Pergamon

Tetrahedron Letters, Vol. 35, No. 27, pp. 4793-4796, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)00961-9

Acid-catalyzed Rearrangement of Phenylsubstituted 1,3-Bishomocubanone *via* Several Equilibrating Non-classical Bicyclobutonium Ions

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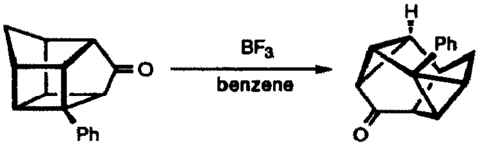
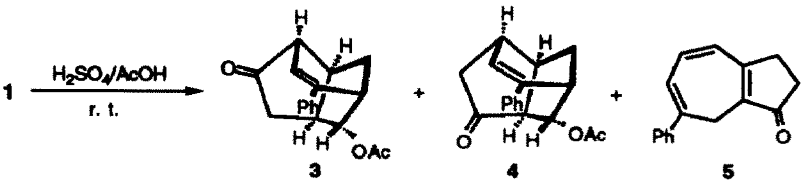
Abstract: 4-Phenylpentacyclo[5. 3. 0. $0^{2,5}$. $0^{3,9}$. $0^{4,8}$]decan-6-one in acetic acid undergoes H_2SO_4-catalyzed rearrangement to give two isomeric acetoxyketones having a novel tricyclo[5. 2. 1. $0^{4,8}$]dec-2-ene ring system besides a small amount of 2,3-dihydro-7-phenyl-1(8*H*)-azulenone. The formation of the acetoxyketones can best be accounted by assuming equilibration of several structurally different non-classical bicyclobutonium ion intermediates.

It is well documented that cubane and homocubane derivatives undergo Ag(I)-catalyzed skeletal reorganization to cuneane and its homologs.[1] The mechanism of these reactions is thought to involve carbocation intermediates,[2,3] and Ag(I) ion is generally considered to act as Lewis acid in these catalyzed rearrangement. Although simple 1,3-bishomocubane derivatives only undergo ring opening of cyclobutane rings to give dienes by Ag(I)-catalyzed reaction,[4] we recently showed that 4-phenylpentacyclo[5. 3. 0. $0^{2,5}$. $0^{3,9}$. $0^{4,8}$]decan-6-one **1** undergoes BF_3- or Ag(I)-catalyzed rearrangement to give a product having the cuneane-like structure **2** (eq 1).[5] We now wish to report more remarkable rearrangement caused by H_2SO_4 in AcOH of **1** to two isomeric products, **3** and **4**, having a novel tricyclo[5. 2. 1. $0^{4,8}$]dec-2-ene ring system besides a small amount of 2,3-dihydro-7-phenyl-1(8*H*)-azulenone **5** (eq 2). The formation of **4** seems somewhat apprehensible since its structure is easily correlated to that of **2**, whereas the formation of **3** is particularly unusual because of unexpected 1,2-migration of the carbonyl group. Furthermore, interconversion of **3** and **4** were observed at elevated temperature. These anomalous phenomena can only be



1 **2**

(1)



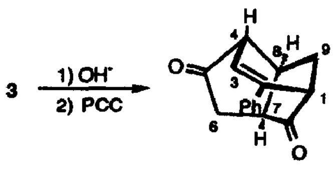
3 **4** **5**

(2)

rationalized by a mechanism in which several equilibrating non-classical bicyclobutonium ions are involved. These facts also support the non-classical cationic nature of the intermediates involved in the Ag(I)-catalyzed rearrangements of cubane and its homologs.

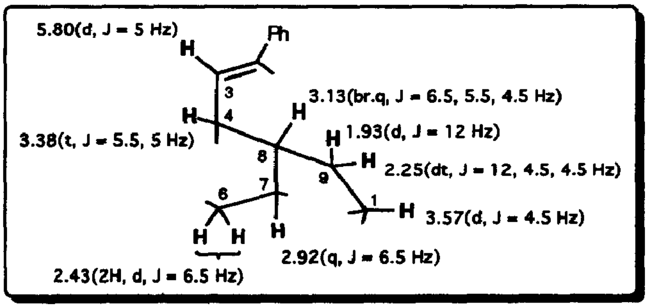
A solution of **1** (2.74 mmol) in acetic acid (5 ml) was treated with several drops of conc. H_2SO_4 at room temperature overnight and chromatographic separation of the products yielded compound **3** (mp 112–4°), **4** (mp 113–4°), and **5** (yellow liquid) in 35%, 28% and 6% yield, respectively. The IR and UV spectra of **3** [ν_{max} 1740, 1720 cm^{-1}; λ_{max}(cyclohexane) 254 nm (ε 12600)] and **4** [ν_{max} 1740, 1720 cm^{-1}; λ_{max}(cyclohexane) 249 nm (ε 12600)] are similar to each other, suggesting the presence of cyclopentanone ring, acetoxyl group and styrene chromophore in both the compounds.

Although the structures of **3** and **4** were finally determined through the analyses of 600 MHz ^{1}H NMR,[6] the unexplainable position of the carbonyl group in **3** was further proved by the following experiments. Alkaline hydrolysis of **3** followed by oxidation with PCC gave a diketone **6** (mp 94-7°, ν_{max} 1740 cm^{-1})(eq 3). ^{1}H NMR (200 MHz) of **6** displayed well resolved signals for all methylene and methine protons and analyses of these signals using decoupling technique led to the partial bond sequence of 8 skeletal carbon atoms shown below. This result, combined together with the fact that **6** has two cyclopentanone rings, exclusively establishes the structure of **6**.



6

(3)

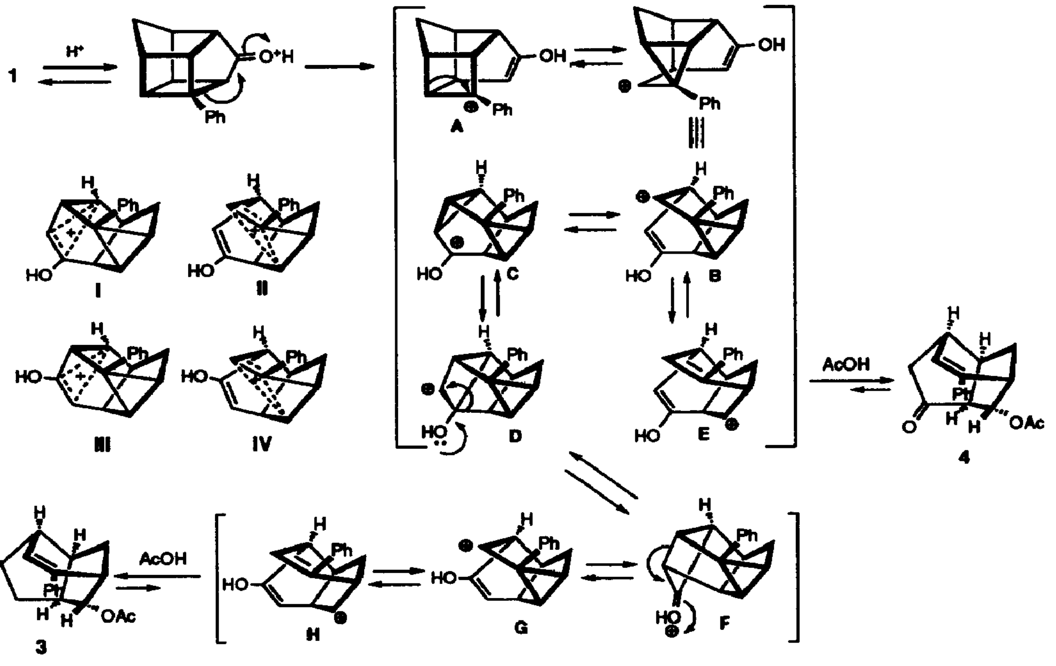


Treatment of the compound **2** with H_2SO_4 in acetic acid at room temperature gave a mixture of **3** and **4** in a ratio of 1:9 (eq 4), suggesting that **2** is not the common intermediate for the products of the reaction of **1**. Both **3** and **4** are unreactive when treated with H_2SO_4 in acetic acid at room temperature, whereas they interconvert to each other at higher temperature. Thus, upon treatment with H_2SO_4 in acetic acid at 70°C for 95 hours, pure **3** afforded a mixture of **3** and **4** in a ratio of 2:1, and pure **4** gave the mixture in a ratio of 1:3 (eq 5).

$$\mathbf{2} \xrightarrow[\text{r.t.}]{H_2SO_4/AcOH} \underset{10\%}{\mathbf{3}} + \underset{90\%}{\mathbf{4}} \qquad (4)$$

$$\mathbf{3} \underset{70\ {}^\circ C}{\overset{H_2SO_4/AcOH}{\rightleftarrows}} \mathbf{4} \qquad (5)$$

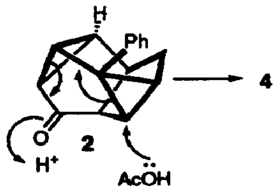
The transformation of **1** to **3** and **4** as well as the interconversion of the latters can be rationalized by



Scheme 1

assuming a series of carbocations as the common intermediates (Scheme 1). The initially formed cyclobutyl carbocation **A** rearranges to a series of carbocations **B**–**E**, which could actually be represented in the forms of non-classical bicyclobutonium ions[7] such as **I** and **II**, or a degenerate form of those cations having the positive charge delocalized more extendedly on the molecule. Being trapped by AcOH at the less hindered side in the form of **E**, the carbocations give the compound **4**. The cations also undergo a pinacol type rearrangement in the form of **D** to give a protonated cyclobutanone **F**, which in turn gives carbocations **G** and **H** by successive ring opening. Being trapped with acetic acid at the less hindered side of **H**, the carbocations thus formed give the compound **3**. It should be noted that **G** and **H** are strikingly similar to **B** and **E**, respectively, and hence can also be represented by non-classical formulations such as **III** and **IV**.

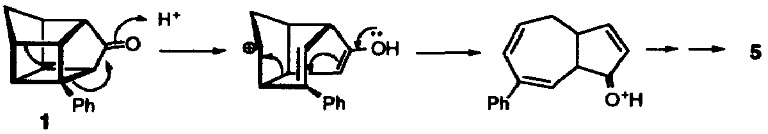
The formation of compound **2** in the reaction of **1** with BF_3 in benzene[5] can also be related to the non-classical cations system **A**–**H**, because deprotonation in the form of **C** is the only route to neutralize the positive charge of the cations in the absence of nucleophiles. On the contrary, **2** does not appear so much to enter the equilibrating cations system upon acid treatment, since, as noted above, it gives **4** much more favorably than expected from the cations system. This may be due to the fact that **2** can undergo concerted ring opening of the two cyclopropanes to give **4** before it gives the non-classical cations (Scheme 2). It seems likely that conversion of **2** to the non-classical cation **I** requires somewhat higher activation energy than the concerted transformation to **4** owing to partial bond reorganization and



Scheme 2

introduction of positive charge into the carbon skeleton.

The structure of compound **5** was determined by spectral data.[8] Its formation from **1** can be interpreted



Scheme 3

by the pathway shown in Scheme 3. This reaction path is independent of the carbocations **A–H**, since **5** was never obtained when **3** and **4** were interconverted.

Acknowledgment: The authors wish to express their thanks to Dr. M. Ueno, Tohoku University, and Mr. M. Kato, Niigata University, for the measurements of NMR spectra.

References and Notes

1. For reviews see: a) Paquette, L. A. *Synthesis*, **1975**, 347-357. b) Bishop III, K. C. *Chem. Rev*., **1976**, *76*, 461-486.
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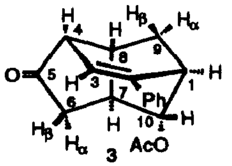
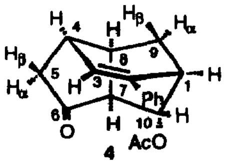
6. 600 MHz ^{1}H NMR Spectra of 3 and 4 (ppm)[a]

	 **3**	 **4**
C_1–H	3.03 (d, $J_{1,9\alpha}$ = 4.5 Hz)	2.99 (d, $J_{1,9\alpha}$ = 4.5 Hz)
C_3–H	5.76 (d, $J_{3,4}$ = 5 Hz)	5.71 (d, $J_{3,4}$ = 3.5 Hz)
C_4–H	3.14 (t, $J_{4,8}$ = 5.5 Hz, $J_{4,3}$ = 5 Hz)	3.12 (br.q, $J_{4,5\alpha}$ = 7 Hz, $J_{4,8}$ = 6 Hz, $J_{4,3}$ = 3.5 Hz)
C_5–H_α		2.52 (dd, $J_{5\alpha,5\beta}$ = 16.5 Hz, $J_{5\alpha,4}$ = 7 Hz)
C_5–H_β		2.21 (d, $J_{5\beta,5\alpha}$ = 16.5 Hz)
C_6–H_α	2.48 (dd, $J_{6\alpha,6\beta}$ = 20 Hz, $J_{6\alpha,7}$ = 10 Hz)	
C_6–H_β	2.59 (br. d, $J_{6\beta,6\alpha}$ = 20 Hz)	
C_7–H	2.78 (br. t, $J_{7,6\alpha}$ = 10 Hz, $J_{7,8}$ = 6.5 Hz)	2.73 (d, $J_{7,8}$ = 7.5 Hz)
C_8–H	2.99 (q, $J_{8,7}$ = 6.5 Hz, $J_{8,4}$ = 5.5 Hz, $J_{8,9\alpha}$ = 4.5 Hz)	3.06 (br.q, $J_{8,7}$ = 7.5 Hz, $J_{8,4}$ = 6 Hz, $J_{8,9\alpha}$ = 4.5 Hz)
C_9–H_α	2.22 (dt, $J_{9\alpha,9\beta}$ = 12 Hz, $J_{9\alpha,1}$ = $J_{9\alpha,8}$ = 4.5 Hz)	2.22 (dt, $J_{9\alpha,9\beta}$ = 11.5 Hz, $J_{9\alpha,1}$ = $J_{9\alpha,8}$ = 4.5 Hz)
C_9–H_β	1.82 (d, $J_{9\beta,9\alpha}$ = 12 Hz)	1.90 (d, $J_{9\beta,9\alpha}$ = 11.5 Hz)
C_{10}–H	4.77 (s)	5.04 (s)

a) *J* Values were determined with the aid of decoupling technique.

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8. **5**: IR ($CHCl_3$) 1680, 1610 cm^{-1}; UV (EtOH) 251(ε 19000), 331(ε 4500) nm; ^{1}H NMR (200 MHz, $CDCl_3$) 2.54(2H, br.t, *J* = 5 Hz, -CH_2-), 2.70(2H, br.t, *J* = 5 Hz, -CH_2-), 3.17(2H, s, -CH_2-), 6.49(1H, d, *J* = 6.5 Hz, =CH-), 6.68(1H, d, *J* = 11 Hz, =CH-), 6.88(1H, dd, *J* = 11, 6.5 Hz, =CH-), 7.25-7.65(5H, m, Ph).

(*Received in Japan* 7 *March* 1994; *accepted* 14 *April* 1994)