1-methyl-2-(benzoylmethylamino)pyridinium iodide, 65442-14-0; 2-methylaminopyridine 1-oxide, 54818-70-1.

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A Novel Intramolecular Homologation of a Phthalimide Group. 1,5,8-Trioxobenz[*f*]indolizidine[1a]

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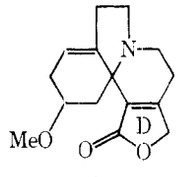
The Reformatsky reaction between ethyl bromoacetate and 1-acetoxy-4-phthalimido-2-butanone (**4**) produces in modest yield β-acetoxy-β-(2-phthalimidoethyl)butyrolactone (**10**), a product of normal addition to the ketone carbonyl, and in low yield a second compound, which arises from transformation of the phthalimide group. The latter product is shown to be 1,5,8-trioxobenz[*f*]indolizidine (**13**), a material which is of synthetic interest because of its structural relationship to the phenanthroindolizidine and Amaryllidaceae alkaloids. The precursor to ketone **4**, 1-diazo-4-phthalimido-2-butanone (**7**), was found to give **13** directly in preparatively acceptable yield via a novel rearrangement of its derived ketocarbene (**17**).

We are presently investigating a synthetic approach to the ring system of cocculolidine (**1**),[2] a member of the D-ring lactone subgroup of the Erythrina group of alkaloids. This approach requires the as yet unknown aminobutenolide **2**, and our immediate synthetic goal was the amine-protected lactone **3**.



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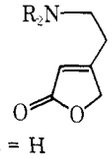
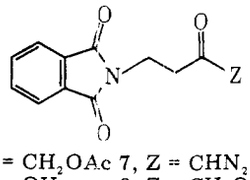
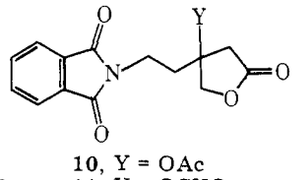


2, R = H
3, R = *o*-phthaloyl

The key step in an initial sequence designed to produce **3** was the Reformatsky reaction between ethyl bromoacetate and 1-acetoxy-4-phthalimido-2-butanone (**4**). This ketone was



4, Z = CH_2OAc
5, Z = OH
6, Z = Cl
7, Z = CHN_2
8, Z = CH_2OCHO
9, Z = CH_2Cl



10, Y = OAc
11, Y = OCHO
12, Y = OH

readily prepared in four steps from β-alanine (3-aminopropionic acid) via intermediates **5**, **6**, and **7**, respectively.

The major product of the Reformatsky reaction was the acetoxylactone **10**, which was formed in modest yield (20%) and presumably arose from normal addition to the ketone followed by transesterification and cyclization. This reaction also produced a second, highly colored, product "A" in lower yield (5%), whose elemental analysis indicated an empirical formula of $C_{12}H_9NO_3$ and whose spectral data indicated that it was not derived from normal addition to the starting ketone. The structure of this product was assigned on the basis of the following.

The ^1H NMR spectrum of the ketone **4** shows a typical A_2X_2 pattern for the adjacent methylene groups: a pair of two-proton triplets at δ 2.9 and 4.1. (J = 8 Hz). The spectrum of A shows these signals unchanged, implying that the NCH_2CH_2CO grouping remains intact in the product. In contrast, the singlets due to the acetate methyl group [δ 2.2 (3 H)] and the 1-methylene group [δ 4.7 (2 H)] in the starting material are absent in the product. In addition, the aromatic protons in **4** show the compact, symmetrical multiplet [δ 7.8 (4 H)] which is typical of N-substituted phthalimides, whereas in A a complex signal [δ 7.6–8.2 (4 H)] appears, suggesting a loss of symmetry in the substitution pattern of the aromatic ring. The only remaining peak in the spectrum of A is a broadened singlet [δ 6.5 (1 H)] which disappears on addition of D_2O.

The transformation of the phthalimide group and loss of ester functionality are both immediately evident from the IR spectrum: the peaks of the starting material **4** at 1715 (strong) and 1780 cm^{-1} (moderate), characteristic of phthalimides, and at 1750 cm^{-1} (OAc) are absent in A. Somewhat surprising is that A also lacks the absorption of **4** at 1730 cm^{-1} due to the simple ketone group. Instead, the product exhibits a strong peak at 1685 cm^{-1}, moderately strong peaks at 1700 and 1675 cm^{-1}, and a very strong band at 1630 cm^{-1}. The spectrum of A shows additionally a broad peak at 3240 cm^{-1}, which correlates with the singlet at δ 6.5 in the NMR spectrum.

Consideration of mechanistic possibilities in view of the above data leads to the benzindolizidine **13** as the structure of A.

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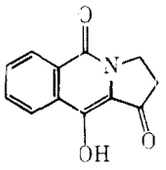

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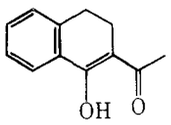

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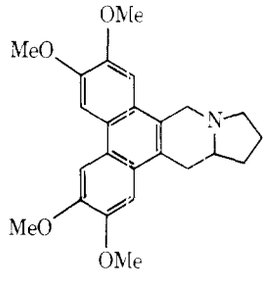
The β-diketone structure is supported both by a positive ferric chloride test and by the IR spectrum. Enol diketones exhibit[3] a very strong principal carbonyl peak in the range 1640–1580 cm^{-1}. Some also show two peaks at somewhat higher frequency. For example, 1-benzoylacetone and 2-acetyl-1-tetralone (**14**) both show[4] moderately strong peaks at 1715 and 1670 cm^{-1} as well as an intense band at 1605 cm^{-1}. These correlate well with the peaks in A at 1700, 1675, and 1630 cm^{-1}. The remaining adsorption in A at 1685 $^{-1}$ can be reasonably assigned to the δ-lactam carbonyl group. The ^1H NMR spectrum described above is completely consistent with structure **13**, as is the ^{13}C NMR spectrum (see Experimental Section). It should be noted that the absorption of the hydroxyl hydrogen at δ 6.5, an unusually high field for enolic protons, can be explained by assuming a low degree of intramolecular hydrogen bonding[5] and that the relative lack of this bonding is reflected as well in the IR spectrum by the prominence and high frequency of O–H stretch (3240 cm^{-1}).[6]

A plausible pathway for the formation of **13** is shown in Scheme I. Zinc enolates such as B are known[7] to exist in Reformatsky mixtures, and the formation of these species is considered[7] to be responsible for lowered yields of addition product and recovery of starting carbonyl compound, regenerated from the enolate during the hydrolysis. We believe that this factor is particularly important here and that large amounts of B are formed, evidence for which, besides the relatively low yield of **10**, is that considerable amounts (ca. 30%) of starting ketone were found in product mixtures. The unusual ease of conversion of **4** to its enolate would presumably be due to inductive stabilization by the electron-withdrawing group in the 1 position in B.

Beyond its unexpected nature we felt that the formation of **13** is of potential synthetic interest as this compound contains substantial portions of the carbon skeletons of at least two otherwise structurally diverse groups of alkaloids, exemplified by tylophorine (**15**) (phenanthrindolizidine)[8a] and lycorine (**16**) (Amaryllidaceae).[8b] In particular, the synthesis



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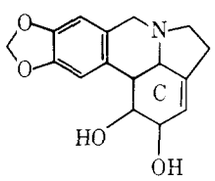

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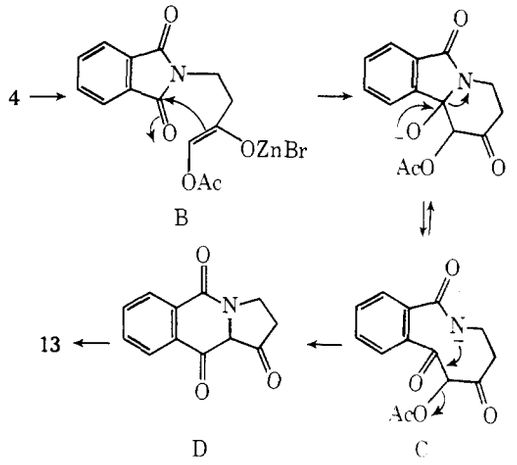
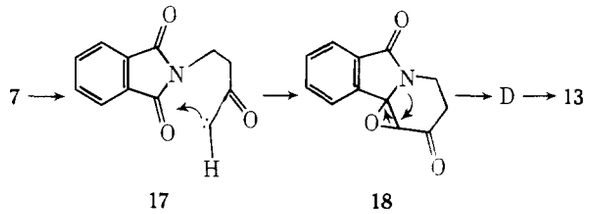
of the Amaryllidaceae ring system could be accomplished by direct elaboration of **13** since the β-diketone functionality is located at the exact points of attachment of the C ring. Consequently, a brief investigation of some possibilities of increasing the yield of **13** to a preparatively useful level seemed justified.

Since our postulated mechanism (Scheme I) implies a key role for the 1-acetoxy group, particularly with respect to its leaving ability, two other 1-substituted 4-phthalimido-2-butanones were prepared and subjected to Reformatsky conditions for comparison. 1-Formyloxy-4-phthalimido-2-butanone (**8**) gave a decreased yield of the analogous normal addition product (**11**, 10%) and a somewhat increased yield of **13** (8%). This is qualitatively consistent with the proposed mechanism and the properties of the formyloxy group relative to the acetoxy group, i.e., more electron withdrawing (greater stabilization in B, disfavoring normal addition) and better leaving ability (greater ease of loss in C, favoring **13**). The effect of replacing acetate by chlorine is less predictable, particularly from a steric point of view, and in fact the 1-chloro derivative **9** gave a lower yield of the normal addition product (**12**, 10%) and none of **13**.

Scheme I



Scheme II



17 18

It then occurred to us that material already in hand, the diazo ketone **7**, would serve as a ready source of a different type of reactive species that might be used to exploit the susceptibility of the imide carbonyls to attack from the δ position of the *N*-butanone chain. This approach is illustrated in Scheme II.

Thus, it seemed that the carbene derived from **7** (**17**) could undergo rearrangement to **13**, initiated by intramolecular insertion[10] across the imide carbonyl and proceeding via the resulting epoxide **18** through the diketo tautomer D.[9] In the event of $CuSO_4$-catalyzed[10] decomposition of **7** in xylene at 120 °C, **13** was indeed produced directly. The yield was 25%, which, though modest, is acceptable from a practical standpoint in view of the ease of product isolation and the efficiency and simplicity of the sequence leading to **7** (96% overall in three steps from β-alanine). The conditions used were adopted when other experiments indicated that both lower and higher temperatures gave lower yields. For example, at 35 °C the decomposition gave a virtually quantitative yield of a new and apparently polymeric phthalimide (**19**) and only a trace of **13**.

While the use of the intact phthaloyl grouping in an amine-protecting role is well established, the elaboration of phthalimides to more complex heterocyclic systems has received little attention.[11] The results reported here suggest that the sensitivity of the phthalimide carbonyls to intramolecular attack, which in this work provided a facile entry to the benz[*f*]indolizidine nucleus, could form the basis for a variety of new synthetic approaches to such systems.

Experimental Section

Melting points are uncorrected. IR spectra were determined with a Beckman 4230 instrument on Nujol mulls. ^1H NMR spectra were obtained on a Perkin-Elmer R-24 instrument and ^{13}C spectra on a Jeol PS-100 instrument operating in the FT mode, using Me_4Si as an internal reference. Combustion analyses were performed on a Perkin-Elmer Model 240 automatic elemental analyzer.

β-Phthalimidopropionic Acid (5).[12] Phthalic anhydride (148 g, 1.00 mol) and β-alanine (89.1 g, 1.00 mol) were refluxed together overnight in excess glacial HOAc. The solvent was evaporated and the white solid residue recrystallized from H_2O to give **5**, 213 g (97%), in two crops as pure white crystals, mp 150–151.5 °C (lit.[13] 150–151 °C).

β-Phthalimidopropionyl Chloride (6). β-Phthalimidopropionic acid (**5**; 2.19 g, 0.0100 mol) was heated in excess thionyl chloride until gas was no longer evolved (ca. 0.5 h). The resulting solution was evaporated to an oil from which most of the residual $SOCl_2$ was removed by alternative solution in CH_2Cl_2 and evaporation. The crystalline residue was dried in vacuo to give **6** as a white solid: 2.36 g (99%); mp 104.5–105.5 °C. In a similar run evaporation of a microsample of the original reaction mixture followed by thorough drying in vacuo gave analytically pure material, mp 107.5–108 °C (lit.[14] 107–108 °C).

Anal. Calcd for $C_{11}H_8ClNO_3$: C, 55.60; H, 3.39; N, 5.89. Found: C, 55.50; H, 3.35; N, 5.89.

1-Diazo-4-phthalimido-2-butanone (7). To a solution of an excess of diazomethane (undistilled, from nitrosomethylurea) in Et_2O was added β-phthalimidopropionyl chloride (**6**; 11.9 g, 0.0500 mol) in portions over ca. 0.25 h. The resulting suspension was stirred for an additional 0.5 h and the remaining diazomethane destroyed with HOAc. The mixture was filtered to give, after drying in vacuo, 8.50 g of **7** as fine pale green crystals, mp 125.5–127 °C. Evaporation of the filtrate gave a second crop, mp 125–126.5 °C, of 2.70 g (total yield 12.2 g, 100%). An analytical sample had mp 128–129 °C; IR 2160 (C=N=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.8 (t, J = 7 Hz, 2 H), 4.0 (t, J = 7 Hz, 2 H), 5.3 (s, 1 H), 7.8 (m, 4 H).

Anal. Calcd for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73; N, 17.28. Found: C, 59.27; H, 3.70; N, 17.55.

1-Acetoxy-4-phthalimido-2-butanone (4). A solution of 9.14 g (0.0376 mol) of diazo ketone **7** in 150 mL of glacial HOAc was heated to 40–45 °C for 5.5 h and then stirred overnight at room temperature. Evaporating the HOAc and drying the residue in vacuo to a constant weight gave a white solid, mp 122–129 °C, 10.27 g (100% crude yield). An analytical sample had mp 130.5–131 °C; IR 1730 (C=O), 1750 (OAc) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2 (s, 3 H), 2.9 (t, J = 8 Hz, 2 H), 4.1 (t, J = 8 Hz, 2 H), 4.7 (s, 2 H), 7.8 (m, 4 H).

Anal. Calcd for $C_{14}H_{13}NO_5$: C, 61.09; H, 4.76; N, 5.09. Found: C, 61.12; H, 4.72; N, 5.10.

1-Formyloxy-4-phthalimido-2-butanone (8). To 25 mL of 91% HCO_2H was added 2.48 g (0.0100 mol) of **7** in portions, and the resulting mixture was stirred for several minutes until no further gas was evolved. The mixture was diluted with H_2O, made basic with $NaHCO_3$, and extracted with 3 × 100 mL of $CHCl_3$. The combined extracts were dried ($CaSO_4$), evaporated, and dried in vacuo to a constant weight, giving 2.48 g (95% crude yield) of **8** as a pure white solid. An analytical sample had mp 154–154.5 °C; IR 1740 (OCHO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.9 (t, J = 8 Hz, 2 H), 4.1 (t, J = 3 Hz, 2 H), 4.7 (s, 2 H), 7.8 (m, 4 H), 8.0 (s, 1 H).

Anal. Calcd for $C_{13}H_{11}NO_5$: C, 59.77; H, 4.24; N, 5.36. Found: C, 59.64; H, 4.27; N, 5.35.

1-Chloro-4-phthalimido-2-butanone (9). To a stirred solution of 8.56 g (0.0352 mol) of **7** in 150 mL of Me_2CO was added concentrated HCl dropwise until gas was no longer evolved and the initial pale green color was discharged. The solvent was evaporated and the resulting residue dried in vacuo to give a pure white solid, 8.81 g (99% crude yield). An analytical sample had mp 120–120.5 °C; IR 1730 ($COCH_2Cl$) cm^{-1};[15] ^1H NMR ($CDCl_3$) δ 3.0 (t, J = 7 Hz, 2 H), 4.0 (t, J = 7 Hz, 2 H), 4.1 (s, 2 H), 7.8 (m, 4 H).

Anal. Calcd for $C_{12}H_{10}ClNO_3$: C, 57.27; H, 4.01; N, 5.57. Found: C, 57.35; H, 4.05; N, 5.57.

Reformatsky Reaction of 1-Acetoxy-4-phthalimido-2-butanone (4). To a flask containing a stirred solution of 22.90 g (0.0833 mol) of **4** in 200 mL of dry refluxing benzene and 5.45 g (0.0833 g-atom) of granulated zinc was added, under dry nitrogen, a solution of 10 mL (0.090 mol) of ethyl bromoacetate in 100 mL of benzene dropwise over 1.5 h. After 3.5 h (total time) an additional 1 g of zinc and 2 mL of ethyl bromoacetate were added and refluxing was continued for 1 h. To the cooled mixture was added 100 mL of 1 N H_2SO_4 with rapid stirring. The two resulting liquid layers were decanted and separated. After 3 days the crystals that formed in the acid layer[16] were collected on a filter to give 0.881 g (5%) of **13** as orange–yellow[17] needles, mp 219–220 °C. An analytical sample had mp 220–221 °C; IR 3240 (very broad), 1700, 1685, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.9 (t, J = 8 Hz, 2 H, CH_2CO), 4.2 (t, J = 8 Hz, 2 H, NCH_2), 6.5 (s, 1 H, exchangeable with D_2O, OH), 7.6–8.3 (m, 4 H, aromatic); ^{13}C NMR (Me_2SO-d_6; multiplicities in coupled spectrum and relative peak heights indicated) δ 34.8 (t, 0.75), 36.4 (t, 0.90), 122.9 (d, 0.91), 124.6 (d, 0.82), 128.7 (s, 0.56), 130.0 (d, 0.89), 130.0 (s, not distinguishable in decoupled spectrum), 132.2 (d, 1.00), 132.7 (s, 0.60), 133.6 (s, 0.53), 163.9 (s, 0.44), 189.8 (s, 0.55); UV (EtOH) λ_{max} 375 nm (ε 19 000).

Anal. Calcd for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51; mol wt 215. Found: C, 66.74; H, 4.27; N, 6.40; mol wt 238 (Rast); *m/e* 215 (base peak).

Evaporation of the dried ($MgSO_4$) benzene layer gave a dark oily solid; trituration with 65 mL of EtOAc left 5.28 g (20%) of acetoxylactone **10** as light crystals, mp 158–160.5 °C. An analytical sample had mp 161 °C; IR 1735 (OAc), 1770 (γ-lactone C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 2.4 (t, J = 8 Hz, 1 H), 2.5 (t, J = 8 Hz, 1 H), 2.85 (s, 1 H), 2.95 (s, 1 H), 3.8 (t, J = 3 Hz, 2 H), 4.3 (d, J = 11 Hz, 1 H), 4.7 (d, J = 11 Hz, 1 H), 7.8 (m, 4 H).

Anal. Calcd for $C_{16}H_{15}NO_6$: C, 60.57; H, 4.77; N, 4.41. Found: C, 60.53; H, 4.71; N, 4.34.

Reformatsky Reaction of 1-Formyloxy-4-phthalimido-2-butanone (8). The procedure, using 2.95 g (0.0113 mol) of **8**, was analogous to that described above and the isolation of **13** (0.191 g, 8%) was the same. The formyloxylactone **11** was initially obtained as an oil which crystallized on standing. Recrystallization (EtOAc–cyclohexane) gave 0.345 g (10%) of **11**, mp 140–142 °C. An analytical sample had mp 144–144.5 °C; IR 1780, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50 (t, J = 8 Hz, 1 H), 2.55 (t, J = 8 Hz, 1 H), 2.9 (s, 1 H), 3.0 (s, 1 H), 3.8 (t, J = 8 Hz, 2 H), 4.4 (d, J = 12 Hz, 1 H), 4.7 (d, J = 12 Hz, 1 H), 7.8 (m, 4 H), 8.0 (s, 1 H).

Anal. Calcd for $C_{15}H_{13}NO_6$: C, 59.41; H, 4.32; N, 4.62. Found: C, 59.56; H, 4.35; N, 4.45.

Reformatsky Reaction of 1-Chloro-4-phthalimido-2-butanone (9). The procedure, using 2.52 g (0.0100 mol) of **9**, was analogous to that described for **4**. No **13** was obtained, and the hydroxylactone **12** was obtained as an oil which crystallized on standing. Recrystallization (EtOH) gave 0.268 g (10%) of **12** as a white solid, mp 160–164 °C. An analytical sample had mp 168–168.5 °C; IR 3480 (OH), 1770 (γ-lactone C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1 (t, J = 7 Hz, 2 H), 2.6 (s, 2 H), 3.9 (t, J = 7 Hz, 2 H), 4.18 (s, 1 H), 4.24 (s, 1 H), 7.8 (m, 4 H).

Anal. Calcd for $C_{14}H_{13}NO_5$: C, 61.09; H, 4.76; N, 5.09. Found: C, 60.75; H, 4.68; N, 5.13.

Decomposition of Diazo Ketone 7. To a stirred suspension of 0.58 g of anhydrous $CuSO_4$ in 100 mL of dry xylene at 120 °C was added dropwise a solution of 0.565 g (0.00233 mol) of **7** in 50 mL of xylene over 1 h. The solution was filtered hot, the cooled filtrate extracted with 2 N NaOH, and the separated basic layer acidified (H_2SO_4) to pH 1. Extraction of the resulting solution with $CHCl_3$, drying ($MgSO_4$), evaporation, and drying in vacuo gave 0.13 g (25%) of **13** as a yellow–green[17] solid.

The pale yellow solid that had precipitated from the aqueous layers was collected on a filter; this highly insoluble material was purified by refluxing in acetone, and refiltration gave 0.1 g of **19**, mp 210–230 °C dec; IR 1710, 1770 (phthalimide) cm^{-1}.

Anal. Calcd for $(C_{12}H_9NO_4)_n$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.21; H, 4.18; N, 6.07.

Registry No.—**4**, 65465-66-9; **5**, 3339-73-9; **6**, 17137-11-0; **7**, 7504-49-6; **8**, 65465-67-0; **9**, 65495-45-6; **10**, 65465-68-1; **11**, 65465-69-2; **12**, 65465-70-5; **13**, 23428-84-4; phthalic anhydride, 85-44-9; β-alanine, 107-95-9.

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(1) (a) This work was presented in part at the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977, Abstracts, ORGN 223. (b) Taken from the Ph.D. Thesis of S. F. K.
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(15) On long standing **9** changes its crystalline form; the new polymorph, mp 121–123 °C, shows the ketone carbonyl stretch shifted to 1740 cm^{-1} and the appearance of the fingerprint region substantially altered.

(16) On some runs the same yields could be obtained within 24 h. On much longer standing the product begins to redissolve, eventually giving a clear colorless solution. The same phenomenon was observed in neutral H_2O.

(17) This compound crystallizes in several forms, whose apparent colors range from green through yellow to red-orange; however, when the macrocrystalline structure is destroyed, such as by fine grinding or solution, the same yellow-green material is obtained. Solutions of **13** show a bright blue fluorescence under 365-nm light.

Studies on the Intramolecular Addition of Vinyl Nitrenes to Olefins

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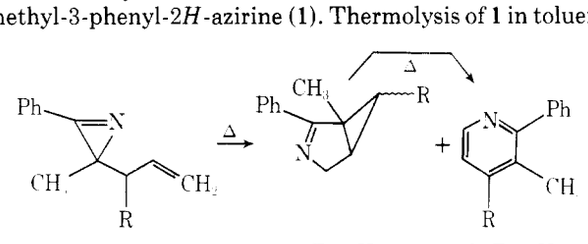
A series of 2-allyl-substituted 2*H*-azirines were found to undergo smooth rearrangement to afford 3-azabicyclo[3.1.0]hex-3-enes in high yield on thermolysis. The reactions can best be rationalized in terms of an equilibration of the 2*H*-azirine ring with a transient vinyl nitrene which subsequently adds to the adjacent π bond. The initially formed bicycloaziridine rearranges to the 3-azabicyclohexene ring system by means of a 1,3-sigmatropic shift. Evidence favoring this pathway is provided by the isolation of 2-phenyl-3-methyl-5-vinyl-Δ^1-pyrroline from the thermolysis of 2-(2-butenyl)-2-methyl-3-phenyl-2*H*-azirine. The formation of the Δ^1-pyrroline ring system can be rationalized as proceeding via a homo[1,5] hydrogen migration from a 6-endo methyl-substituted bicycloaziridine intermediate. Thermolysis of 3-methyl-2-phenyl-2-allyl-substituted 2*H*-azirines affords mixtures of 3-azabicyclohexenes and indoles. The distribution of products with this ring system is controlled by the rates of nitrene attack on the double bond vs. electrocyclization on the adjacent phenyl ring. Finally, the thermolysis of methyl 4-(3-methyl-2-phenyl-2*H*-azirin-2-yl)-2-butenoate results in a novel rearrangement and produces 2-methyl-3-phenyl-5-carbomethoxypyridine as the major product. A tentative but reasonable mechanistic rationale is advanced to rationalize this reaction.

The ready availability of 2*H*-azirines has spurred considerable activity in the chemistry of these strained heterocycles.[1,2] Photochemical and thermal cleavage preferences in 2*H*-azirines appear to be quite distinct.[1,2] Photolysis of 2*H*-azirines leads to irreversible ring opening and the formation of nitrile ylides as intermediates.[3,4] These species may be intercepted by a variety of dipolarophiles to form five-membered heterocyclic rings.[5,6] In certain cases the initially formed 1,3-dipole can be intramolecularly trapped to give novel azabicyclohexenes.[7-10] For example, irradiation of allyl-substituted 2*H*-azirines produces 2-azabicyclo[3.1.0]hex-2-enes via an unusual 1,1-cycloaddition reaction of the 1,3-dipole.[7] Products formed on thermal excitation of the 2*H*-azirine system, on the other hand, appear to involve vinyl nitrenes as intermediates.[11-23] Since examples of the direct addition of vinyl nitrenes to olefins to give aziridines have appeared infrequently in the literature,[24] we decided to investigate the thermal chemistry of a number of allyl-substituted 2*H*-azirines in order to determine whether the initially generated vinyl nitrene would undergo addition to the neighboring double bond. We report here the results of these studies.[25]

Results

The synthesis of the 2-allyl-substituted 2*H*-azirine system was straightforward and involved a modified Neber reaction in which variously substituted 2-methyl-1-phenyl-4-penten-1-ones were allowed to react with dimethylhydrazine. Treatment of the resulting dimethylhydrazone with methyl iodide followed by reaction with base gave the desired 2-allyl-substituted 2*H*-azirines in good yield.

We initially examined the thermal behavior of 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**1**). Thermolysis of **1** in toluene



1, R = H **2**, R = H **3**, R = H
4, R = CH_3 **5**, R = CH_3 **6**, R = CH_3

at 195 °C for 180 h or in the absence of solvent at 250 °C for 1.5 h gave 1-methyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**2**, 90%) and 3-methyl-2-phenylpyridine (**3**, 10%). The identity of **2** was determined by its straightforward spectral characteristics [NMR (100 MHz) τ 9.55 (t, 1 H, J = 4.0 Hz), 9.04 (dd, 1 H, J = 8.0, 4.0 Hz), 8.57 (s, 3 H), 8.36 (m, 1 H), 6.25 (dd, 1 H, J = 17.5, 2.0 Hz), 6.02 (dd, 1 H, J = 17.5, 5.0 Hz), 2.2–2.8 (m, 5 H)] as well as its facile conversion into **3** on further heating. Thermolysis of the closely related 2-(1-methylallyl)-substituted azirine **4** gave 1,6-dimethyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**5**, 58%) as a 1:1 mixture of endo and exo isomers as well as 3,4-dimethyl-2-phenylpyridine (**6**, 25%). The mixture of exo and endo isomers of **5** was smoothly converted into pyridine **6** on further heating.

Subjection of azirine **7** to similar pyrolysis conditions gave 1,4-dimethyl-2-phenyl-3-azabicyclo[3.1.0]hex-2-ene (**8**, 71%), 2-phenyl-3-methyl-5-vinyl-Δ^1-pyrroline (**9**, 21%) as an inseparable cis–trans mixture, and a trace amount (<5%) of

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