These observations, in addition to the general trend in the relaxation times of the other carbons, corroborated our carbon assignments in T-2 toxin.

Experimental Section

All spectra were obtained with a Bruker HX-90E spectrophotometer operating at 22.624 MHz in the pulse Fourier transform mode. Field-frequency stabilization was obtained from the deuterium resonance of the solvent (Me_2SO-d_6). Proton decoupling was accomplished with a broad band modulator of Bruker design. Free induction decay (FID) data were averaged with a Nicolet 1080 computer.

In the case of spectra for the Birdsall plots, 25000 transients of T-2 toxin (600 mg/ml) were averaged before multiplication (TC = −1) of the accumulated FID.

Partially relaxed Fourier transform (PRFT) spectra of T-2 toxin (600 mg/ml) were obtained by the inversion recovery method using a $(-180°-t-90°-T-)_X$ sequence where T (= 15 sec) was greater than $5T_1$ with the FID being accumulated after the 90° pulse. Different t values were employed (0.005–9.99 sec) with X = 1000 (sweeps) before multiplication (TC = −1) of the accumulated FID.

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Registry No.—**1,** 21259-21-2; **2,** 21259-20-1; **3,** 26934-87-2; **4,** 34114-98-2; **5,** 34114-99-3; **6,** 2270-40-8; **7,** 637-96-7; **8,** 21284-11-7.

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Organic Reactions at Alumina Surfaces. Elimination Reactions Effected by Dehydrated Chromatographic Alumina

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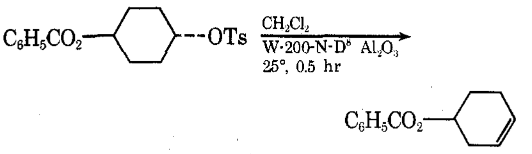
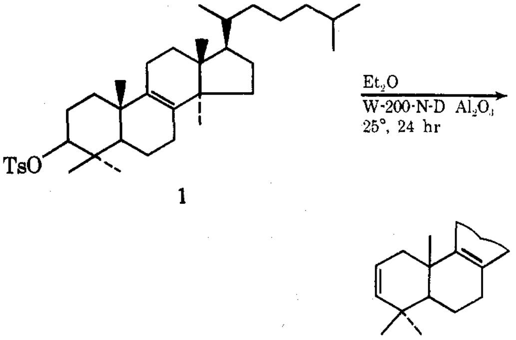
We have reported that stirring solutions of secondary *cyclic* *p*-toluenesulfonate esters over neutral, activity I, Woelm, chromatographic alumina at 25° produces olefins in high yields.[1] The simplicity and mildness of this procedure compare favorably with other methods for overall dehydration of alcohols,[2] and this method has been used recently in other laboratories to prepare some cycloalkenes.[3] Secondary *acyclic* tosylates, however, are converted by activity I alumina to 2:1 mixtures of olefins and alcohols. We reasoned that high temperature, vacuum dehydration of the alumina might form an activated alumina having some useful properties. We report here that Woelm W-200 (Brockmann activity super I),[4] neutral alumina dehydrated at 400° and 0.06 Torr for 24 hr is indeed a mild, effective, new reagent (1) for conversion of *acyclic* secondary tosylates and sulfamates to roughly 10:1 mixtures of olefins and alcohols, (2) for elimination of *cyclic* secondary tosylates to olefins even in presence of normally base and acid labile functionalities, and (3) for elimination of some rearrangement-prone tosylates and sulfamates to olefins *without any rearrangement*. The predominant mechanism of these alumina promoted reactions appears to be an anti elimination, with a syn elimination pathway occurring to some extent.

When 2-octyl tosylate or 2-octyl *N,N*-dimethylsulfamate was stirred in ether at 25° for 24 hr over neutral, dehydrated Woelm W-200 alumina, octenes and 2-octanol were formed in approximately 10:1 ratio and in 70–95% yields; the *cis*-2-octene predominated over the *trans*-2-octene and over the 1-octene.[5]

In contrast to activity I Woelm alumina, which transforms cyclohexyl tosylates to cyclohexenes (~90%) *and* cyclohexanols (~5%),[1] dehydrated W-200 alumina converts cyclohexyl tosylates to cyclohexenes without any detectable trace of cyclohexanols. Thus, 3β-cholestanyl tosylate was converted to 2-cholestene in 83% isolated yield with no cholestanol(s) being formed. This result should be compared with previous alumina-promoted reactions of 3β-tosyloxy sterols, which gave olefin and alcohol mixtures.[6] *p*-Toluenesulfonic acid elimination from *trans*-4-benzoyloxycyclohexyl tosylate illustrates the functional group selectivity of dehydrated W-200 alumina (eq 1).[7] Control experiments establish that the following compounds can be recovered in 70–90% yields after being stirred over dehydrated W-200 alumina for 24 hr at 25°: 1-iodooctane, 2-iodooctane, 5-nonanone, and diethyl dodecanedioate. Thus selective elimination of *p*-toluenesulfonic acid from bifunctional tosylates containing halo, keto, and carboxylic ester groups is practical with dehydrated alumina.



80% (1)



1

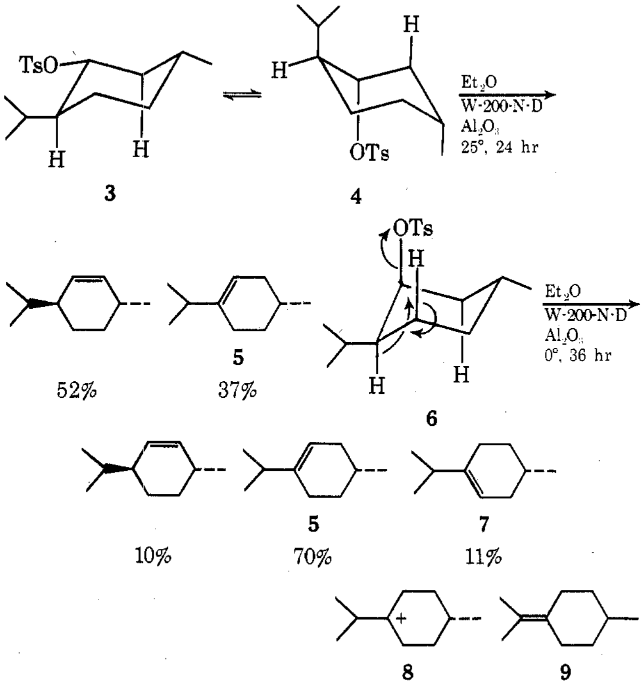
90% (2)

2

Neopentyl tosylates are known to undergo facile solvolytic rearrangements, and several 3-tosyloxy-4,4-dimethyl sterols suffer 4 → 3 methyl migration when exposed to alumina.[9] We have found that stirring 3β-tosyloxy-4,4-dimethyl sterol **1** over dehydrated W-200 alumina produced Δ^2 olefin **2** cleanly in 90% isolated yield with no detectable amount of alcohol or of rearranged material (eq 2). Likewise, cyclohexylmethyl *N,N*-dimethylsulfamate in acetonitrile reacted with dehydrated W-200 alumina to form methylenecyclohexane and 1-methylcyclohexene in 14:1 ratio; in a separate control experiment, methylenecyclohexane was found to be stable to the alumina reaction conditions.

Menthyl (**3**) and neomenthyl (**6**) tosylates reacted with dehydrated alumina to produce 2- and 3-menthenes as shown in Scheme I.[10] Formation of 3-menthenes from menthyl tosylate involves either a syn β-elimination[11] or an E_1 (carbonium ion) process. We have ruled out the E_1 process by using optically active (−)-menthyl tosylate and showing that only (+)-3-menthene (**5**) is formed; had carbonium ion **8** been an intermediate, both enantiomers **5** and **7** of 3-menthene should have been formed in equal amounts (i.e., racemic 3-menthene). Formation of 2-menthene from menthyl tosylate could be either an anti 1,2 elimination from conformer **4** or a syn 1,2 elimination from conformers **3** or **4**. Thus menthyl tosylate reacts at least to the extent of about 37% via a syn 1,2 elimination.[10] Formation of mainly (+)-3-menthene (**5**) from (+)-neomenthyl tosylate (**6**) involvss predominantly an anti 1,2 elimination, and production in small amount of (−)-3-menthene (**7**) involves either a syn 1,3 elimination or an E_1 process; although the E_1 mechanism cannot be ruled out by our data in this case, it seems unlikely because no tetrasubstituted olefin **9** was detected.[10,12] Thus neomenthyl tosylate reacts over dehydrated alumina predominantly but not exclusively via an anti 1,2 elimination. Control experiments showed that no menthene isomerization occurred under the alumina reaction conditions.

Scheme I



Experimental Section

Analytical gas–liquid phase chromatography was performed on a Varian Aerograph Model 1200 chromatograph, and preparative gas–liquid phase chromatography was done on a Varian Aerograph Model 90-P3 chromatograph. Spectral data were obtained with a Perkin-Elmer 457-A infrared spectrometer and a Varian A-60 NMR spectrometer. Optical rotations were measured on chloroform solutions with a Perkin-Elmer Model 141 polarimeter.

All solvents were commercial reagent grade and were purified before use. The esters were prepared from the corresponding alcohols and acid chlorides in pyridine or from the alcoholates and acid chlorides in glyme and gave appropriate spectral and physical data. *trans*-4-Benzoyloxycyclohexyl tosylate was prepared by the method of Owen and Robins.[13]

General Procedure for Alumina Dehydration. Woelm W-200 (neutral, activity grade Super I) is activated by heating in a quartz tube at 400°C and 0.06 Torr for 24 hr, water condensing in a dry ice–acetone cooled trap (3–4% by weight water is removed). The quartz tube is then opened to nitrogen, removed from the vacuum line, and quickly stoppered while hot. The freshly prepared, dehydrated alumina is then transferred to the reaction flasks in the dry nitrogen atmosphere of a glove bag.

General Procedure for Elimination Reactions. To an amount (about 7 g of alumina per millimole of substrate) of dehydrated alumina plus magnetic stir bar in a stoppered round-bottom flask was added quickly via pipet the appropriate amount of substrate in solvent. The resultant thin slurry was rapidly stirred for the duration of the reaction period. At the end of the reaction, the alumina was then stripped of reaction materials by washing in a filter funnel with ether–methylene chloride (1:1); rotary evaporation yields products. (Note that the eliminated sulfonic acid is retained on the catalyst.)

Octenes from 2-Octyl *N,N*-Dimethylsulfamate. A solution of 124.4 mg (0.53 mmol) of 2-octyl *N,N*-dimethylsulfamate in 4 ml of dry ether was stirred over 2.98 g of dehydrated alumina at 25° for 1 day. Gas–liquid phase chromatography (7 ft × 0.125 in., 5% SE-30 on Chromosorb G 100/120 using *n*-nonane as calibrated, added internal standard) showed 82% octenes (1-octene:*cis*-2-octene:*trans*-2-octene, 1.5:3:1) and 9% 2-octanol.

5α-Cholest-2-ene from 5α-Cholestan-3β-yl Tosylate. A solution of 63.3 mg (0.12 mmol) of 5α-cholestan-3β-yl tosylate in 3 ml of carbon tetrachloride was stirred over 1.99 g of dehydrated alumina at 25° for 1 day. Rotary evaporation of the ether–methylene chloride filtrate gave 36 mg (83%) of 5α-cholest-2-ene: NMR (CCl_4) δ 0.60–2.4 (m, 44 H), 5.55 (m, 2 H, olefinic[14]); mp 72–74° (lit.[14] 74–75°) after passage through a silica gel column (29.1 mg, 68%).

4-Benzoyloxycyclohexene from *trans*-4-Benzoyloxycyclohexyl Tosylate. A solution of 66.0 mg (0.18 mmol) of *trans*-4-benzoyloxycyclohexyl tosylate in 3 ml of dry methylene chloride was stirred over 2.67 g of dehydrated alumina at 25° for 20 min. Filtering and rinsing the alumina with 30 ml of ether–methylene chloride (1:1) in a Hirsch funnel, followed by removal of solvent by rotary evaporation and Kugelrohr distillation, afforded 28.4 mg (80%) of 4-benzoyloxycyclohexene: ir (neat) 1712 (s, C=O), 1650 (w, C=C), 1275 cm^{-1} (s, C–O); NMR (CCl_4) δ 1.7–2.5 (m, 6 H, methylenes), 5.21 (m, 1 H, carbinol), 5.66 (d, *J* = 1.5 Hz, 2 H, olefinic), 7.25–8.10 ppm (m, 5 H, aromatic); $n^{22}D$ 1.5221 (lit.[7] $n^{26}D$ 1.5336).

Lanosta-2,8-diene (2) from Lanost-8-en-3β-yl Tosylate (1). A solution of 254.0 mg (0.43 mmol) of lanost-8-en-3β-yl tosylate in 4 ml of dry ether was stirred over 2.83 g of dehydrated alumina at 25° for 1 day. Rotary evaporation of the ether–methylene chloride filter gave 159 mg (90%) of a white solid, lanosta-2,8-diene: NMR ($CDCl_3$) δ 0.65–2.5 (m, 48 H), 5.45 ppm (m, 2 H, olefinic); 150 mg (85%), mp 77–81° (lit.[15] mp 79–81°), after passage through a silica gel column.

Methylenecyclohexane from Cyclohexylmethyl *N,N*-Dimethylsulfamate. A solution of 202.3 mg (0.91 mmol) of cyclohexylmethyl *N,N*-dimethylsulfamate and 44.8 mg of *trans*-2-octene (as internal, calibrated GLC standard) in 6.5 ml of dry acetonitrile was stirred over 7.43 g of dehydrated alumina at 50° for 1 day. Vapor phase chromatography (9 ft × 0.125 in., 5% SE-30 on Chromosorb G 100/140) showed 44% methylenecyclohexane and 3% 1-methylcyclohexene; these products were identified by preparative GLC isolation and comparison with known samples. Cyclohexyl *N,N*-dimethylsulfamate (43%) was also recovered.

Menthenes from (−)-Menthyl Tosylate (3). A solution of 223.7 mg (0.72 mmol) of (−)-menthyl tosylate (**3**) in 5 ml of dry ether was stirred over 5.26 g of dehydrated alumina at 25° for 1 day. Gas–liquid phase chromatography (10 ft × 0.25 in., 10% FFAP on Chromosorb W 60/80, using *p*-cymeme as added, calibrated, internal standard) showed 89% menthenes (Δ^2 and Δ^3 combined). Careful distillation removed most of the solvent and preparative GLC (20 ft × 0.375 in., 20% QF-1 on Chromosorb W 45/60) afforded 60 mg of pure menthenes (Δ^2, Δ^3 combined). Analysis of this material by NMR and optical rotation showed 43% (+)-menth-3-ene ($[\alpha]^{23}{}_{589}$ + 106°, giving 97% optical purity) and 57% (+)-menth-2-ene.

Menthenes from (+)-Neomenthyl Tosylate (6). A solution of 99.0 mg (0.32 mmol) of (+)-neomenthyl tosylate (**6**) in 3 ml of dry ether was stirred over 2.72 g of dehydrated alumina at 0° for 1.5 days. Gas–liquid chromatography (10 ft × 0.25 in., 10% FFAP on Chromosorb W 60/80; using *p*-cymene as added, calibrated, internal standard) showed 91% menthenes (Δ^2 and Δ^3 combined). Careful distillation removed most of the solvent and preparative GLC (20 ft × 0.375 in., 20% QF-1 on Chromosorb W 45/60) afforded a pure sample of the Δ^2- and Δ^3-menthene mixture. Analysis of this material by NMR and optical rotation showed 89% (+)-menth-3-ene ($[\alpha]^{23}{}_{589}$ + 86.1°, giving 74% optical purity) and 11% (+)-menth-2-ene.

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Registry No.—**1**, 57346-50-6; **2**, 35652-87-0; **3**, 2230-82-2; **6**, 2230-77-5; alumina, 1344-28-1; 2-octyl *N,N*-dimethylsulfamate, 57346-51-7; 5α-cholest-2-ene, 570-73-0; 5α-cholestan-3β-yl tosylate, 3381-52-0; 4-benzoyloxycyclohexene, 36978-27-5; *trans*-4-benzoyloxycyclohexyl tosylate, 57346-52-8; cyclohexylmethyl *N,N*-dimethylsulfamate, 57346-53-9.

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Reaction of Substituted Benzodioxoles with Methylmagnesium Iodide under Heterogeneous Conditions

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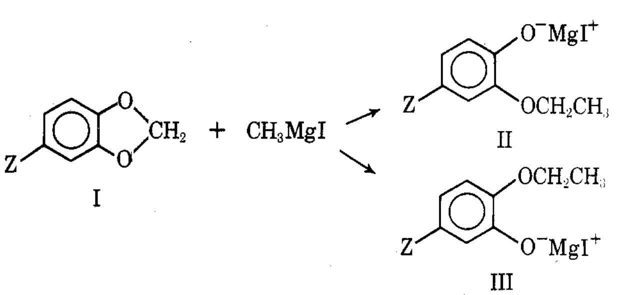
Grignard reagents, when complexed and dissolved by the common ethers, are often unreactive toward C–O single bonds.[2] A typical case is the reaction of 1,3-benzodioxoles with methylmagnesium iodide, which had to be carried out under heterogeneous conditions, between the substrate dissolved in an aromatic hydrocarbon and the insoluble organomagnesium compound.[3]

Reinvestigating such reaction, it has now been found that it proceeds as follows.



a, Z = CH_3
b, Z = H
c, Z = Cl

A partial report has been given.[4]

Results

Stoichiometry. By cleavage of one or the other of the two O–CH_2 bonds, different products, i.e., II and III, are obtained when Z is not hydrogen.

According to a previous report[3] Ia and Ic give only IIa and IIc, respectively. This claim was based on GLC analysis of the corresponding phenols in the hydrolyzed product. Both couples of possible phenolic products IIa–IIIa and IIc–IIIc have been now prepared and it has been shown that in the conditions of the GLC analysis (see Experimental Section) the isomers cannot be resolved. Therefore the reaction products, after hydrolysis and extraction of the phenolic fraction, were analyzed by NMR spectroscopy. Methylethoxyphenols exhibit slightly different CH_2 quartets and CH_3 triplets (at higher fields by 0.02 ppm for IIa); both isomers could be identified and determined in the product mixture from Ia. For the chloroethoxyphenols IIc and IIIc, besides an analogous pattern of the CH_2 and CH_3 signals, an additional difference was found in the peaks of the aromatic protons: an apparent singlet centered at δ 6.70 ppm for IIc and a multiplet with resonance bands centered at 6.77 and 6.59 ppm for IIIc. Both isomers were identified in the product from Ic; their determination was made using the aromatic region of the spectrum.

Ratios x_p = II/(II + III) and $x_m = 1 - x_p$ were evaluated. Results at different conversions and temperatures (from 50 to 68°C) were identical within experimental error. For the reaction of Ia, $x_p \simeq 0.58$ and $x_m \simeq 0.42$, while for the case of Ic, $x_p \simeq 0.25$ and $x_m \simeq 0.75$ were found.

Ethers I and the Grignard reagent were consumed in a 1:1 molar ratio. However, a twofold excess of CH_3MgI was required in order to complete the reaction with good yields of phenols. The formation of a stoichiometric compound between I and the Grignard reagent was not detected. In fact, the solution, separated from the solid phase after a short reaction time, contained the theoretical amount of I and did not evolve gas by water treatment. On the contrary, when phenetole was added to the solution, in the presence of excess CH_3MgI, some of the latter was carried over into the solution. Product IIb bound CH_3MgI in an approximate 1:1 ratio.

Usually, the reactions were carried out on 6 mmol of I in 20 ml of toluene and 18 mmol of CH_3MgI. The latter was partially coordinated to diethyl ether (about 0.1 mol of