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Photochemical and Thermal Ring Transformations of 8-Oxa-3,4-diaza- and 3,4,8-Triazatricyclo[5.1.0.$0^{2,6}$]oct-4-enes

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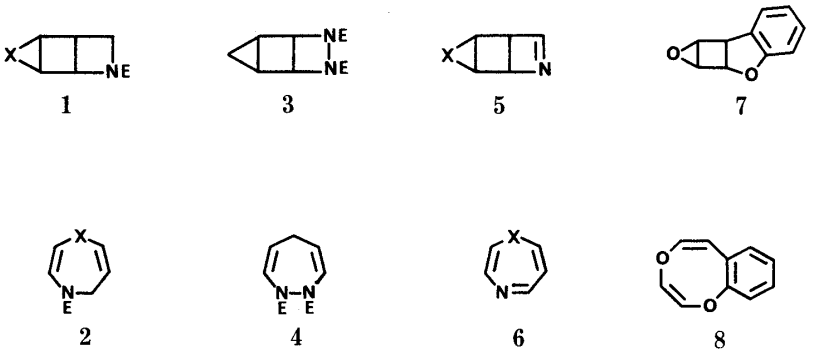
Photolysis of the 8-oxa-3,4-diazatricyclo[5.1.0.$0^{2,6}$]oct-4-enes (**17**) prepared from the 1,2-diazepines (**9**) *via* five steps resulted in a ring transformation to give the 2,3-diazabicyclo[3.1.0]hex-3-enes (**20**), whereas the 8-aza analogues (**18**) gave the 2-amino-3-cyano-5-azabicyclo[2.1.0]pentanes (**23**) by cleavage of the N–N bond. On the other hand, flash vacuum pyrolysis of the 8-oxa compounds **17** resulted in rearrangement to give the 1-amino-2-formylpyrroles (**27**), presumably *via* the expected 1,4,5-oxadiazocines (**29**), whereas the 8-aza compounds **18** gave the 3a,6a-dihydropyrrolo[2,3-*c*]pyrazoles (**33**) through a different type of rearrangement.

Keywords——photolysis; flash vacuum pyrolysis; ring transformation; rearrangement; 8-oxa-3,4-diazatricyclo[5.1.0.$0^{2,6}$]oct-4-ene; 3,4,8-triazatricyclo[5.1.0.$0^{2,6}$]oct-4-ene; 2,3-diazabicyclo-[3.1.0]hex-3-ene; dihydropyrrolopyrazole

It has shown that tricyclic compounds having a highly strained bicyclopentane ring system undergo thermal or photochemical valence isomerization with ring opening, and thus can be used as synthons for seven- and eight-membered heterocycles.[1–5] For example, the thermolysis of the 3-azatricyclo[4.1.0.$0^{2,5}$]heptanes (**1**)[1] and the 3,4-diazatricycloheptanes (**3**)[2] in solvents gives the corresponding dihetero seven-membered ring compounds **2** and **4**. The fully unsaturated 1,4-oxazepines (**6**: X = O) and 1,4-diazepines (**6**: X = NCO_2Et) can be prepared from the corresponding 3-azatricyclopentenes (**5**) by irradiation.[3] The tetrahydro-oxirenocyclobutabenzofurans (**7**), upon flash vacuum pyrolysis, afford the 1,4-benzodioxocins (**8**).[4] These results prompted us to examine the photochemical and thermal behaviors of the title tricyclo-octenes, and we report here that the photolysis[6a] and the flash vacuum pyrolysis[6b] of them gave interesting ring transformation products, although the expected ring expansion products such as oxadiazocines and triazocines could not be obtained.



1 3 5 7

2 4 6 8

X=O, NCO_2Et, S E=CO_2Et

Chart 1

Synthesis of the Starting Tricyclo-octenes

The synthetic routes to the 8-oxa-3,4-diaza- (**17a—c**) and 3,4,8-triazatricyclo[5.1.0.$0^{2,6}$]-oct-4-enes (**18a—c**) used in the present reactions are shown in Chart 2. The 3-unsubstituted 2,3-diazabicyclo[3.2.0]hept-6-enes (**11a—c**) were prepared from the corresponding 1,2-diazepines (**9**)[7] *via* the 2,3-dihydro-1,2-diazepines (**10**) by sodium borohydride reduction followed by photocyclization, according to the procedure reported for the preparation of **11a**.[8] The products **11** were treated with benzyl chloroformate to afford the 3-benzyloxycarbonyl compounds **12a—c** in high yields. Treatment of **12** with *m*-chloroperbenzoic acid (*m*-CPBA) gave the 8-oxa tricyclic compounds **13a—c** in 85—95% yields. The reaction of **12** with ethoxycarbonylnitrene[9] generated from ethyl *p*-nitrobenzenesulfonoxycarbamate by treatment with benzyltriethylammonium bromide and sodium hydrogencarbonate gave the 8-aza tricyclic compounds **14a—c** in 30—60% yields. The protecting benzyloxycarbonyl group of **13** and **14** was removed by catalytic hydrogenation to give the corresponding N(3)-free compounds **15a—c** and **16a—c** in high yields. The compounds **15** and **16** thus obtained were successively treated with *tert*-butyl hypochlorite and 1,5-diazabicyclo-[5.4.0]undec-5-ene (DBU) in dimethylformamide, giving rise to the corresponding desired tricyclo-octenes (**17a—c** and **18a—c**) in 70—90% yields by dehydrogenation.

The 2,3-diazabicyclo[3.2.0]hept-3,6-dienes (**19**) were also prepared from **9** by photocyclization, but they were decomposed by treatment with *m*-CPBA or ethoxycarbonylnitrene and thus gave neither **17** nor **18**. In addition, the direct conversion of the N-unsubstituted bicycloheptenes (**11**) into the tricyclic compounds **17** and **18** was also unsuccessful. The tricyclic compounds **13—18** reported were characterized by their spectral data (see Experimental). Although their stereochemistry was not examined in detail, their stereostructures are tentatively assigned to be *anti-endo*, by analogy with those of the tricycloheptenes (**5**)[3] and 3,7-dihetero-4-oxotricyclo[4.1.0.$0^{2,5}$]heptanes.[10]

Photolysis of the Tricyclo-octenes

Even when the tricyclo-octenes (**17** and **18**) were irradiated with a 400 W high-pressure Hg lamp using a Pyrex filter, no reaction occurred. However, irradiation (30 W, low-pressure Hg lamp) of the 8-oxa compounds **17a—c** for 15—20 min in acetonitrile with ice cooling resulted in a ring transformation to give the 2,3-diazabicyclo[3.1.0]hex-3-enes (**20a—c**) having a formyl or an acetyl group in the 6-position in 30—40% yields, as the sole characterizable products. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **20a** showed signals

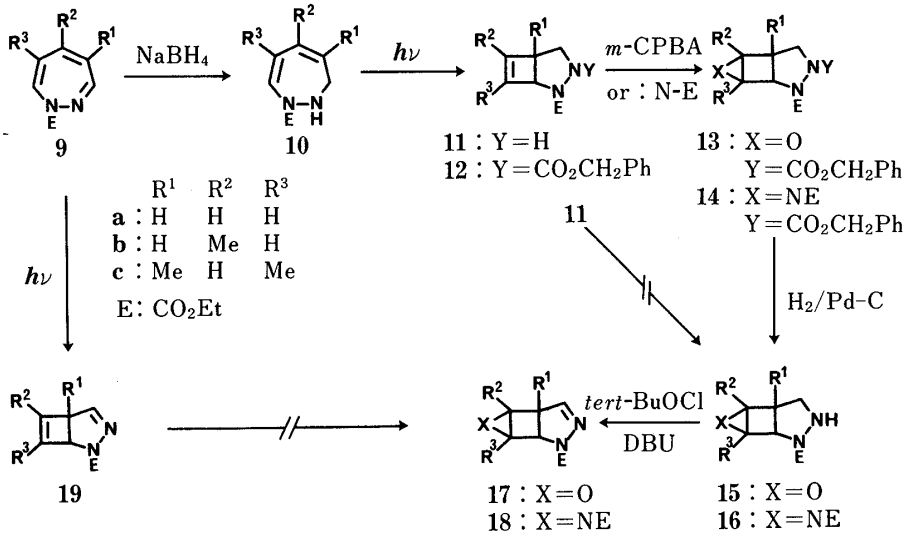
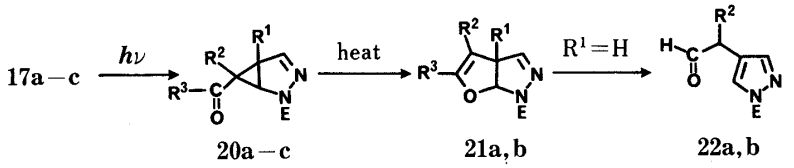


Chart 2



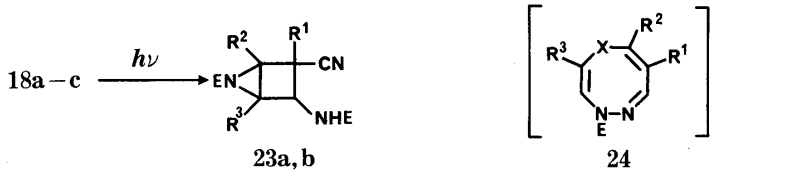


Chart 3

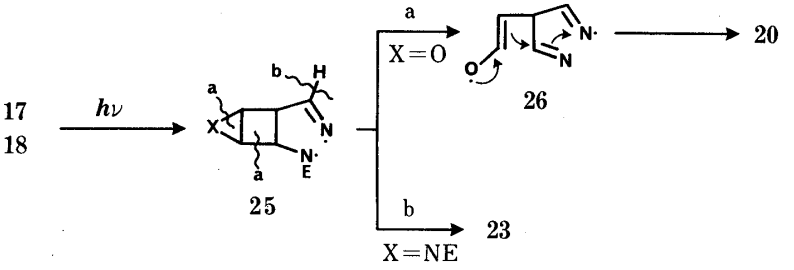


Chart 4

assignable to 1-H (δ 4.82, dd, J=6, 2 Hz), 5-H (δ 3.38, dd, J=3, 2 Hz), 6-H (δ 1.50, ddd, J=3, 2, 2 Hz), 4-H (δ 7.15, s), and CHO (δ 9.93, d, J=2 Hz). The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **20a** showed signals due to three sp^3 ring carbons at δ 26.47 (d, 6-C), 36.00 (d, 5-C), and 48.65 (d, 1-C). These spectral data indicate the presence of a cyclopropane ring and a formyl group, and are consistent with the proposed structure **20**, which was also confirmed by the results of the following thermal studies.

The cyclopropane derivatives (**20a, b**: R^1 = H) were heated at 60 °C in benzene for *ca.* 1 h to form the 3a,6a-dihydrofuro[2,3-*c*]pyrazoles (**21a, b**) and the 4-(formylmethyl)pyrazoles (**22a, b**) in 30—40% and 5—10% yields, respectively. The furopyrazoles (**21**) were readily converted into the pyrazoles (**22**) by further heating at 70 °C and prolonged heating (70 °C, 4—5 h) of **20a, b** in benzene gave only **22a, b** in 40—50% yields; indicating that the pyrazoles (**22**) are derived from **20** *via* **21**.

However, **20c** (R^1 = Me) was decomposed by heating under similar conditions to give no isolable product, probably because the initially formed furopyrazole (**21c**) does not undergo isomerization to **22** owing to the presence of the methyl group in the 3a-position.

In contrast, the 8-aza compounds **18a, b**, upon irradiation under the same conditions, underwent only N–N bond fission to afford the 2-amino-3-cyano-5-azabicyclo[2.1.0]pentanes (**23a, b**) in 50—60% yields. However, irradiation of **18c** resulted only in decomposition, giving no characterizable product. The structures of the nitrile compounds **23** were elucidated from their spectral data. The infrared (IR) spectra of **23** showed two characteristic absorption bands at 3300 (NH) and 2250 (CN) cm^{-1}, in addition to two carbonyl bands at 1720 and 1680 cm^{-1}. The ^{1}H- and ^{13}C-NMR spectra (see Experimental) indicate the presence of a 5-azabicyclopentane ring similar to that of the starting **18**.

In the photolysis of either the oxiranes (**17**) or the aziridines (**18**), the formation of the expected eight-membered ring compounds **24** such as 1,4,5-oxadiazocines and 1,4,5-triazocines was not observed.

Although the detailed mechanisms are not clear, we assume that the photo-induced ring contraction of **17** and **18** proceeds by initial homolytic N–N bond fission to the diradical intermediates (**25**). In the case of the oxirane compounds **17**, the intermediates (**25**) would undergo synchronous homolytic ring contraction of the cyclobutane and the oxirane rings as shown in the structure **25** (Chart 4, path a). In the case of the aziridine compounds **18**, an intramolecular transfer of the hydrogen atom of the imine group to the aminyl centre may occur to give the nitrile products **23** (path b). The difference between **17** and **18** may depend on the different reactivity of C–O and C–N bonds toward homolytic fission. In the case of the aziridines (**18**), the less reactive C–N bond may not favor synchronous ring contraction and thus the transfer of the hydrogen atom becomes predominant.

Pyrolysis of the Tricyclo-octenes

Upon heating in solvents at 100—160 °C, the 8-oxa compounds **17a, b** were not changed and the 8-aza compounds **18a, b** were decomposed to give complex mixtures, but no characterizable product. However, the flash vacuum pyrolysis (f.v.p.)[11] of the 8-oxa compounds **17a—c** at 390 °C (3—5 × 10^{-5} Torr) gave complex mixtures, from which the rearrangement products **27a—c**, 1-ethoxycarbonylamino-2-formylpyrroles, were isolated in 25—40% yields by chromatography as the sole characterizable products. The compounds **27** were characterized by spectral comparison with 2-formylpyrroles.[12] It should be noted that the position of the formyl group in **27c**[13] is different from that in **27a, b**.

A possible mechanism for the pyrolysis of **17** is shown in Chart 5. The pyrolysis may proceed by initial formation of the expected 1,4,5-oxadiazocines (**29**) *via* the diradical intermediates **28** by analogy with the cases of **7**.[4] The oxadiazocines (**29**) might rearrange to the pyrrolinium imides (**32**) *via* the oxirane intermediates **30** and **31** successively, then the imides (**32**) are aromatized to the products **27**. In the case of **32c** (R^3 = Me), the formyl group may migrate to the opposite α-position, because the methyl group prevents aromatization. The presence of the imide intermediates **32** was confirmed by the following result. The key intermediate **32c** could be isolated in 52% yield by heating **17c** in refluxing toluene for 48 h, together with the pyrrole (**27c**: 2—3% yield). Further heating of the imide (**32c**) at 140 °C in xylene for 4 d resulted in the formation of the pyrrole (**27c**) in 73% yield.

On the other hand, flash vacuum pyrolysis of the 8-aza compounds **18a—c** at 430 °C

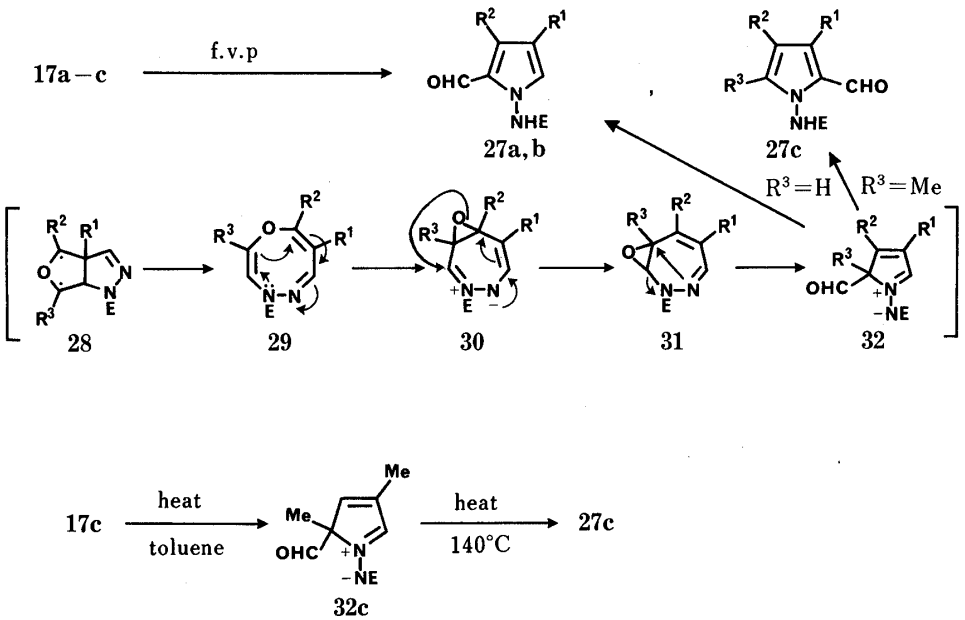


Chart 5

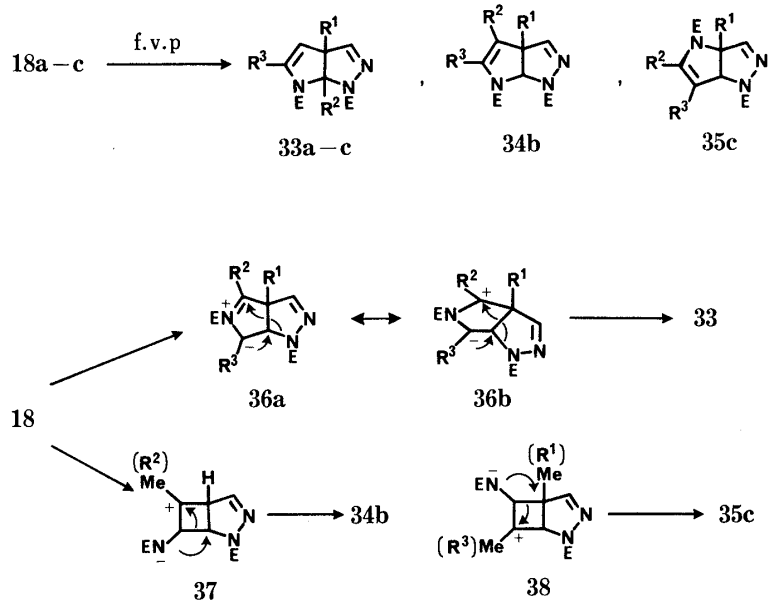


Chart 6

under similar conditions gave the different type of rearrangement products **33a**—**c**, 3a,6a-dihydropyrrolo[2,3-*c*]pyrazoles, in 20—40% yields. In the cases of **18b**, **c**, the isomeric products **34b** and **35c** were also obtained in 18% and 38% yields, respectively. The structures of these dihydropyrrolopyrazoles (**33**—**35**) were elucidated mainly from their ^{1}H- and ^{13}C-NMR spectral data. For example, the ^{1}H-NMR spectrum of **33a** showed an AB pair of doublets (J=4 Hz) at δ 5.04 and 6.72 assignable to 4-H and 5-H, respectively, and each of them coupled with the methine proton signal (3a-H, δ 4.48, $J_{3a,4}$=3, $J_{3a,5}$=2 Hz), which coupled further with both of two signals due to 3-H (δ 6.93, J=1 Hz) and 6a-H (δ 6.54, J=8 Hz). The ^{13}C-NMR spectrum of **33a** showed signals due to two sp^3 ring carbons at δ 57.12 (d, 3a-C) and 74.77 (d, 6a-C), indicating that the latter is adjacent to two nitrogen atoms. These spectral data were consistent with the proposed dihydropyrrolopyrazole structures.

The pyrolysis of **18** would proceed by two competing pathways. The formation of **33** may proceed by initial C–C bond cleavage in the aziridine ring to the ionic intermediates **36**, which might undergo rearrangement as shown in the structures **36** (Chart 6) to give the products **33**. On the other hand, the formation of **34** and **35** may proceed *via* initial ionic C–N bond fission in the aziridine ring to the intermediate **37** or **38**, which might give the product **34** or **35** *via* the paths illustrated in the structures **37** and **38**. The direction of the initial ionic C–N bond fission in the aziridine ring may depend on the position of the methyl group, forming predominantly the cation intermediate stabilized by the methyl group. In the case of **18a** having no methyl group, the product **33a** would be derived *via* both pathways.

The difference in pyrolysis between the oxiranes (**17**) and the aziridines (**18**) may depend on the different mode of the initial bond fission in the three-membered ring. The pyrolysis of **17** might proceed *via* homolytic fission only at a high temperature, and thus would not proceed in solution at 160 °C except for **17c**. On the other hand, the aziridines (**18**) might undergo ionic bond cleavage even at a relatively low temperature (100—160 °C), but the ionic intermediates thus formed would decomposed preferentially in solution, and the rearrangement products could be obtained only by the flash vacuum pyrolysis.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected.

IR spectra were determined with a Hitachi 270-30 spectrometer and mass spectra (MS) were measured with a JEOL DX-300 instrument. ^{1}H-NMR spectra were recorded on a JEOL JNM-MH100 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated; spectral assignments were confirmed by spin-decoupling experiments and, in the case of NH protons, by exchange with D_2O. ^{13}C-NMR spectra were recorded on a JEOL FX-100 spectrometer in $CDCl_3$. Microanalyses were performed in the Microanalytical Laboratory of this school by Mrs. R. Igarashi. Photolyses were carried out under a nitrogen atmosphere in an immersion apparatus equipped with a 400 W high-pressure or a 30 W low-pressure Hg lamp, which was cooled internally with running water.

Starting Materials——The 1-ethoxycarbonyl-1*H*-1,2-diazepines (**9a—c**) were prepared from the corresponding pyridines by the reported method.[7]

1-Ethoxycarbonyl-2,3-dihydro-1*H*-1,2-diazepines (10a—c)——General Procedure: The procedure[8] reported for the preparation of **10a** was employed. Solid $NaBH_4$ (10—12 g) was added in small portions with stirring to a solution of **9** (7—9 g) in methanol (200—300 ml) in an ice bath. The reaction mixture was stirred for a further 6—7 h at room temperature and then was evaporated below 30 °C. The residue was cooled in an ice bath and treated with ice-water (*ca.* 100 ml). The resulting aqueous mixture was extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane–ether (1 : 1) as an eluent to give **10** as a yellow oil.

10a: 90% yield.[8]

10b: 92% yield. MS *m/z*: 182 (M^+). IR (neat): 3300 (NH), 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 4.15 (3H, t, and 2H, q, CO_2Et), 1.82 (3H, s, 5-Me), 3.60 (2H, br s, 3-H_2), 4.18 (1H, br, NH), 4.90 (1H, d, 6-H), 5.58 (1H, s, 4-H), 6.78 (1H, d, 7-H), $J_{6,7}$=9 Hz. *Anal.* Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.06; H, 7.76; N, 15.11.

10c: 96% yield. MS *m/z*: 196 (M^+). IR (neat): 3300 (NH), 1690 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 4.15 (3H, t, and 2H, q, CO_2Et), 1.78 (6H, br s, 4- and 6-Me), 3.60 (2H, br s, 3-H), 4.40 (1H, br, NH), 5.44 (1H, br s, 5-H), 6.42 (1H, br s, 7-H). *Anal.* Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.28. Found: C, 60.97; H, 8.30; N, 14.09.

2-Ethoxycarbonyl-2,3-diazabicyclo[3.2.0]hept-6-enes (11a—c)——General Procedure: The procedure[8] reported for the preparation of **11a** was employed. A solution of **10** (4—5 g) in dry benzene (300 ml) was irradiated (400 W high-pressure Hg lamp, Pyrex filter) for 10—15 h. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using hexane–ether (1 : 1) as an eluent to give **11** as a yellow oil.

11a: 76% yield. MS *m/z*: 168 (M^+). IR (neat): 3400 (NH), 1690 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.26 and 4.22 (3H, t, and 2H, q, CO_2Et), 2.78 (2H, q, 4-H), 3.60—3.72 (1H, m, 5-H), 4.74 (1H, br, NH), 5.14—5.24 (1H, m, 1-H), 6.04 (1H, dd, 7-H), 6.20 (1H, dd, 6-H), $J_{1,6}$=2, $J_{4,5}$=1, $J_{5,7}$=1, $J_{6,7}$=1 Hz. *Anal.* Calcd for $C_8H_{12}N_2O_2$: C, 57.13; H, 7.19; N, 16.66. Found: C, 57.11; H, 7.03; N, 16.73.

11b: 82% yield. MS *m/z*: 182 (M^+). IR (neat): 3300 (NH), 1690 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 4.18 (3H, t, and 2H, q, CO_2Et), 1.72 (3H, s, 6-Me), 2.30—2.86 (2H, m, 4-H), 3.40—3.50 (1H, m, 5-H), 4.70 (1H, br, NH), 4.90—5.00 (1H, m, 1-H), 5.64 (1H, d, J=1 Hz, 7-H). *Anal.* Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.43; H, 7.72; N, 15.09.

11c: 84% yield. MS *m/z*: 196 (M^+). IR (neat): 3400 (NH), 1690 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.32 and 4.28 (3H, t, and 2H, q, CO_2Et), 1.36 (3H, s, 5-Me), 1.72 (3H, s, 7-Me), 2.60 (2H, q, J=6 Hz, 4-H), 4.56 (1H, br s, 1-H), 4.88 (1H, br, NH), 5.90—6.04 (1H, m, 6-H). *Anal.* Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.28. Found: C, 61.02; H, 8.41; N, 14.14.

3-Benzyloxycarbonyl-2-ethoxycarbonyl-2,3-diazabicyclo[3.2.0]hept-6-enes (12a—c)——General Procedure: Benzyl chloroformate (*ca.* 2 mol eq) was added dropwise with stirring to a mixture of **11** (6—10 g), potassium carbonate (*ca.* 2 mol eq), and ethanol (150—200 ml) in an ice bath. The reaction mixture was further stirred for 7—8 h at room temperature and then evaporated *in vacuo*. The residue was extracted with CH_2Cl_2. The extract was washed with water, dried, and evaporated *in vacuo*. The residue was chromatographed on alumina using hexane–ether (3 : 1) as an eluent to give **12** as a yellow oil.

12a: 95% yield. MS *m/z*: 302 (M^+). IR (neat): 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.26 and 4.22 (3H, t, and 2H, q, CO_2Et), 2.94 and 4.12 (each 1H, m, 4-H_2), 3.66 (1H, m, 5-H), 5.22 (3H, br s, 1-H and CH_2Ph), 5.92 (1H, br s, 7-H), 6.05 (1H, s, 7-H), 7.35 (5H, s, Ph-H). *Anal.* Calcd for $C_{16}H_{18}N_2O_4$: C, 65.56; H, 6.00; N, 9.27. Found: C, 65.59; H, 5.77; N, 9.07.

12b: 91% yield. MS *m/z*: 316 (M^+). IR (neat): 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.24 and 4.16 (3H, t, and 2H, q, CO_2Et), 1.60 (3H, s, 6-Me), 2.84 and 4.10 (each 1H, m, 4-H_2), 3.40 (1H, m, 5-H), 5.04 (1H, br s, 1-H), 5.15 (2H, s, CH_2Ph), 5.40 (1H, s, 7-H), 7.32 (5H, s, Ph-H). *Anal.* Calcd for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.86. Found: C, 64.28; H, 6.36; N, 8.69.

12c: 95% yield. MS *m/z*: 330 (M^+). IR (neat): 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.26 and 4.26 (3H, t, and 2H, q, CO_2Et), 1.27 (3H, s, 5-Me), 1.54 (3H, s, 7-Me), 2.74 and 4.06 (each 1H, d, J=12 Hz, 4-H_2), 4.54 (1H, br s, 1-H), 5.23 (2H, s, CH_2Ph), 5.80 (1H, br s, 6-H), 7.37 (5H, s, Ph-H). *Anal.* Calcd for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.54; H, 6.50; N, 8.38.

4-Benzyloxycarbonyl-3-ethoxycarbonyl-8-oxa-3,4-diazatricyclo[5.1.0.0^{2,6}]octanes (13a—c)——General Proce-

dure: A solution of *m*-chloroperbenzoic acid (2—3 mol eq) in CH_2Cl_2 (10 ml) was added dropwise with stirring to a solution of **12** (5—7 g) in CH_2Cl_2 (50 ml) at room temperature. After being stirred for an additional 8—10 h, the reaction mixture was diluted with CH_2Cl_2 (100 ml). The solution was successively washed with saturated $NaHCO_3$ and saturated NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on alumina using hexane–ether (2 : 1) as an eluent to give **13** as a colorless oil.

13a: 87% yield. MS *m/z*: 318 (M^+). IR (neat): 1710 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.24 and 4.20 (3H, t, and 2H, q, CO_2Et), 2.96 (1H, m, 6-H), 3.05 and 4.23 (1H, dd, and 1H, d, 5-H_2), 3.58 (1H, dd, 1-H), 3.74 (1H, dd, 7-H), 4.64 (1H, dd, 2-H), 5.20 (2H, s, $C\underline{H}_2Ph$), 7.30 (5H, s, Ph-H), $J_{1,2}=3$, $J_{1,7}=2$, $J_{2,6}=4$, $J_{2,7}=3$, $J_{5,5'}=12$, $J_{5,6}=5$ Hz. *Anal.* Calcd for $C_{16}H_{18}N_2O_5$: C, 60.37; H, 5.70; N, 8.80. Found: C, 60.39; H, 5.51; N, 8.69.

13b: 83% yield. MS *m/z*: 332 (M^+). IR (neat): 1710 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.24 (3H, s, 7-Me), 1.24 and 4.21 (3H, t, and 2H, q, CO_2Et), 2.93 (1H, m, 6-H), 3.02 and 4.21 (1H, dd, 1H, d, 5-H_2), 3.60 (1H, br s, 1-H), 4.51 (1H, d, 2-H), 5.10 and 5.26 (each 1H, d, $J=12$ Hz, $C\underline{H}_2Ph$), 7.31 (5H, s, Ph-H), $J_{2,6}=4$, $J_{5,5'}=12$, $J_{5,6}=5$ Hz. *Anal.* Calcd for $C_{17}H_{20}N_2O_5$: C, 61.43; H, 6.07; N, 8.43. Found: C, 61.60; H, 5.82; N, 8.40.

13c: 95% yield. MS *m/z*: 346 (M^+). IR (neat): 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.12 (3H, s, 6-Me), 1.22 and 4.26 (3H, t, and 2H, q, CO_2Et), 1.35 (3H, s, 1-Me), 2.97 and 4.23 (each 1H, d, $J=12$ Hz, 5-H_2), 3.58 (1H, br s, 7-H), 4.19 (1H, br s, 2-H), 5.16 and 5.38 (each 1H, d, $J=12$ Hz, $C\underline{H}_2Ph$), 7.40 (5H, s, Ph-H). *Anal.* Calcd for $C_{18}H_{22}N_2O_5$: C, 62.41; H, 6.40; N, 8.09. Found: C, 62.52; H, 6.25; N, 7.82.

4-Benzyloxycarbonyl-3,8-diethoxycarbonyl-3,4,8-triazatricyclo[5.1.0.0^{2,6}]octanes (14a—c)——General Procedure: Benzyltriethylammonium bromide (0.54 g, 0.1 mol eq) and aqueous 0.5 N $NaHCO_3$ (100 ml, *ca.* 3 mol eq) were added with stirring to a solution of **12** (7—8 g, 20—25 mmol) in CH_2Cl_2 (120 ml). Ethyl *p*-nitrobenzenesulfonoxycarbamate (10—11 g, *ca.* 2 mol eq) was added in small portions over a 1 h period to the above mixture with vigorous stirring in an ice bath. The reaction mixture was stirred for a further 8 h at room temperature and diluted with CH_2Cl_2 (100 ml). The organic layer was separated, washed with saturated NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane–ether (3 : 1) as an eluent to give **14** as a pale yellow oil.

14a: 57% yield. MS *m/z*: 389 (M^+). IR (neat): 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.22 and 1.28 (each 3H, t, $OCH_2C\underline{H}_3$), 4.16 and 4.20 (each 2H, q, $OC\underline{H}_2CH_3$), 2.6—3.1 (3H, m, 1-, 6-, and 7-H), 3.08 and 4.20 (1H, dd, and 1H, d, 5-H_2), 4.60 (1H, dd, 2-H), 5.18 (2H, br s, CH_2Ph), 7.28 (5H, s, Ph-H), $J_{2,6}=4$, $J_{2,7}=3$, $J_{5,5'}=12$, $J_{5,6}=5$ Hz. *Anal.* Calcd for $C_{19}H_{23}N_3O_6$: C, 58.60; H, 5.95; N, 10.79. Found: C, 58.67; H, 6.07; N, 10.51.

14b: 28% yield. MS *m/z*: 403 (M^+). IR (neat): 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.18 (3H, s, 7-Me), 1.24 and 1.28 (each 3H, t, $OCH_2C\underline{H}_3$), 2.6—3.5 (3H, m, 1-H, 2-H, and one of 5-H_2), 4.18 (1H, d, $J=12$ Hz, one of 5-H_2), 4.16 and 4.18 (each 2H, q, $OC\underline{H}_2CH_3$), 4.54 (1H, d, $J=4$ Hz, 6-H), 5.10 and 5.28 (each 1H, d, $J=12$ Hz, $C\underline{H}_2Ph$), 7.30 (5H, s, Ph-H). *Anal.* Calcd for $C_{20}H_{25}N_3O_6$: C, 59.54; H, 6.25; N, 10.42. Found: C, 59.43; H, 6.23; N, 10.18.

14c: 38% yield. MS *m/z*: 417 (M^+). IR (neat): 1710 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.18 (3H, s, 6-Me), 1.24 (6H, t, $2\times OCH_2C\underline{H}_3$), 1.28 (3H, s, 1-Me), 2.96 and 4.22 (each 1H, d, $J=12$ Hz, 5-H_2), 4.30 (1H, br s, 2-H), 4.24 (4H, q, $2\times OC\underline{H}_2CH_3$), 5.14 and 5.32 (each 1H, d, $J=12$ Hz, $C\underline{H}_2Ph$), 7.32 (5H, s, Ph-H). *Anal.* Calcd for $C_{21}H_{27}N_3O_6$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.33; H, 6.67; N, 9.87.

3-Ethoxycarbonyl-8-oxa-3,4-diazatricyclo[5.1.0.0^{2,6}]octanes (15a—c)——General Procedure: Compound **13** (2—5 g) was hydrogenated over 5% Pd–C (0.2—0.3 g) in methanol (100 ml) at room temperature under atmospheric pressure for 3—4 h. The catalyst was filtered off and the filtrate was evaporated *in vacuo*. The residue was chromatographed on silica gel using ether as an eluent to give **15**, which was recrystallized from benzene–isopropyl ether to give colorless needles.

15a: 93% yield, mp 77.5—79 °C. MS *m/z*: 184 (M^+). IR (KBr): 3250 (NH), 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.46 and 4.18 (3H, t, and 2H, q, CO_2Et), 2.86 and 3.22 (1H, dd, and 1H, d, 5-H_2), 3.12 (1H, m, 6-H), 3.80 (1H, dd, 7-H), 3.90 (1H, dd, 1-H), 4.62 (1H, dd, 2-H), 4.8 (1H, br, 4-NH). $J_{1,6}=3$, $J_{1,7}=2$, $J_{2,6}=4$, $J_{2,7}=3$, $J_{5,5'}=13$, $J_{5,6}=6$ Hz. *Anal.* Calcd for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.57; N, 15.21. Found: C, 52.13; H, 6.54; N, 15.17.

15b: 86% yield, mp 30—32 °C. MS *m/z*: 198 (M^+). IR (KBr): 3250 (NH), 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.30 and 4.19 (3H, t, and 2H, q, CO_2Et), 1.50 (3H, s, 7-Me), 2.86 and 3.16 (1H, dd, and 1H, d, 5-H_2), 3.02 (1H, m, 6-H), 3.84 (1H, d, 1-H), 4.4 (1H, br, 4-NH), 4.54 (1H, d, 2-H), $J_{1,6}=3$, $J_{2,6}=4$, $J_{5,5'}=13$, $J_{5,6}=6$ Hz. *Anal.* Calcd for $C_9H_{14}N_2O_3$: C, 54.53; H, 7.12; N, 14.13. Found: C, 54.85; H, 7.35; N, 14.31.

15c: 95% yield, mp 86—88 °C. MS *m/z*: 212 (M^+). IR (KBr): 3250 (NH), 1710 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.16 (3H, s, 6-Me), 1.30 and 4.26 (3H, t, and 2H, q, CO_2Et), 1.44 (3H, s, 1-Me), 2.68 and 3.18 (each 1H, d, $J=13$ Hz, 5-H_2), 3.72 (1H, d, $J_{2,7}=2.5$ Hz, 7-H), 4.14 (1H, d, 2-H), 4.4 (1H, br, 4-NH). *Anal.* Calcd for $C_{10}H_{16}N_2O_3$: C, 56.59; H, 7.60; N, 13.20. Found: C, 56.68; H, 7.68; N, 13.13.

3,8-Diethoxycarbonyl-3,4,8-triazatricyclo[5.1.0.0^{2,6}]octanes (16a—c)——Compound **14** (2—3 g) was hydrogenated and worked up as described for **15** to give **16**.

16a: 61% yield, mp 83—85 °C, colorless needles (from benzene–isopropyl ether). MS *m/z*: 255 (M^+). IR (KBr): 3450 (NH), 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 1.32 (each 3H, t, $OCH_2C\underline{H}_3$), 2.8—3.5 (5H, m, 1-, 6-, 7-, and 5-H), 4.18 and 4.26 (each 2H, q, $OC\underline{H}_2CH_3$), 4.60 (1H, dd, 2-H), 4.8 (1H, br, 4-NH), $J_{2,6}=3$, $J_{2,7}=3$, $J_{5,5'}=12$, $J_{5,6}=5$ Hz. *Anal.* Calcd for $C_{11}H_{17}N_3O_4$: C, 51.75; H, 6.71; N, 16.46. Found: C, 52.04; H, 6.80; N, 16.58.

16b: 72% yield, colorless oil. MS *m/z*: 269 (M^+). IR (neat): 3450 (NH), 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.30 and 1.34 (each 3H, t, $OCH_2C\underline{H}_3$), 1.44 (3H, s, 7-Me), 2.74 and 3.12 (1H, dd, and 1H, d, 5-H_2), 3.05 (2H, m, 1- and 6-H), 4.18 and 4.24 (each 2H, q, $OC\underline{H}_2CH_3$), 4.5 (1H, br, 4-NH), 4.58 (1H, d, 2-H), $J_{2,6}=3$, $J_{5,5'}=12$, $J_{5,6}=5$ Hz. *Anal.* Calcd for $C_{12}H_{19}N_3O_4$: C, 53.52; H, 7.11; N, 15.60. Found: C, 53.70; H, 6.97; N, 15.52.

16c: 80% yield, colorless oil. MS *m/z*: 283 (M^+). IR (neat): 3450 (NH), 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.16 (3H, s, 6-Me), 1.24 (6H, t, 2 × $OCH_2C\underline{H}_3$), 1.36 (3H, s, 1-Me), 2.72 and 3.20 (each 1H, d, 5-H_2), 3.12 (1H, d, 7-H), 4.20 and 4.23 (each 2H, q, $OC\underline{H}_2CH_3$), 4.2 (1H, br, 4-NH), 4.22 (1H, d, 2-H), $J_{2,7}=3$, $J_{5,5'}=12$ Hz. *Anal.* Calcd for $C_{13}H_{21}N_3O_4$: C, 55.11; H, 7.47; N, 14.83. Found: C, 55.08; H, 7.18; N, 14.92.

3-Ethoxycarbonyl-8-oxa-3,4-diazatricyclo[5.1.0.0^{2,6}]oct-4-enes (17a—c)——General Procedure: *tert*-Butyl hypochlorite (1.2 mol eq) was added dropwise over a 5 min period to a stirred solution of **15** (2—3 g) and DBU (1.5 mol eq) in dry tetrahydrofuran (20—30 ml) in an ice bath. After stirring for a further 30 min at 0—5 °C, dimethylformamide (20—30 ml) was added to the reaction mixture, and then the mixture was stirred for 3—4 h at room temperature and diluted with ether (100 ml). The mixture was washed with saturated NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane–ether (1 : 3) as an eluent to give **17**, which was recrystallized from benzene–isopropyl ether.

17a: 75% yield, mp 69.5—70.5 °C, colorless plates. MS *m/z*: 182 (M^+). IR (KBr): 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.34 and 4.23 (3H, t, and 2H, q, CO_2Et), 3.84 (1H, m, 6-H), 4.07 (2H, m, 1- and 7-H), 4.64 (1H, m, 2-H), 6.82 (1H, d, 5-H), $J_{1,6}=2.5$, $J_{2,6}=4$, $J_{2,7}=2.5$, $J_{5,6}=1.5$ Hz. *Anal.* Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.64; H, 5.55; N, 15.29.

17b: 82% yield, mp 76—78 °C, colorless needles. MS *m/z*: 196 (M^+). IR (KBr): 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.38 and 4.30 (3H, t, and 2H, q, CO_2Et), 1.55 (3H, s, 7-Me), 3.78 (1H, m, 6-H), 4.04 (1H, d, 1-H), 4.58 (1H, d, 2-H), 6.80 (1H, d, 5-H), $J_{1,6}=3$, $J_{2,6}=5$, $J_{5,6}=1.5$ Hz. *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.28; H, 6.24; N, 14.50.

17c: 71% yield, mp 45—48 °C, colorless needles. MS *m/z*: 210 (M^+). IR (KBr): 1700 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.24 (3H, s, 6-Me), 1.32 and 4.28 (3H, t, and 2H, q, CO_2Et), 1.44 (3H, s, 1-Me), 3.86 (1H, d, 7-H), 4.19 (1H, d, 2-H), 6.60 (1H, s, 5-H), $J_{2,7}=3$ Hz. *Anal.* Calcd for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.33. Found: C, 57.41; H, 6.82; N, 13.31.

3,8-Bis(ethoxycarbonyl)-3,4,8-triazatricyclo[5.1.0.0^{2,6}]oct-4-enes (18a—c)——Compounds **16a—c** (2—3 g) were successively treated with *tert*-butyl hypochlorite and DBU, and worked up as described for **17** to give **18** as yellow oils.

18a: 75% yield. MS *m/z*: 253 (M^+). IR (neat): 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.34 and 1.36 (each 3H, t, $OCH_2C\underline{H}_3$), 3.38 (1H, dd, 7-H), 3.42 (1H, dd, 1-H), 3.80 (1H, m, 6-H), 4.25 and 4.32 (each 2H, q, $OC\underline{H}_2CH_3$), 4.60 (1H, dd, 2-H), 6.87 (1H, d, 5-H), $J_{1,6}=2$, $J_{1,7}=2$, $J_{2,6}=4$, $J_{2,7}=2.5$, $J_{5,6}=1.5$ Hz. *Anal.* Calcd for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59. Found: C, 52.33; H, 5.86; N, 16.46.

18b: 84% yield. MS *m/z*: 267 (M^+). IR (neat): 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.32 and 1.35 (each 3H, t, $OCH_2C\underline{H}_3$), 1.47 (3H, s, 7-Me), 3.29 (1H, d, 1-H), 3.78 (1H, m, 6-H), 4.24 and 4.30 (each 2H, q, $OC\underline{H}_2CH_3$), 4.54 (1H, d, 2-H), 6.88 (1H, d, 5-H), $J_{1,6}=2$, $J_{2,6}=4$, $J_{5,6}=1.5$ Hz. *Anal.* Calcd for $C_{12}H_{17}N_3O_4$: C, 53.92; H, 6.41; N, 15.72. Found: C, 53.83; H, 6.31; N, 15.60.

18c: 90% yield. MS *m/z*: 281 (M^+). IR (neat): 1710 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.24 (3H, s, 6-Me), 1.32 and 1.35 (each 3H, t, $OCH_2C\underline{H}_3$), 1.36 (3H, s, 1-Me), 3.40 (1H, d, 7-H), 4.24 and 4.32 (each 2H, q, $OC\underline{H}_2CH_3$), 4.38 (1H, d, 2-H), 6.68 (1H, s, 5-H), $J_{2,7}=2.5$ Hz. *Anal.* Calcd for $C_{13}H_{19}N_3O_4$: C, 55.50; H, 6.81; N, 14.94. Found: C, 55.49; H, 6.99; N, 14.68.

Photolysis of 17a—c: Formation of 6-Formyl- (20a, b) and 6-Acetyl-2,3-diazabicyclo[3.1.0]hex-3-ene (20c)——General Procedure: A solution of **17** (0.3—0.5 g) in acetonitrile (200—300 ml) was irradiated with a 30 W low-pressure Hg lamp for 15—20 min under a nitrogen atmosphere in an ice bath. After removal of the solvent *in vacuo* below 30 °C, the residue was chromatographed on silica gel using hexane–ether (3 : 1) as an eluent to give **20**.

20a: 30—35% yield, colorless oil. IR (neat): 1710 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.36 and 4.34 (3H, t, and 2H, q, CO_2Et), 1.50 (1H, ddd, 6-H), 3.38 (1H, dd, 5-H), 4.82 (1H, dd, 1-H), 7.15 (1H, s, 4-H), 9.93 (1H, d, CHO), $J_{1,5}=6$, $J_{1,6}=2$, $J_{5,6}=3$, $J_{CHO,6}=2$ Hz. ^{13}C-NMR δ: 26.47 (d, 6-C), 36.00 (d, 5-C), 48.65 (d, 1-C), 146.89 (d, 4-C), 198.77 (d, CHO), 14.53, 63.30, and 151.89 (q, t, and s, CO_2Et). High-resolution MS *m/z*: M^+ Calcd for $C_8H_{10}N_2O_3$: 182.0691. Found: 182.0693.

20b: *ca.* 40% yield, colorless oil. IR (neat): 1710 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.00 (3H, s, 6-Me), 1.38 and 4.38 (3H, t, and 2H, q, CO_2Et), 3.38 (1H, d, 5-H), 4.74 (1H, d, 1-H), 7.04 (1H, s, 4-H), 9.83 (1H, s, CHO), $J_{1,5}=6$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_9H_{12}N_2O_3$: 196.0848. Found: 196.0841.

20c: *ca.* 30% yield, mp 65—66 °C, colorless needles (from isopropyl ether). MS *m/z*: 210 (M^+). IR (KBr): 1710 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.33 and 4.32 (3H, t, and 2H, q, CO_2Et), 1.44 (3H, s, 5-Me), 1.50 (1H, d, 6-H), 2.28 (3H, s, 6-COMe), 4.75 (1H, d, 1-H), 7.02 (1H, s, 4-H), $J_{1,6}=2$ Hz. ^{13}C-NMR δ: 8.71 (q, 5-Me), 30.24 and 204.60 (q and s, COMe), 32.36 (d, 5-C), 44.12 (s, 6-C), 51.30 (d, 1-C), 151.95 (d, 4-C), 14.59, 63.00, and 152.00 (q, t, and s, CO_2Et). *Anal.* Calcd for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.33. Found: C, 57.11; H, 6.62; N, 13.06.

Thermolysis of 20a, b: Formation of 4-(Formylmethyl)pyrazoles (22a, b) *via* 3a,6a-Dihydrofuro[2,3-*c*]pyrazoles

(21a, b)——General Procedure: i) A solution of **20** (*ca.* 100 mg) in benzene (10 ml) was heated at 60 °C for *ca.* 1 h and then evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 5—1 : 1) as an eluent to give **21** (30—40% yield) and **22** (5—10% yield) successively, as colorless oils. The product **21** was heated at 70 °C in benzene for 3 h and worked up as described above to give **22** in 50—60% yield. ii) A solution of **20** (*ca.* 50 mg) in benzene (8 ml) was heated at 70 °C for 4—5 h and worked up as described for procedure i to give **22** in 40—50% yield as the sole isolated product.

21a: This compound was unstable and gradually decomposed on standing, and thus was characterized only by ^{1}H-NMR spectral data: (toluene-d_6) δ: 1.09 and 4.03 (3H, t, and 2H, q, CO_2Et), 3.92 (1H, m, 3a-H), 4.36 (1H, dd, 4-H), 5.95 (1H, dd, 5-H), 6.16 (1H, d, 6a-H), 6.22 (1H, d, 3-H), $J_{3,3a}=1$, $J_{3a,4}=1.5$, $J_{3a,5}=1.5$, $J_{3a,6a}=8$, $J_{4,5}=1.5$ Hz.

21b: IR (neat): 1715 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.36 and 4.34 (3H, t, and 2H, q, CO_2Et), 1.75 (3H, d, 4-Me), 4.20 (1H, m, 3a-H), 6.10 (1H, m, 5-H), 6.50 (1H, d, 6a-H), 7.02 (1H, d, 3-H), $J_{3,3a}=1$, $J_{3a,4}=1$, $J_{3a,5}=1.5$, $J_{4\text{-Me},5}=1$ Hz. ^{13}C-NMR (ring carbons) δ: 62.77 (d, 3a-C), 91.83 (d, 6a-C), 107.48 (s, 4-C), 140.66 (d, 5-C), 145.83 (d, 3-C). High-resolution MS *m/z*: M^+ Calcd for $C_9H_{12}N_2O_3$: 196.0848. Found: 196.0842.

22a: IR (neat): 1730 and 1750 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.44 and 4.48 (3H, t, and 2H, q, CO_2Et), 3.64 (2H, d, $J=1$ Hz, $C\underline{H}_2CHO$), 7.63 (1H, s, 5-H), 8.21 (1H, s, 3-H), 9.74 (1H, t, $J=1$ Hz, $CH_2C\underline{H}O$). High-resolution MS *m/z*: M^+ Calcd for $C_8H_{10}N_2O_3$: 182.0691. Found: 182.0702.

22b: IR (neat): 1730 and 1750 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.44 and 4.50 (3H, t, and 2H, q, CO_2Et), 1.43 [3H, d, $J=7$ Hz, $CH(CHO)C\underline{H}_3$], 3.58 [1H, m, $C\underline{H}(CHO)CH_3$], 7.62 (1H, s, 5-H), 8.02 (1H, s, 3-H), 9.60 (1H, d, $J=1$ Hz, CHO). High-resolution MS *m/z*: M^+ Calcd for $C_9H_{12}N_2O_3$: 196.0848. Found: 196.0845.

Photolysis of 18a, b: Formation of 5-Ethoxycarbonyl-2-ethoxycarbonylamino-3-cyanobicyclo[2.1.0]pentanes (23a, b)——General Procedure: A solution of **18** (0.1—0.2 g) in acetonitrile (250—300 ml) was irradiated with a 30 W low-pressure Hg lamp for 15 min and worked up as described for **17** to give **23**, which was recrystallized from isopropyl ether.

23a: 50—55% yield, mp 98—100 °C, colorless needles. MS *m/z*: 253 (M^+). IR (KBr): 3300 (NH), 2250 (CN), 1720 (C=O), 1680 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 1.35 (each 3H, t, $O\text{–}CH_2C\underline{H}_3$), 3.28 (1H, d, $J=4$ Hz, 3-H), 3.43 and 3.50 (each 1H, m, 1- and 4-H), 4.05 (1H, m, 2-H), 4.19 and 4.27 (each 2H, q, $O\text{–}C\underline{H}_2CH_3$), 5.90 (1H, br d, $J=8$ Hz, NH). *Anal.* Calcd for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59. Found: C, 52.25; H, 5.87; N, 16.42.

23b: 55—60% yield, mp 120—121 °C, colorless needles. MS *m/z*: 267 (M^+). IR (KBr): 3250 (NH), 2250 (CN), 1720 (C=O), 1680 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.27 and 1.33 (each 3H, t, $O\text{–}CH_2C\underline{H}_3$), 1.62 (3H, s, 4-Me), 3.28 (1H, br, 1-H), 3.32 (1H, d, $J=4$ Hz, 3-H), 4.05 (1H, m, 2-H), 4.17 and 4.24 (each 2H, q, $O\text{–}C\underline{H}_2CH_3$), 5.80 (1H, br d, $J=8$ Hz, NH). ^{13}C-NMR δ: 14.47 (q, 4-Me), 38.12 (d, 2-C), 45.00 (s, 4-C), 45.29 (d, 1-C), 49.60 (d, 3-C), 116.07 (s, CN), 14.47 and 14.82 (each q, $O\text{–}CH_2\underline{C}H_3$), 62.00 and 63.30 (each t, $O\text{–}\underline{C}H_2CH_3$), 156.01 and 158.94 (each s, $-CO_2-$). *Anal.* Calcd for $C_{12}H_{17}N_3O_4$: C, 53.92; H, 6.41; N, 15.72. Found: C, 54.11; H, 6.38; N, 15.72.

Flash Vacuum Pyrolysis of 17a—c: Formation of 1-Ethoxycarbonylamino-2-formylpyrazoles (27a—c)——General Procedure: Compound **17** (1.1—1.5 g) was distilled over a 1.5 h period through a quartz pyrolysis tube (1.0 cm × 20 cm; heated at 390 °C with a furnace) from a small flask heated with an air bath under reduced pressure ($3\text{—}5\times10^{-5}$ Torr). The distillate was collected in a trap cooled in a liquid N_2 bath. The trap was washed with CH_2Cl_2 and the washing was concentrated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 1) as an eluent to give **27**, which was recrystallized from hexane–isopropyl ether.

27a: 25—30% yield, mp 63.5—65 °C, colorless prisms. MS *m/z*: 182 (M^+). IR (KBr): 3360 (NH), 1730 (C=O), 1660 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 4.34 (3H, t, and 2H, q, CO_2Et), 6.44 (1H, dd, 4-H), 7.16 (1H, dd, 3-H), 7.26 (1H, dd, 5-H), 8.68 (1H, br, NH), 9.84 (1H, s, CHO), $J_{3,4}=4$, $J_{3,5}=2$, $J_{4,5}=3$ Hz. ^{13}C-NMR δ: 14.35 and 62.77 (q and t, OEt), 108.48 (d, 4-C), 121.89 (d, 3-C), 130.36 (s, 2-C), 131.77 (d, 5-C), 156.65 (s, CO_2-), 179.42 (CHO). *Anal.* Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.68; H, 5.55; N, 15.34.

27b: 30—35% yield, mp 77—79 °C, colorless needles. MS *m/z*: 196 (M^+). IR (KBr): 3350 (NH), 1750 (C=O), 1640 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 4.20 (3H, t, and 2H, q, CO_2Et), 2.34 (3H, s, 3-Me), 5.98 (1H, d, 4-H), 6.87 (1H, d, 5-H), 8.26 (1H, br, NH), 9.60 (1H, s, CHO), $J_{4,5}=3$ Hz. ^{13}C-NMR δ: 14.41 and 62.77 (q and t, OEt), 11.35 (q, 3-Me), 109.89 (d, 4-C), 126.83 (s, 3-C), 130.83 (d, 5-C), 133.83 (d, 5-C), 133.30 (s, 2-C), 156.83 (s, CO_2-), 178.37 (d, CHO). *Anal.* Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.09; H, 6.20; N, 14.24.

27c: *ca.* 40% yield, mp 90.5—91.5 °C, colorless prisms. MS *m/z*: 210 (M^+). IR (KBr): 3360 (NH), 1740 (C=O), 1640 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 4.23 (3H, t, and 2H, q, CO_2Et), 2.15 (3H, s, 3-Me), 2.27 (3H, s, 5-Me), 5.82 (1H, s, 4-H), 7.83 (1H, br, NH), 9.58 (1H, s, CHO). ^{13}C-NMR δ: 10.83 (q, 3-Me), 11.06 (q, 5-Me), 14.41 and 62.82 (q and t, OEt), 109.42 (d, 4-C), 126.48 (s, 3-C), 133.71 (s, 2-C), 140.42 (s, 5-C), 156.65 (s, CO_2-), 177.01 (d, CHO). *Anal.* Calcd for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.33. Found: C, 57.32; H, 6.75; N, 13.07.

Thermolysis of 17c in Toluene——A solution of **17c** (400 mg) in toluene (10 ml) was refluxed for 48 h and then evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 2—2 : 1) as an eluent to give **27c** (2—3% yield) and 2-formyl-2,4-dimethyl-2*H*-pyrrole 1-ethoxycarbonylimide (**32c**): 210 mg, 52% yield, mp 85—86 °C, colorless needles (from benzene). MS *m/z*: 210 (M^+). IR (KBr): 1730 (C=O), 1690 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.36 and 4.36 (3H, t, and 2H, q, CO_2Et), 1.43 (3H, s, 2-Me), 1.83 (3H, d, 4-Me), 5.28 (1H, m, 3-H), 6.95 (1H, d, 5-H), 9.60 (1H, s, CHO), $J_{3,5}=2$, $J_{3,4\text{-Me}}=1.5$ Hz. ^{13}C-NMR δ: 14.47 and 63.65 (q and t, OEt), 18.35 and 19.70

(each q, 2- and 4-Me), 65.77 (s, 2-C), 125.36 (d, 3-C), 126.13 (s, 4-C), 141.24 (d, 5-C), 155.24 (s, CO_2–), 194.84 (d, CHO). *Anal.* Calcd for $C_{10}H_{14}N_2O_3$: C, 57.13; H, 6.71; N, 13.33. Found: C, 57.05; H, 6.79; N, 13.19.

Thermolysis of 32c in Xylene——A solution of **32c** (200 mg) in xylene (10 ml) was refluxed for 4 d and then evaporated *in vacuo*. The residue was chromatographed on silica gel using ether–hexane (1 : 2) as an eluent to give **27c**: 145 mg, 73% yield.

Flash Vacuum Pyrolysis of 18a—c: Formation of Pyrrolopyrazoles (33a—c, 34b, and 35c)——Compounds **18a—c** (*ca.* 500 mg) were pyrolyzed at 430 °C/1—2×10^{-5} Torr over a 40 min period and worked up as described for **17** to give the 3a,6a-dihydropyrrolo[2,3-*c*]pyrazoles (**33a—c**) as colorless oils. From **18b** and **18c**, the isomeric products **34b** and **35c** were also obtained, respectively.

33a: 35% yield. IR (neat): 1730 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 1.32 (each 3H, t, $OCH_2C\underline{H}_3$), 4.22 and 4.30 (each 2H, q, $OC\underline{H}_2CH_3$), 4.48 (1H, m, 3a-H), 5.04 (1H, dd, 4-H), 6.54 (1H, d, 6a-H), 6.72 (1H, dd, 5-H), 6.93 (1H, d, 3-H), $J_{3,3a}=1$, $J_{3a,4}=3$, $J_{3a,5}=2$, $J_{3a,6a}=8$, $J_{4,5}=4$ Hz. ^{13}C-NMR (ring carbons) δ: 57.12 (d, 3a-C), 74.77 (d, 6a-C), 104.01 (d, 4-C), 132.07 (d, 5-C), 146.01 (d, 3-C). High-resolution MS *m/z*: M^+ Calcd for $C_{11}H_{15}N_3O_4$: 253.1062. Found: 253.1061.

33b: 38% yield. IR (neat): 1730 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.28 and 1.32 (each 3H, t, $OCH_2C\underline{H}_3$), 2.00 (3H, s, 6a-Me), 4.04 (1H, m, 3a-H), 4.22 and 4.30 (each 2H, q, $OC\underline{H}_2CH_3$), 4.94 (1H, dd, 4-H), 6.76 (1H, dd, 5-H), 6.88 (1H, d, 3-H), $J_{3,3a}=1$, $J_{3a,4}=3$, $J_{3a,5}=2$, $J_{4,5}=4$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_{12}H_{17}N_3O_4$: 267.1219. Found: 267.1218.

33c: 20% yield. IR (neat): 1730 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.34 (6H, t, $2 \times OCH_2C\underline{H}_3$), 1.35 (3H, s, 3a-Me), 2.14 (3H, s, 5-Me), 4.25 and 4.31 (each 2H, q, $OC\underline{H}_2CH_3$), 4.72 (1H, s, 4-H), 6.18 (1H, s, 6a-H), 6.77 (1H, s, 3-H). High-resolution MS *m/z*: M^+ Calcd for $C_{13}H_{19}N_3O_4$: 281.1376. Found: 281.1387.

34b: 18% yield, colorless oil. IR (neat): 1730 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.29 and 1.34 (each 3H, t, $OCH_2C\underline{H}_3$), 1.78 (3H, d, 4-Me), 4.10 (1H, m, 3a-H), 4.22 and 4.30 (each 2H, q, $OC\underline{H}_2CH_3$), 6.37 (1H, m, 5-H), 6.50 (1H, d, 6a-H), 7.00 (1H, d, 3-H), $J_{3,3a}=1$, $J_{3a,6a}=8$, $J_{4\text{-Me},5}=1$ Hz. High-resolution MS *m/z*: M^+ Calcd for $C_{12}H_{17}N_3O_4$: 267.1219. Found: 267.1230.

35c: 38% yield, mp 58—60 °C, colorless prisms (from isopropyl ether). IR (KBr): 1720 (C=O) cm^{-1}. ^{1}H-NMR δ: 1.32 and 1.34 (each 3H, t, $OCH_2C\underline{H}_3$), 1.63 (3H, s, 6a-Me), 2.12 (3H, br s, 5-Me), 4.22 and 4.28 (each 2H, q, $OC\underline{H}_2CH_3$), 5.02 (1H, d, 3a-H), 5.24 (1H, br s, 6-H), 7.00 (1H, d, 3-H), $J_{3,3a}=1$ Hz. ^{13}C-NMR (ring carbons) δ: 70.83 (s, 6a-C), 75.77 (d, 3a-C), 109.77 (d, 6-C), 141.60 (s, 5-C), 142.13 (d, 3-C). High-resolution MS *m/z*: M^+ Calcd for $C_{13}H_{19}N_3O_4$: 281.1376. Found: 281.1373.

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