Photocycloaddition in the β-Naphthyl-Substituted Azirine System[1]

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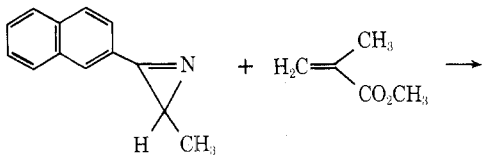
Upon irradiation with ultraviolet light, β-naphthyl-substituted azirines undergo ring opening to give nitrile ylide intermediates which are subsequently trapped with electron-deficient olefins to produce Δ^1-pyrrolines. The regiospecificity of the cycloaddition is discussed in terms of the frontier orbital method. The cycloaddition reaction was shown to proceed from the excited singlet state; the corresponding triplet was demonstrated to be unreactive. Excited singlet lifetimes of a number of substituted naphthylazirines as well as quantum yields for cycloaddition were determined. The rate of opening of the excited azirine ring was found to decrease with increasing methyl substitution. The observed order of photoreactivity is discussed in terms of upper excited singlet states.

In previous papers we reported on the photocycloaddition of arylazirines with electron deficient olefins.[3] The formation of the adducts was interpreted as proceeding by way of irreversible ring opening of the azirine ring to form a nitrile ylide intermediate, which was subsequently trapped by a suitable dipolarophile.[3,4] Irradiation of an arylazirine in the absence of a dipolarophile gave rise to 1,3-diazabicyclo[3.1.0]hex-3-enes as primary photoproducts. The formation of these dimers was attributed to the 1,3-dipolar addition of the initially generated nitrile ylide onto a ground-state azirine molecule. The cleavage of the C–C bond of the azirine ring was also shown to proceed from the n–π* excited singlet state and was rationalized in terms of an electrocyclic transformation by analogy with the cyclopropyl → allyl cation rearrangement.[5] The fact that the singlet state of the azirine was involved was substantiated by our inability to quench or sensitize the cycloaddition with a variety of triplet quenchers and sensitizers.[3]

It is well known that a considerable amount of information on the reactivity of singlet excited states of organic molecules can be obtained from a study of molecular fluorescence properties.[6] In order to secure additional information on the reactivity of the excited singlet state(s) involved in the photocycloaddition reaction, we decided to study the photochemistry of a number of substituted naphthylazirines. Marked differences in the photochemistry of phenyl- and naphthyl-substituted ketones are known and have been ascribed to the difference in nature of the lowest excited state involved in the reaction.[7] It is reasonable to assume that in the naphthylazirine excited states, both singlet and triplet, the excitation energy will be heavily localized on the naphthyl portion of the molecule. Concentration of the excitation at one end of the molecule seemed a possible way of modifying the photobehavior of the azirine ring. The present paper reports on the photocycloaddition reaction of a number of naphthyl-substituted azirines and also describes some fluorescence emission data which permit approximation of the rate constants involved in the ring opening step.

Photocycloaddition in the β-Naphthylazirine System. Our initial experiments revealed that naphthyl-substituted azirines were highly photochemically reactive. Thus, direct irradiation of 2-(β-naphthyl)azirine (**1**) with methyl acrylate and acrylonitrile occurred smoothly and gave rise to good yields of photoadducts **2** and **3**.[3] Irradiation of **1** in the presence of electron-rich acyclic or cyclic olefins produced no photoadduct, but instead gave a dimeric material, whose structure was assigned as 4,5-di(β-naphthyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (**4**).

The photochemical cycloaddition reactions of 3-methyl-2-(β-naphthyl)azirine (**5**) and 3,3-dimethyl-2-(β-naphthyl)-azirine (**6**) with electron-deficient olefins were also investigated. Irradiation of a pentane solution of **5** and acrylonitrile produced a 3:1 mixture of *cis*- and *trans*-4-cyano-5-methyl-2-(β-naphthyl)-Δ^1-pyrroline (**7** and **8**). The structures of photoadducts **7** and **8** are derived from consideration of the nmr data (see Experimental Section), which proved to be remarkably similar to the nmr of the adducts obtained from the photolysis of 3-methyl-2-phenylazirine with acrylonitrile.[3] Similar irradiation of a solution of **5** in pentane which contained an excess of methyl methacrylate proceeded to give a mixture of *cis*- and *trans*-4-carbomethoxy-4,5-dimethyl-2-(β-naphthyl)-Δ^1-pyrroline (**9** and **10**). The ratio of the two cycloadducts (**9**:**10** = 3:2) was determined by nmr analysis of the singlets associated with the methyl groups in the crude photolysate.



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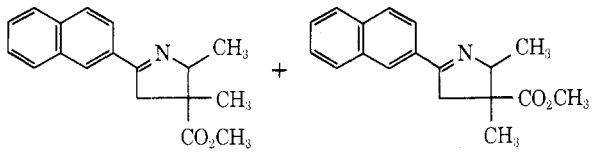
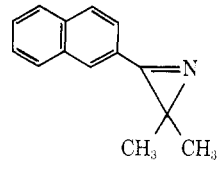
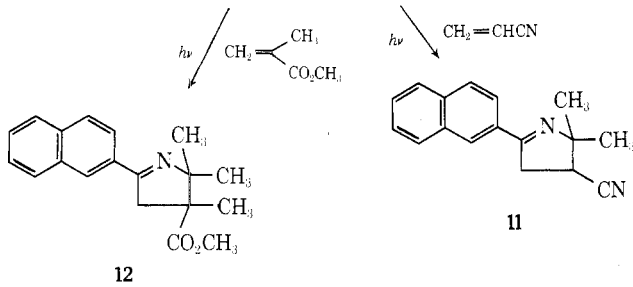


9 10

Photoaddition of 3,3-dimethyl-2-(β-naphthyl)azirine (**6**) with the same two electron-deficient olefins affords Δ¹-pyrrolines **11** and **12**. The configurations of the adducts were readily established by examination of their characteristic nmr spectra (see Experimental Section).



6



12 11

The orientation of the groups in the Δ¹-pyrrolines obtained from the above photoadditions is essentially identical with that observed by Huisgen in related 1,3-dipolar additions.[8,9] The origin of the orientation or regioselectivity in this and related 1,3-dipolar cycloadditions has been one of the major unsolved problems in this area of chemistry. Huisgen has suggested that a subtle interplay of steric and electronic factors controls the regioselectivity in 1,3-dipolar additions.[10] Firestone, on the other hand, has attempted to explain the direction of orientation by estimating the relative energies of two possible diradical intermediates.[11] In a recent report, Houk has successfully employed the frontier orbital method for rationalizing the effect of substituents on rates and regioselectivity of 1,3-dipolar cycloadditions.[12] According to the perturbation model,[12] the relative reactivity of a given 1,3 dipole toward a series of dipolarophiles will be determined primarily by the extent of stabilization afforded the transition state by interaction of the frontier orbitals of the two reactants. When nitrile ylides are used as 1,3 dipoles, the dipole highest occupied (HO) and dipolarophile lowest unoccupied (LU) interaction will be of greatest importance in stabilizing the transition state. The favored cycloadduct will be that formed by union of the atoms with the largest coefficient in the dipole HO and the dipolarophile LU. An electron-deficient olefin has the largest coefficient on the unsubstituted carbon in the lowest unoccupied (LU) orbital while the imine carbon atom of the nitrile ylide has the largest coefficient in the (HO) orbital.[14] With this information, it becomes possible to accommodate the regiochemical data found in the above cycloaddition reactions.

Table I
Quantum Yields, Singlet Lifetimes, and Rates of Reaction in the β-Naphthylazirine System

Azirine	$\Phi_{cycloaddition}$	$\tau_s \times 10^9$, sec	$k_r \times 10^{-8}$, sec
2-(β-Naphthyl)azirine (**1**)	0.37	1.1	3.4
3-Methyl-2-(β-naphthyl)-azirine (**5**)	0.44	2.0	2.2
3,3-Dimethyl-2-(β-naphthyl)azirine (**6**)	0.41	2.5	1.6

Quantum Yield Studies. Quantum yields for adduct formation were determined using benzophenone-benzhydrol actinometry.[15] Degassed and sealed Pyrex tubes containing solutions of the naphthylazirine and the dipolarophile were irradiated along with antinometer tubes in the rotating photochemical assembly. The light from a 450-W Hanovia lamp was filtered through a nickel-cobaltous solution (transmission 300–340 nm). Reactions were carried to low conversions to prevent appreciable light absorption by the products, and yields of products were determined by glpc using internal standards. The quantum yields for cycloaddition at high dipolarophile concentration (see Table I) showed no wavelength dependence. The naphthylazirines proved to be unreactive when irradiated in the presence of acetophenone. In these experiments, the concentrations were adjusted so that acetophenone absorbed more than 98% of the light. The concentration of the naphthylazirine was kept sufficiently low to ensure unimolecular destruction of acetophenone singlet molecules prior to collision with ground-state azirine, yet sufficiently high to guarantee collision of acetophenone triplets with azirine at a rate faster than acetophenone decay.[16] Under these conditions, no photocycloaddition whatsoever was detected. This observation suggests that the excited singlet state of the naphthylazirine is the reacting species.

Absorption and Emission Spectra of the Naphthyl-Substituted Azirines. The ultraviolet absorption spectra of the naphthylazirines studied exhibit strong absorption maxima in the naphthalene region of the spectrum.[17] The fluorescence emission curves for the β-naphthylazirines were essentially identical in shape and wavelength with that of naphthalene.[18] However, the fluorescence quantum efficiencies of these systems were only *ca.* 10% of that of naphthalene. The considerably diminished fluorescence of the naphthylazirine system may be attributed to the shorter lifetime of the excited singlet state of these systems. Most importantly, the fluorescence emission of these azirines was not quenched with added quantities of dipolarophile.

Interpretative Discussion

The first point to be noted from our results is that the photocycloaddition of the naphthyl-substituted azirines still occurs with high quantum efficiency (*i.e.*, $\Phi \sim 0.40$) despite the fact that the excitation energy in the reactant is heavily localized on the naphthyl end of the molecule. Another point which can be made is that the reaction does not proceed *via* T_1, the first excited triplet. The evidence presented above showed that efficient triplet energy transfer from acetophenone to the naphthylazirine occurred, and yet no photocycloaddition was observed. The possibility that the cycloaddition occurs through a T_2 state cannot be totally excluded since acetophenone, with its 74-kcal/mol excitation energy, will not be able to generate the second triplet of naphthalene.[19] It should be pointed out, however, that the singlet excited state of these naphthyl-substituted azirines lies 88 kcal/mol above ground state and therefore should not have sufficient en-

Scheme I

$$A_0 \xrightarrow{h\nu} A^{*1}$$

$$A^{*1} \xrightarrow{k_f} A_0 + h\nu'$$

$$A^{*1} \xrightarrow{k_d} A_0$$

$$A^{*1} \xrightarrow{k_r} NY$$

$$NY + O \xrightarrow{k_1} \text{adduct}$$

$$NY + A_0 \xrightarrow{k_2} \text{dimer}$$

ergy to lead to T_2.[19] Hence, photocycloaddition from S_1 seems the most likely possibility for these systems, but reaction from T_2 cannot be excluded with rigor. Zimmerman and coworkers have also noted the general difficulty in differentiating between the involvement of S_1 and T_2 states in photochemical reactions as a result of their similarities in lifetime and energy.[21,22]

The structural details of the above photocycloaddition reactions are consistent with the mechanism outlined in Scheme I, where A_0 = naphthylazirine, NY = nitrile ylide, and O = dipolarophile. The fact that the fluorescence emission of these systems was not quenched with added quantities of dipolarophile suggests that the opening of the azirine ring to the nitrile ylide (*i.e.*, k_r) is an extremely fast process. One can, in principle, obtain all the desired rate constants of the excited singlet state provided that Φ_r, Φ_f, and one of the rate constants are known. Here k_f is the rate constant of fluorescence, k_r is the rate of opening of the excited azirine ring, and k_d is the sum of all radiationless modes of excited singlet destruction (including any intersystem crossing)

$$\Phi_r = k_r/(k_f + k_d + k_r) \quad (1)$$

$$\Phi_f = k_f/(k_f + k_d + k_r) \quad (2)$$

The above two equations (1 and 2) may be combined to give eq 3. The excited singlet lifetimes of naphthylazirines

$$\Phi_r/k_r = \Phi_f/k_f = \tau_s \quad (3)$$

($\tau_s = \Phi_f/k_f$) were measured by single-photon counting and are shown in Table I. Since the quantum yield for cycloaddition (Φ_a) of the naphthylazirines with the various dipolarophiles used is high (Φ_a = 0.37–0.44), we can estimate that the quantum yield for ring opening (Φ_r) lies somewhere between Φ_a and unit efficiency. The fact that the quantum yield for adduct formation at infinite dipolarophile concentration did not vary significantly as a function of dipolarophile structure indicates that all the nitrile ylides are being efficiently trapped.[23] Consequently, we can estimate Φ_r as being approximately equal to Φ_a. Values of k_r can now be calculated using the measured singlet lifetimes and Φ_r. These are summarized in Table I.

The large magnitude of k_r (*i.e.*, 1.6–3.4 × 10^8 sec) is compatible with a rapid opening of the excited azirine ring to give a nitrile ylide intermediate. The substituent effects noted, although admittedly small, seemingly indicate that methyl groups diminish the rate of ring opening. Moreover, there does not appear to be any correlation of the quantum yields for cycloaddition with the values obtained for k_r. As was pointed out earlier,[24] quantum yields do not necessarily have any relation to excited state reactivity. A correlation of the excited state rate constants with the stability of the photochemically generated nitrile ylide intermediate does not apply in this system either. The precise reasons for this are not known at this time. One possibility worth mentioning is that the reaction leading to the nitrile ylide may proceed from an upper n–π^* excited singlet state. This is not so unreasonable, since Ullman and Singh have already shown that the rearrangements observed with the related 2-aroyl-3-arylazirine system proceeds from a S_2 state.[25,26] If this were the case here, then the photoreactivity of the naphthylazirine system could arise from the equilibrium concentration of the upper n–π^* singlet state. Alternatively, the ring opening reaction might occur from the naphthalene singlet state, which is mostly π–π^* in character but has enough n–π^* character mixed in to cause it to be slightly reactive. At any rate, the photoreactivity of the system would be expected to decrease as the energy gap between the S_1 and S_2 state increases. A similar situation was noted by Wagner in the Norrish Type II reactions of substituted aromatic ketones.[27] If the energy gap of the two excited singlet states increases with methyl substitution, one might expect to see a diminution in the chemical reactivity of the azirine ring as it becomes more heavily substituted. Additional experiment work is required for any further understanding of the problem.

Experimental Section[28]

3-Methyl-2-(β-naphthyl)azirine (5). To a solution of 15 g of sodium azide in 100 ml of acetonitrile cooled in a methanol–ice bath was added a solution of 18.3 g of iodine monochloride in 15 ml of acetonitrile. The mixture was allowed to stir for an additional 30 min while maintaining the temperature at 0°. To this solution was added 13.4 g of β-propenylnaphthalene.[29] The mixture was kept at 0° for 2 hr and was then allowed to warm to room temperature over a 12-hr period. The resultant orange slurry was added to 600 ml of water and extracted with ether. The ether extracts were washed with three 100-ml portions of a 5% sodium thiosulfate solution and then with three 100-ml portions of water. After the organic layer was dried over magnesium sulfate, it was concentrated under reduced pressure to give 25.8 g (96%) of an orange oil which was identified as 1-azido-2-iodo-1-(β-naphthyl)propane: ir (neat) 3.38, 4.76, 6.21, 6.90, 7.91, 9.33, 12.20, and 13.36 μ; nmr ($CDCl_3$) τ 8.13 (3 H, d, J = 7.0 Hz), 5.54 (1 H, m), 5.04 (1 H, d, J = 7.0 Hz), and 1.8–2.6 (7 H, m).

To a stirred and cooled solution of 25.8 g of the above iodine azide adduct in 250 ml of ether was added 15.3 g of potassium *tert*-butoxide over 30 min. The mixture was then allowed to stir at 0° for 1 hr. The slurry was extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 15.6 g of an orange oil which was purified by passing it through a column of neutral alumina with benzene. The resulting light yellow oil was identified as 1-azido-1-(β-naphthyl)-1-propene: ir (neat) 3.30, 4.78, 6.03, 7.34, 7.90, 11.60, 12.17, and 13.30 μ; nmr ($CDCl_3$) τ 8.20 (3 H, d, J = 8.0 Hz), 4.35 (1 H, q, J = 8.0 Hz), and 1.8–2.7 (7 H, m).

A 1.0-g sample of the above azide was refluxed for 24 hr in 5 ml of chloroform. After being concentrated under reduced pressure, the residue was sublimed at 75° (0.1 mm) to give 690 mg (80%) of 3-methyl-2-(β-naphthyl)azirine (5): mp 76–77°; ir (KBr) 3.48, 5.79, 7.23, 10.20, 11.01, 11.46, 12.10, 13.23, and 14.16 μ; nmr τ 8.57 (3 H, d, J = 0 Hz), 7.59 (1 H, q, J = 5.0 Hz), and 1.5–2.4 (7 H, m); uv (cyclohexane) 241, 247, 280, 284, 294, and 339 nm (ε 54,500, 55,800, 9,300, 11,200, 9,400, and 1,200); m/e 181 (M^+), 153 (base), 127, 126, and 101.

Anal. Calcd for $C_{13}H_{11}N$: C, 86.16; H, 6.12; N, 7.73. Found: C, 85.92; H, 6.15; N, 7.56.

3,3-Dimethyl-2-(β-naphthyl)azirine (6). In a Carius tube was placed 5.0 g of β-isobutyronaphthone,[30] 3.0 g of unsymmetrical dimethylhydrazine, 0.05 g of *p*-toluenesulfonic acid, and 1.5 g of anhydrous magnesium sulfate. The tube was sealed under reduced pressure and the mixture heated at 110° for 3 days. To the cooled mixture was added 10 ml of ether, and the resulting solids were removed by filtration. Concentration of the solution under reduced pressure gave 7.3 g of a dark oil which was used in the next reaction without further purification.

The above hydrazone (7.3 g) was placed in a flask which contained 5 ml of ethanol and 28 g of methyl iodide. The mixture was heated at reflux for 6 hr after it was cooled in ice and triturated with ether until a dark solid crystallized out. Recrystalliza-

tion from a 9:1 mixture of ethyl acetate–ethanol gave 7.0 g (61%) of a white crystalline solid, mp 164–166°, which was identified as β-isobutyronaphthone-*N,N,N*-trimethylhydrazonium iodide.

To a stirred solution of the above iodide in 350 ml of isopropyl alcohol was added a solution of sodium isopropoxide (prepared from 0.46 g of sodium in 100 ml of isopropyl alcohol). After the addition was complete, the mixture was allowed to stir for an additional hour at 35°. The solvent was removed under reduced pressure and the residue was extracted with ether. Removal of the ether left 3.25 g (84%) of a pale yellow oil which solidified upon standing. Distillation of this material at 75–80° (0.04 mm) gave 3,3-dimethyl-2-(β-naphthyl)azirine (**6**), as a white crystalline solid: mp 30–31°; ir (neat) 3.40, 5.77, 7.27, 8.88, 12.18, and 13.16 μ; nmr ($CDCl_3$) τ 8.46 (6 H, s) and 1.6–2.5 (7 H, m); *m/e* 195 (M^+), 180, 154 (base), 127, and 126.

Anal. Calcd for $C_{14}H_{13}N$: C, 86.11; H, 6.71; N, 7.17. Found: C, 85.92; H, 6.80; N, 7.18.

Photoaddition of 3-Methyl-2-(β-naphthyl)azirine with Acrylonitrile. A solution of 1.2 g of 3-methyl-2-(β-naphthyl)azirine and 7 ml of acrylonitrile in 250 ml of pentane was irradiated for 2 hr using a Corex filter. After filtration of polymeric materials, the reaction mixture was evaporated to yield an off-white solid (62%) which proved to be a 3:1 mixture of stereoisomers. Repeated recrystallization and chromatography failed to separate the isomers. Spectral and elemental analysis of the mixture of *cis*- and *trans*-4-cyano-5-methyl-2-(β-naphthyl)-Δ^1-pyrroline (**7** and **8**) showed the following features: ir (KBr) 3.40, 4.49, 6.21, 7.00, 7.42, 8.88, 9.12, 11.53, 12.00, and 13.40 μ; nmr (cis) τ 8.45 (3 H, d, J = 7 Hz), 6.63 (3 H, m) 5.40 (1 H, m), and 1.7–2.5 (7 H, m); nmr (trans) τ 8.47 (3 H, d, J = 7 Hz), 6.40–7.50 (3 H, m), 5.40 (1 H, m), and 1.7–2.5 (7 H, m); uv (cyclohexane) λ 339 nm (ε 1130), 330 (790), 323 (1130), 306 (sh, 2220), 293 (11,500), 282, (13,500), 273 (10,600), 521 (60,200), 243 (58,500), and 237 (43,700); *m/e* 234 (M^+), 182, 181 (base), 180, 154, 153, and 127. An elemental analysis was obtained on the mixture.

Anal. Calcd for $C_{16}N_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.86; H, 6.06; N, 11.92.

Photoaddition of 3-Methyl-2-(β-naphthyl)azirine with Methyl Methacrylate. A solution of 0.95 g of 3-methyl-2-(β-naphthyl)-azirine and 8 ml of methyl methacrylate in 250 ml of pentane was irradiated for 2 hr using a Cortex filter. After filtering polymeric side products, 1.05 g of an orange oil was obtained, which by nmr ananlysis was shown to be a 3:2 mixture of *cis*- and *trans*-4-carbomethoxy-4,5-dimethyl-2-(β-naphthyl)-Δ^1-pyrrolines (**9** and **10**). The mixture of pyrrolines could not be separated into the individual isomers by distillation or chromatography. Characterization was accomplished by elemental analysis of the picrate of the mixture and from the following spectral properties: ir (neat) 3.38, 5.80, 6.20, 7.71, 8.31, 11.60, 12.11, and 13.35 μ; nmr (major isomer) τ 8.56 (3 H, s), 8.50 (3 H, d, J = 7 Hz), 6.63 (2 H, ABq, J = 17 Hz), 5.64 (1 H, q, J = 7 Hz), and 1.6–2.4 (7 H, m); nmr (minor isomer) τ 8.76 (3 H, d, J = 7 Hz), 8.71 (3 H, s), 6.47 (2,H, ABq, J = 17 Hz), 5.42 (1 H, 2, J = 7 Hz), and 1.6–2.4 (7 H, m); *m/e* 281 (M^+), 229, 228, 181 (base), 180 154, 153, 128, 127, 111, and 69.

Anal. Calcd for $C_{24}H_{22}N_4O_9$: C, 56.47; H, 4.34; N, 10.98. Found: C, 56.38; H, 4.38; N, 10.88.

Photoaddition of 3,3-Dimethyl-2-(β-naphthyl)azirine with Acrylonitrile. A solution of 1.0 g of 3,3-dimethyl-2-(β-naphthyl)-azirine and 7 ml of acrylonitrile in 250 ml of pentane was irradiated for 1 hr using a Corex filter. After filtration of polymeric materials and removal of the solvent under reduced pressure, the resultant oil was triturated with hexane to yield an off-white solid which was recrystallized from ether to give white crystals, mp 107–108°. This material was identified as 4-cyano-5,5-dimethyl-2-(β-naphthyl)-Δ^1-pyrroline (**11**) (71%): ir (KBr) 3.45, 4.47, 6.23, 7.40, 8.16, 8.82, 11.16, 12.17, and 13.40 μ; nmr τ 8.50 (3 H, s), 8.44 (3 H, s), 6.24–7.10 (3 H, m), and 1.7–2.4 (7 H, m); uv (cyclohexane) λ 339 nm (ε 1090), 330 (750), 323 (1070), 305 (sh, 2240), 293 (11,600), 283 (13,800), 273 (10,800), 251 (62,900), 243 (60,900), and 236 (sh, 44,300); *m/e* 248 (M^+), 194 (base), 154, 153, 127, and 81.

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.27; H, 6.59; N, 11.05.

Photoaddition of 3,3-Dimethyl-2-(β-naphthyl)azirine with Methyl Methacrylate. A solution of 1.0 g of 3,3-dimethyl-2-(β-naphthyl)azirine and 7 ml of methyl methacrylate in 250 ml of pentane was irradiated for 1 hr using a Corex filter. After filtration of polymer and removal of the solvent, an orange oil remained. Trituration of this material in hexane gave 0.93 g of an off-white oily solid. Repeated recrystallization from pentane yielded an analytical sample, mp 76–77°, identified as 4-carbomethoxy-2-(β-naphthyl)-4,5,5-trimethyl-Δ^1-pyrroline (**12**) (50%): ir (KBr) 3.42, 5.80, 6.20, 7.77, 9.21, 11.53, 12.09, and 13.32 μ; nmr τ 8.80 (3 H, s), 8.68 (3 H, s), 8.45 (3 H, s), 7.02 (1 H, d, J = 17.5 Hz), 6.20 (3 H, s), 6.01 (1 H, d, J = 17.5 Hz), and 1.6–2.4 (7 H, m); uv (cyclohexane λ 337 nm (ε 900), 328 (780), 322 (900), 306 (sh, 1920), 293 (10,400), 282 (13,200), 273 (10,700), 249 (54,400), 242 (60,400), and 236 (sh, 47,600); *m/e* 295 (M^+), 236, 195 (base), 194, 179, 154, 153, 127, 81, and 69.

Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H. 7.17; N, 4.74. Found: C, 77.13; H, 7.22; N, 4.72.

Emission Studies. Fluorescence emission studies were made on an Aminco-Bowman spectrophotofluorometer. The spectrofluorometer was equipped with a 1P21 photomultiplier and a high-pressure Xenon lamp, as supplied by the manufacturer. The fluorescence spectra of the azirines were determined in cyclohexane solution at 25°. The values obtained were carefully corrected for any residual solvent emission. No interference due to solvent was found at any time. The concentration of each substrate was 5×10^{-3} *M*. All slits were set at 3 mm and the excitation wavelength (310–356 nm) was chosen so as to yield the highest substrate emission. The shape of the emission envelopes for the naphthyl-substituted azirines were essentially identical with that of naphthalene. The singlet lifetime (τ_s) of the naphthyl-substituted azirines was measured by single-photon counting and was found to be in the order of $1.1\text{–}2.5 \times 10^{-9}$ sec.

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Registry No.—**1**, 41413-91-6; **5**, 51051-84-4; **6**, 51051-85-5; **7**, 51051-86-6; **8**, 51051-87-7; **9** picrate, 51051-89-9; **10** picrate, 51051-91-3; **11**, 51051-92-4; **12**, 51051-93-5; β-propenylnaphthalene, 51051-94-6; 1-azido-2-iodo-1-(β-naphthyl)propane, 51051-95-7; 1-azido-1-(β-naphthyl)-1-propene, 51051-96-8; β-isobutyronaphthone, 51051-97-9; β-isobutyronaphthone-*N,N,N*-trimethylhydrazonium iodide, 51051-98-0; acrylonitrile, 75-05-8; methyl methacrylate, 80-62-6.

References and Notes

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Acid-Catalyzed Angular Methyl Migration in a Substituted Octalin[1]

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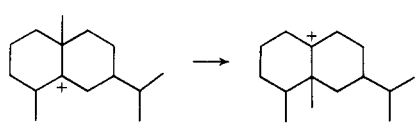
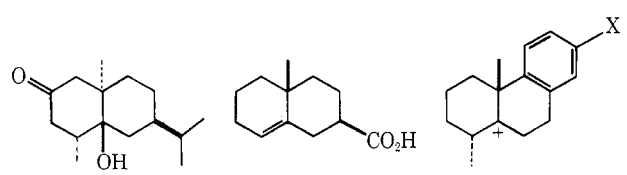
The acid-catalyzed isomerization of optically active 2,2,8,8,10-pentamethyl-1(9)-octalin (12) of known absolute configuration affords two major olefin products, 13 and 14, whose gross structure was determined by a combination of spectral data and chemical transformations of each product to the common derivative, alcohol 17. The absolute configuration at the chiral angular methyl center in 13 and 14 was determined by the ORD curves of the corresponding trans-fused 1-decalone derivatives 25 and 20. The isomerization pathway of 12 to 13 and 14 therefore involves a specific spiro[4.5]decalyl cation to key intermediate 29a which undergoes angular methyl migration. Intermediate 29a was generated independently and shown to undergo rapid conversion to octalins 13 and 14.

A vast amount of literature has appeared over the years dealing with the solvolytic and acid-catalyzed rearrangements of a wide variety of organic molecules found in nature.[2] Backbone rearrangements and angular methyl migrations have been well documented in the biosynthetic pathways leading to the multicyclic triterpenes.[3] Similarly, angular methyl migration has long been considered for the derivation of the eremophilane-type sesquiterpenes from the eudesmane skeleton (1 → 2).[4]

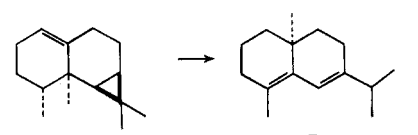


1 2

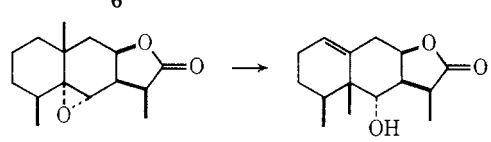
Angular methyl migrations of the above type, however, have been difficult to achieve in decalin systems under laboratory conditions. Attempts to dehydrate ketol 3 with concomitant angular methyl migration failed to afford any methyl-migrated products.[5] The apparent methyl migration observed[6] in the rearrangement of 4 has subsequently been shown to proceed *via* spiro intermediates.[7] Some angular methyl migration has been observed in the rearrangement products arising from cation 5 generated by appropriate solvolysis conditions, although the same cation generated by acid from the corresponding olefin gave only small amounts of such products.[8] Formic acid treatment of 6 has, however, been reported to afford the angular methyl migrated product, diene 7.[9] Likewise, a recent communication[10] shows that formic acid–acetone treatment of epoxydihydroalantolactone (8) gives reasonable yields of the angular methyl migrated product 9.



3 4 5

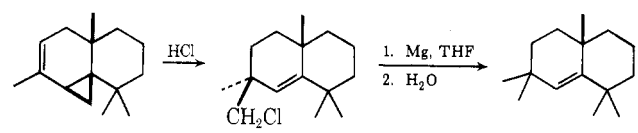


6 7



8 9

Scheme I



10 11 12

Both of the latter two examples which give rise to angular methyl migration products contain more than simple double-bond functionality. We wish to report now a substituted simple octalin system whose acid-catalyzed rearrangement proceeds *via* both a spiro[4.5]decalyl cation system and an angular methyl migration.

Results

Synthesis of (+)-(*S*)-2,2,8,8,10-Pentamethyl-1(9)-octalin (12). The octalin employed in this study was readily obtained from (−)-thujopsene (10) *via* the two-step sequence outlined in Scheme I. Treatment of 10 with hydrogen chloride eventually formed the most stable addition product, neopentyl chloride 11.[11] Reduction of 11 to the desired octalin 12 was conveniently effected by aqueous treatment of the corresponding Grignard complex. The nmr spectrum of 12 showed five methyl singlets and a sharp vinyl proton singlet at δ 5.13, in full agreement with the assigned structure.

It is important to note that the pentamethyloctalin 12 thus obtained is optically active and possesses the absolute configuration depicted. The absolute stereochemistry