Dioxopyrroline. L.[1] Skeletal Rearrangements of 7-Vinyl-7-trimethylsilyloxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]heptane-3,4-diones under Thermal, Basic, and Acidic Conditions

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The oxyvinylcyclobutanes (2), photoadducts of the dioxopyrrolines (1) to trimethylsilyloxybutadienes, undergo two different types of skeletal rearrangements depending on the reaction conditions. Thermolysis of 2 caused expansion of the cyclobutane ring by a 1,3-shift of the C_1–C_7 bond toward the vinyl group, giving rise to the hydroindoles (3) in moderate yields. This 1,3-shift was enormously accelerated when an alkoxide was generated by the action of tetrabutylammonium fluoride (TBAF) on trimethylsilyloxyvinylcyclobutanes. Thus, 2a—d, on treatment with TBAF at −30 °C, provided hydroindole derivatives in good yields, though in some cases (2a, b) accompanied with by-products (10). This demonstrates that the [2+2] photoannulation of dioxopyrroline, when coupled with the anionic 1,3-shift, provides an efficient synthetic route to functionalized hydroindoles. Under acidic conditions, the oxyvinylcyclobutanes (2) rearranged to give exclusively the 2-azatricyclo[4.3.0.0^{4,9}]nonanes (10), whose formation was rationalized in terms of the intramolecular Prins-type cyclization with concomitant expansion of the cyclobutane ring by 1,2-shift of the C_1–C_7 bond toward the vinyl group.

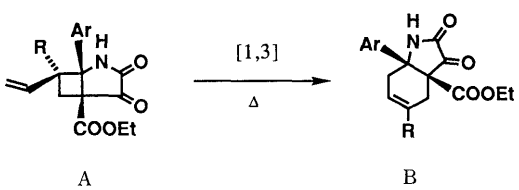
Keywords dioxopyrroline; photocycloaddition; 2-azabicyclo[3.2.0]heptane-3,4-dione; oxyvinylcyclobutane; thermolysis; tetrabutylammonium fluoride; 1,3-shift; hydroindole; Prins-type cyclization; 2-azatricyclo[4.3.0.0^{4,9}]nonane

In a preceding paper[2] we reported that thermolysis of 1-aryl-5-ethoxycarbonyl-7-vinyl-2-azabicyclo[3.2.0]-heptane-3,4-dione (A) (vinylcyclobutane) causes a 1,3-shift to form the hydroindole (B). This ring enlargement reaction is attractive as a synthetic method for hydroindoles, which are found in the structures of various alkaloids. Our observation that introduction of an additional methyl group at the 7-position favors this 1,3-shift[2b] and the fact that the presence of an electron-donating group at the migrating center usually facilitates thermal 1,3-shift,[3] led us to the idea that the 7-oxy-7-vinyl derivative of 5-ethoxycarbonyl-1-aryl-2-azabicyclo[3.2.0]heptane-3,4-dione (oxyvinylcyclobutane) might be a potential precursor for the synthesis of a functionalized hydroindole. In this paper we describe in detail the skeletal rearrangements of 7-vinyl-7-trimethylsilyloxy-5-ethoxycarbonyl-1-phenyl-2-azabicyclo[3.2.0]-heptane-3,4-diones under thermal, basic, and acidic conditions.[4]

Results and Discussion

Thermal 1,3-Shift of Oxyvinylcyclobutanes (2) The oxyvinylcyclobutanes (**2**) were readily prepared by the photoannulation of the dioxopyrrolines (**1**) with 2-trimethylsilyloxybutadiene or 1-methoxy-3-trimethylsilyloxybutadiene in good yields. The reaction is highly site-, regio-, and stereoselective, giving rise to a single product. The structure including stereochemistry of the product was unambiguously established by X-ray crystallographic analysis of the photoadduct **2a**.[5]

Heating of the oxyvinylcyclobutane **2a** in boiling toluene for 3 h caused the 1,3-shift, as expected, to give the hydroindole **3a** in 70% yield. Compound **3a** showed an absorption characteristic of the double bond of an enol ether group in the infrared (IR) spectrum at 1660 cm^{-1} and exhibited an olefinic proton signal in the nuclear magnetic resonance (NMR) spectrum at δ 4.7—4.8, supporting the assigned structure. Hydrolysis of **3a** with 5% hydrochloric acid (HCl) afforded the diketone **4a**, while treatment of **3a** with potassium fluoride in tetrahydrofuran (THF) gave the ketol **5a**, which is the intramolecular aldol condensation product of **4a**. This proves *cis*-juncture of the hydroindole ring in **3a**. Such a facile intramolecular aldol condensation of a 2,3,5-trioxo-*cis*-hydroindole derivative has already been found in the transformation of 2,7,8-trioxoerythrinan derivatives into 3,7-cycloerythrinans under acidic conditions.[6]



A B

Chart 1

Pyrolyses of the *N*-methyl derivative **2b** and the methoxyvinyl analogues, **2c** and **2d**, under similar conditions gave similar results. Although the products, the enol ethers **3c, d**, could not be isolated in pure form because of their instability to moisture and protic solvents, they were well characterized as either triketones **4c, d**, ketols **5c, d**, or conjugated enones **6a, b**, after treatment with 5% HCl or potassium fluoride, as shown in Chart 2.

In addition to the IR and ^{1}H-NMR spectral data, the ^{13}C-NMR spectra (see Experimental) of **5, 6** were consistent with the assigned hydroindole structures. The stereochemistry of C_5-OMe in **5c** and **5d** was concluded to be α, based on the consideration that this 1,3-shift should proceed *via* the six-membered transition state **7a** rather than **7b**, since the latter transition state is destabilized by a severe 1,3-diaxial interaction between the OMe and the COOEt groups (Chart 3). The absence of coupling between C_6-H and C_5-H (J=0 Hz) in the ^{1}H-NMR spectra of **5c** and **5d** indicates that the dihedral angle between these protons is *ca.* 90°. On the other hand, in the demethoxy derivatives **5a** and **5b** the coupling constant between $C_{6\beta}$-H and $C_{5\alpha}$-H is observed to be 6 Hz, while that between $C_{6\beta}$-H and $C_{5\beta}$-H is 0 Hz (see Fig. 1). These findings are consistent with the

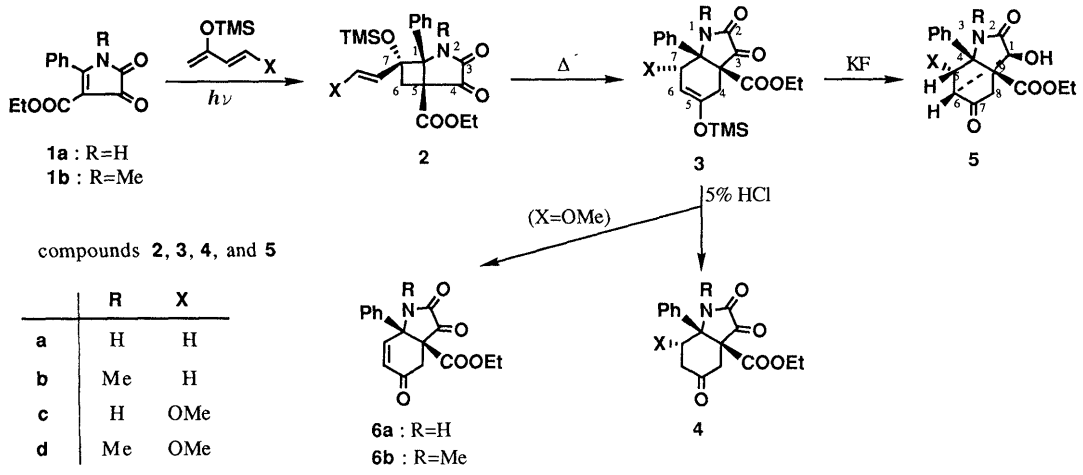


Chart 2

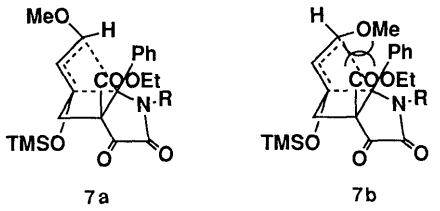


Chart 3

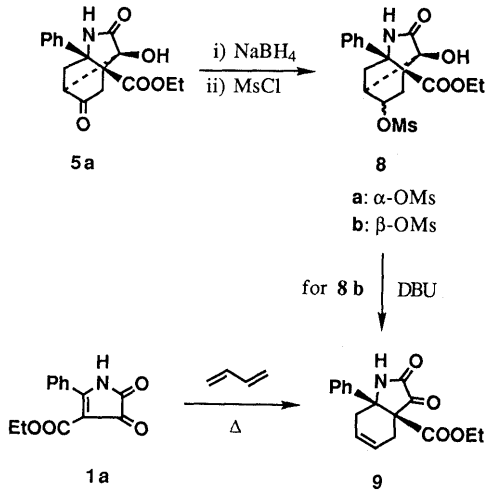


Chart 4

above stereochemical assignment.

The structure of **5a** was confirmed by the following chemical transformations. Reduction of **5a** with sodium borohydride followed by mesylation gave a mixgure of the mesylates **8a** and **8b**, one of which, **8b**, on demesylation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), afforded the olefinic compound **9**. This was proved to be identical with the Diels–Alder adduct of **1a** to butadiene (Chart 4).[7]

The above results indicate that thermolysis of **2** caused the expected 1,3-shift to give the hydroindoles in moderate yields. However, this thermolysis is sometimes accompanied with a side reaction, the cycloreversion of the cyclobutane ring, to an appreciable extent. The formation of dioxopyrroline (**1**), the cycloreversion product, was often indicated by thin layer chromatography (TLC) of the crude product, although it was seldom isolated from the reaction mixture.

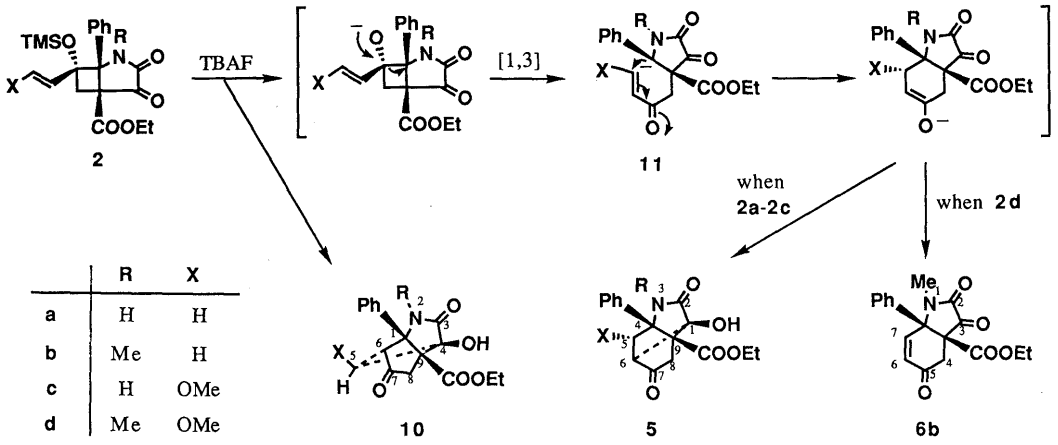
Tetrabutylammonium Fluoride-Induced Anionic Oxyvinyl 1,3-Shift The 1,3-shift of an oxyvinyl system is known to be enormously accelerated, when an alkoxide anion is generated by the action of alkali metal hydrides on a free or masked hydroxyl group.[8] However, the method using metal hydride failed in this case. For example, treatment of **2a** with potassium hydride in THF at 0 °C merely caused extensive decomposition of the substrate. This failure may be attributed to the instability of **2a** to strong bases. Eventually, we discovered that the anionic oxyvinyl 1,3-shift occurs under very mild conditions, when an alkoxide is generated by the action of tetrabutylammonium fluoride (TBAF) on a trimethylsilyloxy group. This, treatment of **2a** with TBAF in THF at −30 °C for 10 min gave the ketol **5a** in 57% yield. The *N*-methyl derivative **2b**, on similar treatment with TBAF, afforded the ketol **5b** in 63% yield. The ketols (**5**) were identical with the products obtained from the thermal 1,3-shift described above (Chart 5).

However, the reactions of **2a** and **2b** were accompanied with the formation of isomeric ketols, **10a** (28%) and **10b** (32%), respectively. These were identified as the products of an intramolecular Prins-type cyclization with concomitant 1,2-shift (see next section).

The methoxyvinyl derivative **2c** and its *N*-methyl analog **2d**, on treatment with TBAF in THF at −30 °C, exclusively gave the 1,3-shift products, the ketol **5c** (88%) and **5d** (83%), respectively.

The above results indicate that TBAF induces the 1,3-shift of oxyvinylcyclobutanes under extremely mild conditions, though the reaction is sometimes accompanied with a side reaction due to Prins-type addition of the carbonyl group to the vinyl group. Although there is too little information available as yet to elucidate the mechanism of this anionic 1,3-shift, the rearrangement presumably involves an anion (**11**) formed by fragmentation of the C_1–C_7 bond as an intermediate. Formation of the anion would be facilitated by the electronic stabilization effect of the C_7-phenyl group. Recently, Bhupathy and Cohen reported some evidence for the fragmentation mechanism in the anionic 1,3-shift of a simple oxyvinylcyclobutane system.[8e]

Acid-Catalyzed Skeletal Rearrangement of Oxyvinylcyclobutanes (2) Treatment of the oxyvinylcyclobutanes (**2**) with



	R	X
a	H	H
b	Me	H
c	H	OMe
d	Me	OMe

Chart 5

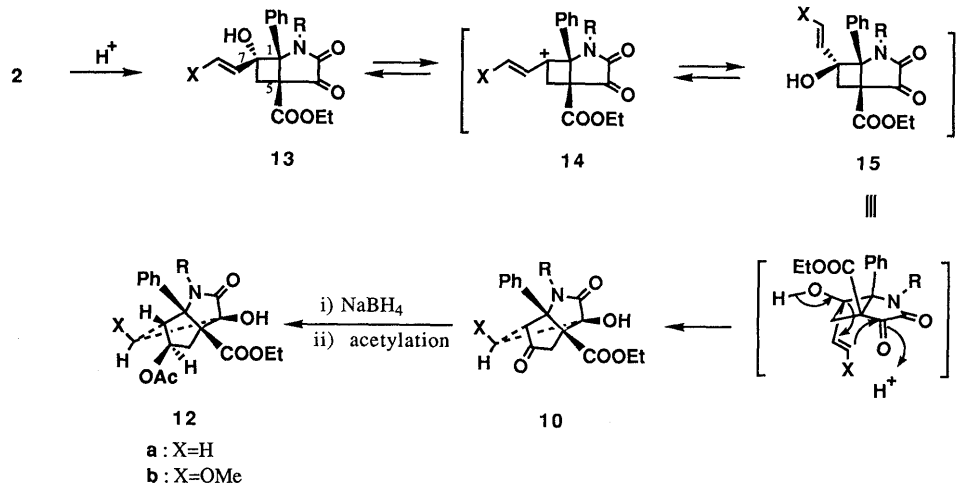


Chart 6

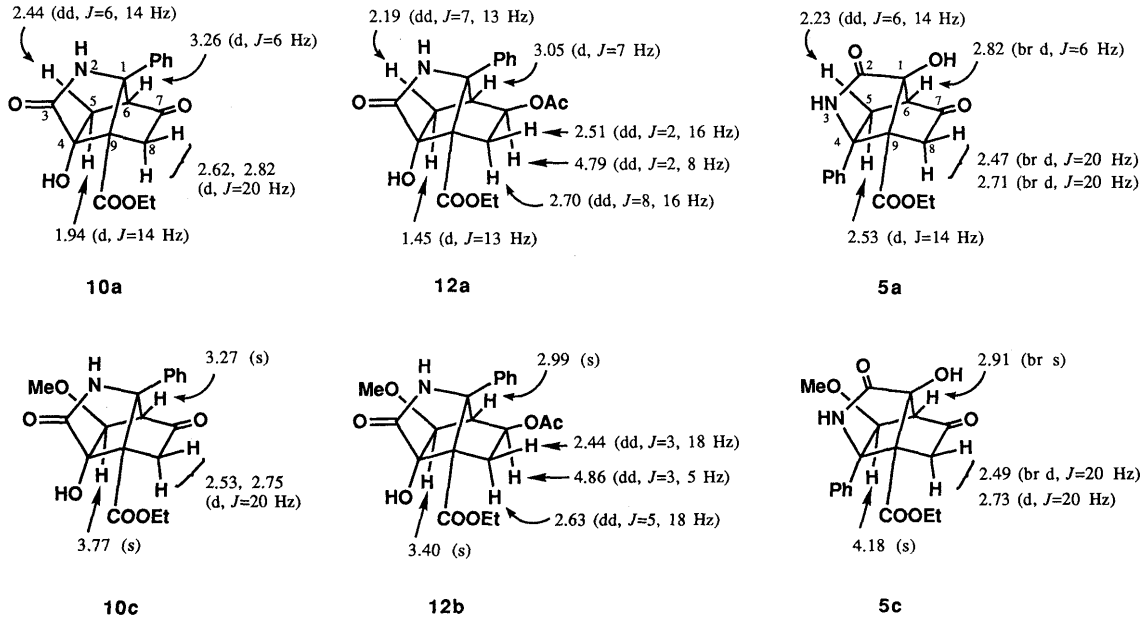


Fig. 1. ^{1}H-NMR Data for Azabicyclo[4.3.0.0^{4,9}]nonanes **5a**, **5c**, **10a**, **10c**, **12a**, and **12b**

acids causes another skeletal rearrangement. Thus, **2a**, on treatment with boron trifluoride etherate in dichloromethane or 5% HCl in THF, formed the ketol **10a** exclusively. The *N*-methyl derivative **2b**, on treatment with 5% HCl in THF at room temperature, gave the hydroxyvinylcyclobutane **13b**, which, on further treatment

with boron trifluoride etherate in dichloromethane under reflux, provided the ketol **10b** in 90% yield. The methoxyvinyl analogues **2c** and **2d** similarly afforded the ketols **10c** and **10d**, respectively, in excellent yields (Chart 6).

The ketols (**10**) showed IR, ^{1}H- and ^{13}C-NMR spectroscopic properties similar to those of the ketols (**5**), suggesting that they are isomeric. The spectra of **10** and the derived acetates (**12**), prepared by sodium borohydride reduction followed by acetylation, taken together with mechanistic considerations, lead to a caged structure of norbornane type for **10**. The observed coupling constants of the ring protons assigned by ^{1}H-NMR decoupling experiments (Fig. 1) were consistent with the reported coupling constants of a norbornane system,[9] thus supporting the assigned structure. The stereochemistry of C_5-OMe in **10c** and **10d** was also deduced from the ^{1}H-NMR spectra. The lack of coupling ($J=0$ Hz) between C_5-H and C_6-H indicated that the OMe group occupies the position *exo* to the norbornane ring. If it is in *endo* orientation, the coupling constant should be 6—7 Hz, since in the demethoxy derivative **10a** the coupling constant between C_5-*exo*-H and C_6-H was observed to be 6 Hz, while that between C_5-*endo*-H and C_6-H was 0 Hz.

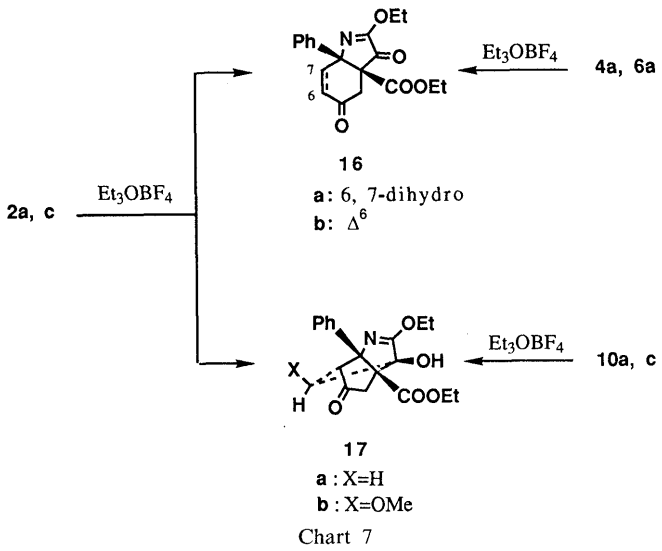


Chart 7

Formation of those products of norbornane structure can be rationalized in terms of an intramolecular Prins-type cyclization of the vinyl group to the C_4-carbonyl group with concomitant expansion of the cyclobutane ring due to the 1,2-shift of the C_1–C_7 bond (Chart 6).

Obviously, this cyclization is geometrically impossible when the C_7-vinyl group is in *exo* configuration, thus requiring the 7-epimerization of the *exo* vinyl group into the *endo* position prior to the cyclization (**13**→**15**). We believe that this epimerization occurs at the stage of the hydroxy derivative (**13**) *via* the carbocation (**14**). Although this epimerization should be reversible, the following irreversible cyclization step leads the reaction toward the formation of **10**. However, the possibility of epimerization due to a C_1–C_5 bond fission-recyclization process as observed in the thermolytic reactions[10] can not be ruled out completely.

Triethyloxonium fluoroborate (Meerwein reagent) was able to effect the two reactions, the Prins-type cyclization and the 1,3-shift, competitively (Chart 7). Thus, treatment of **2a** with Meerwein reagent at room temperature produced two imidates, **16a** (39%) and **17a** (47%). The methoxymethyl derivative **2c**, on similar treatment, also gave two products, **16b** (69%) and **17b** (12%). These imidates were identical with the compounds prepared by imidation of the corresponding lactams, **4a**, **6a**, **10a**, and **10b**, with Meerwein reagent, respectively.

Table I. Skeletal Rearrangements of Oxyvinylcyclobutanes

Substrate	Reagent and product (yield, %)					
	Δ, KF	*Δ*, HCl	TBAF	BF_3–Et_2O	HCl	Et_3OBF_4
2a	**5a** (50)	**4a** (61)	**5a** (57), **10a** (28)	**10a** (75)	**10a** (57)	**16a** (39), **17a** (47)
2b	**5b** (52)	**4b** (51)	**5b** (63), **10b** (32)	**10b** (98)	**13b** (60)[c]	
2c	**5c** (57)	**4c** (62)[a]	**5c** (88)	**10c** (46)	**10c** (86)	**16b** (69), **17b** (12)
2d	**5d** (44)	**4b** (21),[b] **6b** (24)[b]	**5d** (83)	**10d** (55)	**10d** (85)	

a) This gave **6a** (94%) on treatment with boiling HCl–THF (see Experimental). *b*) The crude thermolysis product was treated with boiling HCl–THF (see Experimental). *c*) This gave **10b** (90%) on treatment with BF_3–Et_2O.

Table II. ^{13}C-NMR Data for Azatricyclo[4.3.0.0^{4,9}]nonanes (in $CDCl_3$)

	1	2	3	4	5	6	7	8	9
5a[a]	88.1	167.8	—	68.0	37.7	53.4	207.4	35.2	67.6
5b	86.4	166.9	—	71.6	33.8	53.7	206.0	30.5	65.4
5c	85.6	165.4	—	68.5	80.3	60.6	203.8	34.1	67.6
5d	86.6	167.9	—	75.4	83.2	59.5	205.7	36.1	69.2
10a	71.0	—	168.0	83.7	35.8	53.5	208.6	35.1	67.3
10b	76.0	—	168.2	83.4	35.9	56.0	207.3	35.2	66.0
10c	70.5	—	167.5	89.4	84.2	64.5	206.7	36.7	69.8
10d	75.3	—	167.6	89.1	84.2	62.2	205.8	36.6	67.8
12a[a]	71.0	—	167.9	82.9	35.2	51.1	73.2	29.1	65.1
12b[a]	69.6	—	167.8	88.1	84.2	55.8	70.8	29.1	67.0

a) Solvent, $CDCl_3$–DMSO-d_6.

Conclusions

The oxyvinylcyclobutanes (**2**) readily undergo skeletal rearrangement of two different types with enlargement of the cyclobutane ring by 1,3-shift or 1,2-shift of the C_1–C_7 bond toward the vinyl group depending on the reaction conditions, as summarized in Table I. Thermolysis causes the 1,3-shift. Under ionic conditions, the pathways of the two reactions are affected by the acidity of the reagent: TBAF mainly causes the 1,3-shift to give the hydroindole derivatives, while acids (BF_3 or HCl) produce the 1,2-shift product exclusively. A neutral reagent (Meerwein reagent) yields the two types of rearrangement product competitively.

All of these rearrangements are initiated by O–Si bond fission and proceed, in a highly regioselective manner, *via* the C_1–C_7 bond fission. This easy and selective fission of the C_1–C_7 bond should be attributable not only to the torsional strain of a highly substituted cyclobutane ring but also to the unusually elongated C_1–C_7 bond (1.632 Å) compared to the bond lengths of the other cyclobutane positions (C_1–C_5 = 1.572 Å, C_5–C_6 = 1.542 Å, C_6–C_7 = 1.558 Å), as demonstrated by the X-ray crystallographic analysis of **2a**.[5)]

For hydroindole synthesis, the TBAF method is superior to the thermolysis in terms of the yields and the mildness of the reaction condition, though the reaction often gives the over-reaction (intramolecular aldol condensation) product and is sometimes accompanied with the side reaction (1,2-shift). The results obtained here indicate that [2+2] cycloaddition of a cyclic enone and a trimethylsilyloxybutadiene, when coupled with anionic 1,3-shift, provides a general synthetic method leading to a six-membered carbocyclic compound, which should have a different regio chemistry from the compound obtainable by a Diels–Alder reaction of the same substrates.[7b,11)] Examples of the successful application of this methodology for the synthesis of erythrinan and homoerythrinan alkaloids will be presented in forthcoming publications.

Experimental

Unless otherwise noted, the following procedures were adopted. All melting points are uncorrected. IR spectra were measured as Nujol mulls and are given in cm^{-1}. NMR spectra were taken on a JEOL JNM-FX 100 (^{1}H-NMR, 100 MHz; ^{13}C-NMR, 25 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard and the chemical shifts are given in δ values. For compounds **5a**, **5c**, **10a**, **10c**, **12a**, and **12b**, some data are given in Fig. 1 in addition to those given below. The following abbreviations are used; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were determined with a JEOL JMS-D 300 spectrometer at 30 eV by using a direct inlet system. Ultraviolet (UV) spectra were measured in EtOH and are given in λ_{max} nm (ε). Preparative TLC (PTLC) was performed with precoated silica gel plates, Merck 60 F_{254} (0.5 mm thick). Column chromatography was carried out with silica gel (Wakogel C-200). Medium-pressure liquid chromatography (MPLC) was performed on a Kusano CIG prepacked silica gel column. All organic extracts were dried over anhydrous sodium sulfate before concentration. Identities were confirmed by comparisons of TLC behavior and IR and NMR spectra.

Photocycloaddition of Dioxopyrrolines (1) to Activated 1,3-Butadienes. General Procedure A mixture of a dioxopyrroline (**1**) (1.0 g) and a 1,3-butadiene (2—5 mol eq) in dimethoxyethane (DME) (300 ml) was irradiated with a 300 W high-pressure mercury lamp with a Pyrex filter for 40—60 min at 0 °C with stirring. After removal of the solvent below 30 °C *in vacuo*, the residue was purified by passing it through a short column of SiO_2 with CH_2Cl_2 as an eluent or by MPLC [AcOEt : hexane = 1 : 2] followed by crystallizations from an appropriate solvent.

Photoadduct **2a**: Yield, 70%. Colorless prisms from ether–CH_2Cl_2, mp 176—178 °C. IR: 3180, 3090, 1775, 1725. ^{1}H-NMR (60 MHz): 0.08 (9H, s, $SiMe_3$), 0.77 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 2.37, 3.53 (each 1H, d, J = 14 Hz, C_6-H), 3.88 (2H, q, J = 7 Hz, $OC\underline{H}_2CH_3$), 5.0—5.6 (3H, m, olefinic H), 7.32 (5H, s, Ar-H), ^{13}C-NMR: 1.8 (q × 3), 13.6 (q), 37.6 (t), 57.1 (s), 61.9 (t), 71.9 (s), 82.5 (s), 118.4 (t), 126.4 (d × 2), 128.2 (d), 128.3 (d × 2), 133.2 (s), 137.5 (s), 164.3 (s), 166.1 (s), 195.0 (s). HRMS: m/z (M^+) Calcd for $C_{20}H_{25}NO_5Si$: 387.1502. Found: 387.1538.

Photoadduct **2b**: Yield, 52%. Colorless prisms from ether–hexane, mp 141—143 °C. IR: 1760, 1720. ^{1}H-NMR (60 MHz): 0.12 (9H, s, $SiMe_3$). 0.87 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 2.33, 3.38 (each 1H, d, J = 14 Hz, C_6-H), 3.03 (3H, s, N-Me), 3.78 (2H, q, J = 7 Hz, $OC\underline{H}_2CH_3$), 5.3—6.4 (3H, m, olefinic H), 7.35 (5H, br s, Ar-H). ^{13}C-NMR: 1.8 (q × 3), 13.6 (q), 31.4 (q), 37.2 (t), 55.4 (s), 62.0 (t), 81.5 (s), 117.6 (t), 128.1 (d × 2), 128.6 (d × 3), 132.5 (s), 139.1 (d), 162.8 (s), 165.9 (s), 194.0 (s). HRMS: m/z (M^+) Calcd for $C_{21}H_{27}NO_5Si$: 401.1640. Found: 401.1638.

Photoadduct **2c**: Yield, 79%. Colorless prisms from ether–CH_2Cl_2, mp 172—176 °C. IR: 3170, 3080, 1770, 1725, 1650. ^{1}H-NMR: 0.10 (9H, s, $SiMe_3$), 0.77 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 2.39, 3.40 (each 1H, d, J = 14 Hz, C_6-H), 3.30 (3H, s, OMe), 3.88 (2H, q, J = 7 Hz, $OC\underline{H}_2CH_3$), 4.41, 6.51 (each 1H, d, J = 14 Hz, olefinic H), 7.38 (5H, br s, Ar-H). ^{13}C-NMR: 1.9 (q × 3), 13.6 (q), 39.1 (t), 56.0 (q), 57.5 (s), 61.9 (t), 72.1 (s), 81.2 (s), 103.4 (d), 126.5 (d × 2), 128.1 (d), 128.2 (d × 2), 133.5 (s), 151.1 (d), 164.6 (s), 166.1 (s), 194.9 (s). HRMS: m/z (M^+) Calcd for $C_{21}H_{27}NO_6Si$: 417.1608. Found: 417.1638.

Photoadduct **2d**: Yield, 49%. Colorless needles from ether, mp 150—152 °C. IR: 1760, 1725, 1645. ^{1}H-NMR: 0.10 (9H, s, $SiMe_3$), 0.80 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 2.35, 3.32 (each 1H, d, J = 13 Hz, C_6-H), 3.30 (3H, s, N-Me), 3.57 (3H, s, OMe), 4.87, 6.64 (each 1H, d, J = 13 Hz, olefinic H), 7.3—7.5 (5H, m, Ar-H). ^{13}C-NMR: 1.8 (q × 3), 13.4 (q), 31.4 (q), 38.0 (t), 56.1 (s), 61.7 (t), 80.2 (s), 104.4 (d), 128.0 (d × 2), 128.2 (d), 128.6 (d × 2), 132.3 (s), 151.0 (d), 163.9 (s), 165.7 (s), 194.0 (s). HRMS: m/z (M^+) Calcd for $C_{22}H_{29}NO_6Si$: 431.1763. Found: 431.1768.

Thermal Rearrangement of Photoadducts (2). General Procedure A solution of a photoadduct (**2**) (100 mg) in anhydrous toluene (5 ml) was heated at 120—150 °C for 3—4 h in a sealed tube with stirring. After cooling, the reaction mixture was concentrated *in vacuo* to afford the crude rearrangement product **3**. Compounds **3a** and **3b** were purified by passing them through a short column of Al_2O_3 with CH_2Cl_2 as an eluent or by crystallizations. Compounds **3c** and **3d** were used for the next steps without further purification.

3a: Yield, 69 mg, 69%. Colorless prisms from ether–hexane, mp 140—142 °C. IR: 3100, 1780, 1730, 1660. ^{1}H-NMR: 0.21 (9H, s, $SiMe_3$), 0.70 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 2.46 (1H, dd, J = 7, 16 Hz, C_7-H), 2.8—3.3 (3H, m, C_4-H_2 and C_7-H), 3.3—3.8 (2H, m, $OC\underline{H}_2CH_3$), 4.7—4.8 (1H, m, olefinic H), 7.2—7.6 (5H, m, Ar-H), 9.62 (1H, br s, NH). HRMS: m/z (M^+) Calcd for $C_{20}H_{25}NO_5Si$: 387.1501. Found: 387.1506.

3b: Yield, 48 mg, 48%. Colorless prisms from acetone–hexane, mp 144—146 °C. IR: 1765, 1720, 1645. ^{1}H-NMR (60 MHz): 0.17 (9H, s, $SiMe_3$), 0.80 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 2.1—3.9 (6H, m, $OC\underline{H}_2CH_3$, C_4-H_2, and C_7-H_2), 2.98 (3H, s, N-Me), 4.6–4.9 (1H, m, olefinic H), 7.33 (5H, br s, Ar).

Transformation of the Photoadducts (2) into 3-Azatricyclo[4.3.0.0^{4,9}]-nonanes (5) A photoadduct (**2**) (100 mg) was thermolyzed as described above to give **3**. Thermolysis temperatures and reaction times are given in each individual experiment. The product was dissolved in anhydrous THF (5 ml) and stirred with KF (75 mg, 5 mol eq) for 16—20.5 h at room temperature. The reaction mixture was diluted with CH_2Cl_2, washed with water, and concentrated to give a 3-azatricyclo[4.3.0.0^{4,9}]nonane (**5**), which was crystallized from an appropriate solvent. Yields are given in Table I.

5a: Thermolysis of **2a** was done at 120 °C for 3 h. Colorless prisms from ether–acetone, mp 195—196 °C. IR: 3200, 1760, 1720. ^{1}H-NMR (60 MHz): 0.99 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 4.01 (2H, q, J = 7 Hz, $OC\underline{H}_2CH_3$), 6.70 (1H, br s, NH), 7.41 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{17}H_{17}NO_5$: 315.1104. Found: 315.1087.

5b: Thermolysis of **2b** was done at 140 °C for 4 h. Colorless prisms from ether–MeOH, mp 173—174 °C. IR: 3200, 1760, 1720, 1690. ^{1}H-NMR: 1.12 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 2.66 (3H, s, N-Me), 4.11 (2H, br q, J = 7 Hz, $OC\underline{H}_2CH_3$), 7.2—7.6 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{18}H_{19}NO_5$: 329.1261. Found: 329.1240.

5c: Thermolysis of **2c** was done at 120 °C for 3 h. Colorless prisms from ether–acetone, mp 203—208 °C. IR: 3200, 1760, 1720. ^{1}H-NMR: 0.99 (3H, t, J = 7 Hz, $OCH_2C\underline{H}_3$), 3.28 (3H, s, OMe), 4.01 (2H, q, J = 7 Hz, $OC\underline{H}_2CH_3$), 6.03 (1H, br s, NH), 7.44 (5H, s, Ar-H). HRMS: m/z (M^+) Calcd for $C_{18}H_{19}NO_6$: 345.1209. Found: 345.1208.

5d: Thermolysis of **2d** was done at 150 °C for 3 h. Colorless prisms from

ether–hexane, mp 164—166 °C. IR: 3370, 1765, 1730, 1710. ^{1}H-NMR: 1.15 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.34 (1H, d, J=19 Hz, C_8-H), 2.60 (1H, dd, J=1, 19 Hz, C_8-H), 2.77 (3H, s, N-Me), 2.88 (1H, d, J=1 Hz, C_6-H), 3.39 (3H, s, C_5-OMe), 4.15 (2H, br q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.35 (1H, s, C_5-H), 7.2—7.5 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{19}H_{21}NO_6$: 359.1368. Found: 359.1393.

Transformation of the Photoadducts (2) into the Ketones (4) and/or the Conjugated Ketones (6). General Procedure i) A thermolysis product (**3**) (50—300 mg) was dissolved in 5% HCl–THF (1 : 1, 10—20 ml) and stirred at room temperature for 0.5—2 h. The mixture was diluted with CH_2Cl_2, washed with water, and concentrated. The residue was purified by crystallizations from acetone–hexane to give **4**. Yields are given in Table I.

4a: Colorless prisms from ether–AcOEt, mp 158—160 °C. IR: 3075, 1765, 1740, 1720, 1715. ^{1}H-NMR: 0.76 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 7.43 (5H, br s, Ar-H). ^{13}C-NMR: 13.3 (q), 34.8 (t), 35.3 (t), 42.0 (t), 60.2 (s), 62.6 (t), 62.9 (s), 125.6 (d × 2), 128.9 (d × 3), 139.7 (s), 160.7 (s), 165.9 (s), 196.1 (s), 204.8 (s). HRMS: m/z (M^+) Calcd $C_{17}H_{17}NO_5$: 315.1107. Found: 315.1130.

4b: Colorless prisms from acetone–hexane, mp 141—142 °C. IR: 1760, 1740, 1720, 1705, 1600. ^{1}H-NMR: 0.87 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.8—3.8 (8H, m, $OC\underline{H}_2CH_3$, C_4-H_2, C_6-H_2, and C_7-H_2), 3.06 (3H, s, N-Me), 7.2—7.5 (5H, m, Ar-H).

4c: Colorless prisms from ether–acetone, mp 197—199 °C. IR: 3170, 3060, 1770, 1745, 1705. ^{1}H-NMR (60 MHz, $CDCl_3$–DMSO-d_6): 0.70 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.2—4.2 (7H, m, $OC\underline{H}_2CH_3$, C_4-H_2, C_6-H_2, and C_7-H), 3.20 (3H, s, OMe), 7.43 (5H, br s, Ar-H), 10.45 (1H, br s, NH).

ii) The ketone **4c** (40 mg) in 5% HCl–THF (1 : 1, 5 ml) was heated under reflux for 5 h. After cooling, the mixture was diluted with $CHCl_3$, washed with water, and concentrated to give **6a** (34 mg, 94%) as colorless prisms from ether–hexane, mp 191—192 °C. IR: 3280, 3230, 1780, 1740, 1720, 1680. ^{1}H-NMR: 1.01 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.16, 3.37 (each 1H, d, J=18 Hz, C_4-H), 3.81 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.19, 6.69 (each 1H, d, J=10 Hz, olefinic H), 7.45 (5H, br s, Ar-H), 9.68 (1H, br s, NH). HRMS: m/z (M^+) Calcd for $C_{17}H_{15}NO_5$: 313.0950. Found: 313.0965.

iii) Thermolysis product **3d** (300 mg) was heated under reflux with 5% HCl–THF (1 : 1, 10 ml) for 1.5 h. Work-up of the product gave, on MPLC (AcOEt : hexane = 3 : 5), **4d** (53 mg, 21.2%) and **6b** (54 mg, 23.7%).

4d: Colorless prisms from ether, mp 160—162 °C. IR: 1770, 1750, 1735, 1705. ^{1}H-NMR: 0.85 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.61 (1H, dd, J=9, 18 Hz, C_6-H), 2.83, 3.14 (each 1H, d, J=17 Hz, C_4-H), 3.07 (3H, s, N-Me), 3.1—3.9 (3H, m, $OC\underline{H}_2CH_3$ and C_6-H), 3.39 (3H, s, OMe), 4.62 (1H, dd, J=3, 9 Hz, C_7-H), 7.1—7.6 (5H, m, Ar-H). ^{13}C-NMR: 13.3 (q), 31.0 (q), 39.0 (t), 43.2 (t), 57.7 (q), 59.2 (s), 62.7 (t), 69.5 (s), 103.8 (d), 127.2 (d × 2), 128.8 (d × 2), 129.2 (d), 135.4 (s), 159.7 (s), 167.1 (s), 193.7 (s), 202.1 (s). HRMS: m/z (M^+) Calcd for $C_{19}H_{21}NO_6$: 359.1366. Found: 359.1355.

6b: Colorless platelets, mp 170—171.5 °C. IR: 1780, 1745, 1720, 1680. ^{1}H-NMR: 1.06 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.14 (2H, s, C_4-H_2), 3.16 (3H, s, N-Me), 3.84 (2H, dq, J=1.5, 7 Hz, $OC\underline{H}_2CH_3$), 6.31, 6.84 (each 1H, d, J=11 Hz, olefinic H), 7.2—7.6 (5H, m, Ar-H). ^{13}C-NMR: 13.5 (q), 28.3 (q), 36.4 (t), 61.1 (s), 63.1 (t), 66.2 (s), 126.9 (d × 2), 129.3 (d), 129.5 (d × 2), 129.9 (d), 132.8 (s), 142.9 (d), 160.0 (s), 165.7 (s), 192.2 (s), 193.3 (s). HRMS: m/z (M^+) Calcd for $C_{18}H_{17}NO_5$: 327.1107. Found: 327.1112. *Anal.* Calcd for $C_{18}H_{17}NO_5$: C, 66.05; H, 5.24; N, 4.28. Found: C, 66.01; H, 5.31; N, 4.27.

Transformation of 5a into the Diels–Alder Adduct 9 i) A mixture of **5a** (200 mg) and $NaBH_4$ (48 mg) in EtOH (20 ml) was stirred at 0 °C for 30 min. After addition of water, the mixture was extracted with CH_2Cl_2 to give alcohols.

ii) The above product was dissolved in anhydrous pyridine (5 ml) and treated with methanesulfonyl chloride (110 mg) at room temperature for 2 d. The product, obtained on usual work-up, was subjected to MPLC (AcOEt : hexane = 3 : 1) to give the β-mesylate **8b** (43 mg, 17%), as colorless needles from ether–MeOH, mp 224—226°C. IR: 3460, 3230, 1725. ^{1}H-NMR ($CDCl_3$–DMSO-d_6): 0.94 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.12 (3H, s, Ms), 3.93 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.5—5.7 (1H, m, C$\underline{H}$-OMs), 7.41 (5H, s, Ar-H). HRMS: m/z (M^+) Calcd for $C_{18}H_{21}NO_7S$: 395.1036. Found: 395.1016. The following eluate give the α-mesylate **8a** (66 mg, 26%), as colorless needles from ether–acetone, mp 169—171 °C (dec.). IR: 3300, 1730, ^{1}H-NMR: 0.95 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.12 (3H, s, Ms), 3.91 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.11 (1H, br d, J=6 Hz, C$\underline{H}$-OMs), 5.29, 8.07 (each 1H, br s, NH and OH), 7.37 (5H, s, Ar-H). HRMS: m/z (M^+) Calcd for $C_{18}H_{21}NO_7S$: 395.1036. Found: 395.1019.

iii) A mixture of the β-mesylate **8b** (43 mg) and DBU (100 mg) in anhydrous benzene (10 ml) was heated under reflux for 1.5 h. The mixture was diluted with benzene, washed with 5% HCl, and concentrated. The residue in CH_2Cl_2 was passed through a short column of SiO_2 to afford a hydroindole **9** (12 mg, 88%) as colorless prisms from MeOH, mp 228—231 °C. This was identical with compound **9** previously reported.[7]

Treatment of the α-mesylate **8a** with DBU under the above conditions gave a complex mixture.

TBAF-Induced Anionic Rearrangement of the Photoadducts (2). General Procedure A solution of **2** (100 mg) in anhydrous THF (10 ml) was stirred with a 1.0 M solution of TBAF in THF (1.2 mol eq) at −30 °C for 2—10 min under an argon atmosphere. The reaction mixture was diluted with CH_2Cl_2, washed with water, and concentrated to give **5** (and **10**), which was purified by crystallizations or by MPLC (in the cases of **2a** and **2b**). Products and yields are given in Table I.

Rearrangement of the Photoadducts (2) by $BF_3 \cdot Et_2O$. General Procedure BF_3–etherate (5 mol eq) was added to a stirred solution of **2** (100 mg) in CH_2Cl_2 (10 ml) at room temperature and the mixture was stirred for a further 0.5—18 h at 20—40 °C. The mixture was diluted with CH_2Cl_2, washed with water, and concentrated to give the corresponding crude 2-azatricyclo[4.3.0.0^{4,9}]nonane (**10**), which was purified by crystallizations from an appropriate solvent. Yields are given in Table I.

10a: Reaction of **2a** was done at 20 °C for 18 h. Colorless needles from ether–MeOH, mp 235—236.5 °C (dec.). IR: 3460, 3175, 3090, 1760, 1725. ^{1}H-NMR: 1.16 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 4.17 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.3—7.4 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{17}H_{17}NO_5$: 315.1106. Found: 315.1126.

10b: Reaction of **2b** was done at 40 °C for 4 h. Colorless needles from ether–acetone, mp 163.5—165 °C. IR: 3400, 1755, 1725, 1700. ^{1}H-NMR: 1.21 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.92 (1H, d, J=14 Hz, C_5-H), 2.26 (1H, dd, J=6, 14 Hz, C_5-H), 2.56, 2.86 (each 1H, d, J=20 Hz, C_8-H), 2.61 (3H, s, N-Me), 3.33 (1H, d, J=6 Hz, C_6-H), 4.20 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.2—7.5 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{18}H_{19}NO_5$: 329.1264. Found: 329.1281.

10c: Reaction of **2c** was done at 20 °C for 4 h. Colorless prisms from MeOH, mp 235—237 °C. IR: 3250 (br), 1760, 1725, 1690. ^{1}H-NMR ($CDCl_3$–D_2O): 1.17 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.43 (3H, s, OMe), 4.18 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.2—7.4 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{18}H_{19}NO_6$: 345.1212. Found: 345.1227. *Anal.* Calcd for $C_{18}H_{19}NO_6$: C, 62.60; H, 5.55; N, 4.06. Found: C, 62.70; H, 5.60; N, 4.03.

10d: Reaction of **2d** was done at 20 °C for 0.5 h. Colorless prisms from ether–acetone, mp 178—180 °C. IR: 3390, 1755, 1720. ^{1}H-NMR: 1.21 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.50, 2.75 (each 1H, d, J=20 Hz, C_8-H), 2.60 (3H, s, N-Me), 3.29 (1H, br s, C_6-H), 3.48 (3H, s, OMe), 3.76 (1H, s, C_5-H), 4.21 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.1—7.4 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{19}H_{21}NO_6$: 359.1367. Found: 359.1361.

Rearrangement of the Photoadducts (2) by Hydrochloric Acid. General Procedure i) A mixture of **2** (100 mg) (except **2b**) and 5% HCl–THF (1 : 1, 5 ml) was stirred at 20 °C for 4 h, then extracted with CH_2Cl_2. The organic layer was washed with water and concentrated to give **10**. Yields are given in Table I.

ii) A mixture of **2b** (100 mg) and 5% HCl–THF (1 : 1, 5 ml) was stirred at room temperature for 4 h, then extracted with CH_2Cl_2. The organic extract was washed with water, and concentrated to give a residue, which was crystallized from ether–MeOH to afford **13b** (49 mg, 60%) as colorless prisms, mp 144—146 °C. IR: 3370, 1780, 1720, 1705. ^{1}H-NMR: 1.01 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.66, 3.26 (each 1H, d, J=13 Hz, C_6-H), 2.96 (3H, s, N-Me), 3.95 (2H, dq, J=2, 7 Hz, $OC\underline{H}_2CH_3$), 5.35 (1H, dd, J=2, 11 Hz), 5.64 (1H, dd, J=2, 17 Hz), 6.37 (1H, dd, J=11, 17 Hz, olefinic H), 7.35 (5H, br s, Ar-H). HRMS: m/z (M^+) Calcd for $C_{18}H_{19}NO_5$: 329.1262. Found: 329.1250.

On treatment with BF_3–etherate (5 mol eq) in boiling CH_2Cl_2 for 4 h, **13b** gave **10b** in 90% yield.

$NaBH_4$ Reduction of 10a A mixture of **10a** (50 mg) and $NaBH_4$ (60 mg) in EtOH (25 ml) was stirred at 0 °C for 1.5 h. After addition of ice-water, the mixture was extracted with $CHCl_3$–MeOH to give an alcohol, which was acetylated with pyridine (2 ml) and acetic anhydride (1 ml) for 16 h at room temperature. Usual work-up of the mixture gave **12a** (18 mg, 32%), as colorless prisms from ether–MeOH, mp 215—220 °C. IR: 3340, 1720. ^{1}H-NMR: 1.28 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.33 (3H, s, OAc), 4.28 (2H, br q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.33 (5H, s, Ar-H). HRMS: m/z (M^+) Calcd for $C_{19}H_{21}NO_6$: 359.1369. Found: 359.1379.

$NaBH_4$ Reduction of 10c A mixture of **10c** (300 mg) and $NaBH_4$ (360 mg, 10 mol eq) in EtOH (150 ml) was stirred at 0 °C for 2.5 h. The product obtained as described for the reduction of **10a** gave the alcohol (200 mg, 66%) as colorless plates from ether–MeOH, mp 256—258 °C. IR: 3430, 3280, 1735, 1720. m/z 347 (M^+).

The alcohol (54 mg) was acetylated with acetic anhydride (1 ml) and pyridine (2 ml) for 16 h at room temperature to give the acetate **12b** (50 mg, 55% from **10c**), as colorless needles from ether–acetone, mp 243—245 °C (dec.). IR: 3300, 3190, 1745, 1710. ^{1}H-NMR: 1.27 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.34 (3H, s, OAc), 3.43 (3H, s, OMe), 4.29 (2H, br q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.33 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{20}H_{23}NO_7$: 389.1473. Found: 389.1470.

Reaction of Photoadduct 2a with Meerwein Reagent A mixture of **2a** (160 mg) and Et_3OBF_4 (500 mg, large excess) in anhydrous CH_2Cl_2 (10 ml) was degassed and purged with argon, then stirred at room temperature for 15 h. The reaction mixture was diluted with CH_2Cl_2, washed with 5% $NaHCO_3$, and concentrated to give **17a** (67 mg, 47%) as colorless prisms from ether, mp 165—168 °C. IR: 3410, 1740, 1705, 1615. ^{1}H-NMR: 1.07, 1.44 (each 3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.53 (1H, d, J=3 Hz, C_5-H), 2.23 (1H, dd, J=6, 13 Hz, C_5-H), 2.55, 2.78 (each 1H, d, J=19 Hz, C_8-H), 3.07 (1H, d, J=6 Hz, C_6-H), 4.2—4.6 (2H, m, $OC\underline{H}_2CH_3$), 4.29 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.32 (5H, s, Ar-H). HRMS: m/z (M^+) Calcd for $C_{19}H_{21}NO_5$: 343.1420. Found: 343.1425. The mother liquor of **17a** was chromatographed on Florisil with benzene to afford **16a** (55 mg, 39%) as colorless prisms from ether–hexane, mp 111—113 °C. IR: 1765, 1735, 1725, 1640. ^{1}H-NMR: 0.67, 1.53 (each 3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.2—3.7, 4.5—4.8 (each 2H, m, $OC\underline{H}_2CH_3$), 7.2—7.5 (5H, m, Ar-H). HRMS: m/z (M^+) Calcd for $C_{19}H_{21}NO_5$: 343.1418. Found: 343.1415.

Reaction of Photoadduct 2c with Meerwein Reagent A solution of **2c** (500 mg) in anhydrous CH_2Cl_2 (30 ml) was treated with Et_3OBF_4 and worked up as described above. The product was chromatographed on Florisil with benzene. The eluate from the less polar fraction was crystallized from ether–hexane to give **16b** (280 mg, 69%) as colorless needles, mp 70—72 °C. IR: 1760, 1730, 1690, 1675, 1630. ^{1}H-NMR: 0.90, 1.53 (each 3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.13, 3.49 (each 1H, d, J=18 Hz, C_4-H), 3.4—3.8, 4.4—4.8 (each 2H, m, $OC\underline{H}_2CH_3$), 6.01, 6.70 (each 1H, d, J=10 Hz, olefinic H), 7.38 (5H, s, Ar-H). HRMS: m/z (M^+) Calcd for $C_{19}H_{19}NO_5$: 341.1262. Found: 341.1287.

The eluate from the more polar fraction was crystallized from ether to afford **17b** (54 mg, 12%) as colorless prisms, mp 124—125 °C. IR: 3475, 1750, 1715, 1630. ^{1}H-NMR: 1.07, 1.41 (each 3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.57 (2H, br s, C_8-H_2), 3.06 (1H, s, C_6-H), 3.43 (3H, s, OMe), 3.72 (1H, s, C$\underline{H}$–OMe), 4.04, 4.41 (each 2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.20 (5H, s, Ar-H). HRMS: m/z (M^+) Calcd for $C_{20}H_{23}NO_6$: 373.1523. Found: 373.1507.

Preparation of Imidic Esters (16 and 17) A solution of **4a**, **6a**, **10a**, or **10c** (50—100 mg) in anhydrous CH_2Cl_2 (10—20 ml) was treated with Et_3OBF_4 (200—300 mg, large excess). The reaction mixture was worked up as described above to give the imidic esters **16** or **17**.

16a: 98 mg from **4a** (100 mg), 90.0%. Colorless prisms from ether–hexane, mp 111—113 °C.

16b: 104 mg from **6a** (100 mg), 94.9%. Colorless prisms from ether, mp 70—72 °C.

17a: 88 mg from **10a** (100 mg), 80.8%. Colorless prisms from ether, mp 166—168 °C.

17b: 51 mg from **10c** (50 mg), 94.3%. Colorless prisms from ether, mp 124—125 °C.

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