Tetrahedron Letters No. 31, pp 2685 - 2688, 1975. Pergamon Press. Printed in Great Britain.

SILVER ION ASSISTED HYDROLYSIS OF 5,5-DICHLOROTETRACYCLO-$[5.3.1.1.^{3,9}0^{4,6}]$DODECANE.[1] A NOVEL γ-LACTONE FORMATION

Tadashi Sasaki,* Shoji Eguchi, and Masato Mizutani
Institute of Applied Organic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464, Japan

(Received in Japan 8 March 1975; received in UK for publication 16 June 1975)

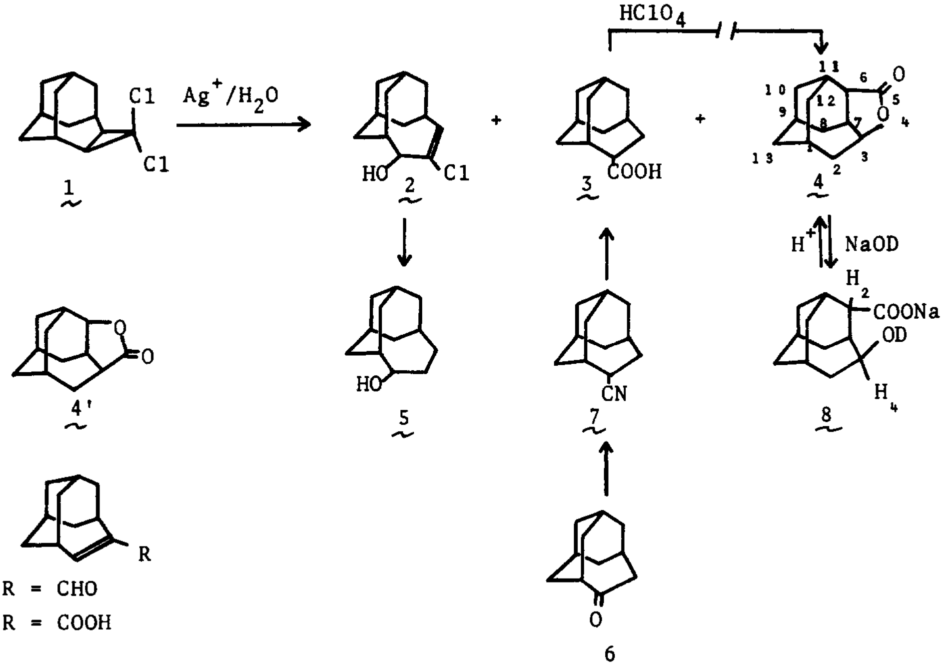
In recent years there has been considerable interest in the ring-opening reactions of constrained halocyclopropane derivatives because of their utility for the synthesis of certain *trans*-cycloalkenes,[2] bridgehead olefins,[3] and for angular carboxylation *via* cyclopropanone derivatives.[4] We report here the ring-opening reaction of 5,5-dichlorotetracyclo$[5.3.1.1.^{3,9}0^{4,6}]$dodecane (**1**),[5] a dichlorocarbene adduct of 4-homoadamantene as one of the most geometrically constrained 8,8-dihalobicyclo[5.1.0]octane system for both favored and unfavored modes of the ring-opening,[2a] in which a novel γ-lactone formation was observed.

In contrast to the reported facile Ag^+ promoted solvolytic ring-expansion of 8,8-dihalobicyclo[5.1.0]octane to *trans*-2-halo-3-hydroxycyclooctene,[2] solvolysis of **1** proceeded under much vigorous conditions. Thus, on refluxing in aqueous dioxane containing $AgBF_4$ **1** afforded three major products **2**-**4** after chromatography (silica gel-$CHCl_3$)(Scheme and Table). Compound **2**, mp 106-107.5°[6] was characterized as 5-chloro-1,1-bishomoadamant-5-ene-4-ol, a ring-expansion product on the basis of mass spectral ion peaks at *m/e* 214 and 212 (35:100) and nmr ($CDCl_3$, 60MHz) signals at δ 6.32 (d, *J*=12.3 Hz, 1H), 3.94 (d, *J*=4.5 Hz, 1H), 2.38 (s, 1H, OH), and 2.8-1.4 (m, 14H), and of conversion to 1,1-bishomoadamantanol **5**[7] on catalytic hydrogenation (10%Pd-C). The second product **3**, mp 122-126° was 4-homoadamantanecarboxylic acid based on the spectral data and an alternative synthesis from 4-homoadamantanecarbonitrile (**7**), mp 165-169° which was prepared by the cyanation of 4-homoadamantanone (**6**) with *p*-tosylmethylisonitrile in 37% yield.[8] Product **4**, mp 262-265° was a γ-lactone and was assigned as 4-oxatetracyclo[7.3.1.0.^{3,7}0^{6,11}]tridecan-5-one from the following data: *m/e* 192(M^+, 8%), 176(10), and 148(100); ir (KBr) 1778 cm^{-1}; nmr ($CDCl_3$) δ 4.79 (d, d, *J*=7.5 and 5.7 Hz, 1H), 3.15-2.47 (m, 2H), and 2.6-1.2 (m, 13H). On addition of $Eu(dpm)_3$[9] [$Eu(dpm)_3$/**4** =0.223] the spectrum revealed signals at δ 6.05 (d, d, *J*=7.8 and 5.3 Hz, 1H), 4.73 (d, d, *J*=7.2 and 5.8 Hz, 1H), 4.31-3.10 (m, 4H), and 3.05-1.60 (m, 10H), suggesting structure **4** or **4'** (Scheme). The location of an OH function at C_4 of homoadamantane skeleton was indicated by the nmr spectrum of sodium salt **8** (ν_{CO}1570 cm^{-1}) derived from **4** in D_2O-NaOD, which had signals at δ (H_2O reference) 3.59 (t, d, *J*=9.0 and 1.5 Hz, 1H), 2.54 (broad t, *J*=4 Hz, 1H), and 2.49-0.9 (m, 14H); the coupling pattern of the signal at δ 3.59 assignable to H_4 of **8** was very similar to that of C_4H signal of 4-homoadamantanol (δ 3.89, t, d, *J*=8.5 and 2.0 Hz) but quite different from that of C_2H signal of 2-adamantanol (δ 3.75, broad t, *J*=4 Hz),[10] while the signal at δ 2.54 assignable to H_2 was similar to C_2H of 2-adamantanecarboxylic acid (δ 2.68, broad t, *J*=3.5 Hz) and different from that of C_4H of **3** (δ 2.23, t, d, *J*=9.0 and 1.8 Hz). On acidification **8** was converted to the same γ-lactone **4**, indicating no occurrence of isomerization or skeletal rearrangement during the alkaline hydrolysis. Furthermore, pyrolysis of **8** with soda lime at 320° gave 4-homoadamantanol on glc analysis, supporting the assigned structure **4**.

The relative yields of **2**-**4** were considerably depending on the hydrolysis conditions (Table). The fact that the use of aqueous dioxane of higher water content favors the formation of **3** and **4**, and the use of perchlorate instead of fluoroborate favors the formation of **4** indicates clearly a very slow ring-opening of **1** possibly *via* a half-opened cyclopropylcation intermediate:[11,12] the reaction of water as a nucleophile with the cationic intermediate can give rise to afford **3** *via* the corresponding cyclopropanone or its equivalent.[4] The γ-lactone **4** could be produced *via* unsaturated aldehyde **9** and/or acid **10** followed by 1,2-Wagner-Meerwein rearrangement under the acidic hydrolysis conditions (formation of HBF_4 or $HClO_4$).[13,14] In fact, **9** and **10**[15] were detectable in the hydrolysis products (glc) as very minor components and furthermore, both **9** and

10 produced 4 under the hydrolysis conditions, while 3 did not, supporting above mechanism.

Almost exclusive formation of 4 with $AgClO_4$ from 1 might be of interest from both synthetic and mechanistic view points.



Scheme

TABLE Products of Ag^+ Assisted Hydrolysis of 1 under Various Conditions

Ag salt	Ag^+/1 (mol/mol)	Diox./H_2O (vol%)	Conc. M x 10^{-1}	React. time,hr[a]	Total yield,%[b]	Product ratio,%[c] 2	3	4	others
$AgBF_4$	4.9	95	1.1	35	66	45	36	19	d
$AgBF_4$	10	95	0.3	14	57[e]	46	10	33	f
$AgBF_4$	3.0	90	1.0	72	25	0	29	71	d
$AgClO_4$	3.0	98	0.8	17	34	11	2	87	d
$AgClO_4$	2.4	96	0.6	48	88[e]	1	13	74	f
$AgClO_4$	3.0	96	0.5	15	51	0	1	99	d

[a] Under refluxing. [b] Isolated yield. [c] Glc analysis. [d] Not identified. [e] Conversion. [f] 9 and 10 were detectable among complex mixtures (ca.11-12%) of other minor products.

REFERENCES AND FOOTNOTES

1. Synthesis of Adamantane Derivatives. XXIX. Part XXVIII: T. Sasaki, S. Eguchi, F. Hibi and O. Hiroaki, *J. Org. Chem.*, **40**, 845 (1975).
2. (a) C. B. Reese and A. Shaw, *J. Amer. Chem. Soc.*, **92**, 2566 (1970); (b) M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 4637 (1971).
3. (a) P. Warner, J. Fayos and J. C. Clardy, *ibid.*, 4473 (1973); (b) C. B. Reese and M. R. D. Stebles, *Chem. Commun.*, 1231 (1972); (c) P. Warner, R. LaRose, C.-m. Lee and J. C. Clardy, *J. Amer. Chem. Soc.*, **94**, 7607 (1972).
4. (a) J. T. Groves and K. W. Ma, *Tetrahedron Lett.*, 909 (1974); (b) D. B. Ledlie, J. Knetzer and A. Gitterman, *J. Org. Chem.*, **39**, 708 (1974).
5. T. Sasaki, S. Eguchi and M. Mizutani, *Org. Prep. and Proc. Int.*, **6**, 57(1974).
6. All melting points were measured in sealed tube and are corrected. All new compounds gave satisfactory analysis.
7. T. Sasaki, S. Eguchi, T. Toru and K. Itoh,*J. Amer. Chem. Soc.*,**94**,1357(1972).
8. *Cf.* O. H. Oldenziel and A. M. van Leusen, *Tetrahedron Lett.*, 1357 (1973).
9. A. F. Cockerill, G. L. O. Davies, R. C. Harden and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).
10. F. W. van Deursen and P. K. Korver, *Tetrahedron Lett.*, 3923 (1967); G. Snatzke and D. Marquarding, *Chem. Ber.*, **100**, 1710 (1967).
11. P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust and K. Fellenberger, *J. Amer. Chem. Soc.*, **94**, 125 (1972); W. F. Sliwinski, T. M. Su and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972).
12. The ring-opening of **1** to **2** is expected to suffer a considerable strain increase; the calcd. strains for homoadamantane and 1,1-bishomoadamantane are 14.6 and 23.5 kcal/mol(Engler force field) respectively:E. M. Engler, J. D. Andose and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973).
13. *Cf.* C. B. Reese and M. R. D. Stebles, *Tetrahedron Lett.*, 4427 (1972).
14. *Cf.* J. E. Nordlander, F. Y.-H. Wu, S. P. Jindal, J. B. Hamilton, *J. Amer. Chem. Soc.*, **91**, 3962 (1969); P. v. R. Schleyer, E. Funke and S. H. Liggero, *ibid.*, **91**, 3965 (1969).
15. Compounds **9** (2,4-dinitrophenylhydrazone, mp 276-277°) and **10**, mp 147-149° were prepared from **3** *via* 4-hydroxy-4-homoadamantanecarboxylic acid.