Tetrahedron. Vol. 33, pp. 2603 to 2607 Pergamon Press 1977. Printed in Great Britain

UNCONVENTIONAL NUCLEOTIDE ANALOGUES—XVII[1]

RING-TRANSFORMATIONS OF URACIL DIHALOCARBENE ADDUCTS

H. P. M. THIELLIER,[2] G. J. KOOMEN and U. K. PANDIT*
Organic Chemistry Laboratory, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

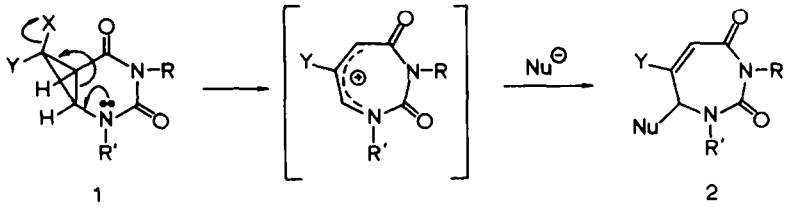
(*Received in UK 4 April 1977; Accepted for publication 13 May 1977*)

Abstract—Halocarbene adducts of 1,3-disubstituted uracil (**3a, b, d**) undergo ring-enlargement to yield 1,3-diazepine derivatives (**4a–d**). The ring-opening of the cyclopropane system is controlled by the stereochemical configuration of the halogen atom, which can be eliminated as a halide ion. Reduction of the adducts with n-Bu_3SnH leads to a variety of 1,3-diazepines. Details of the mechanism of formation of the diazepines and their further transformations are discussed.

We have recently described the addition of carbenes to the 5,6-double bond of uracil and uridine derivatives.[1,3] Since halo-adducts of type **1** constitute potentially suitable precursors for the synthesis of 2,4-dioxo-1,3-diazpine derivatives (**2**), it was envisaged that such a ring-transformation approach could provide a convenient access to novel diazepine nucleosides.[4] This communication discusses the 3-ring opening reaction of 1,3-diazabicyclo [4.1.0]heptanes (**1**).

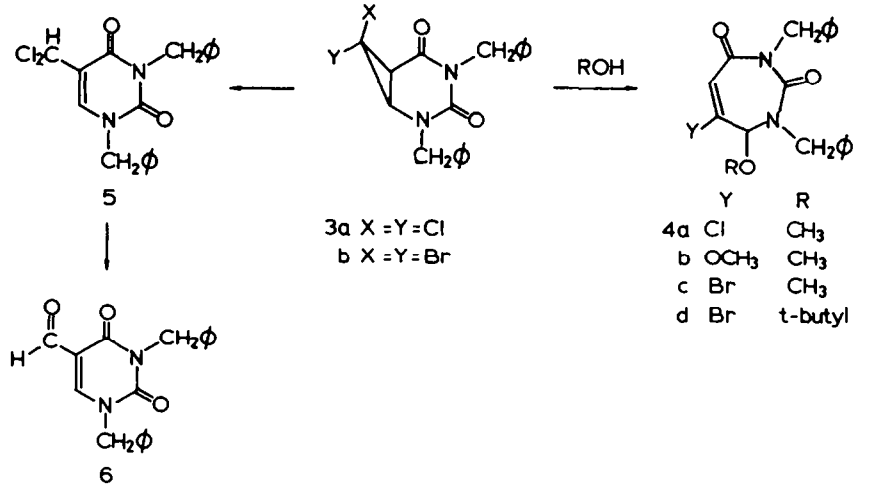
The electrocyclic ring-opening reaction of cyclopropane derivative has received considerable attention.[5] In the case of 7-halo-substituted bicyclo[4,1,0]heptanes, it has been demonstrated[6] that the *bi-* → *mono*-cyclic ring conversion occurs via a concerted disrotatory process[7] in which an *endo*-halogen is extruded from the system. Ring-opening involving the expulsion of *exo*-halides has been, however, observed in special cases, where unique structural features[8] or reaction conditions[9] influence the course of the reaction.

In view of the foregoing discussion, the dihalocarbene adducts **3a, b** (Scheme 2) were expected to undergo a skeletal transformation to a 1,3-diazepine derivative with relative facility; the latter because of the fact that the carbenium ion (Scheme 1) formed upon ionization of the *endo*-halogen would derive stabilization by virtue of the neighbouring N atom. Consistent with these considerations, heating of adducts **3a, b** in methanol (110°, sealed tube, 5 hr) resulted in the formation of **4a** and **4c** in 35% and quantitative yield, respectively (Scheme 2). The structures of the dioxodiazepines (**4a** and **4c**) was



1 2

Scheme 1.



5 6

3a X = Y = Cl
b X = Y = Br

	Y	R
4a	Cl	CH_3
b	OCH_3	CH_3
c	Br	CH_3
d	Br	t-butyl

Scheme 2.

attested by their spectro-analytical data (Experimental); particularly diagnostic being the C_5 vinylic proton which, for example, in the case of **4a**, was observed at δ 6.30, with an allylic coupling of 1.5 Hz. When **3a** was subjected to more drastic reaction conditions (MeOH, 130°, sealed tube, 24 hr), besides formation of **4a** (39%), two further products, viz. **4b** (13%) and **6** (19%) could be isolated from the mixture. The formation of **4b** can be rationalized in terms of nucleophilic addition of methanol to **4a**, followed by elimination of hydrochloric acid. This was confirmed by demonstrating the formation of **4b** by heating **4a** in methanol (130°, 24 hr), in a separate experiment. While the details of the steps leading to **6** are not known at present, a possible sequence of events could involve: (a) C_6–C_7 ring-opening in an S_N2 reaction with methanol (**5a**), (b) loss of methanol (**5b**) and (c) hydrolysis of the gem-dichloride system in **5b**, during isolation, to 1,3-dibenzyl-5-formyluracil (**6**).[10] Apparently, under forcing conditions (130°, 24 hr), the C_6–C_7 cleavage begins to compete effectively with the C_5–C_6 ring-opening (synchronous with chloride elimination) observed at 110°.

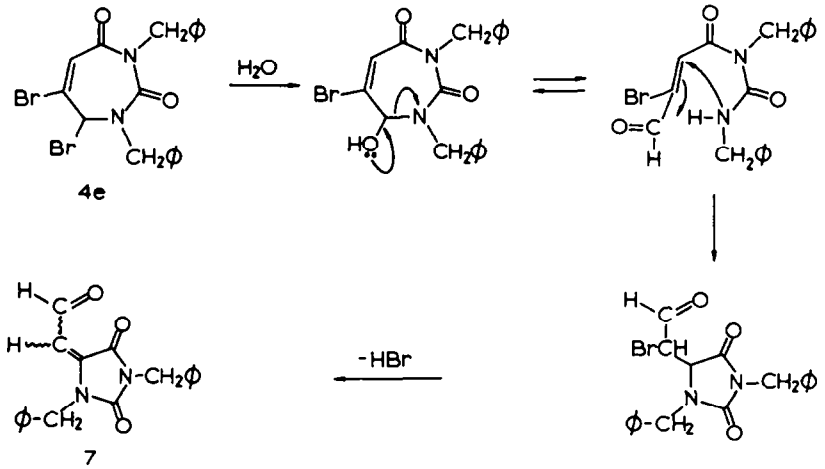
It should be noted that reaction of **3a**, **b** in methanol leads to an overall production of one equivalent of a hydrogen halide. Moreover, methanol has been observed to complicate the reactivity pattern by acting as a nucleophile towards both the starting material (**3a** → **6**) and the primary product (**4a** → **4b**). To eliminate the formation of acid in the mixture and to suppress the consequences of a *nucleophilic* alcohol, the reaction of **3b** with t-butanol (100°), in the presence of triethylamine, was examined. From the latter mixture two products were isolated, which could be assigned structures **4d** (36%) and **7** (4%, Scheme 3) on the basis of their spectral data. Hydantoin **7** was recognized, in particular, by bands in the IR (1780, 1720, 1700, 1650) and the doublet in the NMR, due to the aldehyde proton (δ 10.62, J = 7 Hz). Since product **4d** is stable under the reaction conditions, it is suggested that, in view of the steric bulk of t-butanol, formation of **4e** (Scheme 3) competes with the afore-mentioned type of reaction leading to **4d**. Conversion of **4e** into **7** may follow the route shown in Scheme 3; the water originating from the reaction conditions employed during the workup. The steric requirements of the t-Bu group in **4d** has significant influence upon its structure. The NMR spectrum of **4d** showed that a duplicate set of signals was present (2:3) corresponding to the expected pattern (Experimental). These sets of signals coalesced when the spectrum was run at 110°. These results are explicable on the basis of two conformational isomers of **4d** which interconvert by a movement of the adjacent t-BuO group and the Br atom past each other. Available data at present do not permit structural assignment to the two conformers.

Information on the mechanism of **3**→**4** type transformation was derived from the study of isomeric chlorofluorocarbene-uracil adducts (**3c**, **d**[1], Scheme 4).

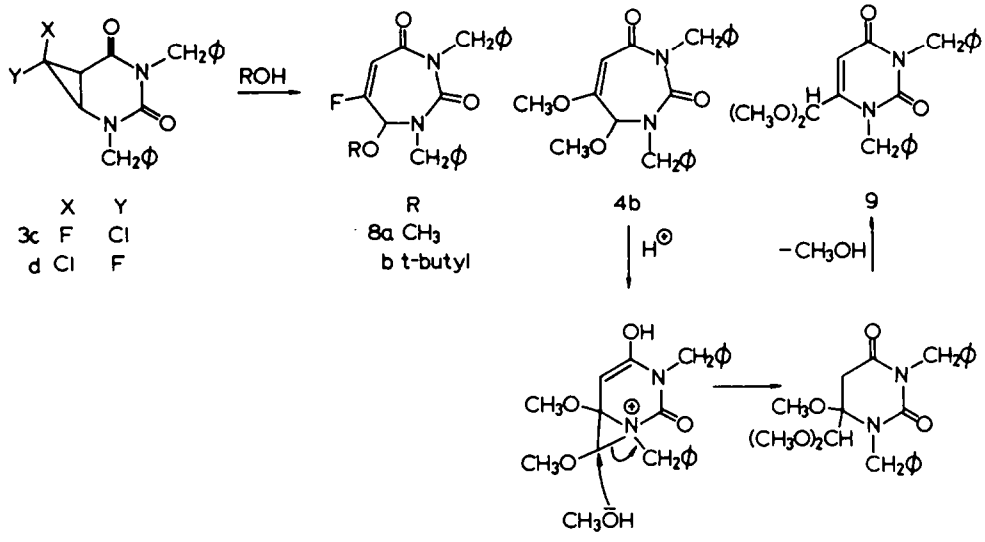
The attempted reaction of *exo*-chloro isomer **3c** (MeOH, 110°, 5 hr) led to recovery of the total starting material. Under identical conditions, the *endo*-chloro isomer yielded a mixture of two products, **4b** (30%) and **9** (30%), which were isolated and identified. Structure of **9** readily followed from its spectral data and its hydrolysis to the corresponding aldehyde. Since compound **4b** represents a cyclopropane ring-opening involving C_5–C_6 bond cleavage in **3d**, the results, in conjunction with the behaviour of **3c**, constitute strong evidence that elimination of the chloride ion and ring-opening are subject to a stereoelectronic control imposed by the orbital symmetry rules.

The formation of **9** deserves further comment. It was suspected that **9** was produced by reaction of **4b** with the acid generated during the ring-opening process. Confirmation of this was found in the fact that treatment of **4b** with *p*-toluenesulfonic acid (MeOH, 110°, 5 hr) converted it quantitatively into **9**. Furthermore, when the ring-transformation of **3d** was carried out in the presence of triethylamine, the formation of **4b** (100%) was observed. The acid catalyzed conversion of **4b** to **9** can be envisaged as proceeding according to the mechanistic sequence described in Scheme 4.

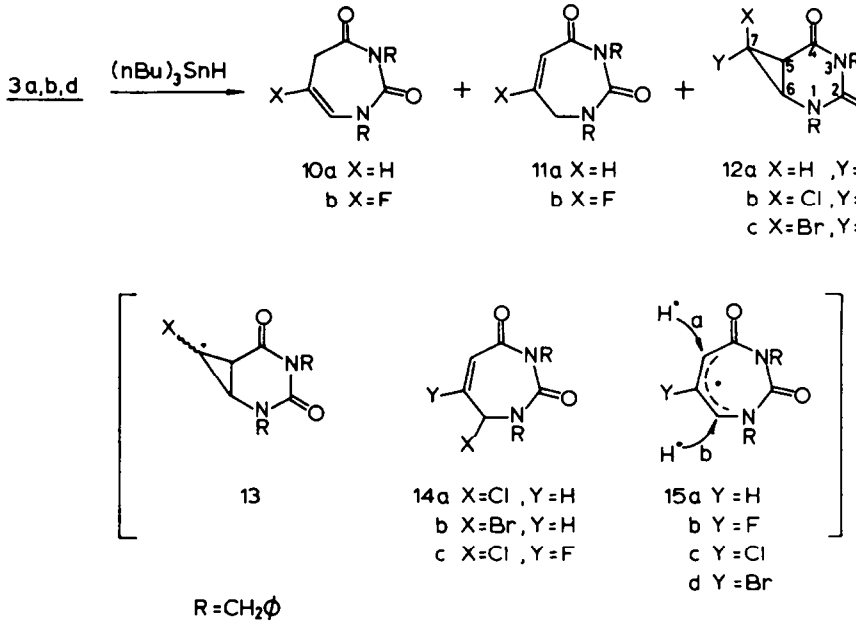
From the foregoing results, it appeared that while **4b** was produced via an electrocyclic (cyclopropane) ring-opening process, it was, however, not the primary product of the reaction and was presumably formed by reaction of **8a** (Scheme 4) with excess of methanol, under the conditions of the reaction. Support for this assumption came from the reaction of **3d** with 2 equiv. of methanol in benzene, in the presence of triethylamine. Under these conditions, the fluoro derivative **8a** was formed in 83% yield. As expected, **8a** could be converted to **4b** in a fast reaction (15 min) by heating with methanol and triethylamine. Since the last reaction involves a nucleophilic attack of methanol on **8a** (C_6), bulky alcohols would not be expected to undergo such a process.



Scheme 3.



Scheme 4.



Scheme 5.

In agreement herewith, refluxing of **3d** in t-butanol (110°, 2.5 hr, Et_3N) yielded the fluorodiazepine system **8b** quantitatively.

With a view to applying the ring-expansion reaction of uracil-carbene adducts to the synthesis of modified nucleosides, the potential selective reduction of the halogens on the cyclopropane framework was undertaken. While a number of methods have been used to reduce cyclopropyl halides,[11] in context of the present work, reduction with n-Bu_3SnH[12] appeared to be the most practical procedure. Reduction of **3a**, at 130°, without use of a solvent, yielded three isolable products, viz **10a** (12%), **11a** (21%) and **12a** (8%). The *exo*-chloro configuration of **10a** followed from the coupling constants of H_7 with H_5 and H_6 (Experimental). In dioxodiazepines **11a** and **12a**, the position of the double bond could be elucidated from both their IR and NMR spectra.[13] Particularly relevant to the structure assignment was the chemical shifts of the methylene and the vinyl protons. In **12a**, consistent with expectation, the latter groups of protons were at lower field, as compared to similar protons in **11a**. In a related reaction, treatment of **3b** with the tinhydride led to the exclusive formation of **11a** (43%). The isomeric adducts **3c** and **3d** revealed the sensitivity of the reduction reaction to the stereochemistry of the halogens. While **3c** was inert towards the tinhydride, in refluxing xylene (40 hr), a similar treatment of the *endo*-chloro isomer (**3d**) gave a high yield of **11b** (>90%). The latter product was contaminated with small amounts of **12b**, from which it could not be completely separated, despite considerable effort.

The mechanism of the reductive ring-opening reactions can be discussed in the following terms. Formation of **10a** and **11a** (from **3a**, **b**) may be visualized as proceeding via the sequence **3a**, **b** → **13** (X=Cl, Br) → **12(b**, **c)** → **14(a**, **b)** → **15a** → **10a** + **11a**. Support for the formation of the

radical **13**, in the first step, is derived from the formation of the inert *exo*-chloro isomer **12a**. The corresponding *endo*-halo primary reduction products **12b, c** would be expected to isomerize to **14a, b** under the condition of the reactions. The latter, in turn, should lose their allylic halogens by reaction with the tin hydride and, through the intermediacy of **15a**, give the products of the reaction (**10a** + **11a**). A direct ring-opening of radical **13** (X=Cl, Br) to the intermediates **15c, d** is considered unlikely since such a process usually involves a driving-force in the form of factors, such as steric strain[14] in the three-membered ring or special stabilization[15] of the (product) allylic radical. Formation of the fluorodiazepinones **10b** and **11b**, from **3d**, can be most adequately rationalized by invoking an initial ring-opening reaction leading to **14c**, which is then reduced, by the formation and quenching of radical **15b**, via paths (a) and (b). The exceptional tendency of **3d** towards ring-opening may be ascribed to the electronegative character of the fluorine atom at C_7. The ring-opening process appears to be increasingly facile, within the series of adducts of $:CCl_2$, $:CBr_2$ and :CFCl, as the electronegativity of the halogen increases. Thus, the dibromo adduct **3b** is quantitatively converted to **4c** under the same reaction conditions which result in a 34% conversion of the dichloro adduct **3c** to the corresponding diazepine **4a**.

Application of the ring-transformation reaction of uracil-carbene adducts, to the synthesis of modified nucleosides, are described in the accompanying communication.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were recorded on a Unicam SP 200 spectrometer and NMR spectra were run on Varian Associates Model A-60D, HA-100 and XL-100 instruments, using TMS as an internal standard. UV spectra were recorded on a Cary-14 spectrophotometer. Unless stated otherwise, IR and NMR spectra are taken in $CHCl_3$ and $CDCl_3$, respectively. The oily products were purified by chromatography and their purity was attested by a single spot in TLC.

Reaction of dichlorocarbene adduct **3a** *in methanol*

A. A soln of **3a** (38 mg, 0.10 mmole) in 1.0 ml MeOH was heated in a sealed tube at 110° during 5 hr. On TLC (silica; ethylacetate/cyclohexane 1:3) **4b** and the starting material appeared as a single spot. According to the NMR spectrum **4a** was formed in 34% yield.

4a: colourless oil. IR: 1680, 1650, 1630 cm^{-1}, NMR δ 2.78 (s, OCH_3), 4.71 (1H, d, J = 1.5, H-7), 4.59, 4.85 (2H, AB-system, J = 15, CH_2-N-1), 5.00, 5.40 (2H, AB-system, J = 14, CH_2-N-3), 5.30 (1H, d, J = 1.5, H-5), 7.3 (m, arom.).

B. Heating **3a** (100 mg) in 2.5 ml MeOH and 0.1 ml triethylamine at 130° (sealed tube) during 24 hr, resulted in a mixture of **4a** (37%), **4b** (13%) and **6** (19%) isolated by TLC.

4b: colourless oil. IR: 1700, 1670, 1640 cm^{-1}. NMR δ 2.77 (s, 7-OCH_3), 3.50 (s, 6-OCH_3), 4.52 (1H, d, J = 2, H-7), 4.68, 4.75 (AB-system, J = 15, CH_2-N-1), 4.97, 5.41 (2H, AB-system, J = 14, CH_2-N-3), 5.21 (1H, d, J = 2, H-5), 7.3 (m, arom.). Mass: *m/e* = 366.

6: colourless oil. IR: 1720, 1695, 1660, 1610 cm^{-1}. NMR δ 5.00 (s, CH_2-N-1), 5.16 (s, CH_2-N-3), 7.3 (m, arom.), 8.04 (s, H-6), 10.00 (s, CHO).

Reaction of dibromocarbene adduct **3b**

A. A soln of **3b** (46 mg, 0.10 mmol) was heated in 1.0 ml MeOH at 110° (sealed tube) during 5 hr. After evaporation of excess of MeOH the resulting oil, according to TLC and IR/NMR spectra was the pure diazepine **4c**.

4c: colourless oil. IR: 1680, 1650, 1630 cm^{-1}. NMR δ 2.78 (s, 7-OCH_3), 4.84 (d, J = 1.5, H-7), 4.59, 4.85 (AB-system, J = 15, CH_2-N-1), 5.02, 5.39 (AB-system, J = 14, CH_2-N-3), 6.53 (d, J = 1.5, H-5), 7.3 (m, arom.).

B. A soln of **3b** (50 mg, 0.11 mmol) and 0.020 ml triethylamine in 1.0 ml t-BuOH was heated in a sealed tube at 110° during 4 hr. Volatile material was evaporated and the residue purified over a silica-plate (EtOAc/cyclohexane 1:3). Besides 3 mg (6%) starting material, **4d** (18 mg, 36%) and **7** (2 mg, 4%) were isolated.

4d: colourless oil. IR: 1670, 1640, 1620 cm^{-1}. According to NMR **4d** existed as an equilibrium of 2 conformers (2:3, $CDCl_3$), at 110° (DMSO-D_6) only one isomer being visible. NMR I δ 0.94 (s, OtBu), 4.35, 4.64 (AB-system, J = 15, CH_2-N-1), 5.00, 5.25 (AB-system, J = 15, CH_2-N-3), 4.87 (d, J = 1.5, H-7), 6.38 (d, J = 1.5, H-5). II δ 0.87 (s, O-t-Bu), 4.79, 5.00 (AB-system, J = 15, CH_2-N-1), 5.05, 5.36 (AB-system, J = 15, CH_2-N-3), 5.59 (d, J = 1.5, H-7), 6.38 (D, J = 1.5, H-5).

7: IR: 1780, 1720, 1700, 1650, 1630 cm^{-1}. NMR δ 4.83 (s, CH_2-N-1), CH_2-N-3), 5.68 (d, J = 7, vinylproton), 7.3 (m, arom.), 10.62 (d, J = 7, aldehyde proton).

Reaction of chloro-fluoro carbene adduct **3d** *in methanol*

A. A soln of **3d** (36 mg, 0.10 mmol) in 1.0 ml MeOH was heated at 110° during 5 hr (sealed tube). After evaporation the residue was purified over a silica-plate (EtOAc/cyclohexane 1:1). Besides 12 mg of **4b** (32%) a mixture of products was obtained, according to NMR containing **9**.

B. A soln of **3d** (72 mg, 0.20 mmol) in 0.050 ml triethylamine and 1.0 ml MeOH was heated at 110° during 1.5 hr. The mixture was dissolved in chloroform, washed with 5% HCl, dried over $MgSO_4$ and the solvents evaporated. Pure **4b** was obtained as a colourless oil (72 mg, 100%).

1,3-*Dibenzyl-6-formyluracil dimethylacetal* **9**

A soln of **4b** (50 mg, 0.14 mmol) and *p*-toluenesulphonic acid (27 mg, 0.14 mmol) in 1.0 ml MeOH was heated at 110° during 5 hr (sealed tube). The solvent was evaporated and the residue purified over a silica-plate. **9** was isolated as a colourless oil in quantitative yield; IR: 1700, 1650, 1620 cm^{-1}; UV: 268 nm (8600), NMR δ 3.25 (s, OCH_3), 4.96 (s, H-7), 5.17 (s, CH_2-N-1), 5.26 (s, CH_2N-3), 6.10 (s, H-5), 7.25 (m, arom.).

1,3-*Dibenzyl-6-formyluracil*

A soln of **9** (38 nm, 0.10 mmol) in a mixture of 0.5 ml glacial AcOH, 0.40 ml water and two drops of HCl was heated to 100°. When the reaction was completed (TLC, 5 hr) the mixture was purified over a silica plate, yield 35 mg, 100%. IR: 1700, 1660 cm^{-1}. NMR δ 5.16 (s, CH_2-N-1), 5.50 (s, CH_2-N-3), 6.28 (s, H-5), 9.45 (s, aldehyde proton).

Preparation of **8a**

A soln of **3d** (36 mg, 0.1 mmol), MeOH (7.0 mg, 0.22 mmol) and triethylamine (0.020 ml) in 1.0 ml benzene was heated at 110° during 10 hr (sealed tube). The mixture was filtered, the filtrate evaporated to dryness and the residue purified on a silica-plate (EtOAc/cyclohexane 1:1). Diazepine **8a** was isolated in 83% yield.

8a: oil (slightly coloured). IR: 1700, 1670, 1640 cm^{-1} NMR δ 2.82 (s, OCH_3), 4.57, 4.86 (AB-system, J = 15, CH_2-N-1), 4.94, 5.40 (AB-system, J = 14, CH_2-N-3), 4.66 (d × d, J(5-7) = 1.5, J(H-F) = 13, H-7), 5.85 (d × d, J(5-7) = 1.5, J(H-F) = 13, H-5).

Preparation of **8b**

A soln of **3d** (36 mg, 0.1 mmol) and 0.020 ml triethylamine in 1.0 ml t-BuOH was heated at 110°. After 1.5 hr the mixture was evaporated to dryness and the residue purified on a silica-plate. **8b** was isolated as a colourless oil; IR: 1700, 1670, 1640 cm^{-1}; NMR δ 1.00 (s, otBu), 4.42 (AB-system, J = 15, CH_2-N-1), 5.72 (D × D, J(5-7) = 1.5, J(H-F) = 13, H-5).

Reduction of dichlorocarbene adduct **3a** *with tri-n-butyltinhydride*

A mixture of **3a** (108 mg, 0.30 mmol) and 0.16 ml tri-n-butyltinhydride (0.60 mmol) was heated at 135° during 3 hr. An additional 0.106 ml tri-n-butyltinhydride was added and the mixture heated at 135° for another 3 hr. The resulting mixture was separated by thick-layer chromatography (silica, EtOAc/cyclohexane 1:2) and the resulting 3 fractions purified by preparative

TLC, yields **10a** (12 mg, 12%), **11a** (18 mg, 21%), **12a** (7 mg, 8%).

10a: IR: 1720, 1680 cm^{-1}. NMR δ 2.43 (d × d, J(5-6) = 9, J(5-7) = 3.5, H-5), 2.79 (d × d, J(6-7) = 2, H-7), 3.11 (d × d, H-6), 4.68, 4.79 (AB-system, J = 15, CH_2-N-1), 4.95 (s, CH_2-N-3).

11a: IR: 1710, 1670. NMR δ 3.05 (d, J = 7, C-5 methylene), 4.71, 5.02 (N-1, N-3 CH_2), 5.51 (q, J = 7, H-6), 6.00 (d, J = 7, H-7), 7.2 (arom.).

12a; IR: 1720, 1700, 1670, 1640 cm^{-1}. NMR δ 3.63 (d, J = 7, C-7 methylene), 4.58, 5.12, (CH_2-N-1 and N-3), 6.12 (d, J = 10, H-5), 6.47 (d × t, H-6), 7.3 (m, arom.).

Reduction of chlorofluorocarbene adduct **3d** *with tri-n-butyltinhydride*

A soln of **3d** (40 mg) and tri-n-butyltinhydride (0.1 ml) in 2.0 ml toluene was reflexed under N_2 for 60 hr. After evaporating the solvent, the residue was purified over a silica-plate (EtOAc/cyclohexane 1:3). **11b** was isolated, slightly contaminated with **12b**, yield 35 mg (96%).

11b: IR: 1710, 1670 cm^{-1}. NMR δ 3.30 (d, J(H-F) = 16, C-5 methylene), 4.68 (s, CH_2-N-1), 5.03 (s, CH_2-N-3), (d, J(H-F) = 3, H-7).

Reduction of dibromocarbene adduct **3b** *with tri-n-butyltinhydride*

A soln of **3b** (46 mg, 0.10 mmol) and tri-n-butyltinhydride (0.053 ml, 0.20 mmol) in 5 ml benzene was refluxed for 18 hr. Chromatographic purification yielded **11a** (13 mg, 43%).

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