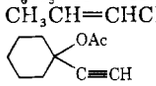
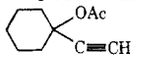
Table I. The Conversion of Ethynylalkanol Acetates to Allenes

$R_2'C(OAc)C{\equiv}CH$	% yield, $RHC{=}C{=}CR_2'$[a]		
	n-Bu_3B[b]	i-Bu_3B[b]	sec-Bu_3B[b]
$(CH_3)_2C(OAc)C{\equiv}CH$	80	90	76
n-$C_5H_{11}CH(OAc)C{\equiv}CH$	87 (78), 90[c]	76, 92[c]	80, 92[c]
$C_6H_5CH(OAc)C{\equiv}CH$	77, 94[c]	70, 91[c]	82, 90[c]
$C_6H_5CH{=}CHCH(OAc)C{\equiv}CH$	(64)[c]		
$CH_3CH{=}CHCH(OAc)C{\equiv}CH$	87 (72)[c]		
	82	78 (75)	81 (73)

[a] % yield based on acetate by VPC (isolated yields are in parentheses). [b] R_3B. [c] −120 °C, other reactions at −78 °C.

Table II. The Conversion of Ethynylalkynol Acetates to Acetylenes

$R_2'C(OAc)C{\equiv}CH$	R_3B	% yield,[a] $RC{\equiv}CCHR_2'$
n-$C_5H_{11}CH(OAc)C{\equiv}CH$	n-Bu_3B	87 (78)
$C_6H_5CH(OAc)C{\equiv}CH$	n-Bu_3B	91
$C_6H_5CH(OAc)C{\equiv}CH$	sec-Bu_3B	91
$CH_3CH{=}CHCH(OAc)C{\equiv}CH$	n-Bu_3B	(60)
	n-Bu_3B	84 (70)

[a] % yield based on acetate by VPC (isolated yields are in parentheses). All reactions were run at −78 °C.

The reaction is quite general and gives high yields of the acetylene (Table II).

The following procedure for the preparation of methyl cyclohexylidenetetradeca-12,13-dienoate (**3**) is representative. The trialkylborane was prepared[3a] in a 50-ml flask under nitrogen from 15.5 mmol of borane–methyl sulfide and 50 mmol of methyl 10-undecenoate using 20 mL of tetrahydrofuran, 5 mL of diethyl ether, and 5 mL of pentane as a solvent.[8] A separate, dry 100-mL flask was flushed with nitrogen and charged with 20 mL of THF, 5 mL of ether, 5 mL of pentane, and 15 mmol of 1-ethynylcyclohexanol acetate. The solution was cooled to −120 °C[8] [petroleum ether (30–60 °C)–isopropyl alcohol–acetone (4:1:1)/1N_2]. n-Butyllithium, 15 mmol (9.6 mL of a 1.56 M solution in hexane) was added dropwise followed by the dropwise addition of the organoborane solution. The solution was then warmed from −120 °C to room temperature. The solution became slightly cloudy. After 15 min at room temperature, 3 mL of dry acetic acid was added. The mixture was stirred for 15 min and then neutralized (phenolphthalein) with 3 M sodium hydroxide. The aqueous layer was separated, and the THF dried (K_2CO_3) and removed under vacuum. Pentane (60 mL) was added, followed by 15 mmol of ethanolamine. The solution was warmed briefly and a heavy solid ethanolamine adduct of R_2BOH was removed by filtration. After removal of the pentane, the residue was distilled to give 3.35 g of product (73%): bp 140–145 °C (0.02 mm); IR (neat) 1950 (allene), 1740 cm^{-1} (carbonyl); ^1H NMR (CCl_4, TMS) δ 1.2–2.3 (br m, 30 H), 3.62 (s, 3 H), 4.9 (br m, 1 H). The product contained ~5% isomer resulting from hydroboration at the internal position of methyl 10-undecenoate. No acetylene was detected. Repetition of the reaction at −78 °C resulted in a 61% isolated yield.

The hydrocarbon allenes were conveniently isolated by column chromatography on silica gel or alumina following oxidation of the organoborane by-product. The acetylenes were prepared by substituting water for acetic acid.

This procedure offers a general method for preparing allenic boranes which can be converted to either allenes or acetylenes. Furthermore, the allenic boranes may be extremely versatile intermediates, similar to allylic boranes in their reactions. For example, preliminary experiments have shown that they will add readily to ketones and aldehydes to give homopropargylic alcohols, $RC{\equiv}CCR_2CR'_2OH$.[9] We are continuing to explore these versatile reagents.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

(1) P. Rona and P. Crabbé, *J. Am. Chem. Soc.*, **91**, 3289 (1969).
(2) T. Leung and G. Zweifel, *J. Am. Chem. Soc.*, **96**, 5620 (1974).
(3) (a) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975; (b) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972.
(4) The ethynylalkanol acetates are readily prepared by the addition of monolithium acetylide to a ketone or aldehyde [M. M. Midland, *J. Org. Chem.*, **40**, 2250 (1975)] followed by acetylation of the propargyl alcohol [H. Rupe, W. Messner, and E. Kambli, *Helv. Chim. Acta*, **11**, 449 (1928)].
(5) We have previously prepared the allenic boranes, **1** (R = n-Bu; R' = C_6H_5, H) [IR 1950 cm^{-1}; NMR δ 6.15 (t, J = 3.0 Hz)] by addition of dilithium trialkylboraacetylides, $(R_3BC{\equiv}CLi)Li$, to aldehydes followed by acetylation (M. M. Midland, the 172nd National Meeting of the American Chemical Society, San Francisco, Aug 29–Sept 3, 1976).
(6) In a few cases up to 10% acetylene was formed.
(7) B. M. Mikhailov, *Organomet. Chem. Rev. A*, 1 (1972).
(8) G. Köbrich and H. Trapp, *Chem. Ber.*, **99**, 680 (1966).
(9) In contrast to our results, Zweifel has found that allenic boranes react with aldehydes to give allenic alcohols.[2]

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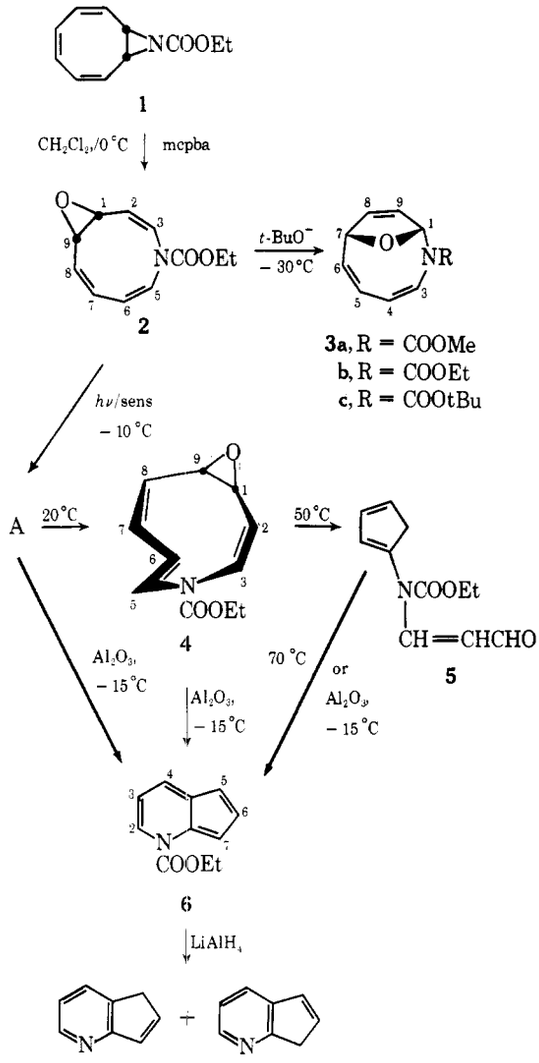
1,2- and 1,4-Oxides of Azonine. A Unique Synthetic Entry into N-Substituted 1-Pyrindines

Summary: The preparation and characterization of three isomeric oxides of azonine, a hitherto unknown C_8H_8XY family of heterobicyclics, and the development of a convenient synthetic scheme for the construction of the interesting, yet rare, N-substituted 1-pyrindine system are described.

Sir: We wish to offer brief description of work which led to (i) the synthesis of three isomeric oxides of azonine, a hitherto unknown C_8H_8XY family of diheterobicyclics and (ii) the development of a general synthetic scheme for the construction of the interesting, but rare,[1] N-substituted 1-pyrindine system depicted as **6**.

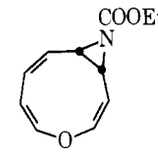
We discovered that reaction between urethane **1** and m-chloroperbenzoic acid (mcpba) leads, in ~55% yield, predominantly[2] to the 1,2-azonine oxide shown as **2**[3] [colorless liquid; ^1H NMR (100 MHz, $CDCl_3$) τ 3.53 (1 H, d, H^3, $J_{3,2}$ = 6.5 Hz), 3.75 (1 H, d, H^5, $J_{5,6}$ = 11.0 Hz), 3.9–4.3 (4 H, m), 5.73 (2 H, q), 6.62 (1 H, m, H^1 or H^9), 6.78 (1 H, m, H^9 or H^1), 8.72 (3 H, t); ^{13}C NMR (25 MHz, $CDCl_3$) 57.64 (C^9 or C^1), 55.76 ppm (C^9 or C^1); λ_{max} (C_6H_{14}) 260 nm (ϵ 2000); m/e 207 (P^+,

28%)]. On contact with strong base, **2** readily isomerizes to the *1,4* counterpart, **3**. Specifically, exposure of **2** to an excess of potassium *tert*-butoxide in THF at −30 °C followed by electrophilic quench with methyl chloroformate at −78 °C yields three structurally related carbamates,[4] **3a**[3] (26%) [colorless



liquid; ^{1}H NMR (100 MHz, benzene-d_6) τ 2.96 (1 H, s, H^1), 3.48 (1 H, d, H^3, $J_{3,4}$ = 11.5 Hz), 4.30 (1 H, dd, H^5, $J_{4,5}$ = 8.0 Hz, $J_{5,6}$ = 11.5 Hz), 4.60 (1 H, dd, H^6, $J_{5,6}$ = 11.5 Hz, $J_{6,7}$ = 6.0 Hz), 4.68 (2 H, s, H^8 + H^9), 4.82 (1 H, dd, H^4, $J_{3,4}$ = 11.5 Hz, $J_{4,5}$ = 8.0 Hz), 4.84 (1 H, d, H^7, $J_{7,6}$ = 6.0 Hz), 6.68 (3 H, s); ^{13}C NMR (20 MHz, $CDCl_3$) 81.79 (C^7), 86.81 ppm (C^1); λ_{max} (C_6H_{14}) 273 (ϵ 7530); *m/e* 193 (P$^+$, 21.8%)], **3b**[5] (18%) (physically and spectroscopically analogous to **3a**), and **3c**[5] (21%) (white crystals; mp 63.5–64.5 °C; spectroscopically analogous to **3a** and **3b**). Exposure to sensitized irradiation (acetone at ca. −10 °C), on the other hand, transforms **2** to an extremely labile substance (A)[6] which, in turn, rearranges to a thermally labile white solid tentatively formulated as **4** [^{1}H NMR (100 MHz, $CDCl_3$, 0 °C) τ 3.24 (1 H, br d, H^3, $J_{3,2}$ = 9.0 Hz), 3.48 (1 H, d, H^7 or H^8, $J_{7,8}$ = 10.0 Hz), 3.66 (1 H, d, H^7 or H^8, $J_{7,8}$ = 10.0 Hz), 3.82 (1 H, br d, H^5 or H^6, $J_{5,6}$ = 14.0 Hz), 4.04 (1 H, d, H^5 or H^6, $J_{5,6}$ = 14.0 Hz), 4.78 (1 H, dd, H^2, $J_{2,3}$ = 9.0 Hz, $J_{2,1}$ = 2.0 Hz), 5.72 (2 H, q), 6.74 (1 H, br s, $W_{1/2}$ ~ 7 Hz, H^9), 7.04 (1 H, dt, H^1, $J_{1,9}$ ~ 3 Hz, $J_{1,2}$ ~ 2 Hz), 8.68 (3 H, t); ^{13}C NMR (20 MHz, $CDCl_3$, −11 °C) 59.13 (C^1 or C^9), 61.94 (C^1 or C^9); λ_{max} (C_6H_{14}) 270 nm (ϵ 2440); *m/e* 207 (P$^+$, 4%)] on warming to 0 °C. The presence in **4** of basically the same [7.1.0] frame as **2** was securely established by catalytic hydrogenation (Rh/C) whereby **2** and **4** were independently converted to the same three-component mixture consisting of an epoxide (IR, mass spectrum, ^{1}H NMR, ^{13}C NMR) (~50% of the mixture), the saturated counterpart of **2** and **4**, and two isomeric alcohols (IR, ^{13}C NMR, mass spectrum). It follows that **2** and **4** must be geometrical isomers, the observation of a large vicinal coupling constant (J = 14 Hz) in the olefinic region of the ^{1}H NMR spectrum of **4** attesting to the presence of a trans double bond in this molecule. Further, the specified location of this key function, i.e., α to nitrogen and not directly linked to the oxirane unit, draws its support primarily from the ready thermal rearrangement of **4** [k (acetone-d_6, 56.2 °C) = 2.38 ± 0.47 × 10^{-4} s^{-1}; $\Delta G^{\ddagger}$ = 24.8 kcal/mol] to **5**.[5,7,8] Besides its key role in the structural elucidation of **4**, **5** is a synthetically useful intermediate cleanly undergoing thermal or alumina-catalyzed cyclodehydration to the hitherto unknown *N*-carbethoxy-1-pyrindine **6**[3,9] [deep purple liquid; ^{1}H NMR (80 MHz, $CDCl_3$) τ 1.80 (1 H, d, H^2, $J_{2,3}$ = 7.0 Hz), 2.25 (1 H, dd, H^4, $J_{4,3}$ = 7.0 Hz, $J_{4,6}$ = 1.5 Hz), 2.75 (1 H, dd, H^6, $J_{5,6}$ = 3.0 Hz, $J_{6,7}$ = 5.0 Hz), 3.20 (1 H, ddd, H^5, $J_{5,6}$ = 3.0 Hz, $J_{5,7}$ = 2.0 Hz, $J_{4,6}$ = 1.5 Hz), 3.46 (1 H, dd, H^7, $J_{6,7}$ = 5.0 Hz, $J_{5,7}$ = 2.0 Hz), 3.50 (1 H, t, H^3, $J_{3,2}$ = $J_{3,4}$ = 7.0 Hz), 5.40 (2 H, q), 8.45 (3 H, t); λ_{max} (C_6H_{14}) 249 nm (ϵ 9900), 326 (6600), 332 (6200), 340 (6900), 357 (3900), 502 sh (1300), 512 sh (1330), 524 (1250, 546 sh (1100), 573 sh (790), 602 (520), 626 sh (260), 662 (110); *m/e* 189 (P$^+$, 5.5%)], a very stable[10] and extensively delocalized (UV) substance.

To conclude it is worth noting that, while the high thermal and chemical instability of photoisomer A precludes the type of direct observation necessary for a firm structural assignment, the close pericyclic association of this substance with isomers **2** and **4** does provide a basis for tentative assignment. Specifically, we propose structure **7** as a mechanistically viable



7

structural possibility for A, i.e., one whose [$_{\sigma}2_s$ + $_{\pi}2_s$ + $_{\pi}4_s$] photogeneration from **2** and [$_{\sigma}2_a$ + $_{\pi}2_s$ + $_{\pi}4_s$] thermal conversion to **4** are fully "allowed" by orbital symmetry. Moreover, the thermal instability of **7** relative to **2** and **4** may reasonably be traced to the well-documented decrease in thermal stability one observes on passing from *cis*-1,2-divinyloxirane (a function present in **2** and **4**) to the aziridine counterpart (a group present in **7**).[11]

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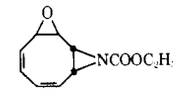
References and Notes

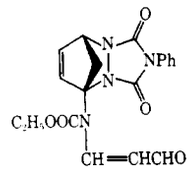
(1) *N*-Methyl-1-pyrindine constitutes the only previously known member of this family: C. B. Reese, *J. Am. Chem. Soc.*, **84**, 3979 (1962). See also A. G. Anderson, Jr., and H. L. Ammon, *Tetrahedron*, **23**, 3601 (1967).

(2) Careful purification of the mixture by column chromatography led to the isolation of small quantities (~2%) of unrearranged product shown (IR, ^{1}H NMR, ^{13}C NMR, mass spectrum) to possess the structure and stereochemistry shown in i.



i

(3) The elemental composition of this substance was established by C. H, and N combustion analysis.
(4) Separation of the mixture into its individual components was accomplished by column chromatography at −15 °C.
(5) This substance was characterized by fully consistent spectroscopic (^{1}H NMR, ^{13}C NMR, IR, UV, mass spectrum) data.
(6) All efforts to purify this substance by column chromatography at −15 °C were frustrated by its tendency to undergo overall dehydration to **6**.
(7) The structure of **5** was further confirmed through low-temperature (−78 °C) cycloadditive coupling with *N*-phenyltriazolinedione to produce a single cycloadduct (mp 70–72 °C dec) whose spectroscopic characteristics (IR, ^{1}H NMR, ^{13}C NMR, mass spectrum) are fully consistent with the structure shown as ii.



ii

(8) For obvious reasons, the primary product generated in the thermolytic ring contraction of **4** must be the symmetrically substituted counterpart of **5** and one which is related to the observed product, **5**, by a simple (1,5) hydrogen shift.
(9) Chemically, the structure of **6** receives unequivocal support from its reductive ($LiAlH_4$) conversion to the previously described [A. G. Anderson, Jr., and H. I. Ammon, *Tetrahedron Lett.*, 2579 (1966)] mixture of 5*H*- and 7*H*-1-pyrindines (^{1}H NMR, UV, IR).
(10) It is significant to note in this connection that compounds **4**, **5**, and A cleanly dehydrate to **6** on passage through alumina at ca. −15 °C.
(11) For pertinent information in this connection see W. Grimme and K. Seel, *Angew. Chem.*, **85**, 514 (1973).
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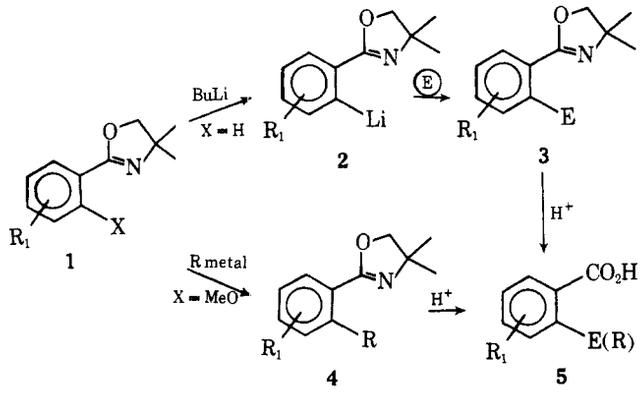
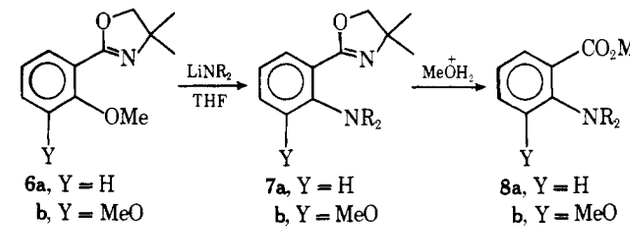
The Displacement of Methoxy by Amino Groups in Aryloxazolines. A Novel Approach to *o*-Amino-, *o*-Alkylamino-, and *o*-Dialkylaminobenzoic Acids

Summary: Treatment of *o*-(methoxyaryl)oxazolines with lithio amides at room temperature results in a facile methoxy displacement furnishing the *o*-(aminoaryl)oxazolines.

Sir: The synthetic utility of aryloxazolines as precursors to various substituted benzoic acids has been demonstrated in this and other laboratories.[1,2] Thus, 2-aryloxazolines **1** (X = H) may be readily metalated using *n*-butyllithium furnishing exclusively the *o*-lithio derivative **2** which, when treated with various electrophiles (E), affords the ortho-substituted aryloxazolines **3**. In contrast to the above, 2-(*o*-methoxyphenyl)oxazolines **1** (X = MeO) were found to react with organometallics (RLi, RMgX) not by metalation, but by direct substitution of the methoxyl group furnishing the *o*-alkyl or *o*-aryl derivative **4**. This latter process occurs under unexpectedly mild conditions (−45–25 °C, THF) in high yields. Both electrophilic (**1** → **3**) and nucleophilic (**1** → **4**) routes lead ultimately to elaborated benzoic acids **5**.



We now wish to describe a significant extension to the methoxy-displacement reaction using various lithio salts of primary and secondary amines as well as lithium amide.[3] When lithio amides are treated with either **6a** or **6b** at room temperature (THF, 1–6 h), the *o*-amino substituent is directly introduced in place of the *o*-methoxyl group in fair-to-excellent yields. The only other major product observed is the starting methoxy derivative which was readily separated and recovered by column or preparative layer chromatography. The aminated oxazolines were transformed into their corresponding methyl benzoates **8** by acidic hydrolysis (3 N HCl, 12–24 h, reflux) followed by esterification using methanolic hydrogen chloride.[4] The versatility of this substitution process can be seen by the examples listed in Table I. Most striking are those examples using so called "nonnucleophilic" bases such as LDA and *tert*-butylamine, indicating that there are virtually no steric effects to inhibit methoxy displacement.[5] In fact, the methoxy group displaced in **6b** is one which is flanked by two ortho substituents and seemingly sterically encumbered. The process may be envisioned as a nucleophilic addition followed by elimination of lithium methoxide en-



6a, Y = H
b, Y = MeO

7a, Y = H
b, Y = MeO

8a, Y = H
b, Y = MeO

Table I. Amination of 2-(*o*-Methoxyphenyl)oxazolines 6 Leading to *o*-Aminated Benzoic Esters

Oxazoline	$LiNR_2$	% 7[a]	% 8[b]
6a	$LiNH_2$	58	45
6a	$LiNEt_2$	98	*c*
6a	$LiN(i\text{-}Pr)_2$	78	*c*
6a	$LiNH(t\text{-}Bu)$	41	*c*
6b	$LiNH_2$	59	72
6b	$LiNEt_2$	93	40
6b	$LiN(i\text{-}Pr)_2$	78	*c*
6b	$LiNH(t\text{-}Bu)$	63	75[d-f]

[a] Yields are those for pure, isolated material. [b] Obtained by heating **7** in 3 N HCl (15–20 h) followed by treatment with methanolic hydrogen chloride. These conditions have not as yet been optimized. [c] Not attempted. [d] Hydrolysis proceeds with dealkylation producing methyl 2-amino-3-methoxy benzoate. [e] All new compounds gave correct analytical data. [f] The alternative basic hydrolysis to remove the oxazoline should allow the *tert*-butyl group to remain intact (see ref 2).