1230, and 3500 cm^{-1}; nmr δ 2.1 (s, 3 H) and 5.1 (s, br, 1 H). *Anal.* Calcd for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81. Found: C, 79.45; H, 10.75. This was converted to the diacetate **9** (pyridine, acetic anhydride), mp 186°, $[\alpha]D$ +64°, M^+ *m/e* 526, identified by direct comparison (tlc, ir, nmr, mixture melting point) with an authentic sample.

3β-Hydroxy-13β,28-epoxy-12α-bromooleanane (20). A solution of bromine in acetic acid (3%, 4.5 ml) was added dropwise to a stirred solution of **6** (500 mg) and NaOAc (2.0 g) in 90% aqueous acetic acid (50 ml). After 3 hr the solution was poured into water containing $Na_2S_2O_3$. Usual work-up furnished **20** (250 mg): mp 180°; $[\alpha]D$ +3.6°; M^+ *m/e* 520; ν_{max} 3400 cm^{-1}; nmr δ 4.3 (m, 1 H), 3.5 (q, 2 H), and no vinyl proton signal. *Anal.* Calcd for $C_{30}H_{49}BrO_2$: C, 69.1; H, 9.5. Found: C, 68.9; H, 9.6.

3β-Hydroxy-13β,28-epoxyoleanane (18) from 20. A solution of **20** (50 mg) in THF (5 ml) was added to a refluxing slurry of $LiAlH_4$ (50 mg) in THF (25 ml). Refluxing and stirring were continued for 8 hr. Usual work-up and crystallization from ether–methanol yielded **18** (15 mg), mp 229°, $[\alpha]D$ +1.9°, M^+ *m/e* 442, identified by tlc, nmr, melting point, and mixture melting point with an authentic sample.

Echinocystic Acid[20] Bromolactone (16). A solution of bromine in acetic acid (3%, 2–3 ml) was added dropwise during the course of 3 hr to a stirred solution of **3** (100 mg) and NaOAc (400 mg) in 90% aqueous acetic acid (10 ml). The reaction mixture was then poured into water containing $Na_2S_2O_3$. The crystalline material was filtered (45 mg) and recrystallized from $CHCl_3$–MeOH to yield **16** (30 mg): mp 246°; $[\alpha]D$ +61°; M^+ *m/e* 550; ν_{max} 1750 cm^{-1}; nmr δ 4.3 (m, 1 H) and absence of vinyl proton signal. *Anal.* Calcd for $C_{30}H_{47}BrO_4$: C, 65.31; H, 8.59. Found: C, 65.62; H, 8.81.

Reduction of 16 (200 mg) with boron trifluoride etherate (2 ml) and $LiAlH_4$ (200 mg) in THF (25 ml) for 8 hr yielded a mixture (185 mg) whose ir spectrum was transparent in the carbonyl region. Its nmr spectrum showed signals at δ 4.3 (m, 1 H) and 3.3 (2 H) and no vinyl proton signal. This was again reduced with $LiAlH_4$ (150 mg) in refluxing THF (30 ml) for 7 hr to yield a mixture (170 mg) which on chromatography on alumina (10 g) did not yield **21** but furnished **10** (38 mg), mp 242°, $[\alpha]D$ +41°, identified by direct comparison (tlc, ir, mixture melting point) with an authentic sample prepared by reducing **4** with $LiAlH_4$. It also gave a compound (34 mg), mp 168–170°, which was not **11** and was not further characterized.

A solution of **10** (200 mg) in $CHCl_3$ (15 ml) was treated with gaseous HCl for 1 hr at room temperature. Usual work-up gave a solid (185 mg) which on chromatography on alumina (10 g) furnished the starting material (98 mg) and another product (48 mg), mp 246°, M^+ *m/e* 486, which was not further characterized.

Echinocystic Acid Lactone (15). A stream of gaseous HCl was passed through a solution of **3** (100 mg) in $CHCl_3$ (50 ml) for 15 min at room temperature. Removal of the unreacted acid with 15% aqueous KOH yielded the neutral **15** (23 mg): mp 280°: $[\alpha]D$ +14°; ν_{max} 1753 cm^{-1}; nmr spectrum showed the absence of vinyl protons. *Anal.* Calcd for $C_{30}H_{48}O_4$: C, 76.22; H, 10.24. Found: C, 76.31; H, 10.41. Reduction of **15** with boron trifluoride etherate and $LiAlH_4$ did not give **21**.

Protoprimulagenin A (21). A solution of **14**[18] (300 mg) in THF (20 ml) containing boron trifluoride etherate (3 ml) was added to a stirred suspension of $LiAlH_4$ (250 mg) in THF (250 ml) at 0°. Stirring was continued for 2 hr at ice-bath temperature. Usual work-up and chromatography on basic alumina gave in benzene–ethyl acetate (1:1) **21** (48 mg): mp 262°; $[\alpha]D$ +22°; ν_{max} 3600–3500 cm^{-1}; nmr δ 3.1–3.5 (m, 3 H) and 3.91 (1 H). This was identified by direct comparison (tlc, ir, nmr, mixture melting point, etc.) with an authentic sample.[10]

Acknowledgments. We are indebted to Professor I. Kitagawa for an authentic sample of protoprimulagenin A and to the CSIR (India) for the award of a junior research fellowship to one of us (A. A. N.).

Registry No.—**3**, 545-88-0; **6**, 545-48-2; **7**, 7089-38-5; **8**, 51820-71-4; **12**, 1721-60-4; **14**, 51830-03-6; **15**, 51829-67-5; **16**, 51829-68-6; **18**, 35738-40-0; **19**, 43059-47-8; **20**, 39701-58-1; **21**, 2611-08-7.

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(20) Echinocystic acid (**3**) was isolated from the seeds of *Albizzia lebbek* by the procedure of I. P. Varshney, *Indian J. Chem.*, **7**, 446 (1949).

Nucleophilic Addition of Aliphatic Hydroxylamines to *p*-Tolylsulfonylacetylenes. Competitive Nitrogen and Oxygen Attack

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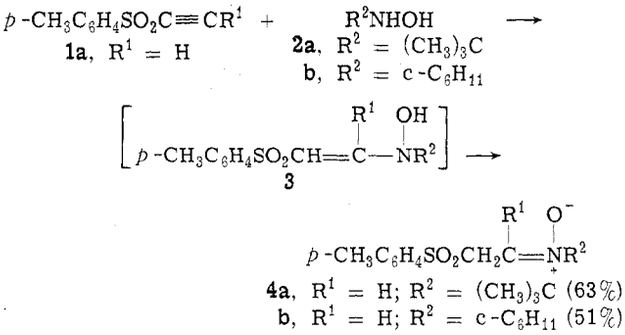
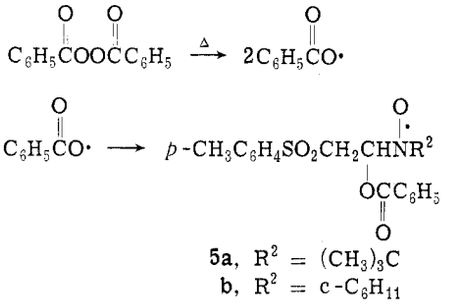
Acetylenes activated by sulfonyl substitution at the triple bond usually undergo facile nucleophilic addition.[1-4] Particularly the addition reactions of primary and secondary amines have been subjected to detailed investigation. However, there seems to be no literature precedent for the reaction of hydroxylamines with acetylenic sulfones. We report here a few examples of such reactions.

When *p*-tolylsulfonylacetylene (**1a**) was allowed to react with *N*-*tert*-butylhydroxylamine (**2a**) or *N*-cyclohexylhydroxylamine (**2b**) in ethanol at room temperature, a smooth reaction occurred. The analytical and spectral properties of the crystalline products obtained were entirely consistent with the nitrone structures[5] **4a,b**. The pres-



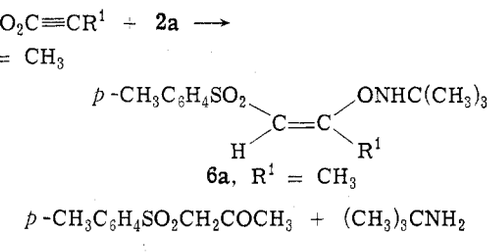
ence of a nitrone functionality in **4a,b** is further supported by the successful utilization of these compounds as spin

traps.[6] Thus, benzoyloxy radicals rapidly add to **4a,b** to give paramagnetic species that exhibit esr spectra in accordance with the nitroxide radical structures **5a,b** (*cf.* Experimental Section).



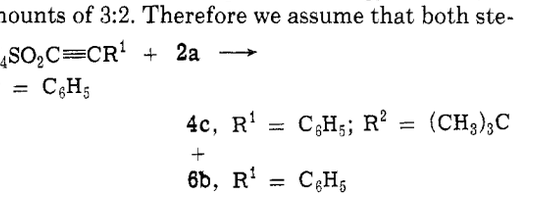
Presumably, the formation of **4a,b** from **1a** proceeds *via* preferential attack of nitrogen[7] on the triple bond, to give initially *N*-hydroxyenamines of type **3,** followed by isomerization through proton shift from oxygen to α-sulfonyl carbon.[8]

Interestingly, the addition of **2a** to the nonterminal sulfonylacetylene **1b** took a completely different course. The 1:1 adduct, isolated in a yield of 86%, possessed spectral properties which were inconsistent with a nitrone product like **4** ($R^1 = CH_3$). We assign the *O*-sulfonylpropenylhydroxylamine structure **6a** to this adduct on the basis of the following observations. First of all, the ir spectrum, taken in carbon tetrachloride, showed a rather sharp absorption at 3248 ± 2 cm^{-1} and no (broad) OH stretch around 3500 cm^{-1} as would be expected for an *N*-hydroxyenamine **3** [$R^1 = CH_3$; $R^2 = (CH_3)_3C$].[9,10] The isolation of *p*-tolylsulfonylacetone (91%) upon mild hydrogenation[11] of **6a** and the failure of **6a** to react with Fehling's reagent[12] lend further support to the proposed structure.[13]



Intramolecular nuclear Overhauser effects (NOE)[14] indicate that **6a** is the *Z* isomer, since saturation of the methyl absorption at δ 2.18 ppm resulted in a 12 ± 2% enhancement of the signal due to the vinyl hydrogen. This provides evidence for trans addition of **2a**,[15] but by analogy with the addition of amines,[2] postisomerization processes may occur. In addition, saturation of the *tert*-butyl signal resulted in a 13 ± 1% increase in the intensity of the vinyl proton absorption. Inspection of molecular models reveals that this result can be reconciled with structure **6a** rather than with **3** [$R^1 = CH_3$; $R^2 = (CH_3)_3C$] since only in **6a** conformations with short vinyl hydrogen–*tert*-butyl hydrogen distances can be attained. There is ample literature precedent for long-range NOE[16] and these effects can also occur if only part of the populated conformations allow for sufficiently short internuclear distances.[14]

The isolation of **6a** indicates that **2a** utilizes oxygen as the nucleophilic site[17] in the addition reaction to **1b.** It is tempting to rationalize this result in terms of the more severe steric demands for addition to **1b,** causing the reaction to occur at the least hindered nucleophilic site in **2a.** The competitive nitrogen *vs.* oxygen attack for addition of **2a** to **1a,b** would then be reminiscent of the behavior of N-monosubstituted hydroxylamines upon acylation. Usually nitrogen is the preferred nucleophilic site but acylation may occur on oxygen when steric hindrance deactivates the nitrogen atom.[18] However, the actual situation is more complicated as demonstrated by the addition of **2a** to the even more hindered **1c.** This reaction afforded in 94% yield a mixture of the nitrone **4c** and the O-substituted hydroxylamine **6b** (structure based on spectral analogy with **6a**) in relative amounts of 3:2. Therefore we assume that both steric and electronic effects are important in determining the preferred nucleophilic site in **2a** and clearly further studies are required in order to obtain further insight into this problem.



Experimental Section

Elemental analyses were carried out in the Analytical Department of this laboratory under the supervision of Mr. W. M. Hazenberg. Melting points were determined using a Mettler FP1 melting point apparatus with a Mettler FP52 microscope attachment. Nmr spectra were recorded on a Varian A-60 spectrometer, using TMS (δ 0) as an internal standard. NOE experiments were performed on a Varian XL-100-15 instrument. Esr spectra were taken on a Varian E-4 apparatus. Ir spectra were measured with a Perkin-Elmer instrument, Model 125 or 257.

The sulfonylacetylenes **1a, 1b,** and **1c** and the hydroxylamines **2a** and **2b** were prepared according to literature procedures.[2-4,7]

Addition of Hydroxylamines to Sulfonylacetylenes. General Procedure. To a solution of the hydroxylamine **2a,b** (1.1 mmol) in 5 ml of ethanol was added dropwise an ethanolic solution of the sulfonylacetylene **1a–c** (1 mmol in 5 ml). After stirring for 2 hr at room temperature the solvent was removed *in vacuo.* Solvents used for crystallization of the obtained solids and yields of analytically pure compounds are given below.

The crude reaction product from the reaction of **1c** with **2a** was dissolved in 100 ml of dichloromethane and washed twice with 100 ml of water. After drying with sodium sulfate and removal of the solvent *in vacuo,* the nmr spectrum of the mixture indicated the presence of 60% of **4c** and 40% of **6b** (total yield 94%). The product composition remained unchanged when the reaction time was doubled. Two crystallizations of the material from petroleum ether (bp 40–60°)–ether (1:1) afforded pure **6b.** Evaporation of the mother liquor gave solid material that was crystallized five times from *n*-pentane–ether (19:1) to give a low yield of **4c.**

C-*p*-**Tolylsulfonylmethyl**-*N*-*tert*-**butylnitrone (4a):** yield 63%; mp 125–126.5° (from CCl_4); nmr ($CDCl_3$) δ 1.35 (s, 9 H, *tert*-butyl), 2.42 (s, 3 H, aryl CH_3), 4.40 (d, J = 6 Hz, 2 H, CH_2), 7.02 (t, J = 6 Hz, 1 H, methine proton), ~7.30–7.91 ppm (AA'BB', 4 H, aryl); ir (KBr) 1582, 1568, 1354, 1310, 1300, 1285, 1148, 1120 cm^{-1}.

Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20; S, 11.91. Found: C, 57.78; H, 7.02; N, 5.06; S, 12.03.

C-*p*-**Tolylsulfonylmethyl**-*N*-**cyclohexylnitrone (4b):** yield 51%; mp 114.5–115.3° (from benzene–*n*-hexane); nmr ($CDCl_3$) δ ~1.0–1.9 (unresolved m, 11 H, cyclohexyl), 2.43 (s, 3 H, aryl CH_3), 4.37 (d, J = 6 Hz, 2 H, CH_2CH=), 6.90 (t, J = 6 Hz, 1 H, methine proton), 7.22–7.88 ppm (AA'BB', 4 H, aryl); ir (Nujol) 1580, 1385, 1310, 1290, 1130 cm^{-1}.

Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74; S, 10.86. Found: C, 61.21; H, 7.43; N, 4.56; S, 10.71.

C-**Phenyl**-*C*-*p*-**tolylsulfonylmethyl**-*N*-*tert*-**butylnitrone (4c):** mp 110–112° (from *n*-pentane–ether); nmr ($CDCl_3$) δ 1.29 (s, 9 H, *tert*-butyl), 2.45 (s, 3 H, aryl CH_3), 4.73 (s, 2 H, CH_2), ~7.20–8.00 ppm (m, 9 H, aryl protons).

Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.06; S, 9.28. Found: C, 65.86; H, 6.79; N, 4.00; S, 9.23.

N-*tert*-**Butyl**-*O*-**2**-*p*-**tolylsulfonylpropenylhydroxylamine (6a):** yield 86%; mp 122–124° [from petroleum ether (bp 40–60°)–ether (1:1)]; nmr ($CDCl_3$) δ 1.02 (s, 9 H, *tert*-butyl), 2.18 [s, 3 H, C=C(CH_3)], 2.40 (s, 3 H, aryl CH_3), ~5.1 (br s, 1 H, NH), 6.42 (s, 1 H, vinyl H), 7.25–7.85 ppm (AA'BB', 4 H, aryl); mass spectrum *m/e* 283 (M^+); ir (KBr) 3245, 3085, 1640, 1380, 1360, 1275, 1127 cm^{-1}; ir (0.01–0.04 *M* solution in CCl_4) 3248 ± 2 cm^{-1}.

Anal. Calcd for $C_{14}H_{21}NO_3S$: C, 59.36; H, 7.47; N, 4.94; S, 11.31. Found: C, 59.33; H, 7.41; N, 4.84; S, 11.17.

Acylation of **6a** with acetyl chloride was attempted under a variety of standard conditions but all experiments led to recovery of **6a** in high yield. Under more drastic conditions extensive decomposition of **6a** was observed. Steric approach to nitrogen is apparently strongly hindered because of the neopentyl-like position. NOE: on a degassed 0.2 *M* solution of **6a** in $CDCl_3$.

***N*-*tert*-Butyl-*O*-2-*p*-tolylsulfonyl-1-phenylethenylhydroxylamine (6b):** yield 32%, mp 152–154°, nmr ($CDCl_3$) δ 1.17 (s, 9 H, *tert*-butyl), 2.38 (s, 3 H, aryl CH_3), 5.63 (s, 1 H, NH), 6.83 (s, 1 H, vinyl H), ~7.20–8.00 ppm (m, 9 H, aryl protons); ir (KBr) 3255, 3085, 1620, 1590, 1365, 1295, 1285, 1127 cm^{-1}.

Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.06; S, 9.28. Found: C, 65.98; H, 6.62; N, 3.79; S, 9.20.

Reduction of 6a. Using a procedure similar to that described by Nicolaus, *et al.*,[11] a 91% yield of pure *p*-tolylsulfonylacetone, mp 50.5–51.5° (lit.[19] mp 52°), was obtained. The spectral data were in accordance with the structure. *tert*-Butylamine was detected in the reaction mixture by glc comparison with an authentic sample.

Esr Experiments. A 0.05 *M* solution of dibenzoyl peroxide in benzene was mixed with an equimolar solution of **4a** or **4b** in benzene, and the mixture was degassed. After 5 min, the esr spectrum of the spin adduct was recorded: **5a,** a_N = 14.7 G, a_H = 2.8 G (1 H); **5b,** a_N = 14.5 G, a_H = 4.0 (1 H), 6.0 G (1 H).

Acknowledgment. We are indebted to Dr. J. H. Wieringa for performing the NOE experiments.

Registry No.—**1a,** 13894-21-8; **1b,** 14027-53-3; **1c,** 24378-05-0; **2a,** 16649-50-6; **2b,** 2211-64-5; **4a,** 51869-11-5; **4b,** 51869-12-6; **4c,** 51869-13-7; **5a,** 51869-14-8; **5b,** 51869-15-9; **6a,** 51869-50-2; **6b,** 51869-16-0.

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(9) It is highly unlikely that the observed peak is due to an OH stretch shifted to lower frequency as a result of hydrogen bonding. To test for intermolecular H bonding, ir spectra were taken at concentrations as low as 10^{-2} mol $l.^{-1}$ but no free OH stretch could be detected. The frequency of the absorption is too low to be the result of intramolecular H bonding of OH in a structure like **3** to a weak H-bond acceptor moiety like the sulfonyl group; see J. W. Dallinga and J. B. F. N. Engberts, *Spectrochim. Acta,* in press.
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(12) Hydroxylamines containing an unsubstituted OH group give a positive test with Fehling's reagent; see ref 7.
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(15) One could imagine that the barrier to rotation around the carbon–carbon double bond in **6a** is substantially lowered owing to resonance interaction involving partial electron pair localization at α-sulfonyl carbon. However, nmr spectra of **6a** taken in CS_2 down to −110° did not show any splitting of the appropriate signals.
(16) See, for instance, R. Rowan, III, A. Warshel, B. D. Sykes, and M. Karplus, *Biochemistry,* **13,** 970 (1974), and references cited therein.
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Thermal Rearrangement of Deltacycline to Indan. A Facile and Deep-Seated Aromatization

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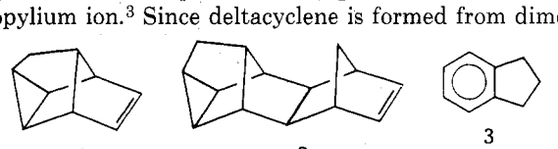
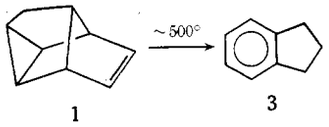
We have been investigating the mass spectral behavior of deltacyclene (tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene, **1**)[1] and a series of related compounds and have observed very strong peaks at *m/e* 118 and 117 in the mass spectra of many of these molecules, especially deltacyclene itself and its thermal precursor, the head-to-side norbornadiene dimer (**2**).[1b,c] This mass spectral pattern is suggestive of the aromatic C_9H_{10} isomer indan (**3**) under similar conditions[2] and indicates that deltacyclene rearranges upon electron impact to indan, which then loses hydrogen in apparent analogy with the mass spectral rearrangement of toluene to the tropylium ion.[3] Since deltacyclene is formed from dimer **2**



1 2 3

via pyrolysis at ~480°,[1] the mass spectrum of **2** first of all indicates that the analogous fragmentation (a retro Diels–Alder reaction) apparently occurs in the mass spectrometer and, secondly, raises the possibility that deltacyclene might undergo pyrolysis to indan.

Accordingly, deltacyclene was pyrolyzed at temperatures between 480 and 510°. This resulted in a strikingly clean aromatization to indan (eq 1).



1 3 (1)

A number of side products, most with molecular weights of 118, were also formed, but their total concentration was low. In a typical experiment, deltacyclene vapor, mixed with dry nitrogen, was pyrolyzed in a flow system by passing a stream of nitrogen over a reservoir of starting material, passing the mixture through a heated Pyrex tube, and then trapping the products at Dry Ice or liquid nitrogen temperatures. Product mixtures were initially analyzed on a gas chromatograph–mass spectrometer combination, and indan was confirmed as the major product by comparing the mass spectrum, gas chromatographic retention times, and nmr spectrum of the product with the corresponding data for commercial indan. All were indistinguishable. When the mixture was analyzed on SE-30 or FFAP columns at least eight products could be detected, but unreacted deltacyclene (16%) and indan (70%) were by far the major components, with the next most plentiful product (also *m/e* 118) having a concentration of 8% (percentages are based on total volatile product; see Experimental Section). When the dimer **2** was pyrolyzed at temperatures higher than 480° and, especially, with larger contact times, the product mixture contained increasing amounts of indan presumably formed *via* secondary pyrolysis of deltacyclene; this system (**2** → **3**) actually constitutes a fairly good synthesis of indan.

The deltacyclene → indan transformation is reminiscent of the thermal conversion of norbornadiene to toluene, which has been postulated to occur *via* initial formation of cycloheptatriene.[4] The analogous pathway in this system,