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Solvolytic Rearrangement of 5,6-Polymethylenebicyclo[4.2.0]octan-2-ol Derivatives to Functionalized Polymethylenebicyclo[3.2.1]- and [3.3.0]octanes

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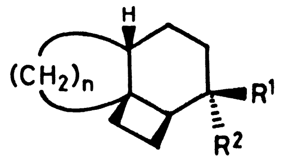
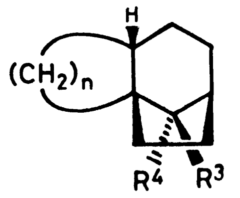
The functionalized polymethylenebicyclo[3.2.1]- and [3.3.0]octane derivatives are newly synthesized from *endo*- and *exo*-5,6-polymethylenebicyclo[4.2.0]oct-2-yl 3,5-dinitrobenzoates by skeletal rearrangement using solvolysis.

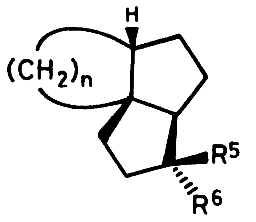
Recently, much attention has been paid on the natural products having bicyclo[3.2.1]- or [3.3.0]octane ring system as a key structure because of their unique carbon skeletons and biological activities.[1)] We have studied on the facile construction of the basic frameworks of polyquinane sesquiterpenes by the acid-catalyzed rearrangement of trimethylenebicyclo[4.2.0]octane derivatives.[2)] 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 *endo*- and *exo*-*cis*,*cis*-5,6-polymethylenebicyclo[4.2.0]oct-2-yl 3,5-dinitrobenzoates **1a-c** and **2a-c**.



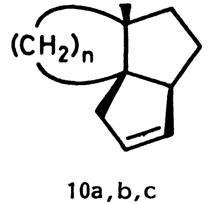
1a,b,c R^1=ODNB, R^2=H
2a,b,c R^1=H, R^2=ODNB
3a R^1=OCO⌬Br, R^2=H



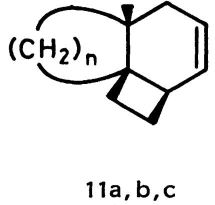
4a,b,c R^3=H, R^4=ODNB
5a,b,c R^3=H, R^4=OH
6a,b,c R^3=OH, R^4=H



7a,b,c R^5=ODNB, R^6=H
8a,b,c R^5=OH, R^6=H
9a,b,c R^5=H, R^6=OH



10a,b,c



11a,b,c

a: n=3, b: n=4, c: n=5
ODNB= 3,5-dinitrobenzoyl

The *endo*- and *exo*-benzoates **1** and **2** were easily prepared from the corresponding alcohols,[4)] and their stereochemistry was determined on the basis of our previous work[5)] and the X-ray analysis of *endo*-p-bromobenzoate **3a**.[6)]

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,[7)] no marked difference was observed between **1** and **2**. The product distribution is shown in Table 1.[8)] The *endo*-benzoates **1a**-**c** gave the bicyclo[3.3.0]octane derivatives **7**-**10** mainly. Although the content of unidentified olefins increased in the case of higher homologues, the *exo*-benzoates **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 control. Namely, in the series of *endo*-benzoates (**1a**-**c**), the central bond of 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**

Benzoate	Products/%									Yield/%
	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	Others[a)]	
1a	-	2	-	19	44	17	10	5	3	58[b)]
1b	-	4	22	24	8	27	9	5	1	92
1c	-	3	-	34	20	16	10	3	14	93
2a	56	29	6	-	-	-	-	5	4	84
2b	48	30	1	-	-	1	-	5	15	82
2c	29	19	-	-	2	3	-	12	35	90

a) Unidentified olefins.
b) A considerable amount of polymeric materials was obtained.

References

1) For recent reviews, see: L. A. Paquette, Top. Curr. Chem., 119, 1 (1984); E. Fujita and M. Node, Progress in the Chemistry of Natural Product, 46, 77(1984).

2) Y. Odaira and K. Kakiuchi, Yuki Gosei Kagaku Kyokai Shi, 44, 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., 1987, 1903.

5) K. Kakiuchi, S. Kumanoya, M. Ue, Y. Tobe, and Y. Odaira, Chem. Lett., 1985, 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: 6.99×10^{-6} s^{-1} ; **1b**: 3.28×10^{-5} s^{-1} ; **1c**: 1.62×10^{-5} s^{-1}.
2a: 1.49×10^{-5} s^{-1} ; **2b**: 9.98×10^{-5} s^{-1} ; **2c**: 1.29×10^{-5} s^{-1}.

8) The structure of solvolytic products were confirmed by transformation to suitable derivatives of which authentic samples were prepared independently.

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