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Solvolytic Rearrangement of 5,6-Polymethylenebicyclo[4.2.0]octan-2-cl Derivatives to Functionalized Polymethylenebicyclo[3.2.1] - and [3.3.0]octanes Masaki UE, \* Teruhisa NAGASHIMA, Masahiko KINUGAWA, Kiyomi KAKIUCHI, Yoshito TOBE, Yoshinobu ODAIRA, Masahide YASUDA, <sup>†</sup> and Kensuke SHIMA <sup>†</sup> Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565 <sup>†</sup> Department of Industrial Chemistry, Faculty of Engineering, Miyazaki University, 7710 Kumano, Miyazaki 889-21

> The functionalized polymethylenebicyclo[3.2.1]- and [3.3.0]octane derivatives are newly synthesized from <u>endo</u>- and <u>exo</u>-5,6-polymethylenebicyclo[4.2.0]oct-2-yl 3,5dinitrobenzoates by skeletal rearrangement using solvolysis.

Recently, much attention has been paid on the natural products having bicyclo[3.2.1]- or [3.3.0]octane ring system as a key structure because of their unique carbon skeletons and biological activities. <sup>1)</sup> We have studied on the facile construction of the basic frameworks of polyquinane sesquiterpenes by the acid-catalyzed rearrangement of trimethylenebicyclo[4.2.0]octane derivatives.<sup>2)</sup> In this connection, we describe herein novel construction of the functionalized bicyclo[3.2.1]- and [3.3.0]octane ring systems by solvolytic rearrangement of the <u>endo-</u> and <u>exo-cis, cis-5,6-polymethylenebicyclo[4.2.0]oct-2-yl 3,5-dinitro-benzoates la-c and 2a-c.</u>



1a, b, c R<sup>1</sup>=ODNB, R<sup>2</sup>=H 2a, b, c R<sup>1</sup>=H, R<sup>2</sup>=ODNB 3a R<sup>1</sup>=OCO $\bigcirc$ Br, R<sup>2</sup>=H





 $\overset{\text{Ha}}{\underset{\text{5a}}{\text{,b},c}}$ ,  $\overset{\text{R}}{\underset{\text{c}}{\text{R}^{3}=\text{H}}}$ ,  $\overset{\text{R}}{\underset{\text{c}}{\text{R}^{4}=\text{ODNB}}}$  $\overset{\text{5a}}{\underset{\text{6a}}{\text{,b},c}}$ ,  $\overset{\text{R}}{\underset{\text{c}}{\text{R}^{3}=\text{OH}}}$ ,  $\overset{\text{H}}{\underset{\text{c}}{\text{R}^{4}=\text{H}}}$ 





b,c

9a.b.c

. R6

 $R^5 = ODNB, R^6 = H$ 

l1a,b,c ∼~~~~ The <u>endo</u>- and <u>exo</u>-benzoates 1 and 2 were easily prepared from the corresponding alcohols,  $\frac{4}{4}$  and their stereochemistry was determined on the basis of our previous work<sup>5</sup> and the X-ray analysis of <u>endo</u>-p-bromobenzoate 3a.<sup>6</sup>

Solvolytic rearrangements of 1a-2c were carried out in 50% (v/v) aqueous dioxane at 160 °C except for 2a at 150 °C. As for the rates of hydrolysis,<sup>7</sup>) no marked difference was observed between 1 and 2. The product distribution is shown in Table 1.<sup>8)</sup> The <u>endo</u>-benzoates 1a-c gave the bicyclo[3.3.0]octane derivatives 7-10 mainly. Although the content of unidentified olefins increased case of higher homologues, the <u>exo</u>-benzoates the in 2a-c gave the bicyclo[3.2.1]octane derivatives 4-6 predominantly. This significantly high selectivity is explained on the ground of the principle of stereoelectronic Namely, in the series of endo-benzoates (1a-c), the central bond of control. the bicyclo[4.2.0]octane unit migrates preferentially, whereas in the case of exo-benzoates (2a-c) migration of the peripheral bond predominates because of the antiperiplanar alignment between the migrating bond and the leaving group.

Table	1.	Product	distribution	for	hydrolysis	of	3,5-dinitrobenzoates	1	and	2
					, ,		,	$\sim$		$\sim$

	Products/%									
Benzoate	4	5	<u>6</u>	Z	8	9	10	11	Others <sup>a)</sup>	Yield/%
1a 1b 1c 2a 2b 2c	- - 56 48 29	2 4 3 29 30 19	22 6 1	19 24 34 - -	44 8 20 - 2	17 27 16 - 1 3	10 9 10 -	5 5 3 5 5 12	3 1 14 4 15 35	58 <sup>b)</sup> 92 93 84 82 90

a) Unidentified olefins.

b) A considerable amount of polymeric materials was obtained.

References

- For recent reviews, see: L. A. Paquette, Top. Curr. Chem., <u>119</u>, 1 (1984);
  E. Fujita and M. Node, Progress in the Chemistry of Natural Product, <u>46</u>, 77(1984).
- 2) Y. Odaira and K. Kakiuchi, Yuki Gosei Kagaku Kyokai Shi, <u>44</u>, 930 (1986).
- 3) All new compounds gave satisfactory spectral and analytical data.
- 4) Prepared by photocycloaddition of the corresponding bicyclic enones to ethylene followed by hydride reduction; see: M. Ue, K. Kobiro, K. Kakiuchi, Y. Tobe, and Y. Odaira, Chem. Lett., <u>1987</u>, 1903.
- 5) K. Kakiuchi, S. Kumanoya, M. Ue, Y. Tobe, and Y. Odaira, Chem. Lett., <u>1985</u>, 989.
- 6) Details will be reported elsewhere.
- 7) The rates of hydrolysis were measured by titrimetric method. The rate constants (50% aqueous dioxane at 150 °C) are as follows: 1a:  $6.99 \times 10^{-6} \text{ s}^{-1}$ ; 1b:  $3.28 \times 10^{-5} \text{ s}^{-1}$ ; 1c:  $1.62 \times 10^{-5} \text{ s}^{-1}$ . 2a:  $1.49 \times 10^{-5} \text{ s}^{-1}$ ; 2b:  $9.98 \times 10^{-5} \text{ s}^{-1}$ ; 2c:  $1.29 \times 10^{-5} \text{ s}^{-1}$ .
- The structure of solvolytic products were confirmed by transformation to suitable derivatives of which authentic samples were prepared independently.

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