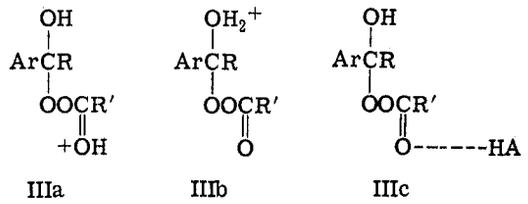
It is also not proper to correlate directly the uncorrected data for a strong electron-attracting group such as NO_2 and CN where methyl group is also a competitive migration one.[7,25]

The ρ value for the migration step cannot be obtained directly from the above data because K_I is unknown. An approximately estimated ρ value for K_I might be near 0.9 if compared with ρ values for other carbonyl addition equilibria in aqueous ethanol (at 20–30°), *e.g.*, ArCHO + H_2O_2 (ρ = 1.6),[2a] ArCHO + $H_2NNHCONH_2$ (ρ = 1.64),[26] and ArCOMe + $H_2NNHCONH_2$ (ρ = 0.91).[27] Thus, the migration in the B–V reaction should possess an approximate ρ value of −3 (σ^+), which is comparable to the ρ value of −4 to −5 for the B–V migration of benzaldehydes[28a] and to other peroxide rearrangements (ρ = −5.1,[28] −4.57,[29] and −3.78[30]).

As for the nature of acid catalysis for the migration step, the protonation on the carbonyl (IIIa),[7] acyloxy oxygen,[7] or hydroxyl oxygen (IIIb)[5,6] has been assumed. However, the present study demonstrates no intervention of conjugate acid of I, *i.e.*, IIIa or IIIb of specific proton catalysis, since the rate is not correlated with H_0 function (the slope of log k_{obsd} *vs.* $-H_0$ is less than 0.4) but accelerated slightly by perchloric acid in aqueous ethanol. The catalysis suggests IIIc of general acid catalysis, the position of hydrogen bonding being either on carbonyl (IIIc) or acyloxy oxygen. Finally, the data in the presence of acetic acid clearly reveals that the uncatalyzed migration from I is also operative.



(25) E. E. Smissman, J. P. Li, and Z. H. Israili, in ref 9 reported an exceptional facile migration of *o*-nitrophenyl group for the B–V reaction of acetophenones, but strangely the anchimeric assistance was not observed for propiophenones.

(26) R. Wolfenden and W. P. Jencks, *J. Amer. Chem. Soc.*, **83**, 2763 (1961).

(27) R. P. Cross and P. Fugassi, *ibid.*, **71**, 223 (1949).

(28) K. Nelson, quoted by S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(29) A. W. De R. Van Stevenick and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **79**, 413 (1960).

(30) G. H. Anderson and J. G. Smith, *Can. J. Chem.*, **46**, 1553, 1561 (1968).

Experimental Section

Materials.—Perbenzoic acids were prepared by the reaction of benzoyl peroxides or chlorides with alkaline hydrogen peroxide[31] and recrystallized from *n*-hexane. *o*- and *p*-hydroxyacetophenones were prepared by the Fries rearrangement of corresponding phenyl esters.[32] Alkyl group and melting or boiling points for *p*-hydroxyphenyl alkyl ketones are as follows: Me, mp 108.8–109.2°; Et, mp 153°; *n*-Pr, mp 90.5–91.5°; *i*-Pr, bp 196–198° (21 mm); CH_2Cl, mp 148–149°; *i*-Bu, bp 175–180° (6 mm); Ph, mp 132–133°. Boiling points for *o*-HOC_6H_4COR are as follows: Me, 109–110° (23 mm); Et, 120–122° (21 mm); *n*-Pr, 91–98° (5 mm); *i*-Pr, bp 121–123° (20 mm). Other ketones were synthesized by Friedel–Crafts acylation and purified by fractional distillation.

Rate and Products.—The B–V reaction of acetophenones in 40 vol. % aqueous ethanol was conducted in the presence of 10^{-4} *M* EDTA to suppress metallic ion catalyzed decomposition of PBA. The rate was determined by iodometry of peracid and/or by uv spectrophotometry of ketone as reported previously.[2]

The produced phenols were determined by uv spectrophotometry or by glc after methylation as reported previously.[2b]

Registry No.—PBA, 93-59-4; *p*-hydroxyphenyl isobutyl ketone, 34887-83-7.

(31) Y. Ogata and Y. Sawaki, *Tetrahedron*, **23**, 3327 (1967).

(32) E. Miller and W. H. Hartung, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1955, p 543.

Nonbenzenoid Aromatic Systems. VII.[1a] Reactions of Azulenes with Ethylene Oxide or Trimethylene Oxide and Lewis Acids

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A direct β-hydroxyethylation method applied to azulene, 5-methylazulene, and certain 6-substituted (OCH_3, CH_3, Br) azulenes is reported. Reaction of azulene and trimethylene oxide with aluminum chloride yielded 3-(1-azulyl)-1-propanol and 1,1-di(1-azulyl)propane.

Presently, only one literature method is available for the introduction of the 2-hydroxyethyl side chain into the 1 position of azulene (**1a**).[2] Since this procedure is rather lengthy (*N*,*N*-dimethylamino methylation, quaternization, cyanide displacement, hydrolysis, and reduction), our interest in the solvolytic behavior of 2-(1-azulyl)ethyl tosylate and ring-substituted derivatives[3] prompted us to examine a more direct route for introducing this side chain. We report here such a procedure, which involves reaction of the azulene with ethylene oxide and Lewis acids.

The reaction is a modification of the procedure by Searles[4] for the β-hydroxyethylation of benzene and anisole; the modifications involve the use of methylene chloride as solvent and shorter reaction times. As can be seen from the results listed in Table I, 2-(1-azulyl)-ethanol (**2a**) was produced in 41–47% yield (81–85% net yield) with either aluminum chloride or stannic chloride as the Lewis acid. A minor component was identified as the disubstitution product, 1,3-bis(2-hydroxyethyl)azulene (**3**), on the basis of its nmr spectrum. Increasing or decreasing the amounts of Lewis

(1) (a) For paper VI see R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **37**, 2703 (1972); (b) Phillips Petroleum Co. Fellowship, 1968–1969.

(2) A. G. Anderson, R. G. Anderson, and T. S. Fujita, *J. Org. Chem.*, **27**, 5435 (1962).

(3) R. N. McDonald and J. R. Curtis, *J. Amer. Chem. Soc.*, **93**, 2530 (1971).

(4) S. Searles, *ibid.*, **76**, 2313 (1954).

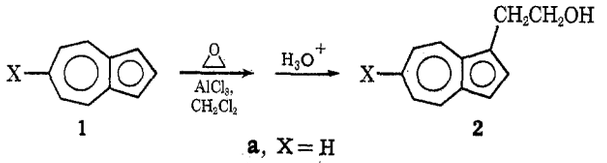
TABLE I

CONDITIONS AND YIELDS FOR β-HYDROXYETHYLATION OF AZULENES[a]

Starting azulene	Solvent	Catalyst	Reaction time	Yield, %	Net yield,[b] %
Azulene	CH_2Cl_2	$AlCl_3$	10 min	47	81
Azulene	CS_2	$AlCl_3$	10 min	20	70
Azulene	CH_2Cl_2	$SnCl_4$	10 min	41	85
Azulene	CH_3NO_2	$AlCl_3$	2 min	0	0
Azulene	CH_2Cl_2	$AlCl_3$	10 hr	45	68
6-Methylazulene	CH_2Cl_2	$AlCl_3$	10 min	46	73
5-Methylazulene	CH_2Cl_2	$AlCl_3$	10 min	45	
6-Bromoazulene	CH_2Cl_2	$AlCl_3$	1 hr	41	90
6-Methoxyazulene	CH_2Cl_2	$AlCl_3$	20 min	48	93
6-Cyanoazulene	CH_2Cl_2	$AlCl_3$	1 hr	0	0[c]

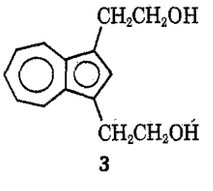
[a] After chromatography of the products **2** on basic alumina, nmr spectral analysis showed the presence of impurities, presumably ethylene chlorohydrin and/or ethylene glycol. The impurities can be removed by (1) repeated, careful chromatography of the product on alumina and recrystallization of solid alcohols **2**; (2) preparation and chromatography of the acetates of **2** followed by hydrolysis; and (3) preparation and recrystallization of the 1,3,5-trinitrobenzene complexes of **2** followed by chromatography. Of these three methods, (2) is the most convenient and gives the best recoveries of alcohols **2**. [b] Based on recovered starting material. [c] 6-Cyanoazulene recovered in 70%.

acid and increasing reaction times led to reduced amounts of **2a**. The procedure has been successfully applied to the β-hydroxyethylation of 6-methoxy- (**1b**), 6-methyl- (**1c**), 6-bromo- (**1d**), and 5-methylazulene;



1 2

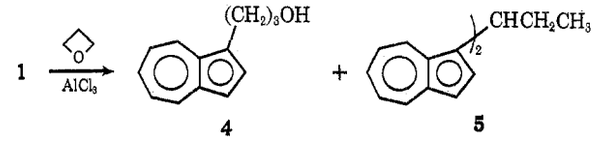
a, X = H
b, X = OCH_3
c, X = CH_3
d, X = Br
e, X = CN



3

the last example gives rise to a mixture of 2-[5- and 2-(7-methylazulyl)]ethanol.[5] 6-Cyanoazulene (**1e**) failed to produce **2e** in this reaction, apparently due to complexation of the cyano group and aluminum chloride with accompanying increased electron withdrawal by the complexed group.

The success of the β-hydroxyethylation of **1** led us to try γ-hydroxypropylation using trimethylene oxide in place of ethylene oxide. 3-(1-Azulyl)-1-propanol (**4**)



4 5

(5) Since this original work, we have successfully used this reaction with several 2-substituted (Cl, Br, CH_3, OCH_3) azulenes.[6]

(6) J. M. Richmond, unpublished results.

was indeed formed, but only in minor amounts. The major product was 1,1-di(1-azulyl)propane (**5**), which was identified on the basis of its nmr and mass spectra; the 100% abundance peak in the mass spectrum of **5** involved the loss of $\cdot C_2H_5$, the process expected for structure **5**.[7] By increasing the amount of aluminum chloride (and trimethylene oxide), the isolated ratio of **5**:**4** increased, as is shown in Table II. Replacing

TABLE II

REACTION OF AZULENE WITH TRIMETHYLENE OXIDE

Azulene, mmol	$AlCl_3$, mmol	$(CH_2)_3O$, mmol	Yield of **4**, %	Yield of **5**, %
2.0	4.0	4.0	1.6	4.8
4.4	9.5	13.8	5.5	12.5
3.2	16.2	16.2	2.2	15.2
4.0	20.0	41.0	0.0	20.0

aluminum chloride with stannic chloride gave neither **4** nor **5**. While the mechanism of formation **5** is unknown, if we assume that **4** or its aluminate ester is the precursor to **5**, a number of mechanistic pathways to **5** appear reasonable, probably involving formation of a 1-azulylcarbinyl cation followed by electrophilic substitution on unreacted azulene.

Experimental Section[8]

β-Hydroxyethylation of Azulene.—To 100 mg (0.78 mmol) of azulene in 25 ml of dichloromethane was added 0.216 g (1.6 mmol) of anhydrous aluminum chloride with stirring at ice bath temperature. After a few minutes the color of the mixture changed from blue to light yellow. Into this was injected 8.0 ml of a 1% (v/v) ethylene oxide–dichloromethane solution by means of syringe. The color of the solution changed immediately back to blue. The mixture was stirred for 10 min and poured onto 500 ml of iced 10% hydrochloric acid. The organic layer was extracted with 10% hydrochloric acid and washed with ten 100-ml portions of water. The dichloromethane layer was dried (Na_2SO_4), the solvent was evaporated, and the blue residue was chromatographed on 40 g of alumina. A mixture of 9:1 hexane–dichloromethane eluted 42 mg of azulene, chloroform eluted a second blue band, and a third smaller blue band was eluted with 1:1 ethanol–chloroform. Solvent removal from the second band yielded 63 mg (47%; 81% net yield) of 2-(1-azulyl)ethanol (**2a**) recrystallized from carbon tetrachloride as blue needles, mp 57–58° (lit.[2,3] mp 57–58°), which was identical in all respects with that previously reported. The third band, 15 mg (9%; 15% net yield), was characterized as 1,3-bis(2-hydroxyethyl)azulene (**3**), assigned on the basis of the nmr spectrum ($CDCl_3$) τ 1.85 (d, 2), 2.36 (s, 1), 2.50–3.25 (m, 3), 6.22 (t, J = 6.0 Hz, CH_2CH_2OH, 4), 6.83 (t, J = 6.0 Hz, CH_2CH_2OH, 4), and 7.66 (s, OH, 2).

2-(6-Methoxy-1-azulyl)ethanol (2b).—To 0.300 g (1.90 mmol) of 6-methoxyazulene dissolved in 150 ml of dichloromethane was added 0.508 g (3.80 mmol) of aluminum chloride at ice bath temperature. After a few minutes stirring, the color changed from violet-red to deep blue. To this mixture was added 10 ml of 2% (v/v) ethylene oxide–dichloromethane, causing the solution to change back to violet-red. After stirring the solution for 20 min, the color had gradually faded to a light pink. Isolation and purification of the product as described previously resulted in 0.145 g of recovered 6-methoxyazulene and 0.184 g (48%; 93% net yield) of **2b**: mp 59.5–61.0°; ir (KBr) 3.04 (s, OH), 6.35 (s), and 12.05 μ (s); nmr ($CDCl_3$, internal TMS) τ 1.82 and 1.86 (2 superimposed d's, J = 11.5 Hz, $C_{4,8}$ ring H's, 2), 2.46 (d, J = 4.0

(7) R. G. Cooks, A. N. Yeo, and D. H. Williams, *Org. Mass Spectrom.*, **2**, 985 (1969).

(8) Melting points were determined on a Kofler hot stage and are uncorrected. Spectra were determined with commercial instruments (ir, P-E 137; nmr, Varian A-60 and T-60; uv, Cary 11; mass, AEI MS-9). Nmr spectral data are listed as centers except for multiplets, where the range of the signals is given. All alumina is F-20 Alcoa, basic alumina, activity I, unless otherwise specified.

Hz, C_2 ring H, 1), 2.78 (d, J = 4.0 Hz, C_3 ring H, 1), 3.28 (broad d, J = 11.5 Hz, $C_{5,7}$ ring H's, 2), 6.11 (t, J = 6.0 Hz, CH_2CH_2-OH, 2), 6.13 (s, OCH_3, 3), 6.76 (t, J = 6.0 Hz, CH_2CH_2OH, 2), and 8.30 (s, OH, 1).

For analysis, a 1,3,5-trinitrobenzene complex was prepared and recrystallized from 1:1 ethyl acetate–hexane: mp 90.0–91.5°; λ_{max} (CH_2Cl_2) 541 (log ϵ 2.42), 371 (3.38), 358 (3.87), 350 (3.80), 342 (3.78), 297 (4.93), and 291 nm (4.93).

Anal. Calcd for $C_{19}H_{17}N_3O_8$: C, 54.91; H, 4.13. Found: C, 55.00; H, 4.10.

2-(6-Methyl-1-azulyl)ethanol (2c).—Following the above procedure, 100 mg (0.705 mmol) of 6-methylazulene, 188 mg (1.41 mmol) of aluminum chloride, and 7.3 ml of 1% ethylene oxide–dichloromethane solution were allowed to react. This reaction netted 37 mg of recovered 6-methylazulene, 60 mg (46%; 73% net yield) of **2c**, identical to that of an authentic sample,[9] and 12 mg (7%; 12% net yield) of what is probably 1,3-bis(2-hydroxyethyl)-6-methylazulene from its nmr spectrum.

2-(6-Bromo-1-azulyl)ethanol (2d).—To 126 mg (0.61 mmol) of 6-bromoazulene in 25 ml of dichloromethane cooled to ice bath temperature 165 mg (1.22 mmol) of aluminum chloride was added, with a corresponding color change from blue to green. Upon addition of 6.3 ml of a 1% (v/v) ethylene oxide–dichloromethane solution, the blue color returned. After 0.5 hr of stirring, 83 mg (0.61 mmol) of aluminum chloride and 3.2 ml of the 1% ethylene oxide solution were added to the solution, with stirring for another 0.5-hr period. The product was isolated and purified as described previously to yield 68 mg of 6-bromoazulene and 63 mg (41%; 90% net yield) of **2d**. This product was crystallized from carbon tetrachloride–hexanes to yield pale blue plates: mp 113–116°; ir (KBr) 3.10 (s, OH), 6.41 (s), 11.27 (m), 12.13 (s), and 12.76 μ (m); nmr ($CDCl_3$, internal TMS) τ 1.80–2.70 (m, 6), 6.05 (t, J = 6.5 Hz, CH_2CH_2OH, 2), 6.85 (t, J = 6.5 Hz, CH_2CH_2OH, 2), and 8.42 (s, OH, 1); λ_{max} (CH_2Cl_2) 724 (log ϵ 1.91), 654 (2.27), 603 (2.47), 430 (1.75), 353 (3.72), 333 (3.62), 292 (4.83), and 286 nm (4.81).

Anal. Calcd for $C_{12}H_{11}OBr$: C, 57.39; H, 4.42. Found: C, 57.10; H, 4.60.

2-[5- and 2-(7-Methyl-1-azulyl)]ethanol.—Following the procedure outlined with azulene, 180 mg (1.27 mmol) of 5-methylazulene in 50 ml of dichloromethane was allowed to react with 366 mg (2.66 mmol) of anhydrous aluminum chloride and 13 ml of a 1% (v/v) ethylene oxide–dichloromethane solution. Upon isolation of the product, 108 mg (45.5%) of a 1:1 mixture of 2-[5- and 2-(7-methyl-1-azulyl)]ethanol was collected as a blue-green oil, containing an impurity.

Purification of the compounds was achieved by recrystallization of the ethanols as their mixed 1,3,5-trinitrobenzene complexes. To 108 mg (0.58 mmol) of product in 3 ml of ethyl acetate was added 124 mg of 1,3,5-trinitrobenzene in 3 ml of ethyl acetate. The solvent volume was reduced to approximately one-half, 3 ml of hexanes was added, and the product was allowed to crystallize at freezer temperature. Recrystallization of the brown solid from 1:1 hexanes–ethyl acetate yielded a red-brown solid: mp 80.0–82.0°; ir (KBr) 3.00 (m, OH) and 7.47 μ (s); nmr ($CDCl_3$, internal TMS) τ 0.71 (s, TNB H's, 3), 1.84–3.30 (m, 6), 6.03 (t, J = 6.0 Hz, CH_2CH_2OH, 2), 6.70 (t, J = 6.0 Hz, CH_2CH_2-OH, 2), 7.33 and 7.37 (s, CH_3, each 1.5), and 8.42 (s, OH, 1); λ_{max} (CH_2Cl_2) 658 (log ϵ 2.52), 610 (2.57), 361 (3.58), 346 (3.70), and 283 nm (4.77).

Anal. Calcd for $C_{19}H_{17}N_3O_7$: C, 57.14; H, 4.29. Found: C, 56.99; H, 4.48.

Reaction of Azulene with Trimethylene Oxide.—To azulene (415 mg, 3.24 mmol) in 200 ml of dichloromethane was added 2.160 g (16.2 mmol) of anhydrous aluminum chloride with stirring at ice bath temperature. After being stirred a few minutes, the solution became bright yellow. To this mixture was added 940 mg (16.2 mmol) of trimethylene oxide (Farchan Research Laboratories) dissolved in 50 ml of dichloromethane, causing an immediate color change from yellow to blue. The mixture was stirred for 10 min and isolation of the blue residue was achieved as described previously. The blue residue was chromatographed on 60 g of alumina with hexanes eluting, after careful solvent volume reduction, 29 mg of azulene. A second band eluted with 9:1 hexanes–dichloromethane gave 73 mg of a bright blue solid, mp 77–77.5°. Chloroform eluted 13 mg of a blue oil after solvent evaporation.

The blue solid was identified as 1,1-di(1-azulyl)propane (**5**) (15%; 51% net yield) based on its analysis and spectral properties: ir (KBr) 6.38 (s), 12.93 (s), 13.08 (s), and 13.62 μ (s); nmr (CCl_4, internal TMS) τ 1.55–3.30 (m, 14), 4.88 (t, J = 7.0 Hz, $CHCH_2CH_3$, 1), 7.63 (m, J = 7.0 Hz, $CHCH_2CH_3$, 2), and 9.00 (t, J = 7.0 Hz, $CHCH_2CH_3$, 3); λ_{max} (cyclohexane) 735 (log ϵ 2.27), 693 (2.38), 662 (2.73), 631 (2.72), 605 (2.80), 584 (2.72), 362 (3.89), 346 (3.94), 292 (4.74), 288 (4.73), 271 (4.85), and 241 nm (4.47); mass spectrum (70 eV, heated inlet) m/e (rel intensity), 296 ($M\cdot^+$, 27), 267 (100), 265 (24), 252 (8), and 239 (5).

Anal. Calcd for $C_{13}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.20; H, 6.82.

The second product band was identified as 3-(1-azulyl)-1-propanol (**4**) (2%; 7% net yield): ir (film) 3.04 (s, OH) and 6.34 μ (s); nmr (CCl_4, internal TMS) τ 1.60–3.30 (m, 7), 6.43 (t, J = 6.0 Hz, CH_2OH, 2), 6.88 (t, J = 6.0 Hz, $CH_2CH_2CH_2$-OH, 2), and 7.90–8.30 (m, $CH_2CH_2CH_2OH$, 2); λ_{max} (CH_2Cl_2) 718 (log ϵ 1.97), 654 (2.40), 602 (2.48), 359 (3.50), 345 (3.73), 289 (4.55), 284 (4.66), and 280 nm (4.69); mass spectrum (70 eV, heated inlet) m/e (rel intensity), 186 ($M\cdot^+$, 25), 155 (9), and 141 (100). A trinitrobenzene complex was prepared from the above oil to aid in its purification which was recrystallized from ethyl acetate–hexanes to give brown needles, mp 102.5–103.5°.

Registry No.—**1a,** 275-51-4; **1b,** 35046-03-8; **1c,** 1654-52-0; **1d,** 35046-05-0; **2b,** 35046-06-1; **2b** (1,3,5-trinitrobenzene complex), 35046-07-2; **2d,** 35096-49-2; **3,** 35046-08-3; **4,** 35046-09-4; **4** (1,3,5-trinitrobenzene complex), 35046-10-7; **5,** 35046-11-8; ethylene oxide, 75-21-8; 5-methylazulene, 1654-55-3; trimethylene oxide, 75-56-9; 2-(5-methyl-1-azulyl)ethanol, 35046-13-0; 2-(7-methyl-1-azulyl)ethanol, 35046-14-1.

Acknowledgment.—The authors wish to thank the National Science Foundation (GP-7818, GP-10691) for support of this research.

(9) J. R. Curtis, Ph.D. Thesis, Kansas State University (1971).