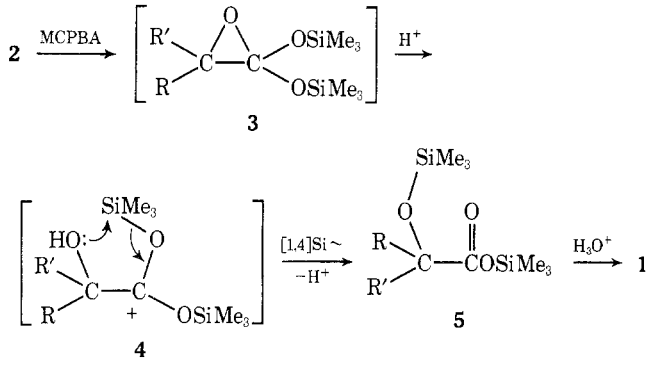
Table I
Preparation of α-Hydroxycarboxylic Acids 1

2[a]	1[a]	% yield of 1[b]	Mp (lit. mp), °C
$Ph_2C{=}C(OSiMe_3)_2$ (2a)	Ph_2COHCO_2H (1a)	81	149–150.5 (148–150[c])
$PhCH{=}C(OSiMe_3)_2$ (2b)	$PhCHOHCO_2H$ (1b)	82	119–120.5 (118–120[c])
p-OMe—$PhCH{=}C(OSiMe_3)_2$ (2c)	p-OMe—$PhCHOHCO_2H$ (1c)	83	101–103 (98–102[c])
t-$BuCH{=}C(OSiMe_3)_2$ (2d)	t-$BuCHOHCO_2H$ (1d)	50	84–86 (91[d])
$C_5H_{10}C{=}C(OSiMe_3)_2$ (2e)	$C_5H_{10}COHCO_2H$ (1e)	80	106–107 (106–107[e])

[a] All compounds show ir, NMR, and mass spectral data consistent with the proposed structure. [b] Yields based on isolated, pure 1; average of at least two runs. [c] Values taken from ref 1. [d] Authentic 1d prepared by the method of M. Charpentier-Morize, *Bull. Soc. Chim. Fr.*, 920 (1962), gave a melting point of 84–86°, and showed no melting point depression upon admixture with 1d prepared by the present method. [e] J. Rouzoud, G. Cauquil, and L. Giral, *ibid.*, 2908 (1964).

Scheme II



the case of the oxidation of trimethylsilyl enol ethers, an analogous epoxide has been isolated,[6b] making 3 a likely intermediate in the oxidation of 2.

Experimental Section

Preparation of Ketene Bis(trimethylsilyl) Acetals, 2. The method of Ainsworth and Kuo[8] afforded the ketene bis(trimethylsilyl) acetals, **2a–e**, in yields of ca. 80%. Physical properties of **2a, 2b, 2d,** and **2e** were in accord with the literature values. Compound **2c**: bp 113–114° (0.5 mm); $n^{26.5}D$ 1.5868; ir ($CHCl_3$) 1655 cm^{-1}; NMR (CCl_4–Me_4Si) δ 0.18 (9 H, s), 0.22 (9 H, s), 3.65 (3 H, s), 4.41 (1 H, s), 6.50–7.30 (4 H, m); MS M^+ *m/e* (rel abundance) 310 (31), 295 (3), 148 (95), 147 (40), 120 (17), 75 (20), 73 (100).

Anal. Calcd for $C_{15}H_{26}O_3Si_2$: C, 58.02; H, 8.44. Found: C, 58.30; H, 8.37.

Preparation of α-Hydroxycarboxylic Acids, 1. General Procedure. A precooled (ice–methanol bath), stirred solution of 1.8 mmol of MCPBA in 10 ml of dry hexane under 1 atm of N_2 was treated with a solution containing 1.8 mmol of 2 in 10 ml of dry hexane (ca. 5 min addition time). After the addition was complete, the resulting slurry was stirred at room temperature for 30 min. After filtration of the mixture to remove the bulk of *m*-chlorobenzoic acid formed in the reaction, the crude filtrate was partitioned between 20 ml of ether and 20 ml of 1.5 *N* hydrochloric acid. After brief shaking, the layers were separated and the aqueous layer was extracted with 3 × 20 ml of ether. The combined ethereal portion was dried with anhydrous magnesium sulfate. Filtration, followed by solvent removal in vacuo, afforded crude 1 which was purified by a combination of sublimation and crystallization from chloroform–hexane mixtures.

Preparation of Trimethylsilyl-α-(trimethylsiloxy) Phenylacetate (5a). To a solution containing 20 mmol of dry triethylamine, 40 mmol of chlorotrimethylsilane, and 120 ml of dry THF was added, with stirring, under N_2, a solution containing 10 mmol of *dl*-mandelic acid (1b) in 30 ml of dry THF (ca. 5 min addition time). The resulting mixture was then stirred overnight at room temperature. The slurry was then filtered and the solvent removed in vacuo. The residue was then diluted with 60 ml of dry ether and the resulting mixture filtered once again. Removal of solvent in vacuo, followed by distillation at reduced pressure, afforded a 91% yield of pure trimethylsilyl-α-(trimethylsiloxy) phenylacetate (**5b**): bp 78–79° (0.65 mm); $n^{22}D$ 1.5688; ir (CCl_4) 1740 cm^{-1}; NMR (CCl_4–CH_2Cl_2) δ 0.18 (9 H, s), 0.22 (9 H, s), 5.10 (1 H, s), 7.2–7.5 (5 H, m); M^+ *m/e* (rel abundance) 296 (1), 281 (4), 179 (100), 147 (26), 75 (9), 73 (65).

Anal. Calcd for $C_{14}H_{24}O_3Si_2$: C, 56.71; H, 8.16. Found: C, 56.65; H, 7.89.

Acid hydrolysis of **5b** (see above) afforded a quantitative yield of **1b**, mp 118.5–119.5°.

Acknowledgments. The authors gratefully acknowledge the Economic Development Administration of the Commonwealth of Puerto Rico (R.M.) and the Research Council of the University of Idaho (G.M.R.) for support of this work.

Registry No.—**1a,** 76-93-7; **1b,** 611-72-3; **1c,** 10502-44-0; **1d,** 4026-20-4; **1e,** 1123-28-0; **2a,** 31469-27-9; **2b,** 31491-21-1; **2c,** 56817-43-7; **2d,** 31469-23-5; **2e,** 40348-04-7; **5a,** 2078-19-5; *m*-chloroperbenzoic acid, 937-14-4.

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Transformation of 1-Azirines to 1*H*-Indoles with Benzyne. Evidence for the Intermediacy of the 3*H*-Indole System

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Received June 18, 1975

The synthetic capabilities of *o*-benzyne have been examined and utilized effectively in recent years.[1] It appears to possess a symmetric singlet ground state,[2] behaves as a highly reactive ethylenic component, and participates in cycloadditions with olefins and dienes in a [2 + 2], [2 + 4], or "ene" fashion.[1-10] Although the reaction of benzyne with enamines has been studied,[5,16] little is known about the reactivity of benzyne toward C=N bonds. We wish to report on the reaction of benzyne with the reactive C=N bond of the 1-azirine ring system.

Results and Discussion

2,3-Diphenyl-1-azirine (1) reacts with excess *o*-benzyne, generated by the thermal decomposition of benzenediazonium 2-carboxylate,[11] to give two products. The major product, a 1:1 adduct produced in 50% yield, was identified as

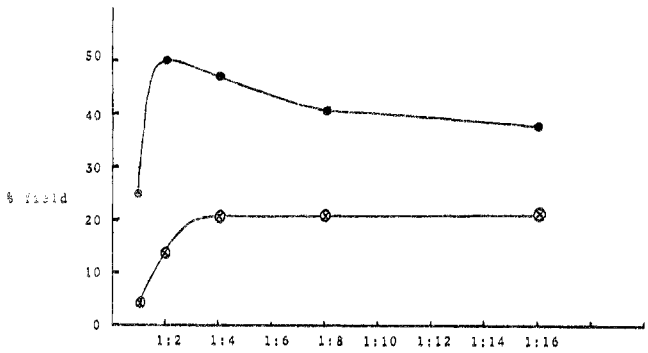
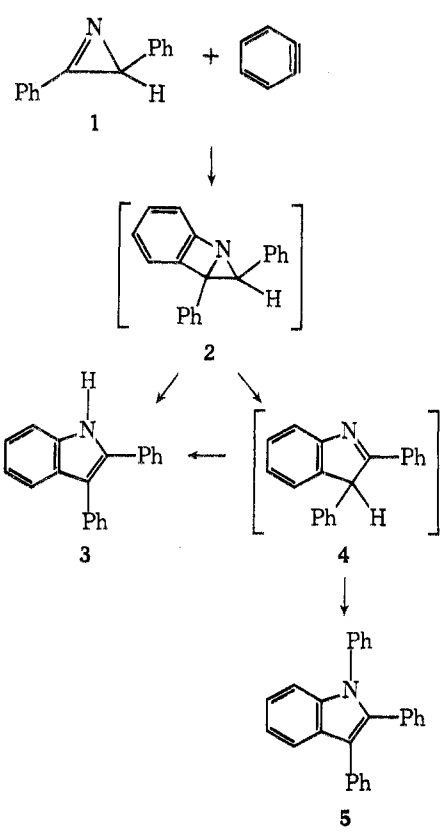
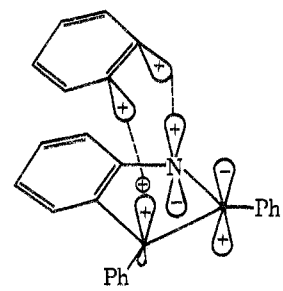


Figure 1. Millimolar ratio of azirine (1) to benzyne: ⊕, indole 5; •, indole 3.

2,3-diphenylindole[12] (3). A 1:2 adduct of azirine and benzyne, identified as 1,2,3-triphenylindole (5),[13] was isolated in 14% yield. Increase in the concentration of benzyne was accompanied by an increase in the yield of 5 as shown in Figure 1. Under the same conditions 2,3-diphenylindole was found to be relatively inert to benzyne, and no triphenylindole (5) could be isolated even after extended reaction times.

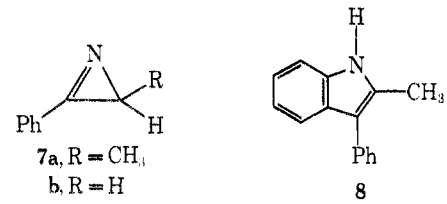
The mechanism of formation of 2,3-diphenylindole (3) may require initial formation of 2, the result of 1,2 addition on the azirine ring system. Initial 1,3 addition may be ruled out by the isolation of 2-methyl-3-phenylindole (8) from the reaction of azirine 7a and benzyne, although it is possible that more than one mechanism is operating depending on the substituent of carbon 3 of the azirine. It is known that the [2 + 2] cycloaddition between benzyne and simple olefins occurs in a nonconcerted fashion.[3,8-10] It can be presumed then that following the stepwise [2 + 2] cycloaddition of benzyne to the 1-azirine and the formation of intermediate 2, two reaction pathways for partitioning of this intermediate are available. A 1,2-hydrogen shift to the nitrogen would give the stable aromatic indole 3. A 1,2 shift to carbon would give the 3*H*-indole system 4, which can be trapped by benzyne to give the 1,2,3-triphenylindole (5). The conversion of indolenine (4) to the indole 3 is a symmetry-forbidden process and it appears likely that in the presence of a large excess of benzyne, partitioning of 4 to 3, a symmetry-forbidden process, is less favorable than the alternate symmetry-allowed "ene" reaction (see 6) to give 5.[6,10,15] That this may indeed be the case is borne out by





the observation illustrated in Figure 1. The yield of 5 reaches a steady maximum value when large excesses of benzyne are used implying efficient trapping of 4. Some natural partitioning of 4 to 3 cannot still be ruled out. Interestingly, no "ene" product from 1 and benzyne was isolated.

When 3-methyl-2-phenyl-1-azirine (7a) was treated with excess benzyne, the only isolable product was 2-methyl-3-phenylindole (8). Under the same conditions, 2-phenyl-1-azirine (7b) gave only polymeric products.



Experimental Section

Benzenediazonium 2-carboxylate was prepared by the method of Friedman.[11]

Reaction of 2,3-Diphenyl-1-azirine (1) with Benzyne. To a solution of 0.386 g (2 mmol) of 2,3-diphenyl-1-azirine (1) in 20 ml of dichloroethane was added 0.592 g (4 mmol) of benzene-wet benzenediazonium 2-carboxylate, and the reaction mixture was heated under reflux for 5 hr. The solvent was then carefully removed in vacuo and the residual material was chromatographed on silica gel PF_{254} plates with 30% ether–pentane as the developing solvent. The top band (R_f 0.85) was cut out and eluted with ether to give, after solvent removal and drying, white crystals (0.097 g, 14%): mp 185–186° (lit.[13] mp 186°); ^1H NMR δ_{Me_4Si} ($CDCl_3$) 7.07 (s, 5 H), 7.16–7.85 (m, 14 H); ^{13}C NMR δ_{Me_4Si} ($CDCl_3$) 110.6, 116.7, 119.6, 120.9, 122.8, 125.9, 127.1, 127.4, 127.6, 127.9, 128.3, 129.1, 130.2, 131.2, 131.6, 134.9, 137.1, 137.9, 138.1; mass spectrum (70 eV) *m/e* 345 (M^+).

The middle band (R_f 0.55) was cut out and eluted with ether to give 0.289 g of pale yellow oil after solvent removal. The oil crystallized from ether–pentane as colorless, rectangular crystals (0.267 g, 50%): mp 122–123° (lit.[12] mp 123–124°); ^1H NMR δ_{Me_4Si} ($CDCl_3$) 7.21–7.72 (m, 14 H), 7.95 (s, br, 1 H); ^{13}C NMR δ_{Me_4Si} ($CDCl_3$) 110.9, 115.0, 119.7, 120.4, 122.6, 126.2, 127.7, 128.2, 128.5, 128.7, 130.2, 132.6, 134.1, 135.1, 135.9; mass spectrum (70 eV) *m/e* 269 (M^+).

Attempted Reaction of 2,3-Diphenylindole (3) and Benzyne. To a solution of 0.538 g (2 mmol) of 2,3-diphenylindole (3) in 10 ml of dichloroethane was added approximately 0.60 g (4 mmol) of benzenediazonium 2-carboxylate and the reaction mixture was heated under reflux for 5 hr. Solvent removal and chromatographic separation gave 0.489 g (91% recovery) of 3. No 1,2,3-triphenylindole was isolated. Some decomposition of 3 does occur in the presence of benzyne (see Figure 1).

Reaction of 3-Methyl-2-phenyl-1-azirine (7a) with Benzyne. The azirine 7a (0.393 g, 3 mmol) in 20 ml of dichloroethane was treated with 0.90 g (6 mmol) of benzenediazonium 2-carboxyl-

ate, and the reaction mixture was heated under reflux for 4 hr. Solvent removal and chromatographic separation gave 0.198 g (32%) of 2-methyl-3-phenylindole (8): mp 58° (lit.[14] mp 59–60°); ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 2.28 (s, 3 H), 7.05–7.76 (m, 10 H); mass spectrum (70 eV) *m/e* 207 (M^+).

Registry No.—1, 16483-98-0; 3, 3469-20-3; 5, 54879-94-6; 7a, 16205-14-4; 8, 4757-69-1; benzyne, 462-80-6.

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Photolysis of 4,4-Dimethylcholesta-1,5-dien-3-one

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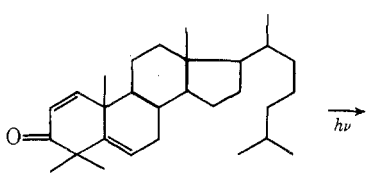
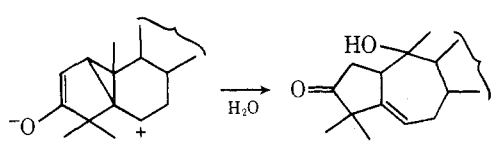
Received July 9, 1974

The photolysis of 4,4-dimethylcholesta-1,5-dien-3-one (1) has been examined in the hope that the AB portion of the steroid nucleus would rearrange to a hydroazulene system of the type found in the grayanotoxins.[1-5] A plausible

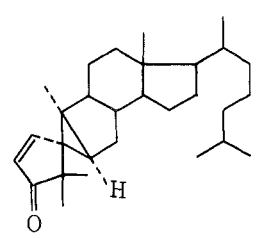


1

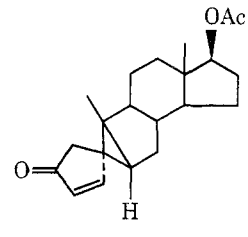


mechanism can be written for this transformation and the change from a decalin system to a hydroazulene skeleton is frequently encountered in the photochemical reactions of dienones. Nonetheless this type of transformation was not encountered. Photolysis of 1 in either 95% ethanol or dioxane in the 250-nm region produced at least eight new compounds. However, photolysis at 300 nm in aqueous dioxane gave predominantly one new compound which is assigned structure 2.

The formation of 2 is entirely expected from the elegant and extensive studies of Jeger, Schaffner, and their collaborators, who examined the photolysis of 3-oxo-17β-acetoxy-$\Delta^{1,5}$-androstadiene which presents the same hexalone system only lacking the two methyl groups at C-4.[7] The photolysis of 3-oxo-17β-acetoxy-$\Delta^{1,5}$-androstadiene afforded the photoisomer 3 accompanied by three of its stereoisomers.



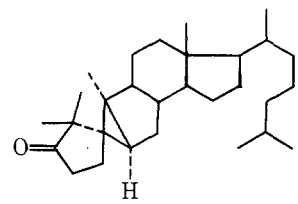
2



3

The structure of 2 follows from a comparison of its spectroscopic properties with those of 3. The ultraviolet spectrum of 2 showed λ_{max} 263 nm (ϵ 8800) whereas 3 exhibited λ_{max} 267 nm (ϵ 9750). The vinyl protons of 2 appeared as an AB quartet (δ 5.98 and 7.03, J = 6 Hz) similar to that found for 3 (δ 6.07 and 7.25, J = 6 Hz). The infrared spectrum of 2 had absorption maxima at 1707 and 1681 cm^{-1} in good agreement with those found for 3.

Photolysis of dienone 1 at 350 nm in dioxane–acetic acid gave 2 along with two new photoisomers, 4 and 5. Photoisomer 4 is clearly a stereoisomer of 2. Moreover, photolysis of 2 leads to the formation of 4. The third photoisomer is assigned structure 5 based on its spectroscopic properties which are very similar to those found for compound 6 obtained from the photolysis of 3-oxo-17β-acetoxy-$\Delta^{1,5}$-androstadiene.



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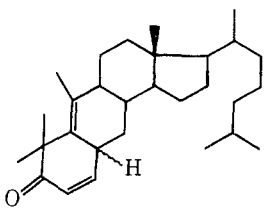
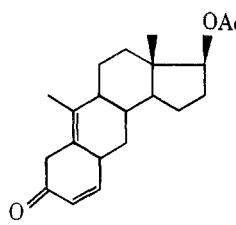


5



6

The infrared spectrum of 5 showed carbonyl absorption at 1667 cm^{-1} and double bond absorption at 1640 cm^{-1}. The ^{1}H NMR spectrum showed an AB quartet (δ 5.79 and 6.45, J = 10 Hz) whereas the ultraviolet spectrum showed a maximum at 227 nm. These spectroscopic characteristics are in good agreement with those found for 6.

The remaining structural problem is the stereochemistry of the spiro photoisomers. It was shown previously in the studies of 3 and its stereoisomers that the four stereoisomers formed two pairs. Members of one pair reached a photostationary state but did not give rise to either member of the other pair. Extensive degradations and circular dichroism measurements indicated that members of a pair were related to one another by change in the stereochemistry of the spiro carbon.

Moreover, members of a pair showed enantiomeric circular dichroism curves. However, in the case at hand, both of the stereoisomers we obtain had positive circular dichroism curves. Although we did not establish that the spiro photoisomers 2 and 4 achieve a photostationary state, it was established that photolysis of 2 gives rise to 4 and following