tate was then recrystallized from methanol, giving 5.35 g (70%) of white needles: mp 138°; $\lambda_{max}^{95\% EtOH}$ 217 nm (ϵ 7000); ν_{max}^{KBr} 3280 (NH stretching), 3040 (aromatic CH stretching), 2950 and 2870 (aliphatic CH stretching), 1695 (very broad, C=O stretching), 1550, 1490, 1445, 1325, 1265, 1190, 1135, 1120, 1035, 1010, 760, 735, and 705 cm^{-1}; nmr (pyridine) δ 5.59 (quartet, $J_{9,10} = 2$ Hz, $J_{9,NH} = 8$ Hz, benzylic proton H_A), 4.84 (multiplet, $W_{1/2} = 4$ Hz, H_{10} proton), and 2.70–0.7 (multiplet, methylene–methine envelope).

Anal. Calcd for $C_{16}H_{20}INO_2$: C, 49.88; H, 5.23; N, 3.64. Found: C, 49.97; H, 5.32; N, 4.01.

***syn*-9,10-Imino-1,2,3,4,4a,9,10,10a(*trans*-4a,10a)-octahydrophenanthrene (1).**—A mixture of 5.0 g (0.013 mol) of the iodocarbamate and 12.9 g of potassium hydroxide in 130 ml of absolute ethanol was refluxed for 3 hr. The ethanol was then removed *in vacuo* and the remaining solid was dissolved in 500 ml of ether and washed with cold water until the aqueous washings were neutral. The ether layer was dried (Na_2SO_4) and evaporated *in vacuo* to a volume of 50 ml, which was then placed in the refrigerator overnight. A total of 2.49 g (93.5%) of white needles, mp 128–129°, were collected. A small portion of the aziridine was recrystallized from ether for the analytical sample: mp 129–130°; ν_{max}^{KBr} 3200 (NH stretching), 3030 (aromatic CH stretching), and 2870 (aliphatic CH stretching), 1550, 1490, 1450, 1420, 1290, 1050, 910, 870, 850, 815, 794, 770, 745, and 735 cm^{-1}; nmr ($CDCl_3$) δ 7.55–6.90 (multiplet, aromatic protons), 2.79 (doublet, $J_{AB} = 6$ Hz, benzylic H_9 proton), and 2.70–0.70 (multiplet, methylene–methine envelope).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.25; H, 8.56; N, 6.82.

9(*a*)-Chloro-10(*e*)-benzamido-1,2,3,4,4a,9,10,10a(*trans*-4a,10a)-octahydrophenanthrene (2).—Into 250 ml of anhydrous ether was placed 450 mg (2.25 mmol) of the aziridine 1 and 177 mg (2.25 mmol) of pyridine. To this mixture was added 315 mg (2.55 mmol) of benzoyl chloride in 20 ml of anhydrous ether. With an ice bath, the cloudy suspension was maintained below 10° at all times during the addition. The mixture was then allowed to warm to room temperature and stirred for an additional 30 min. The ether mixture was filtered, and the filtrate was evaporated *in vacuo* to a volume of 15 ml, with the water bath kept at room temperature, and placed in the refrigerator. The needlelike crystals that formed were removed by filtration, giving a total of 515 mg (68%) of the benzamide 2, mp 142–143°. The benzamide could not be recrystallized, since upon heating in solution it formed oxazoline hydrochloride 3: ν_{max}^{KBr} 3330 (NH stretching), 2900 and 2180 (aliphatic CH stretching), 1630 (C=O stretching), 1520, 1480, and 690 cm^{-1}; nmr ($CDCl_3$) δ 8.05–7.05 (multiplet, 9 aromatic protons), 6.65 (doublet, amide proton), 5.46 (doublet, $J_{AB} = 4$ Hz, benzylic proton H_9), 4.67 (sextet, $J_{BC} = 9$ Hz, proton H_B), and 3.00–0.90 (multiplet, methylene–methine envelope).

Anal. Calcd for $C_{21}H_{22}ClNO$: C, 74.21; H, 6.53; N, 4.12. Found: C, 74.22; H, 6.13; N, 4.27.

2-Phenyloxazoline of 9(*a*)-Hydroxy-10(*e*)-amino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (3). A. Cyclization of 2.—A mixture of 300 mg (0.89 mmol of chlorobenzamide 2, 75 mg (0.90 mmol) of anhydrous sodium bicarbonate, and 200 ml of acetone was refluxed for 5 hr with stirring. The mixture was then evaporated *in vacuo* to dryness and to this was added 100 ml of water. The aqueous mixture was then extracted seversl times with ether. The ether layers were combined, dried (Na_2SO_4), and evaporated *in vacuo* to give 260 mg of solid material. The solid material was passed over a 30-g alumina column (Merck, reagent aluminum oxide) using benzene as an eluent. No material was isolated in the first 160 ml of benzene eluted from the column, but the next 360 ml of benzene solvent eluted afforded 230 mg (86%) of the oxazoline: mp 142–143°; ν_{max}^{KBr} 3050 (aromatic CH stretching), 2910 and 2860 (aliphatic CH stretching), 1640 (C=N stretching), 1575, 1490, 1445, 1080, 1060, 1025, 960, 950, 930, 780, 740, 725, and 685 cm^{-1}; nmr ($CDCl_3$) δ 8.15–7.10 (multiplet, aromatic protons), 5.49 (doublet, $J_{AB} = 9.5$ Hz, benzylic proton H_A), 4.12 (triplet, $J_{BC} = 9.5$ Hz, proton H_B), and 2.80–0.80 (multiplet, methylene–methine envelope).

Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.97; N, 4.61. Found: C, 83.56; H, 6.98; N, 4.82.

B. Oxazoline 3 Synthesis *via* Amino Alcohol 4.—A mixture of 100 mg (0.46 mmol) of amino alcohol 4,[13] 80 mg (0.46 mmol) of ethyl benzimidate prepared by the method of McCasland and Smith,[16] and 100 ml of anhydrous pyridine was refluxed for 5 hr. The pyridine was then removed *in vacuo*, affording 108 mg of an oil which was placed on an alumina column snd eluted with benzene. A total of 94 mg (69%) of the oxazoline (3), mp 141–142°, was isolated. The spectral properties were identical with those of the oxazoline prepared previously.

Acid Hydrolysis of Oxazoline 3.—Oxazoline 3, 300 mg (1.0 mmol), was dissolved in 150 ml of 10% aqueous hydrochloric acid and refluxed for 1 hr. The acidic solution was allowed to cool and extracted with ether to remove benzoic acid. The acidic solution was made alkaline with aqueous 10% NaOH solution and extracted with $CHCl_3$. The $CHCl_3$ was separated, dried (Na_2SO_4), and evaporated *in vacuo*, affording 148 mg (68%) of amino alcohol 4, mp 180°.

Registry No.—1, 23385-94-6; 2, 23385-95-7; 3, 23385-96-8; 3 hydrochloride, 23385-97-9; 9(*a*)-carbomethoxyamino-10(*a*)-iodo-1,2,3,4,4a,9,10,10a(*trans*-4a,10)-octahydrophenanthrene, 23385-98-0.

(16) G. E. McCasland and D. A. Smith, *J. Amer. Chem. Soc.*, **72**, 2190 (1950).

The Rearrangement of 1-Acylaziridines to Oxazolinium Cations in Strong Acid Media[1]

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General interest in the ring-opening reactions of aziridine derivatives developed as a result of their biological[2,3] and industrial[3,4] significance. Many biological alkylating agents, such as cancer-inducing mitomycin,[3c] contain aziridine ring functions. The recent preparation[5] of 1-alkylaziridinium ions, 1-acylaziridinium ions, and O-protonated 1-acylaziridines prompts us to report our studies of 1-acylaziridines in strong acid media.

Heine[6] has reviewed the well-known isomerization reactions of 1-acylaziridines. Fanta[7] and Heine[8] have investigated extensively the pyrolytic and catalytic

(1) (a) Acid-Catalyzed Cyclization Reactions. VIII. For other papers in this series, see S. P. McManus, J. T. Carroll, P. M. Grohse, and C. U. Pittman, *Org. Prep. Proc.*, in press. (b) This work was supported in part by the University of Alabama Research Committee and at Huntsville in part by the Petroleum Research Fund (Grant 3501-B) administered by the American Chemical Society and by the National Aeronautics and Space Administration (Grant NGL-01-002-001).

(2) (a) B. Belleau, *Can. J. Biochem.*, **36**, 731 (1968); (b) W. C. J. Ross, "Biological Alkylating Agents," Butterworth and Co. Ltd., London, 1962; (c) D. A. Karnofsky and F. Bergel in "Chemotherapy in Cancer," P. L. Plattner, Ed., Elsevier Publishing Co., New York, N. Y., 1964, pp 3–18, 21–23.

(3) P. E. Fanta in "Heterocyclic Compounds—Three- and Four-Membered Heterocycles," Part I, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, and references cited therein.

(4) (a) A. G. Pittman and R. E. Lundin, *J. Polym. Sci., Part A*, **2**, 3803 (1964); (b) R. H. Quacchia, D. E. Johnson, and A. J. DiMilo, *Ind. Eng. Chem., Prod. Res. Develop.*, **6**, 268 (1967).

(5) G. Olah and P. J. Szilagyi, *J. Amer. Chem. Soc.*, **91**, 2949 (1969).

(6) H. W. Heine, *Angew. Chem., Int. Ed. Engl.*, **1**, 528 (1962).

(7) P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **31**, 59 (1966), and previous papers in the series.

(8) P. G. Mente, H. W. Heine, and G. R. Scharoubin, *ibid.*, **33**, 4547 (1968), and previous papers in the series. See also references cited therein for other pertinent work.

TABLE I
NMR ASSIGNMENTS OF OXAZOLINIUM CATIONS IN 90% H_2SO_4[a]

Ion	R_1[b]	NH[b]	Ring CH_2CH,[b] C-4/C-5	C-5 CH_3[b]	Yield of oxazoline on drowning, %
2a	CH_3, 2.91 (s)	9.30 (br)	4.62, J_{cis} = 9.9		61
			5.53, J_{trans} = 9.9		
2b	CH_3, 2.70 (s)	9.10 (br)	4.41 (m)[c]	2.02 (d), J = 6.8	
			5.82 (m)		53
2c	CH_3, 2.90 (s)	9.75 (br)	4.34 (s)	2.16 (s)	66
2d	C_6H_6, 7.81–8.40 (m)	10.10 (br)	4.48 (t), J_{cis} = 9.8		
			5.42 (t), J_{trans} = 9.8		68
2e	C_6H_6, 7.75–8.37 (m)	10.02 (br)	4.20 (t),[d] J_{cis} = 9.9	2.01 (d), J = 7.0	
			4.71 (t), J_{trans} = 9.8		
			5.92 (m)		71

[a] Positions given in parts per million downfield from TMS (internal capillary) at 33°. [b] Abbreviations: s, singlet; d, doublets; m, multiplet; br, broadened singlet; t, triplet. [c] The C-4 protons *cis* and *trans* to methyl at C-5 are not well resolved. [d] *cis* to methyl.

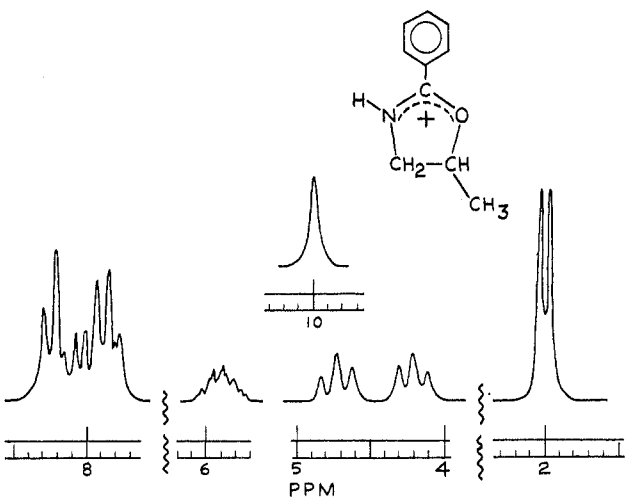
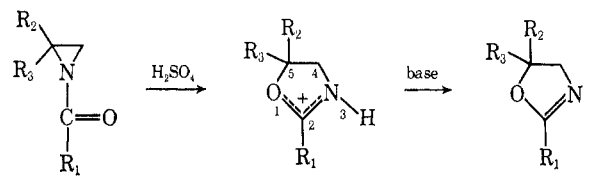


Figure 1.

SCHEME I



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a, $R_1 = CH_3$; $R_2 = R_3 = H$
b, $R_1 = R_2 = CH_3$; $R_3 = H$
c, $R_1 = R_2 = R_3 = CH_3$
d, $R_1 = Ph$; $R_2 = R_3 = H$
e, $R_1 = Ph$; $R_2 = CH_3$; $R_3 = H$

isomerizations of 1-acylaziridines. 1-Acylaziridines undergo thermal rearrangements to 2-oxazolines, N-allylamides, and 2-benzamidobenzalacetophenones.[8] In the presence of various nucleophiles, 1-acylaziridines may isomerize to either a single 2-oxazoline or isomeric 2-oxazolines, depending on the substitution in the 2 and 3 position of the aziridine ring.[4b,8,9] Since Gabriel and Stelzner[10] observed that 1-aziridinethiocarboxanilide is converted into 2-anilino-2-thiazoline by concentrated hydrochloric acid, a few reports[6] of acid-catalyzed isomerizations have appeared. The most pertinent study to our work was that by Heine, Fetter, and Nicholson,[11] who reported the essentially quantitative conversion of 1-*p*-nitrobenzoyl-2,2-dimethylaziridine into 2-*p*-nitrophenyl-5,5-dimethyl-2-oxazoline in concentrated sulfuric acid. As part of our continuing probe into the mechanism of reactions involving carbonyl-group participation in carbonium ion reactions,[12] we decided to record the nmr spectra of some 1-acylaziridines in strong acid media to see whether oxazolinium ion formation, and intermediates leading to them, could be observed.

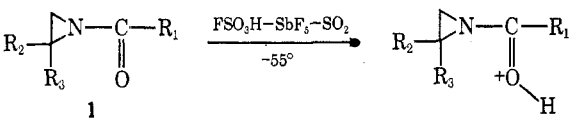
Quantitative rearrangement of 1-acetylaziridines **1a–1c** and 1-benzoylaziridines **1d** and **1e** to the corresponding 2-methyl- and 2-phenyloxazolinium cations **2a–2e**, respectively, occurred in 80–96% sulfuric acid (Scheme I). Careful drownings into base, in each case, liberated the expected 2-oxazolines **3a–3e**.

At 15°, no O- or N-protonated aziridine derivative or open-chain carbonium ion was observed. In each case immediate observation of the oxazolinium cation resulted. The oxazolinium ions were identified by (A) examination of their nmr spectra[13] at 33° (Table I), (B) isolation and subsequent identification of the 2-oxazolines, and (C) regeneration of the same oxazolinium ion from authentic samples of the 2-oxazolines. The nmr spectrum of ion **2e**, shown in Figure 1, is representative of the quality of the spectra obtained. The chemical shifts of the 2-methyl and 2-phenyl substituents in ions **2a–2e** were deshielded with respect to their positions in the spectra of their corresponding 2-oxazolines. The ring protons on C-5, adjacent to oxygen, were always found more than 0.7 ppm downfield from the protons at C-4. No long-range coupling involving the C-2 methyl protons was observed in the cations.[14] The proton on nitrogen appears as a broadened singlet owing to the nitrogen quadrapole,[15] which shortens the spin-lattice relaxation time to a value comparable with the reciprocal of the J_{HN} coupling constant. Observation of the proton on nitrogen rules out fast proton exchange with solvent. However, in 60%

(9) D. E. Johnson, R. H. Quacchia, and A. J. DiMilo, *Ind. Eng. Chem., Prod. Res. Develop.*, **6**, 273 (1967).
(10) S. Gabriel and R. Stelzner, *Chem. Ber.*, **28**, 2929 (1895).
(11) H. W. Heine, M. E. Fetter, and E. M. Nicholson, *J. Amer. Chem. Soc.*, **81**, 2202 (1959).
(12) (a) C. U. Pittman and S. P. McManus, *Chem. Commun.*, 1479 (1968); (b) C. U. Pittman and S. P. McManus, *Tetrahedron Lett.*, 339 (1969).
(13) The values of the chemical shift varied with acidity in H_2SO_4; in trifluoroacetic acid the downfield shifts were not so great as in H_2SO_4.
(14) In 2-oxazolines long-range coupling between the C-2 methyl protons and the C-4 protons are observed; *cf.* S. P. McManus, *Chem. Commun.*, 235 (1969).
(15) (a) J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 4495 (1956). (b) The broadening, due mainly to asymmetric fields near N, indicates the preserved sp^2 hybridization in cations **2a–2c** where the electric field symmetry is far lower than in ammonium ions.[16]
(16) A. D. Tiers and F. A. Bovey, *J. Phys. Chem.*, **63**, 302 (1959).

H_2SO_4 the nitrogen proton is not observed, indicating that, at this lower acidity, the rate of proton exchange with solvent is increased. The *cis* and *trans* vicinal coupling between the ring protons at C-4 and C-5 are equal, within experimental error, in ions **2a**, **2b**, **2d**, and **2e**. While this is an exception to the Karplus equation prediction, this phenomenon has been found in dihydrofuran ring systems[17] and five-membered-ring oxonium ions.[12] These couplings are large, with values of 9–10 Hz in each ion.

Since oxazolinium ions were the only cationic species which could be observed in sulfuric acid, stronger acids[18] were used at lower temperatures. In FSO_3H–SbF_5–SO_2 media at −55°, stable O-protonated 1-acylaziridines **4a**–**4c** were formed with nmr spectra



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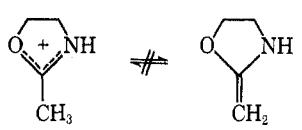
virtually identical with those recently reported by Olah and Szilagyi.[5] This conclusively demonstrates O protonation as opposed to N protonation. See Table II.

TABLE II
NMR ASSIGNMENTS OF PROTONATED 1-ACYLAZIRIDINES[a]

Ion	R_1	OH	Ring CH_2 (CH)	Ring CH_3
4a	CH_3, 2.98 (s)	9.12 (s)	5.10 (m)	
4b	CH_3, 2.89 (s)	9.40 (s)	4.89 (m)	1.86 (d)
			5.20 (m)	
4d	C_6H_6, 8.10[b]	10.60 (s)	4.90 (m)	

[a] s, singlet; d, doublet; m, multiplet; the positions are given in parts per million downfield from TMS. [b] Unlike most protonated aryl ketones, the *ortho*, *meta*, and *para* hydrogens of the ring are not well resolved.

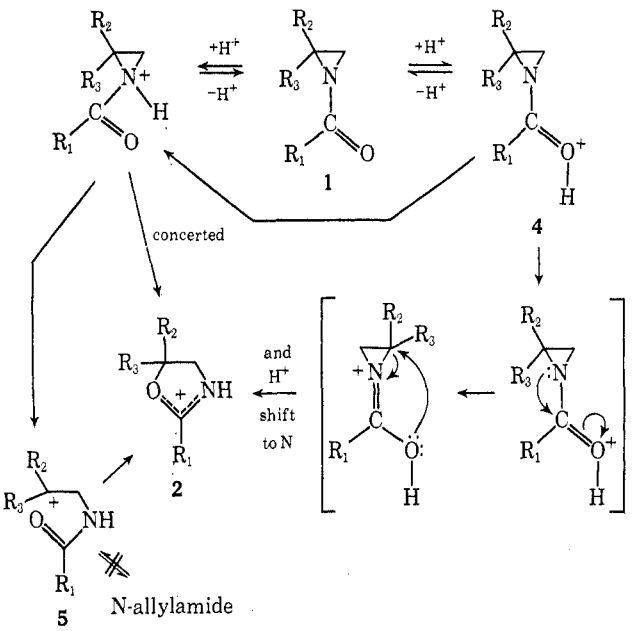
The resistance of oxazolinium ions **2a**–**2c** to H–D exchange is remarkable. When **1a**–**1c** rearrange in 96% D_2SO_4, other than at nitrogen, no H–D exchange occurs even after 14 hr at 120°. In 65% D_2SO_4, no H–D exchange has occurred after 10 min at 122°. Thus oxazolinium cations are similar to dioxolenium cations[12b] in their resistance to exchange but differ from 1-oxoniacyclopent-1-enyl cations[12a] in the H–D exchange propensity of the C-2 methyl group. Upon



heating **1a**–**1c** in 50% sulfuric acid, low molecular weight N-acylpolyethylenimine polymers are formed. Thus facile N-acylaziridine polymerization[4a,b,5,19,20] in the presence of proton acids appears to proceed by prior ring opening to oxazolinium ions.

Our results lead us to refine the Heine ring-opening mechanism[11] (Scheme II). O protonation of the

SCHEME II



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acylaziridines[4] can be followed by concerted ring opening to an O-protonated oxazoline, which immediately converts into the observed oxazolinium ions (**2**). However, N-protonated acylaziridines could exist in equilibrium with O-protonated (**4**) or unprotonated (**1**) acylaziridines. The N-protonated species could rearrange directly by a concerted process to oxazolinium ions (**2**) or proceed through the short-lived carbonium ion **5**. The lack of H–D exchange during the rearrangement demonstrates that, if ion **5** has discrete existence, its lifetime is too short to permit equilibrium with the corresponding N-allylamides, which are known to cyclize to 2-oxazolines in acids.[21] N protonation is analogous to the proposed C protonation in acid-catalyzed ring opening of acylcyclopropanes.[22]

Experimental Section

Materials.—Aziridine and 2-methylaziridine were kindly donated by the Rohn and Haas Co. 2,2-Dimethylaziridine was prepared by the method of Fanta.[23] The 1-acetylaziridines were prepared by reaction of the appropriate aziridine with ketene,[24] and the 1-benzoylaziridines were prepared from the aziridines and benzoyl chloride as described by Stephens, *et al.*[25] Fluorosulfonic acid–antimony pentafluoride was purified as previously described.[26]

Nmr Spectra.—All spectra was recorded using a Varian HA-100 spectrometer with a variable-temperature probe. The chemical shifts are relative to tetramethylsilane as an internal standard (internal capillary).

Rearrangement of 1-Acylaziridines in Sulfuric Acid.—Carbon tetrachloride solutions containing *ca.* 10% of a 1-acylaziridine were added dropwise with rapid stirring to solutions of sulfuric acid at 15° or below. Sulfuric acid concentrations used were 80, 90, and 96%. In all cases portions of the solutions were quickly transferred to nmr tubes and the spectra were recorded. Spectral values at 33° of the oxazolinium ions produced in 90% sulfuric acid are compiled in Table I.

(17) L. M. Jackman, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 87.

(18) (a) R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202 (1968); (b) A. Commeyras and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2929 (1959).

(19) J. W. Cornforth in "Heterocyclic Compounds," Vol. 5, C. R. Elderfield, Ed., John Wiley & Sons, Inc., New York, N Y., 1950, p 383.

(20) T. G. Basseri, A. Levy, and M. H. Litt [*Polymer Lett.*, **5**, 871 (1967)] have reported polymerization of a wide variety of oxazolines to N-acylpolyethylenimines using a variety of Lewis and proton acids.

(21) R. H. Wiley and L. L. Bennett, *Chem. Rev.*, **44**, 447 (1949).

(22) C. U. Pittman and S. P. McManus, *J. Amer. Chem. Soc.*, **91**, 5915 (1969).

(23) P. E. Fanta, U. S. Patent 2,766,236 (Oct 9, 1956).

(24) P. E. Fanta and A. S. Deutsch, *J. Org. Chem.*, **23**, 72 (1958).

(25) W. D. Stephens, L. R. Moffett, H. W. Vaughn, W. E. Hill, and S. P. Brown, *J. Chem. Eng. Data*, **8**, 625 (1963).

(26) G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 1103 (1965).

The oxazolines **3a–3e** were recovered in yields of 53–71% (Table I) by dropwise addition of the acid solution into excess, rapidly stirring aqueous sodium bicarbonate with continuous ether extraction.[1a] Each oxazoline was identified unequivocally by comparison with an authentic sample.[1a,24]

Proton Exchange Studies.—The exchange of the nitrogen proton of ions **2a–2e** in 65% sulfuric acid solution was determined by diluting solutions of the ions to the proper concentration and observing the disappearance of the previously observed nmr signal. The H–D exchange studies required monitoring of the nmr spectra and using peak integration as the measuring device.

Protonation of 1-Acylaziridine.—The aziridine derivatives **1a–1c** were each dissolved in sulfur dioxide and the resulting solutions were added to 1:1 fluorosulfonic acid–antimony pentafluoride at −70°. Their individual spectra were recorded at −55° (Table II).

Registry No.—**2a**, 23704-69-0; **2b**, 23704-70-3; **2c**, 23704-71-4; **2d**, 23704-72-5; **2e**, 23704-73-6; **4a**, 23402-58-6; **4b**, 23402-59-7; **4d**, 23402-60-0.

Acknowledgment.—The authors appreciate the assistance of Mr. J. T. Carroll in the preparation of some of the acylaziridines and thank Dr. C. O. Parker of the Rohm and Haas Co., Huntsville, Ala., for the gift of aziridine samples.

Nenitzescu Indole Synthesis with 2-Chloro-5-methylbenzoquinone

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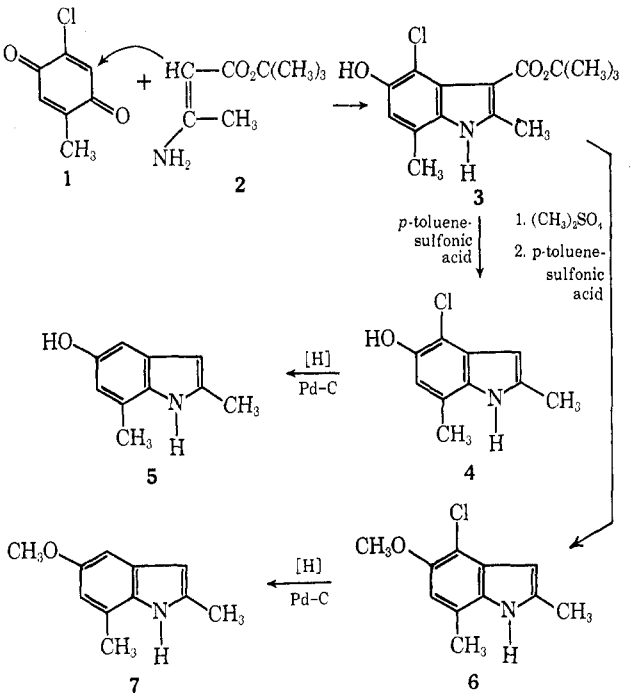
The reaction of aminocrotonate esters (*e.g.*, **2**) with *p*-quinones (*e.g.*, **1**) to form 5-hydroxy-3-carbalkoxyindoles (*e.g.*, **3**) proceeds *via* condensation of the terminal carbon of the enamine triad and one of the C=C carbons of the quinone system.[1,2] With unsymmetrically substituted quinones, the isomeric 5-hydroxyindole that is ultimately produced depends on which of the available double-bond carbons participates in this condensation. In the case of monosubstituted quinones, a 4-substituted 5-hydroxyindole product has been reported only with trifluoromethyl[3] and carbethoxy[4] qunone substituents. Such a product implies condensation of the enamine carbon at the *ortho* position in the quinone ring. With substituents such as alkyl,[1] halogen,[3] and alkoxy,[1] condensation occurs at the *para* or *meta* positions, and leads to 6-substituted and in some cases also 7-substituted 5-hydroxyindoles.

Since neither methyl nor chlorine leads to *ortho* condensation when substituted on the quinone ring, it was of some interest to investigate a Nenitzescu reaction with 2-chloro-5-methylbenzoquinone. In this case condensation would have to take place at an *ortho* position. From this condensation we have been able to detect only one isomer, the product of enamine condensation *ortho* to the chlorine substituent (namely, the 4-chloro-7-methyl isomer **3**), which was obtained in 51% yield. Proof of structure was provided by decarbalkoxylation and dechlorination (hydrogenolysis with Pd–C catalyst) to the known[1] 2,7-dimethyl-5-hydroxyindole (**5**). Although in this instance the dechlorination yield was low, a satisfactory yield (74%) was obtained with the 5-methoxy derivative **6** to give 2,7-dimethyl-5-methoxyindole (**7**). Thus, this procedure appears to offer a potentially useful synthetic method for the preparation of 2,7-dialkyl-5-oxyindoles.



Experimental Section[5]

***t*-Butyl 4-Chloro-5-hydroxy-2,7-dimethylindole-3-carboxylate (3).**—To a hot solution of 5-chloro-2-methyl-1,4-*p*-benzoquinone (**1**)[6] (3.12 g, 0.0199 mol) in glacial acetic acid (15 ml), *t*-butyl 3-aminocrotonate (**2**)[3] (3.14 g, 0.02 mol) was added. After 30 min without application of heat, the solution was cooled, and the resulting pink precipitate was filtered and washed with chilled acetic acid to give 2.99 g (51%) of **3**, mp 178–180° dec.

An analytical sample was obtained by elution from Florisil[7] (magnesia–silica gel adsorbent), followed by recrystallization from methylene chloride: mp 177–179°; λ_{max} 218, 248, 288 mμ (ε 27,300, 15,300, 885); ir 3.08, 6.0, 6.3, 7.05, 8.64, 8.9 μ; nmr, δ 1.53 [s, 9, C(CH$_3$)$_3$], 2.37 (s, 3, 7-CH$_3$), 2.47 (s, 3, 2-CH$_3$), 6.62 (broadened s, 1, 6-H), 8.97 (s, 1, OH), and 11.2 (broadened s, 1, NH) ppm.

Anal. Calcd for $C_{15}H_{18}ClNO_3$: C, 60.91; H, 6.13; Cl, 11.98; N, 4.73. Found: C, 61.14; H, 6.60; Cl, 11.78; N, 4.80.

4-Chloro-5-hydroxy-2,7-dimethylindole (4).—A magnetically stirred solution of *t*-butyl 4-chloro-5-hydroxy-2,7-dimethylindole-3-carboxylate (**3**) (2.99 g, 0.0101 mol) and *p*-toluenesulfonic acid (250 mg) in 250 ml of toluene was heated at reflux for 1 hr. The solution was cooled, filtered, and evaporated to dryness. The residue was dissolved in ethyl acetate and washed with dilute sodium bicarbonate solution and then with water. The organic

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(2) D. Raileanu and C. D. Nenitzescu, *Rev. Roum. Chem.*, **10**, 339 (1965); *Chem. Abstr.*, **63**, 9903 (1965).

(3) R. Littell and G. R. Allen, Jr., *J. Org. Chem.*, **33**, 2064 (1968).

(4) G. R. Allen, Jr., and M. J. Weiss, *ibid.*, **33**, 198 (1968).

(5) Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. Ultraviolet spectra were determined in methanol solution with a Cary recording spectrophotometer, and infrared spectra were determined in potassium bromide disks with a Perkin-Elmer Model 21 spectrophotometer. The proton magnetic resonance spectrum was determined with a Varian A-60 spectrometer in dimethyl sulfoxide-d_6, using tetramethylsilane as an internal standard. Evaporations were done under reduced pressure.

(6) H. H. Hodgson and F. H. Moore, *J. Chem. Soc.*, 2036 (1926).

(7) Florisil is the trademark of the Floridin Co. for a magnesia–silica gel adsorbent.