 100/120) of the methylene chloride/ether (1:1) extract showed 60% 1-fluorocycloheptene and 4% cycloheptanone (comparison to knowns) with no recovered starting material. Preparative VPC (10 ft × ¼ in., 20% SE-30 on Chromosorb W 45/60) of the product of a separate run afforded pure 1-fluorocycloheptene: $n^{21}D$ 1.4360 (lit.[22a] $n^{25}D$ 1.4359); NMR (CCl_4) δ 5.28 (d of

Table III. Physical and Spectral Properties of Cyclohexylmethyl Esters

Z=	n_D, T °C	Mp or bp (torr), °C	IR, cm^{-1}	NMR (CCl_4), δ (ppm)	Comments
SO_2Tol		30–31 (lit.[42] 30–31)	(CCl_4), 1370 (br, $\nu_{AS}SO_2$), 1186 and 1174 (s, sharp, ν_SSO_2)	3.74 (d, J = 6 Hz, 2 H, carbinol H)	
$SO_2C_6H_4NO_2$-p		81–83	($CHCl_3$), 1559 (s, $\nu_{AS}NO_2$), 1365 (sh, $\nu_{AS}SO_2$), 1349 (s, ν_SNO_2), 1183 (s, sharp, ν_SSO_2)	($CDCl_3$), 4.92 (d, J = 6 Hz, 2 H, carbinol H)	Pale yellow crystals. Anal. Calcd for $C_{13}H_{17}NO_5S$: C, 52.20; H, 5.72; N, 4.68; S, 10.71. Found: C, 52.57; H, 5.81; N, 4.85; S, 10.67.
		74–76 (lit.[33] 76–77)	($CHCl_3$), 1355 (s, br, $\nu_{AS}SO_2$), 1176 and 1150 (s, sharp, ν_SSO_2)	($CDCl_3$), 4.11 (d, J = 6 Hz, 2 H, carbinol H)	
SO_2NMe_2	1.4602, 26	85–87 (0.13)	(film), 1360 (s, br, $\nu_{AS}SO_2$), 1171 (s, ν_SSO_2)	3.85 (d, J = 6 Hz, 2 H, carbinol H), 2.83 (s, 6 H, NCH_3)	Anal. Calcd for $C_9H_{19}NO_3S$: C, 48.84; H, 8.65; N, 6.33; S, 14.49. Found: C, 49.33; H, 9.10; N, 6.56; S, 14.34. Straw-yellow oil
SOTol	1.5361, 21.5		(film), 1132 (s, νSO)	3.7 and 3.3 [AB, m, 2 H, $CH_2OS(=O)Ar$]	
CSSMe	1.5498, 21		(film), 1220 (s, br, νC=S), 1060 (s, νCO)	4.33 (d, J = 6 Hz, 2 H, carbinol H), 2.51 (s, 3 H, SCH_3)	Anal. Calcd for $C_9H_{16}OS_2$: C, 52.89; H, 7.89; S, 31.38. Found: C, 52.36; H, 7.80; S, 30.67.
COOMe	1.4467, 18		(film), 1750 (s, νC=O), 1260 (s, br, νCO)	3.85 (d, J = 6 Hz, 2 H, $-CH_2O-$), 3.70 (s, 3 H, $-OCH_3$)	Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.91; H, 9.67.
COOPh[a]	1.4994, 25		(film), 1765 (s, νC=O), 1250 (s, br, νCO)	7.15 (m, 5 H, ArH), 3.97 (d, J = 6 Hz, 2 H, $-CH_2O-$)	Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.90; H, 7.18.
$PO(OPh)_2$	1.5301, 25		(film), 1293 (s, νP=O), 1192 (s, POC_{aryl}), 1160 (m, sharp, νPO)	3.92 (d of d, J_{HH} = 6 Hz, J_{HP} = 15.5 Hz, $-CH_2OP$)	Anal. Calcd for $C_{19}H_{23}O_4P$: C, 65.89; H, 6.69; P, 8.94. Found: C, 65.52; H, 6.69; P, 9.18.
$PS(OMe)_2$	1.4845, 18		(film), 1185 (m, νPO), 1020 (s, br, νC—O)	3.79 (d of d, $-CH_2OP$) and 3.68 (d, J_{HP} = 14 Hz, $POCH_3$, total 8 H)	Anal. Calcd for $C_9H_{19}O_3PS$: C, 45.36; H, 8.04; P, 13.00; S, 13.46. Found: C, 45.10; H, 7.94; P, 12.38; S, 13.33.

[a] Registry no.: 62862-14-0.

t, $J_{CH_2CH=}$ = 6 Hz, $J_{HC=CF}$ = 22 Hz, 1 H, olefinic), 2.5–1.1 (m, 10 H, methylenes); IR (liquid film) 2920 (s), 2840 (s), 1695 (s, νHC=CF), 1446 (s), 1371 (s), 1220 (m), 1091 (s), 1065 (s), 1010 cm^{-1} (m).

***l*-2-Octyl Tosylate (11).** A solution of 288.9 mg (1.02 mmol) of *l*-2-octyl tosylate (**11**) ($[\alpha]^{22}_D$ −8.255 ± 0.10° [cyclohexane][36]) in 8 mL of dry ether was stirred over 5.50 g of W-200-N-Dehydrated alumina at 25 °C for 2 days. Analysis by VPC (9 ft × ⅛ in., 5% SE-30 on Chromosorb G 100/140, using nonane as added, calibrated, internal standard) of the ether/methylene chloride extract showed 22% 1-octene, 12% *trans*-2-octene, 33% *cis*-2-octene, and <0.5% 2-octanol (molar percent yields, VPC comparison with known samples on two columns). No starting ester was recovered.

In a similar manner, a solution of 190.2 mg (0.67 mmol) of *l*-2-octyl tosylate (**11**) in 4.5 mL of dry ether was stirred over 3.73 g of W-200-N-Dehydrated alumina at 25 °C for *2 h*. Filtering and rinsing the alumina with 45 mL of methylene chloride/ether/acetonitrile (1:1:1), followed by rotary evaporation (residue 28.2 mg) and preparative thin layer chromatography (silica gel), gave 8 mg of pure 2-octyl tosylate. Its optical rotation, $[\alpha]^{18}_D$ −8.27 ± 0.43° (cyclohexane), indicated no racemization of starting ester (100.2 ± 6.9% retention of configuration).

5,5-Dideuterio-6-undecyl Tosylate (12). A solution of 105.0 mg (0.32 mmol) of 5,5-dideuterio-6-undecyl tosylate[39] (**12**) in 3 mL of carbon tetrachloride was stirred over 2.56 g of W-200-N-Dehydrated alumina at 25 °C for 1 day. Filtering and washing the alumina with 30 mL of methylene chloride/ether (1:1), followed by removal of solvent by rotary evaporation, gave 40.6 mg (82%) of clear, colorless oil, 5-undecene (cis and/or trans; homogeneous by VPC, 10 ft × ⅛ in., 5% SE-30 on Chromosorb W 100/120). Mass spectral analysis showed *m/e* (peak height, average) 157 (12.4, M + 1 of $C_{11}H_{20}D_2^+$), 156 (82.0, M^+ of $C_{11}H_{20}D_2^+$ + M + 1 of $C_{11}H_{21}D^+$), 155 (4.13, M^+ of $C_{11}H_{21}D^+$ + M + 1 of $C_{11}H_{22}^+$), 154 (1.9, M^+ of $C_{11}H_{22}^+$). Correcting for the interference of isotope peaks (M + 1 of 5-undecenes measured in control experiment as 12.0% of parent peak), we find: 156 (77.0, $C_{11}H_{20}D_2^+$) and 155 (41.1, $C_{11}H_{21}D^+$), giving a value for k_H/k_D of 1.88.

In a similar experiment, run in ether solvent, a value for k_H/k_D of 1.94 was obtained.

2-Methyl-3-octyl Tosylate (13). A solution of 215.8 mg (0.72 mmol) of 2-methyl-3-octyl tosylate[40] (**13**) (n^{25}_D 1.4917) in 5 mL of dry ether was stirred over 3.36 g of W-200-N-Dehydrated alumina at 25 °C for 1 day. Analysis by VPC (9 ft × ⅛ in., 5% SE-30 on Chromosorb G 100/140) and NMR of the concentrated methylene chloride/ether (1:1) extract showed four components, identified as (relative per cent yields by VPC and NMR): *cis*- and *trans*-2-methyl-3-octene (15, 8%), 2-methyl-2-octene (51%), and 2-methyl-1-octene (26%). No starting ester was recovered. Product mixture: NMR (CCl_4) δ 5.2–4.9 (m, olefinic C=CH), 4.60 (br s, terminal $=CH_2$), 2.2–1.7 (vinyl CH_2), 1.65 (m, vinyl CH_3), 1.53 (m, vinyl CH_3), 1.5–0.7 (m, methylenes and methyls). Integration was consistent with VPC.

2,2-Dimethyl-3-dodecyl Tosylate (14). A solution of 228.0 mg (0.62 mmol) of 2,2-dimethyl-3-dodecyl tosylate[41] (**14**) (n^{22}_D 1.4822) in 4 mL of dry ether was stirred over 4.29 g of W-200-N-Dehydrated alumina at 25 °C for 1.5 days. Filtering and rinsing the alumina with 50 mL of methylene chloride/ether/acetonitrile (1:1:1), followed by removal of solvent by rotary evaporation, yielded 111.8 mg of clear colorless liquid. Analysis by VPC (10 ft × ⅛ in., 5% SE-30 on Chromosorb W 100/120) showed (molar percent yields, products identified by NMR and IR of preparative VPC isolated materials): *trans*-2,2-dimethyl-3-dodecene [13%; NMR (CCl_4) δ 5.31 (m, 2 H, olefinic), 2.2–1.6 (m, 2 H, vinyl CH_2), 0.99 (s, *t*-Bu); IR (liquid film) 1665 (w, C=C), 968 cm^{-1} (m, sharp, *trans*-C=C)], *cis*-2,2-dimethyl-3-dodecene [7%; NMR (CCl_4) δ 5.19 (m, 2 H, olefinic), 2.2–1.6 (m, 2 H, vinyl CH_2), 1.09 (s, *t*-Bu); IR (liquid film) 1650 cm^{-1} (w, C=C)], 2,3-dimethyl-1-dodecene (**27**) [60%; NMR (CCl_4) δ 4.61 (m, 2 H, olefinic), 2.3–1.8 (m, 1 H, vinyl CH), 1.61 (m, 3 H, vinyl CH_3); IR (liquid film) 1641 (w, C=C), 885 cm^{-1} (s, sharp, $=CH_2$)], and 2,3-dimethyl-2-dodecene (**28**) [12%; NMR (CCl_4) δ 2.15–1.65 (m, 2 H, vinyl CH_2), 1.61 (s, 9 H, vinyl CH_3)].

Cyclohexanemethyl Tosylate (17). A solution of 156.9 mg (0.59 mmol) of cyclohexanemethyl tosylate (**17**) (mp 30–31 °C; lit.[42] mp

30–31 °C) and 25.8 mg of *trans*-2-octene (calibrated, internal standard) in 4.5 mL of carbon tetrachloride was stirred over 4.08 g of W-200-N-Dehydrated alumina doped with 4% w/w acetonitrile at 25 °C for 1 day. Analysis by VPC (10 ft × ⅛ in., 5% SE-30 on Chromosorb W 100/120) of the methylene chloride/ether/acetonitrile (1:1:1) extract showed (identified by VPC comparison with known samples on three columns) 61% methylenecyclohexane (**18**) and 8% 1-methylcyclohexene. Cyclohexanemethyl tosylate (27%) was also recovered.

Stability of Methylenecyclohexane over Alumina. A. With CCl_4 Solvent. A solution of 37.9 mg (0.39 mmol) of methylenecyclohexane (**18**) in 3 mL of carbon tetrachloride was stirred over 2.81 g of W-200-N-Dehydrated alumina at 25 °C for 1 day. Analysis by VPC (10 ft × ⅛ in., 5% SE-30 on Chromosorb W 100/120) of the ether extract showed (comparison with known samples) 99% 1-methylcyclohexene and a trace of methylenecyclohexane (**18**).

B. With Et_2O Solvent. A solution of 20–30 mg of impure methylenecyclohexane (containing about 20% 1-methylcyclohexene) in 2.5 mL of dry ether was stirred over 1.47 g of W-200-N-Dehydrated alumina at 25 °C for 1 day. Analysis by VPC (9 ft × ⅛ in., 5% SE-30 on Chromosorb G 100/140) of the ether filtrate showed no change in composition (methylenecyclohexane/1-methylcyclohexene, 5:1).

Cyclohexanemethyl 8-Quinolinesulfonate with Methanol-Doped Alumina. A solution of 103.0 mg (0.34 mmol) of cyclohexanemethyl 8-quinolinesulfonate [mp 74–76 °C (lit.[33] mp 76.0–77.0 °C)] and 21.9 mg of *trans*-2-octene (calibrated, internal standard) in 7 mL of carbon tetrachloride was stirred over 4.47 g of W-200-N-Dehydrated alumina doped with 3% w/w methanol (132.4 mg) at 25 °C for 1 day. Analysis by VPC (10 ft × ⅛ in., 5% SE-30 on Chromosorb W 100/120) of the methylene chloride/ether/acetonitrile (1:1:1) extract showed 10% methylenecyclohexane, <1% 1-methylcyclohexene and cycloheptene combined, a trace of cyclohexanemethanol, and 80–85% cyclohexanemethyl methyl ether (**19**) (identified by comparison with a known sample[43]): NMR δ 3.23 (s, 3 H, OCH_3), 3.09 (d, J = 6 Hz, 2 H, CH_2O), 2.0–0.8 (m, 11 H, cyclohexane ring); mass spectrum m/e 128 (M^+), 97 ($M^+ - OCH_3$).

10-Pinanyl Tosylate (21). A solution of 213.4 mg (0.69 mmol) of 10-pinanyl tosylate (**21**) [mp 74–76 °C (lit.[30b] mp 75.5–76 °C)] in 7.5 mL of carbon tetrachloride was stirred over 4.90 g of W-200-N-Dehydrated alumina doped with 4.5% acetonitrile at 25 °C for 1 day. Analysis by VPC (10 ft × ⅛ in., 5% SE-30 on Chromosorb W 100/120) of the methylene chloride/ether/acetonitrile (1:1:1) extract showed (absolute yields, identified by comparison with known samples on two columns): 67% β-pinene (**22**), 12% α-pinene (**23**), and 6% camphene (**24**) (plus two minor components in trace and 3% amounts). No starting tosylate was recovered.

Stability of Pinenes 22 and 23 on Alumina. A. With CCl_4 Solvent. A solution of 88.8 mg (0.65 mmol) of β-pinene (**22**) in 8 mL of carbon tetrachloride was added to 4.60 g of W-200-N-D alumina to which had been added 82.7 mg (0.44 mmol) of *p*-toluenesulfonic acid monohydrate. The mixture was stirred at 25 °C for 1 day, after which time the catalyst was filtered and rinsed with 23 mL of methylene chloride/ether (1:1). Analysis by VPC (10 ft × ⅛ in., 5% SE-30 on Chromosorb W 100/120) showed (relative percent yields) 54% camphene (**24**) and two unidentified isomers suspected (on the basis of relative retention times) to be terpinolene (38%) and fenchene (7%). No pinenes **22** and **23** were detected.

When α-pinene (**23**) was treated in this manner, the same three products were obtained in 55, 37, and 8% relative yields, respectively. When α-pinene was treated in this manner, save for the absence of *p*-toluenesulfonic acid monohydrate, the same three products were obtained in 57, 35, and 8% relative yields, respectively.

B. With Et_2O Solvent. A solution of 85.4 mg (0.63 mmol) of β-pinene (**22**) in 8.5 mL of dry ether was added to 4.52 g of W-200-N-Dehydrated alumina to which had been added 79.5 mg (0.42 mmol) of *p*-toluenesulfonic acid monohydrate. The mixture was stirred at 25 °C for 1 day, after which time the catalyst was filtered and rinsed with 25 mL of methylene chloride/ether (1:1). Analysis by VPC showed only unchanged β-pinene (**22**).

When α-pinene (**23**) was treated in this manner, only unchanged α-pinene was detected (by VPC).

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Registry No.—**3,** 53962-86-0; **4,** 56722-63-5; **5,** 28837-12-9; **6,** 62862-15-1; **9,** 53869-82-2; **10,** 2284-36-8; **19,** 19752-94-4; **21,** 62862-16-2; **22,** 127-91-3; **23,** 80-56-8; **27,** 62862-17-3; **28,** 62060-12-2; *trans*-4-*tert*-butylcyclohexyl tosylate, 7453-05-6; 4-*tert*-butylcyclohexene, 2228-98-0; *trans*-2,2,6-trimethylcyclohexyl tosylate, 62862-18-4; *cis*-2,2,6-trimethylcyclohexyl tosylate, 62862-19-5; *trans*-2-isopropenyl-1-methylcyclopentane, 62862-20-8; 1,5-cyclooctadiene, 111-78-4; 1,4-cyclooctadiene, 1073-07-0; 1,1-difluorocycloheptane, 27371-42-2; 1-fluorocycloheptene, 27415-45-8; *cis*-5-undecene, 764-96-5; *trans*-5-undecene, 764-97-6; *cis*-2-methyl-3-octene, 62862-21-9; *trans*-2-methyl-3-octene, 52937-36-7; 2-methyl-2-octene, 16993-86-5; *trans*-2,2-dimethyl-3-dodecene, 62862-22-0; *cis*-2,2-dimethyl-3-dodecene, 62862-23-1; methylenecyclohexane, 1192-37-6.

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Reductions of Conjugated Carbonyl Compounds with Copper Hydride—Preparative and Mechanistic Aspects

M. F. Semmelhack,* R. D. Stauffer, and A. Yamashita

Department of Chemistry, Cornell University, Ithaca, New York 14853

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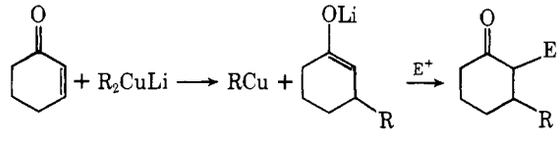
The reaction of lithium trimethoxyaluminum hydride with 0.5 molar equiv of cuprous bromide produces a heterogeneous mixture referred to as the Li complex, while sodium bis(2-methoxyethoxy)aluminum hydride with 1.0 molar equiv of cuprous bromide gives a similar mixture, the Na complex. Both reagents are effective in selective reduction of the olefin unit in conjugated ketones and esters, including two examples of acetylenic esters. The Li complex is more efficient with cyclohexenones, while the Na complex gives better yields in reduction of acyclic enones and enoates, especially in the presence of 2-butanol. Deuterium labeling experiments show that the hydrogen which is transferred to the β position of the conjugated carbonyl compound originates from the hydridocuprate reagent; the 2-butanol appears to serve as a weak acid, inhibiting polymerization. In the absence of 2-butanol, reduction of methyl cinnamate produces dimethyl *meso*-3,4-diphenyladipate as a major product, apparently the result of radical anion intermediates. Aldehyde, ketone, and halide functionality are reduced at rates comparable to the rate of enone reduction, but nitrile and ester units are inert.

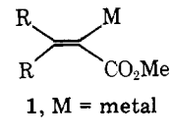
Organocopper reagents have been developed into powerful methods for carbon–carbon bond formation,[1,2] especially utilizing the remarkable preference for delivery of carbon units to the β position of α,β-unsaturated carbonyl compounds.[1] This general method of conjugate addition is selective not only for 1,4 instead of 1,2 addition, but also highly chemiselective: most nonacidic functional groups do not interfere. An added dimension in synthesis is the technique of "enolate trapping", where the product enolate anion from addition to the β position reacts with an electrophile in the α position.[3]



E = electrophilic species

Until recently, addition of hydrogen to the olefin unit in an α,β-unsaturated carbonyl compound was commonly achieved by catalytic hydrogenation[4] and dissolving metal reduction,[5] each method having characteristic technical advantages and conveniences in particular systems, and with shortcomings in chemiselectivity. Recently, hydride transfer reagents involving iron,[6,7] boron,[8] and aluminum[9] have been developed for 1,4 reduction; the boron reagent allows enolate trapping with carbon electrophiles.[8]

In analogy with the alkyl–copper chemistry, hydrido–copper reagents might provide selective conjugate addition of hydride, compatibility with most common functional groups, and would generate an enolate anion which could be trapped with protons (overall reduction of the olefin unit) or with electrophiles at the α position. We were particularly intrigued with the possibility of generation and trapping of α-metalloacrylate anion **1**, perhaps via conjugate addition of a hydrido–copper species to methyl propiolate. A few specific examples of organometal species closely related to **1** have been detected, through dialkyl cuprate addition to propiolate derivatives,[10] through halogen–metal exchange with α-bromo



1, M = metal

Li[H-Cu-R]

2, R = 1-pentynyl
3, R = $OC(CH_3)_3$
4, R = *n*-butyl