point with an authentic sample was undepressed; the infrared spectrum was identical with that of an authentic sample. Conditions were not developed to obtain an optimum yield.

Registry No.—**1**, 16627-75-1; **2**, 37709-20-9; **3**, 37710-01-3; **4**, 37710-02-4; **5**, 32280-93-6; **6**, 5332-26-3; **7**, 37710-05-7; **8**, 37710-06-8; **8** disodium salt, 37710-07-9; **10**, 37710-08-0; **11**, 37710-09-1; **12**, 156-57-0; **13**, 2937-53-3; *N*-(hydroxymethyl)phthalimide, 118-29-6.

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Acid Decomposition of Tosylazocyclohex-1-ene and 3-Tosylazocholesta-3,5-diene

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The decomposition in acetic acid of tosylazocyclohex-1-ene and 3-tosylazocholesta-3,5-diene is described. The first furnishes a mixture of 1,2-cyclohexanediol diacetate (**3**), 1-tosylcyclohex-2-ene (**4**), *cis*-2-tosylbicyclo[3.1.0]hexane (**5**), *trans*-2-tosyl-1-acetoxycyclohexane (**6**), (*Z*)-2-tosylcyclohexan-1-one tosylhydrazone (**7**), and (*E*)-2-tosylcyclohexan-1-one tosylhydrazone (**8**); the second furnishes practically the sole 3-acetoxy-6β-tosylcholest-4-ene (**9**).

The chemical properties of azoalkenes have been of interest to us recently. Tosylazoalkenes in particular showed dual behaviour in their transformations; either they kept the original sequence of CNS bonds during a reaction, or exhibited extensive rearrangement with loss of nitrogen.[1]

Some new reactions of tosylazocyclohex-1-ene (**1**)[2] and 3-tosylazocholesta-3,5-diene (**2**)[3] are reported.

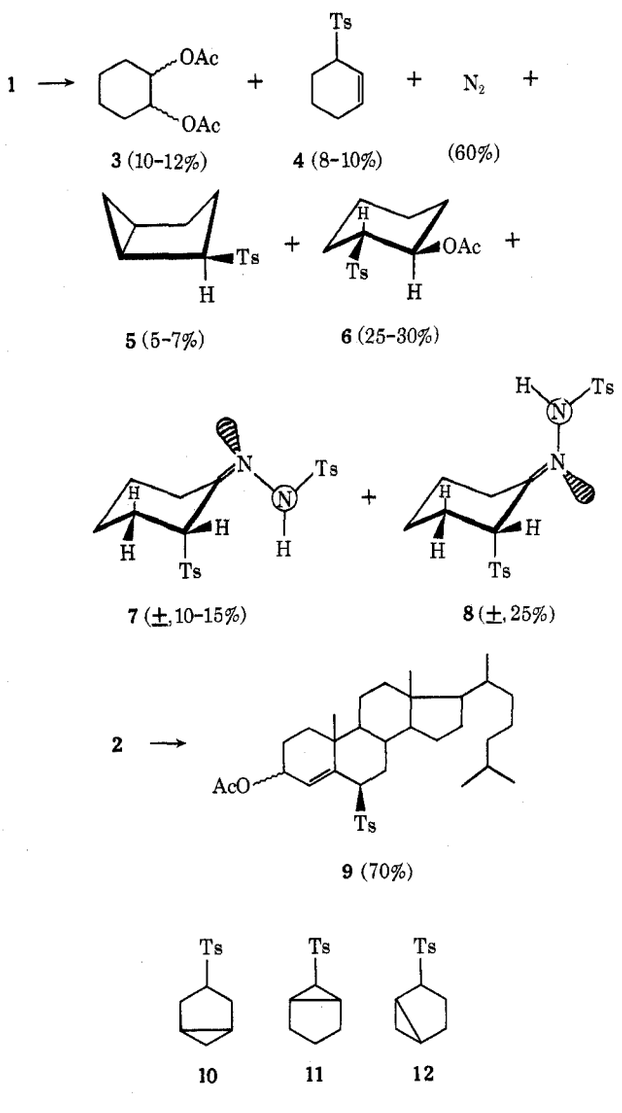
Results

Treatment of **1** and **2** with acetic acid in chloroform at room temperature resulted in the evolution of nitrogen accompanied by the disappearance of the yellow color of the solutions. By absorption chromatography, compounds **3**–**8** were isolated starting from **1** and compound **9** from **2**.

Structures **3** and **4** were determined by direct comparison with specimens prepared by independent routes (ir, pmr, mass spectra).[4] The ir spectrum of **5** revealed the presence of the sulfone function, para-substituted phenyl group, and aliphatic hydrogens. The analytical data indicated the molecular formula $C_{13}H_{16}SO_2$. Osmotic determination of the molecular weight (235.6) and the highest *m/e* peak in the mass spectrum (236) confirmed the monomeric nature of **5**.

The high-resolution pmr spectrum at 100 MHz of compound **5** is reported in Table I.

On the ground of the absence of vinyl hydrogens and as a tetrasubstituted ethane structure is impossible the bicyclic structures **10**, **11**, or **12** are proposed.



(1) L. Caglioti and G. Rosini, *Chem. Ind. (London)*, 1093 (1969).

(2) (a) L. Caglioti, P. Grasselli, F. Morlacchi, and G. Rosini, *ibid.*, 25 (1968); (b) A. Dondoni, G. Rosini, G. Mossa, and L. Caglioti, *J. Chem. Soc. B*, 1404 (1968).

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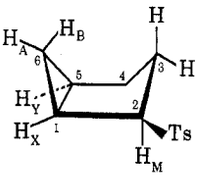
(4) K. B. Wiberg and K. A. Saegebart, *J. Amer. Chem. Soc.*, **79**, 6256 (1957).

TABLE I

Compd	Solvent	δ	
	C_6D_6	H_A	0.20
		H_B	0.74
		$H_X + H_Y$	0.85–1.15
		$2CH_2$	1.15–1.70
		CH_3Ar	2.0
		H_M	3.31
		Aromatic (4 H, q, J = 8 Hz)	6.88–7.82
	$CDCl_3$	H_A	0.44
		H_B	0.69
		$H_X + H_Y$	1.25–1.45
		$2CH_2$	1.45–2.10
		CH_3Ar	2.4
		H_M	3.58
		Aromatic (4 H, q, J = 8 Hz)	7.3–7.8

Irradiation of H_X and H_Y caused H_A and H_B to give an AB system (J_{AB} = 5.5 Hz), while H_M is singly decoupled (J_{MX} = 4.0 Hz), giving rise to a pseudotriplet. The value of the latter coupling constant is in agreement with a dihedral angle H_X–H_M of *ca.* 30°, and the absence of appreciable long-range couplings between the methylene of the cyclopropane ring and H_M infers a cis configuration for the tosyl group relative to the CH_2 bridge.[5]

The boat conformation of the cyclohexane ring would account for the relatively large separation (~8 Hz) of H_M caused by the C_3 hydrogens (no right angles).

On irradiation of H_M the signals of H_A and H_B become narrower, thus indicating some long-range coupling. This type of coupling was observed in an analogous system.[6] The other possible isomer (**10**) would give a J_{MX} value too large to be interpreted as a long-range coupling and has never been observed in similar structures; furthermore, it should exhibit a long-range coupling through four nonplanar bonds. Structure **11** must be ruled out, since it would not show the cyclopropane methylene at high field of the AB system. Structure **12** is therefore proved. Use of pmr was also useful in establishing the conformation of compound **6**; the signals at δ 5.05 and 3.3 with a half-width of 20 Hz suggest the structure of *trans*-2-tosyl-1-acetoxycyclohexane in a diequatorial configuration. It is known that the width of the resonance peak due to the ring protons is considerably larger in the conformer with the diequatorial conformation.[7]

Analytical and spectroscopic data suggest that **7** and **8** structures of which have been established from analytical and spectroscopic data reported in the Experimental Section, are geometric isomers. The broad signal centered at δ 4.75 for **7** and at 3.92 for **8** is assigned to CHTs; the low value of $W_{1/2}$ = 7.5 Hz for both compounds indicates that the protons are equatorial (axial tosyl group), and therefore **7** and **8** are syn and anti isomers.

On the basis of the work of Karabatsos and Taller[8] we have assigned the syn structure to isomer **7** with the α-methine proton resonating at lower magnetic fields and the anti structure **8** to the other.

When **2** was treated with acetic acid the main product was **9**, the structure of which was assigned on the grounds of the analytical and spectroscopic data reported in the Experimental Section. As for the configuration of the sulfonyl group at C_6, the pmr spectrum showed a double doublet centered at δ 3.5 (J_a^{app} = 1.5 and 7.0 Hz) assigned to C_6 H. These values agree with the data available in the case of bulky 6β substituents (Cl, Br, J_{AX}^{app} = 1.8 and J_{BX}^{app} = 3.6 Hz) but very different from the values reported for 6α substituents (J_{AX}^{app} = 12.5 and J_{BX}^{app} = 4.5 Hz). This suggest a 6β configuration for the tosyl group; the slight difference in J should be ascribed to distortion of ring B due to interaction between the 6β tosyl and the C-19 methyl group.[9,10] The pmr spectrum of **9** obtained by decomposition of **2** with CH_3COOD in chloroform showed signals at δ 5.3 (1 H, vinylic proton) and 3.5 (m, 1 H, CHTs), and the disappearance of the signals at 5.0 assigned to CHOAc; the other signals were identical with those of the spectrum of undeuterated **9** (see Experimental Section).

Moreover, if the C_6–H bond is not broken, no isotopic exchange is observed at this position. Therefore, according to the mechanism now proposed, the deuterium enters position 3. It can be deduced from the pmr results reported above that the –OAc group is also in position 3 and thus the tosyl is in position 6.

Discussion

The compounds isolated from the decomposition of **1** with acetic acid in chloroform and the relative yields suggest mechanism 1.

p-Toluenesulfinate anion and acetate anion may add to the β position of C to give the substituted diazoalkanes D and F, which then react with a proton to form the products **3** and **6**.

Alternatively, D and F may be formed by rearrangement of **1** *via* ion pairs A and B.

When the reaction was carried out in CH_3COOD, there was deuterium exchange in compound **6** in the position α to the acetoxy group, but none on the α carbon attached to the tosyl group. This indicates that the neutralization of the carbonium ion G with acetate anion in the scheme was the main route to **6**.

All efforts to isolate compound **13** were unsuccessful. The fact that the intermediate E was not converted into compound **6** and that compound **13** was not appreciably formed can be tentatively rationalized by assuming the high reactivity of intermediates E and G and the relatively high concentration of acetic acid in the mixture.

Alternatively, the α-tosyldiazocyclohexane F could undergo thermal decomposition to form *cis*-2-tosylbicyclo[3.1.0]hexane (**5**) and 1-tosylcyclohex-2-ene (**4**), possibly through the divalent carbon intermediate H.

Compound **5** could be formed by internal rearrangement of the carbonium ion G, but the total absence of deuterium in **5** when the decomposition of **1** is performed with CH_3COOD indicates that the carbene H is the true precursor of **5**.

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(9) M. S. Bhacca and D. M. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 108 and 148.
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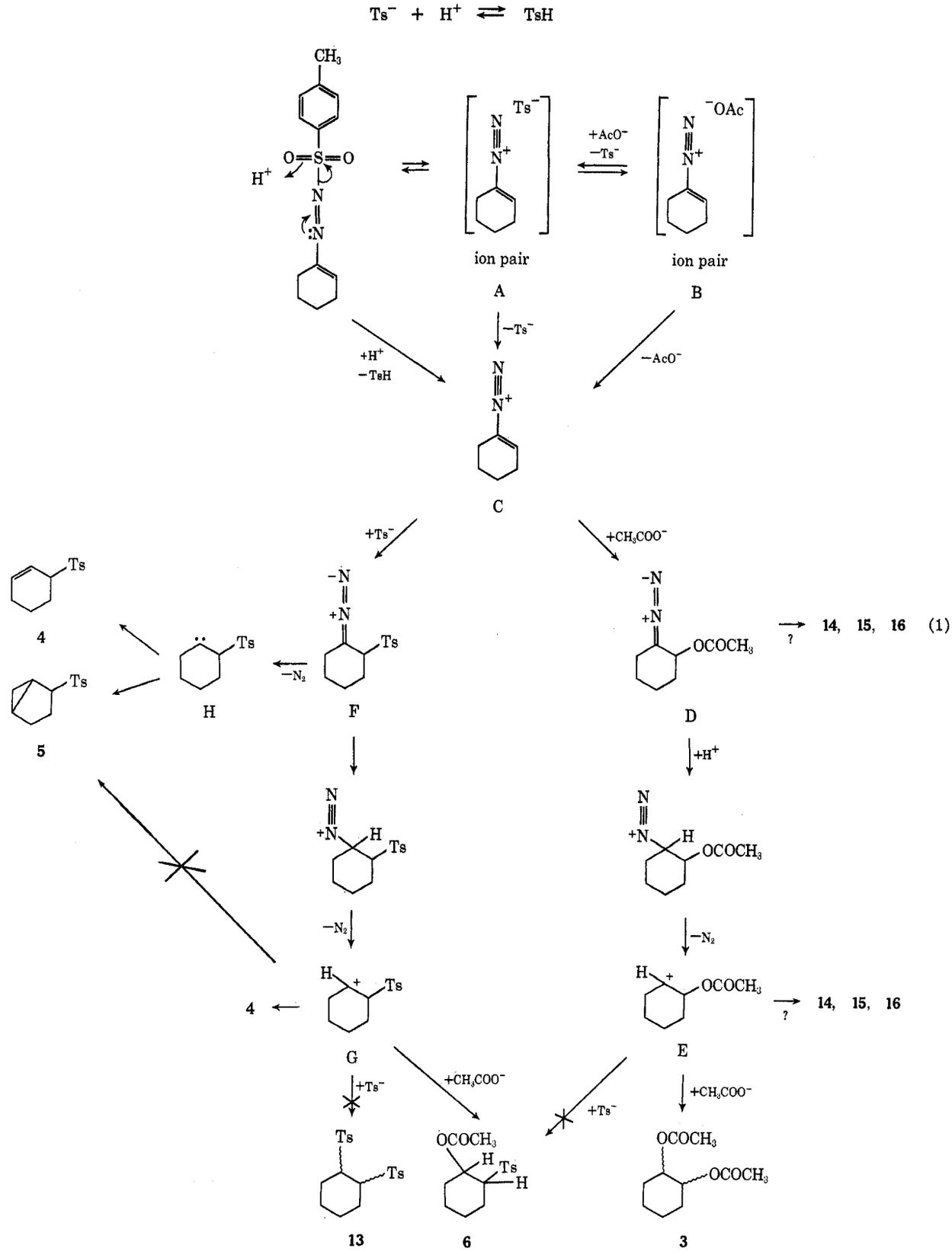
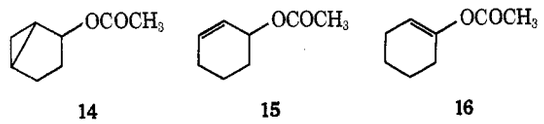


The formation of compounds **7** and **8** can be explained as a 1,4 addition of *p*-toluenesulfinate anion or *p*-toluenesulfinic acid to the azoenic system of compound **1**. The addition of acetate anion or acetic acid would give the α-acetoxycyclohexanone tosylhydrazone, which undergoes a 1,4 elimination to form compound **1**. We have not been able to detect compounds **14**, **15**, or **16**, which could arise from D or E, but the possibility that such compounds are formed during the



14 15 16

reaction cannot be ruled out. The decomposition of tosylazocyclohex-1-ene in methanol[1,2a] and the thermal decomposition of tosylazostilbene[11] are explained in terms of the dissociation of S–N bonds as indicated in the scheme; the data now collected on the acidic decomposition of tosylazocyclohex-1-ene fit the general reactivity patterns of this system well.

Experimental Section

All melting points and boilings points are uncorrected. Spectra were recorded on Beckman IR-5A, Unicam SP 800, Jeol 60-HL, and Varian 100-XL spectrometers. Pmr spectra were recorded using TMS as internal standard. Molecular weights were determined with a Hewlett-Packard Macrolab vapor phase osmometer. Microanalyses were performed using a Hewlett-Packard C, H, N analyzer, Model 185. Gas chromatographic analyses were performed on a Varian Aerograph Model 1440 using SE-30 on Chromosorb W and FFAP (10%) with Chromosorb W columns (2 m).

Reagents.—All reagents were commercial materials. Analytical grade solvents were purified by standard methods.

Apparatus.—Nitrogen evolution was measured by attaching a series of burets through a Dry Ice trap to the outlet of the condenser.

Tosylazocyclohex-1-ene (1).—This was synthesized as previously described.[1,2b] Further purification was achieved by dissolving 1.0 g of 1 in ether (50 ml) and a few drops of benzene. The yellow solution was rapidly filtered and *n*-hexane was added to turbidity; then the solution was allowed to stand in an ice bath (5–10 min). Yellow crystals were collected and dried under reduced pressure, mp 59–61° dec.

Decomposition of Tosylazocyclohex-1-ene (1) **with Acetic Acid.**—1 (8.00 g, 3.00×10^{-2} mol) was added to a solution of 8.65 ml (0.152 mol) of acetic acid in 240 ml of chloroform under magnetic stirring at room temperature. The acidic decomposition of 1 resulted in the evolution of nitrogen and the disappearance of the yellow color of the solution.

The evolved nitrogen, collected and measured at STP, gave a 60% mol yield with respect to 1.

The colorless solution was allowed to stand for 10 hr, placed in a separating funnel and shaken with a saturated aqueous solution of Na_2CO_3, washed several times with water, dried (Na_2SO_4), and evaporated under reduced pressure.

The mixture obtained was dissolved in ethyl acetate (8 ml), and *n*-hexane (12 ml) was added; a white compound was collected and recrystallized. This compound was identified as (*E*)-2-tosylcyclohexanone tosylhydrazone (8).

The filtrate was evaporated under reduced pressure and then a chromatographic separation was performed on a silica gel column using *n*-hexane–ethyl acetate (75:25) as eluent. The first fraction consisted of a mixture of 1,2-cyclohexanediol diacetate (3) and 1-tosylcyclohex-2-ene (4), successively separated by distillation under vacuum; the other fraction consisted of *cis*-2-tosylbicyclo[3.1.0]hexane (5), *trans*-2-tosyl-1-acetoxycyclohexane (6), and (*Z*)-2-tosylcyclohexanone tosylhydrazone (7).

1,2-Cyclohexanediol diacetate (3) was a colorless oil, yield 10–12%; ir and mass spectra are in good agreement with the data reported in the literature[4] for a mixture of *cis*- and *trans*-1,2-cyclohexanediol diacetate.

1-Tosylcyclohex-2-ene (4) was white crystals, mp 59°, yield 8–10%. Ir (KBr) shows peaks at 1280–1140 (SO_2), 725–705 (cis CH=CH–), and 812 cm^{-1} (para-substituted phenyl). Pmr (DMSO-d_6) signals are at δ 7.75 and 7.45 (AA'BB' pattern, 4 H, J = 8.5 Hz, *p*-C_6H_4), 6.08 and 5.6 (AB pattern, J_{AB} = 10.5 Hz, cis vinylic protons), 3.96 (m, 1 H, CHTs), 2.4 (s, 3 H, *p*-$CH_3C_6H_4$), 1.5–2.0 (m, 6 H, other aliphatic protons).

Anal. Calcd for $C_{13}H_{16}SO_2$: C, 66.08; H, 6.82. Found: C, 66.21; H, 6.68.

***cis*-2-Tosylbicyclo[3.1.0]hexane** (5) was white crystals, mp 69–70° (AcOEt–*n*-hexane), yield 5–7%. Ir (KBr) shows peaks at 1280–1140 (SO_2), 812 cm^{-1} (para-substituted phenyl). Pmr ($CDCl_3$) signals are reported in the Discussion. The molecular weight (vapor pressure osmometer, $C_2H_4Cl_2$) was 235.6; mol wt (mass spectrum, 80 eV) 236 m/e (molecular ion).

Anal. Calcd. for $C_{13}H_{16}SO_2$: C, 66.08; H, 6.83. Found: C, 65.85; H, 6.79.

***trans*-2-Tosyl-1-acetoxycyclohexane** (6) was white crystals, mp 105–106° (AcOEt–*n*-hexane), yield 25–30%. Ir (KBr) shows peaks at 1740 (–C=O) 1280–1140 (SO_2), 812 cm^{-1} (para-substituted phenyl). Pmr ($CDCl_3$) signals are at δ 7.78 and 7.35 (AA'BB' pattern, 4 H, J = 8 Hz, *p*-C_6H_4), 5.05 (m, $W_{1/2}$ 2.0 Hz, 1 H, CHOCOCH$_3$), 3.3 (m, $W_{1/2}$ 2.0 Hz, 1 H, CHTs), 2.45 (s, 3 H, $CH_3C_6H_4$), 1.68 (s, 3 H, –OCOCH$_3$), 1.0–2.2 (m, 8 H, other aliphatic protons).

Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.80; H, 6.80. Found: C, 60.72; H, 6.70.

(*Z*)-2-Tosylcyclohexan-1-one tosylhydrazone (7) was white crystals, mp 146–147° (AcOEt–*n*-hexane), yield 10–15%. Ir (KBr) shows peaks at 3150 (–NH), 1280–1140 (SO_2), 812 cm^{-1} (para-substituted phenyl); pmr (DMSO-d_6) δ 10.4 (s, 1 H, $-SO_2NH-$), 7.2–7.8 (m, 8 H, two para-substituted phenyls), 4.75 (m, $W_{1/2}$ = 7.5 Hz, 1 H, CHTs), 2.4 (s, 3 H, $CH_3C_6H_4-$), 2.35 (s, 3 H, $CH_3C_6H_4-$), 1.3–2.2 (m, 8 H, other aliphatic protons).

Anal. Calcd for $C_{20}H_{24}N_2O_4S$: C, 57.13; H, 5.75; N, 6.66. Found: C, 57.34; H, 5.94; N, 6.59.

(*E*)-2-Tosylcyclohexane-1-one tosylhydrazone (8) was white crystals, mp 160–162° (AcOEt–*n*-hexane), yield 25%. Ir (KBr) shows peaks at 3230 (–NH), 1280 and 1140 ($-SO_2$), 812 cm^{-1} (para-substituted phenyl); pmr (DMSO-d_6) δ 1.05 (s, 1 H, $-SO_2NH-$), 7.7-7.0 (m, 8 H, two para-substituted phenyls), 3.92 ($W_{1/2}$ = 7.5 Hz, CHTs), 2.4 (s, 3 H, $CH_3C_6H_4-$), 2.35 (s, 3 H, $CH_3C_6H_4-$), 1.4-2.7 (m, 8 H, other aliphatic protons).

Anal. Calcd for $C_{20}H_{24}N_2O_4S$: C, 57.13; H, 5.75; N, 6.66. Found: C. 57.11; H, 5.58; N, 6.87.

Decomposition of 3-Tosylazocholesta-3,5-diene (2).—2[3] (4.24 g, 7.7×10^{-1} mol) was added to a solution of 8.0 ml (0.140 mol) of acetic acid in 130 ml of chloroform under magnetic stirring at room temperature. The evolved nitrogen, collected and measured at STP, gave 85% yield with respect to 2.

The pale yellow colored solution was treated as given for the decomposition of 1. Chromatographic separation on a silica gel column (0.05–0.20) using a mixture of cyclohexane–AcOEt (80:20) as eluent gave 3-acetoxy-6-β-tosylcholest-4-ene (9) as the main product (yield 70%).

3-Acetoxy-6β-tosylcholest-4-ene (9) was white crystals, mp 147–148°. Ir (KBr) shows peaks at 1748 (ether C=O), 1600 (phenyl), 1280–1140 (SO_2), 820 cm^{-1} (para-substituted phenyl). Pmr (CCl_4) showed signals at δ 7.68 and 7.29 (AA'BB' pattern, 4 H, J = 8 Hz; aromatic protons), 5.3 (d, 1 H, J = 5 Hz, vinylic proton), 5.0 (m, 1 H, –CHOAc), 3.5 (m, 1 H, –CHTs), 2.43 (s, 3 H, $CH_3C_6H_4-$), 0.8–2.2 (other aliphatic protons).

Anal. Calcd for $C_{36}H_{54}SO_4$: C, 74.19; H, 9.34. Found: C, 74.00; H, 9.20.

Registry No.—**1**, 17344-06-8; **2**, 26152-91-0; **4**, 37488-68-9; **5**, 37500-26-8; **6**, 37500-27-9; **7**, 37500-28-0; **8**, 37500-29-1; **9**, 37500-30-4.

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