4,5-Epoxycyclooctyl Acetate (10).—Tetraethylammonium acetate (5.10 g) was added to a solution of **9** (1.15 g) in dry acetone (40 ml) and the mixture was heated under reflux for 46 hr. Removal of the solvent at reduced pressure gave a semisolid which was treated with water (80 ml) and extracted with ether. The ether extracts were washed with water, dried ($MgSO_4$), and concentrated to an oil (0.62 g). Glpc analysis showed the presence of three components, two of which had retention times similar to that of 4,5-epoxycyclooctene. The third component, which had a retention time close to that of epoxy acetate **8**, was obtained by preparative glpc: ir (CCl_4) 1740, 1250, 1035, and 1020 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.02; H, 8.68.

Glpc analysis of a mixture of **8** and **10** showed that these isomers were cleanly separated on a 10-ft 20% LAC-728.

Hydrolysis of the Diepoxide.—A mixture of the diepoxide (10 g) and 0.02 *N* sulfuric acid (100 ml) was heated on a steam bath for 20 hr. After cooling, solid sodium bicarbonate was added followed by sodium chloride. Continuous extraction with ethyl acetate for 12 hr then gave 11 g (97%) of a solid. A sample collected by preparative glpc had mp 60–85°, mol wt (mass spectrometry), 158.19.

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.33; H, 8.90.

Ditosylates of 11 and 12.—To a cold solution of the crude diol mixture (3.1 g) in pyridine (30 ml) was added *p*-toluenesulfonyl chloride (8.2 g). The mixture was stirred at room temperature for 4 hr and was then poured into cold water. The precipitated solid was collected by filtration and dissolved in benzene. The benzene solution was washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate, and water, and dried ($MgSO_4$). Removal of the solvent gave an oil 8.7 g (97%) which solidified on standing, mp 117–125°. Thin layer chromatography indicated the presence of two components. A sample had mp 153° after three recrystallizations from ethyl acetate–hexane.

Anal. Calcd for $C_{22}H_{26}O_7S_2$: C, 56.63; H, 5.62. Found: C, 56.62; H, 5.60.

9-Oxabicyclo[4.2.1]nonane and 9-Oxabicyclo[3.3.1]nonane.—To a solution of potassium hydroxide (1.4 g) in triethyleneglycol (6 ml) in a flask fitted with a condenser set for distillation was added the crude ditosylate mixture (2.0 g). The flask was heated for 30 min with a flame and a mixture of the epoxydienes **13** and **14** (0.6 g) was collected in a cold trap. The mixture was dissolved in ethyl acetate and hydrogenated during 12 hr at room temperature using Adams catalyst. The catalyst was removed by filtration and the filtrate was concentrated at reduced pressure. Preparative glpc of the residue gave 9-oxabicyclo[4.2.1]nonane (75%) and 9-oxabicyclo[3.3.1]nonane (25%), identified by spectral comparisons with authentic samples.

Reaction of the Diepoxide with Sodium Sulfide.—A solution of the diepoxide (2.8 g) in ethanol (20 ml) was mixed with a solution of sodium sulfide (4.8 g) in 50% aqueous ethanol (40 ml) and the mixture was heated under reflux for 14 hr. The mixture was cooled, diluted with water, and extracted with ethyl acetate. The extract was dried (Na_2SO_4) and concentrated to give a mixture of **15** and **16**, 3.1 g (88%), as a solid. Recrystallization from benzene–ethyl acetate gave colorless needles, mp 179°. A sample which was sublimed at 120° (0.5 mm) had mp 175–176°. Thin layer chromatography indicated the presence of both isomers. The major isomer **16**, mp 174°, could be obtained pure by adsorption chromatography of the mixture on alumina.

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10; S, 18.40. Found: C, 55.12; H, 8.05; S, 18.33.

Desulfurization of 15 and 16 with Raney Nickel.—A solution of of the above mixture of **15** and **16** (1.5 g) in 95% ethanol was stirred and heated under reflux with excess W_2 Raney nickel for 15 hr. The catalyst was removed by filtration and the filtrate analyzed by glpc on an 8-ft 20% silicon rubber column at 150°. The three major components (representing 80% of the total) were isolated and identified as 4-hydroxycyclooctanone, 5-hydroxycyclooctanone, and *cis*-1,4-cyclooctanediol.

Registry No.—**1a**, 19740-81-9; **8**, 19740-82-0; **9**, 19740-83-1; **10**, 19740-84-2; **11**, 19771-18-7; **11** (ditosylate), 19740-85-3; **12**, 19740-86-4; **12** (ditosylate), 19740-87-5; **15**, 19740-88-6; **16**, 19740-89-7; *cis,cis*-1,5-cyclooctadiene monoepoxide, 19740-90-0.

Purification of Hydrocarbon Solvents with a Silver Nitrate Column

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Hydrocarbon solvents of the utmost purity were required in a research program dealing with the properties of niobium and tantalum halides in nonaqueous systems. The usual procedures and combinations of procedures for purifying these liquids were tried with little success.

The predominant impurities in commercial and reagent grades of saturated hydrocarbon solvents are olefinic and aromatic compounds. One method[2a] for the removal of these impurities involves washing the hydrocarbon with a nitrating mixture of sulfuric and nitric acids followed by several washings with sulfuric acid, water, and finally with sodium bicarbonate solution. Alternatively, the hydrocarbon can be passed through silica gel columns.[2b,3,4] Maclean, Jencks, and Acree[4] demonstrated that several passes are necessary to obtain reasonably pure solvent by this latter method; their sample of purified cyclohexane had an absorbance of 0.4 in a 1.0-cm cell at 220 $m\mu$. The data of Mair and Farziati[3b] indicate that the yield of pure solvent is equal approximately to the mass of silica gel used in their purification procedure. In our work distillation from solutions containing niobium pentachloride as outlined by Fairbrother, *et al.*,[5] was found to add an impurity which interfered with the measurements being made; a similar phenomenon was observed with the sulfuric acid treatment referred to above. Hydrocarbon solvents which were pure enough for our purposes were not obtained after repeated and frustrating attempts to apply the above methods.

Solid silver nitrate as an adsorbent for the hydrocarbon impurities was then investigated. Reports in the literature indicate that silver nitrate on alumina has been used in columns for the separation of olefinic mixtures in both liquid–solid[6–8] and gas–solid[9–11] partition chromatography; silver nitrate on alumina and on silica gel has been used in thin layer chromatography[12,13] for the separation of unsaturated compounds.

Columns filled with silver nitrate on alumina have been used in our study for the facile preparation of

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TABLE I

COMPARISON OF ABSORBANCES OF PURIFIED *vs.* UNPURIFIED HYDROCARBON SOLVENTS AT SPECIFIC WAVELENGTHS[a,b]

Hydrocarbon	Wavelength, mμ								
	210	220	230	240	250	260	270	280	300
Cyclohexane		2 0.25	0.55 0.12	0.24 0.034	0.31 0.010	0.32 0.005		0.13 0.003	0.02 0.001
Hexane	>2 0.18		>2 0.032		>2 0.008		2 0.003	0.36 0.003	0.10 0.001
Pentane	>2 0.065	>2 0.03	>2 0.018	0.55 0.012		0.10 0.006		0.05 0.003	0.033 0.002
3-Methylpentane	1.15 0.15	1.25 0.055		0.32 0.012		0.25 0.005		0.17 0.003	0.07 0.002
2,2,4-Trimethylpentane		0.40 0.08		0.10 0.015		0.05 0.005		0.03 0.002	0.02 0.001
Methylcyclohexane		0.57 0.2	0.35 0.010	0.22 0.035		0.065 0.007		0.025 0.003	0.015 0.001

[a] The upper number for a specific wavelength in the series of numbers following a given hydrocarbon is the absorbance of the unpurified hydrocarbon, and the lower number is the absorbance of the hydrocarbon after one pass through a silver nitrate on alumina column. [b] Absorbances were obtained on the unpurified hydrocarbons in a 1.0-cm cell while those for the purified liquids were obtained in a 10-cm cell; in order to make comparisons, the latter values were divided by 10 for inclusion in this table.

spectroscopically pure cyclohexane, hexane, pentane, 3-methylpentane, 2,2,4-trimethylpentane, and methylcyclohexane. The exceptional efficiency of this method is reflected in the specific data summarized for each hydrocarbon in Table I. A 90-cm length of the silver nitrate–alumina in a 16-mm (i.d.) column was found to remove effectively the impurities from as much as 6 l. of cyclohexane.

Experimental Section

The silver nitrate–alumina column material was prepared in the following way. A sample of alumina (360 g) was mixed thoroughly with 500 ml of 2 *M* nitric acid. This slurry was filtered through a coarse sintered-glass funnel and the solid was washed with water until the filtrate was neutral to Hydrion paper. Reagent grade silver nitrate (40 g) was dissolved in 20 ml of distilled water and the resulting solution was diluted with 350 ml of reagent grade methanol. This solution was used to wash the damp alumina from the filter into a 2-l. flash evaporator flask. After removal of the solvent by means of the flash evaporator, the solid was poured from the flask and air dried at 140° for 24 hr. The silver nitrate–alumina column material prepared by this procedure is white in contrast to the brown material obtained by Barbour.[6]

A 13-mm (i.d.) column was packed to a depth of 25 cm with the silver nitrate–alumina for the survey experiments reported here. The solvent to be purified was dried over phosphorus pentoxide and then decanted into a reservoir on the top of the column. The column was evacuated with an aspirator before the solvent was allowed to flow; the flow of liquid through the column was then adjusted to approximately 1 drop/sec. One hundred milliliters of solvent was collected and its spectrum was recorded in a 10-cm cell using a Cary Model 14 spectrophotometer.

Registry No.—Silver nitrate, 7761-88-8; cyclohexane, 110-82-7; hexane, 110-54-3; pentane, 109-66-0; 3-methylpentane, 96-14-0; 2,2,4-trimethylpentane, 540-84-1; methylcyclohexane, 108-87-2.

Synthesis of 1-Azatricyclo[7.2.1.0^{6,11}]dodecan-12-one

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In previous work[2] it was found that 7-carboxytetrahydrobenzazepine (**1**) underwent facile cyclization to tricyclic lactam **2** on hydrogenation over ruthenium at 160°. It was thought of interest to determine whether this reaction would be useful in producing other lactams as well.

Homodihydrocarbostyril[3] (**3**) was reduced with lithium aluminum hydride and converted to N-acyltetrahydrobenzazepine (**4**). In contrast to the ultraviolet spectrum of acetanilide [λ_{max} 238 mμ (ϵ 10,500)][4] the spectrum of **4** had λ_{max} at 226 and 265 mμ. The latter peak had an extinction coefficient of 450 and was in the form of a typical benzene fingerprint. The appearance of the benzenoid fine structure indicated a nearly complete lack of conjugation between the amide group and the aromatic ring caused, presumably, by an interaction between the *peri* hydrogen and the amide carbonyl.

Because of this lack of conjugation it was felt that electrophilic attack would most likely take place on C-8 of the benzazepine.[5] Friedel–Crafts acylation of **4** gave

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