CHEMISTRY LETTERS, pp. 649-652, 1975. Published by the Chemical Society of Japan

FACILE FORMATION OF TRICYCLO[4.4.1.$0^{3,8}$]UNDECANE RING SYSTEM FROM 2,4-DEHYDROHOMOADAMANTANE

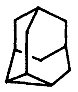
Ryohei YAMAGUCHI and Mituyosi KAWANISI
Department of Industrial Chemistry, Faculty of Engineering
Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

Treatment of 2,4-dehydrohomoadamantane (1) with excess iodine or bromine and silver acetate in acetic acid afforded exo,exo-4,9-diacetoxytricyclo-[4.4.1.$0^{3,8}$]undecane (3) and endo,exo-4,9-diacetoxytricyclo[4.4.1.$0^{3,8}$]undecane (4) as major reaction products.

2,4-Dehydrohomoadamantane (1) is one of cage compounds which containe a strained cyclopropane ring in their frameworks. Since 1 had become available in quantities,1) we have examined reactions of 1 and found that 1 can be transformed into 2-mono- and 2,4-di-substituted homoadamantanes,2) in which a radical type cleavage of the cyclopropane ring of 1 is a key step. In this communication we wish to report a cationic cleavage which gives rise to a novel skeletal rearrangement to the titled ring system.

To a solution of 1 (1.0 g; 6.8 mmol) in acetic acid (42 ml) were added successively iodine (1.8 g; 7.0 mmol) and silver acetate (2.8 g; 16.8 mmol) at room temperature with vigorous stirring. After 1 hr, an additional iodine (1.8 g) and silver acetate (2.8 g) were added to the reaction mixture. The mixture was stirred at 80-90°C for 2 hr and the precipitates were removed off by filtration. Usual work-up (neutralization, extraction, and evaporation) gave an oily material, which was chromatographed on silica gel to afford three diacetates in 59% yield (Table). When bromine was used in place of iodine, the same diacetates were obtained in 56% yield (Table). The major two diacetates, 3 (mp 124-126°C)3) and 4 (140°C/0.1 mmHg), were deduced

Table. The Reaction of 1 with Halogen and Silver Acetate



1

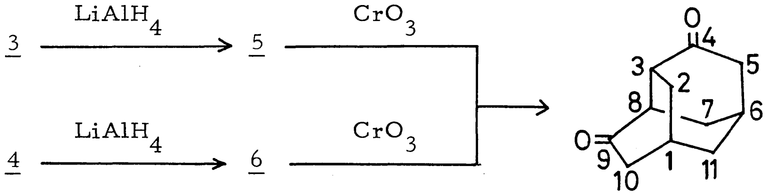
$\xrightarrow[\text{AcOH}]{X_2,\ \text{AgOAc}}$ 2 + 3 + 4

X	Yield (%) a)	Distribution (%) b)		
		2	3	4
I	59	8	38	54
Br	56	10	54	36

a) Isolation yield.
b) Determined by glc (HVSG, 150°C).

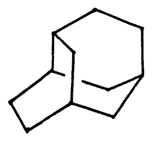
to be exo,exo-4,9-diacetoxytricyclo[4.4.1.0^{3,8}]undecane and endo,exo(exo,endo)-4,9-diacetoxytricyclo[4.4.1.0^{3,8}]undecane, respectively, by the following evidences, although the structure of 2 has not been determined yet.

Reduction of 3 and 4 with $LiAlH_4$ gave the diols, 5 (mp 231-233°C) and 6 (mp 222-224°C), respectively. Subsequent oxidation of each 5 and 6 with chromic anhydride in acetic acid afforded the same diketone (7) as a sole reaction product (Scheme 1). The structure of 7 was determined to be tricyclo[4.4.1.0^{3,8}]undecane-4,9-dione by the following chemical, spectral, and analytical results: (i) molecular formula, $C_{11}H_{14}O_2$ (MS spectrum and elemental analysis); (ii) IR: 1720 cm^{-1} ^{1}H-nmr: no olefinic proton; (iii) H-D exchange under mild conditions (D_2O/dioxane, K_2CO_3 at reflux temp.), an introduction of four deuterium atoms indicating the presence of two CH_2 groups adjacent to the C=O groups; (iv) ^{13}C-nmr: $\delta(CDCl_3)$ 212.6(2C=O) 46.1(2CH) 44.8(2CH_2) 41.5(CH_2) 30.5(2CH) 28.5(2CH_2), this spectrum strongly suggests that 7 belongs to C_2 symmetry; (v) Wolff-Kishner reduction gave a hydrocarbon $C_{11}H_{18}$ (8, mp 183-185°C) identical with the authentic tricyclo[4.4.1.0^{3,8}]undecane $^{4)}$ in comparison with 100 MHz ^{1}H-nmr spectra.



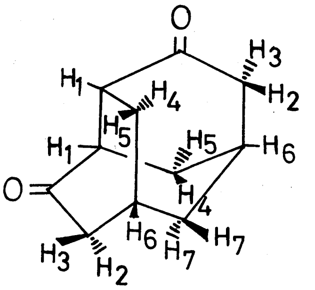
7

Scheme 1



8

Tricyclo[4.4.1.0^{3,8}]undecane-4,9-dione can accomodate itself to the above observed results. Furthermore, in order to confirm the structure of 7 we have examined ^{1}H-nmr shift experiment using $Eu(fod)_3$ (Fig. 1). This result is consistent with that expected from the inspection of Dreiding model of 7. $^{5)}$



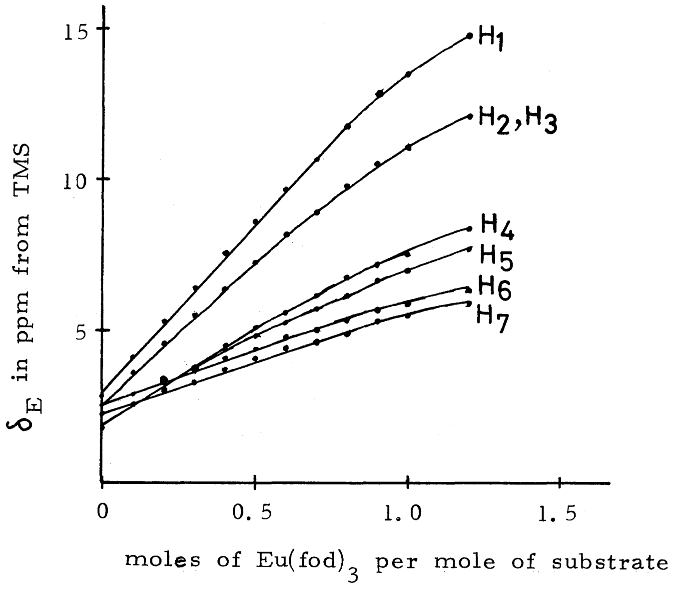


Fig. 1. Variation of Chemical Shift, δ_E, with molar ratio of $Eu(fod)_3$/substrate for 7 in $CDCl_3$ solution.

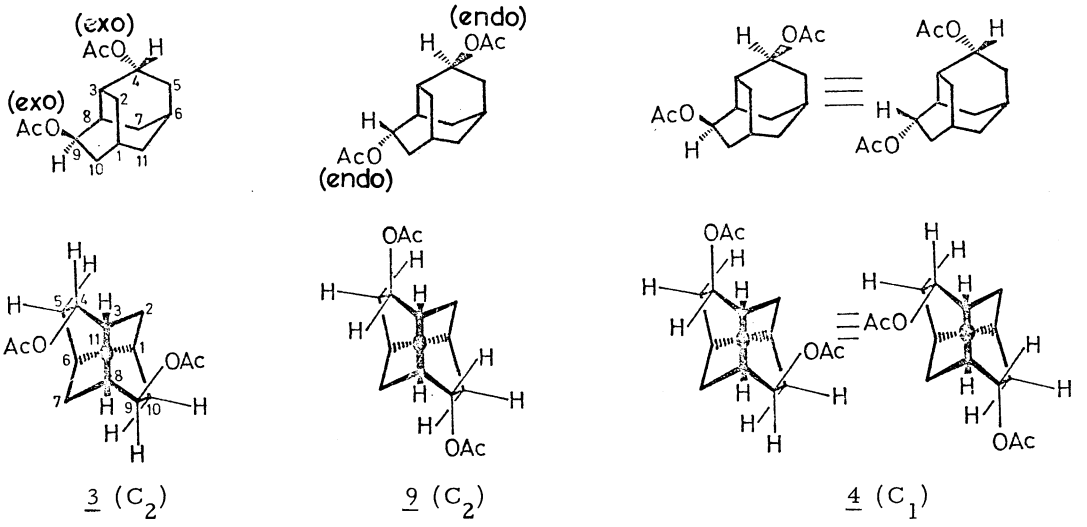
The diketone 7 was reduced ($LiAlH_4$/THF), followed by acetylation (Ac_2O/pyridine) to give a new diacetate (9, mp 101-103°C) as a major product, along with a small amount of 3 and 4

(Scheme 2). The mixture of 3, 4, and 9 were reduced, followed by oxidation to give 7; this proves that no skeletal rearrangement takes place through the above chemical transformations.

$$7 \underset{CrO_3}{\overset{LiAlH_4}{\rightleftarrows}} \underset{LiAlH_4}{\overset{Ac_2O/Py}{\rightleftarrows}} \begin{array}{ccccc} 9 & + & 3 & + & 4 \\ (79 & : & 3 & : & 18) \end{array}$$

Scheme 2

Each of the ^{13}C-nmr spectra of 3 and 9 showed 8 kinds of signals, while that of 4 showed 13 kinds of signals;⁶⁾ this implies that 3 and 9 belong to C_2 symmetry, while 4 does not. Among three possible stereoisomeric diacetates (optical isomers are excluded),⁷⁾ *exo,exo*- and *endo,endo*-4,9-diacetoxytricyclo[4.4.1.$0^{3,8}$]undecanes belong to C_2 symmetry, while *endo,exo*(or *exo,endo*)-4,9- isomer does not (Fig. 2). Therefore, the structure of 4 can be determined to be *endo,exo*-4,9-diacetoxytricyclo[4.4.1.$0^{3,8}$]undecane. Moreover, on the basis of their ^{1}H-nmr spectra 3 and 9 are deduced to be *exo,exo*- and *endo,endo*-4,9-diacetoxytricyclo[4.4.1.$0^{3,8}$]-undecanes, respectively.⁸⁾



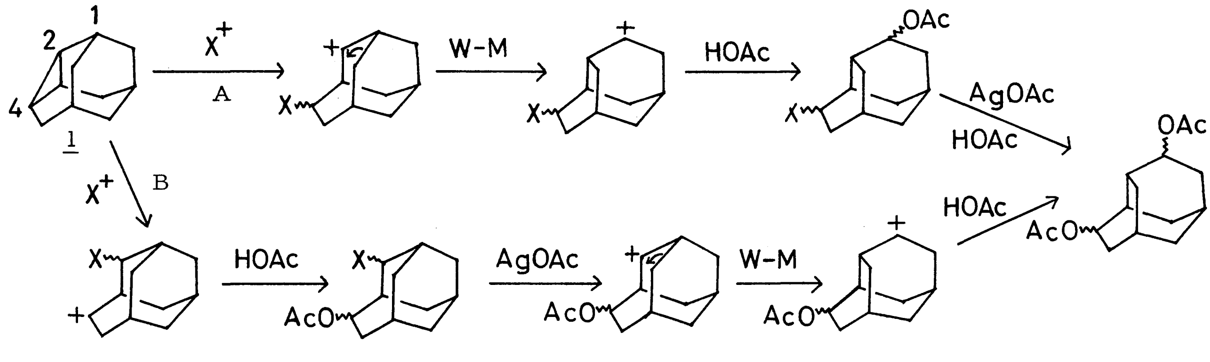
3 (C_2) 9 (C_2) 4 (C_1)

Fig. 2. Projections of Stereoisomeric 4,9-Diacetoxytricyclo[4.4.1.$0^{3,8}$]undecanes

We tentatively construct the reaction pathway as is shown in Scheme 3. It is reasonable to think that the reactive species in this reaction is halonium ion, *i.e.* iodonium or bromonium ion, which is generated *in situ* by the action of halogen with silver acetate.⁹⁾ Two reaction pathways (A and B) may be possible; in path A halonium ion attackes the cyclopropane ring on the 4 position, while in path B on the 2 position. Although it is not clear which pathway the reaction follows, tricyclo[4.4.1.$0^{3,8}$]undecane ring system may be probably produced through a Wagner-Meerwein type rearrangement of 4-substituted 2-homoadamantyl cation into 9(4)-substituted tricyclo[4.4.1.$0^{3,8}$]undec-4(9)-yl cation. However, nothing about the behavior of 2-homoadamantyl cation has been known yet. Further investigation on this point is currently in progress. In addition, the present reaction provides a novel and facile method of preparation of tricyclo[4.4.1.$0^{3,8}$]undecane ring system, only one synthesis of which has been disclosed.⁴⁾

The authors are indebted to Professor C. A. Cupas and Dr. W. C. Schumann, Case

Western Reverse University, for providing ^{1}H-nmr spectra of 8 and related compounds, and also to Dr. T. Imagawa for helpful discussion.



Scheme 3

References and Footnotes

1) R. Yamaguchi, T. Katsushima, T. Imagawa, and M. Kawanisi, Synth. Comm., 83 (1974). R. Yamaguchi, T. Katsushima, and M. Kawanisi, Bull. Chem. Soc. Japan, 47, 2830(1974).

2) R. Yamaguchi, T. Katsushima, and M. Kawanisi, *ibid.*, submitted for publication.

3) All new compounds gave satisfactory elemental analyses and consistent IR, ^{1}H-nmr, and MS spectra.

4) C. A. Cupas, W. E. Heyd, and M.-S. Kong, J. Amer. Chem. Soc., 93, 4623 (1971).

5) Another possibility that 7 would be tricyclo[4.4.1.0^{3,8}]undecane-5,10-dione can be ruled out, because Dreiding model investigation tells us that this structure is inconsistent with the observed result of ^{1}H-nmr shift experiment.

6) Data of the ^{13}C-nmr spectra of 3, 4, and 9 are as follows; 3, δ(CDCl$_3$) 170.5(2C=O) 73.9 (2CHOAc) 45.4(CH$_2$) 36.8(2CH$_2$) 30.3(2CH) 28.0(2CH) 27.1(2CH$_2$) 21.4(2CH$_3$). 4, δ(CDCl$_3$) 170.4(2C=O) 73.8(CHOAc) 72.7(CHOAc) 46.1(CH$_2$) 36.9(CH$_2$) 35.9(CH$_2$) 34.0(CH) 31.5(CH) 30.0(CH) 27.8(CH) 27.1(CH$_2$) 24.4(CH$_2$) 21.3(2CH$_3$). 9, δ(CDCl$_3$) 170.5(2C=O) 72.8(2CHOAc) 46.9(CH$_2$) 36.2(2CH$_2$) 35.4(2CH) 29.9(2CH) 24.5(2CH$_2$) 21.3(2CH$_3$).

7) *Endo,exo*- and *exo,endo*-4,9-diacetoxytricyclo[4.4.1.0^{3,8}]undecane are equivalent to each other, as is shown in Fig. 2.

8) ^{1}H-nmr spectra of 3 and 9 showed half-band widths of 12 and 21 Hz assignable to the methine protons at the 4(9) positions, respectively. Dreiding model investigation as well as Williamson-Johnson equations (K. L. Williamson and W. S. Johnson, J. Amer. Chem. Soc., 83, 4623 (1961)) suggest that *endo*-proton at the 4(9) position must have a half-band width of ca. 10 Hz and *exo*-proton at the same position must have a half-band width of ca. 20 Hz.

9) It has been well known that the reaction of iodine with silver acetate generates a very reactive electrophilic species, I^+OAc^-, which attacks olefinic function (R. B. Woodward and F. V. Brutcher, Jr., J. Amer. Chem. Soc., 80, 209 (1958) and references cited therein). As to the first example that iodonium ion cleaves a strained cyclopropane ring, see the following report; A. C. Udding, J. Strating, and H. Wynberg, Tetrahedron Lett., 1345 (1968).

(Received May 20, 1975)