Tetrahedron Letters No.4, pp. 361-363, 1967. Pergamon Press Ltd. Printed in Great Britain.

REARRANGEMENTS OF THE BENZOBICYCLO[3.2.0] HEPTENYL TO THE 2-(2-INDENYL)ETHYL AND BENZOBICYCLO[2.2.1] HEPTENYL SYSTEMS

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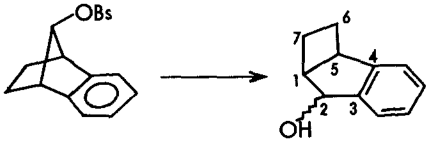
(Received 4 November 1966)

WE wish to report the isomerization of *anti*-2-benzo[3,4]bicyclo[3.2.0]heptenyl acetate (Ia-OAc) to 2-(2-indenyl)ethyl acetate (II) and *syn*-9-benzonorbornenyl acetate (III), an example of a new type of intramolecular rearrangement.

Hydrolysis of *syn*-7-norbornenyl *p*-toluenesulfonate gives predominantly *anti*-bicyclo[3.2.0]hept-3-en-2-ol (1). We observed that, in a similar fashion, hydrolysis of *syn*-9-benzonorbornenyl *p*-bromobenzenesulfonate in a 40 vol.% water - 60 vol.% acetone solvent with added $NaHCO_3$ at 120° for a week led quantitatively to a 98.6 : 1.4 mixture of *anti*-2-benzo[3,4]bicyclo[3.2.0]heptenol (Ia-OH) (its acetate has b.p. 109-110°/4 mm., n^{25}D 1.5335) and its *syn* epimer (Is-OH), m.p. 90-91°.[*1]



anti Ia-OH
syn Is-OH

Heating Ia-OAc in glacial acetic acid at 173° causes conversion to a mixture consisting of 98% the ring-opened II, b.p. 114-115° (2 mm.), and 2% the known III (2). The structure of II was established by comparison with an authentic sample, which was prepared by the modified Wittig reaction of 2-indanone with

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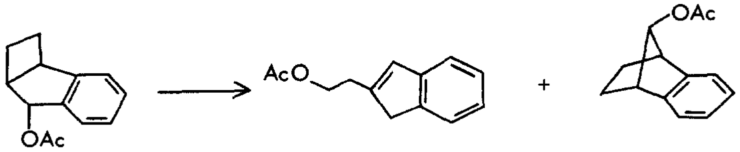
[*1] The structures of both compounds were principally determined by nmr spectra.[*2] Further, the Oppenauer oxidation of Ia-OH gave a benzylic ketone, $\lambda_{max}^{95\%\ EtOH}$ 246 mμ (ε 11600) and 293 (2250), $LiAlH_4$ reduction of which yielded a 1 : 99 mixture of Ia-OH and Is-OH. The reactions studied in this communication also confirm the structures.

[*2] Nmr of Ia-OH in CCl_4: 4 Ar.-H at τ 2.5-2.9 (m), 1 ϕCHOH at 5.34 (s), 1 C_5-H at ~6.3 (m), 1 C_1-H at ~7.2 (m), 2 $C_{6,7}$*exo*-H at 7.5-8.1 (m), and 2 $C_{6,7}$*endo*-H at 8.2-8.6 (m). Nmr of Is-OH in CCl_4: 4 Ar.-H at τ 2.6-3.0 (m), 1 ϕCHOH at 4.74 (d, $J_{1,2}$ = 7.1 cps), 1 C_5-H at ~6.5 (m), 1 C_1-H at ~6.7 (m), 4 $C_{6,7}$-H at 7.4-8.5 (m).

$(C_2H_5O)_2 \cdot P(O)CH_2COOC_2H_5$, followed by $LiAlH_4$ reduction and acetylation. The double bond in II was assigned by UV and nmr.



Ia-OAc II III

The conversion is much accelerated with the addition of $LiClO_4$ (a salt effect) or TsOH (acid catalysis), changing the product composition, as shown in Table I, but it does not proceed with heating in such aprotic solvents as acetic anhydride, benzene, dioxane, nitromethane, and acetonitrile. From the data in Table I, an extraordinarily large <u>b</u> value of 200 is obtained for the $LiClO_4$ addition from the linear salt effect equation, k = k° (1 + <u>b</u>[salt]) (3). These results are consistent with a carbonium ion mechanism.

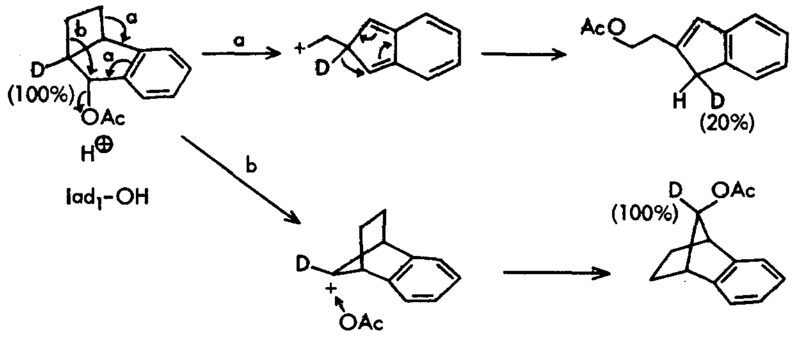
TABLE I
Isomerization of Ia-OAc in Acetic Acid

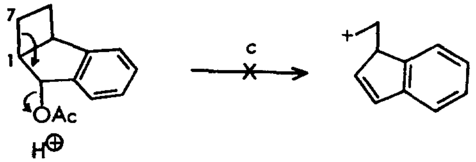
Added reagent	Temp. °C	$k_1 \times 10^5$	Product ratio II	III
None	173	8.4	98	2
0.5[M] NaOAc	173	8.6	98	2
0.001[M] $LiClO_4$	172	9.0		
0.005[M] $LiClO_4$	172	15.2	60	40
0.01[M] $LiClO_4$	173	24.7	29	71
0.5[M] $LiClO_4$	150			100
0.01[M] TsOH	173	140	42	58
0.01[M] TsOH [a]	173	6.5	>98	<2

[a] Solvent was acetic anhydride.

In order to investigate stereospecificity in this reaction, a labeled experiment was carried out. Hydrolysis of <u>syn</u>-9-benzonorbornenyl-9-d <u>p</u>-bromobenzenesulfonate (obtained in turn from $LiAlD_4$ reduction of 9-benzonorbornenone (2), followed by esterification) gave Iad_1-OH (d_1 = 100%). The product III from Iad_1-OAc had 100% deuterium at <u>anti</u>-C_9, while the deuterium content in II was only 20% at C_1.

Accordingly, all experimental findings could be accommodated by a mechanism pictured as follows:





Postulation of the carbonium ion intermediate of an isoindene type seems to be necessary for explanation of the path a which is prefered to the path c, the C_1-C_7 bond cleavage leading to a 2-(1-indenyl)ethyl derivative.[*3] Gain of resonance stabilization due to the isoindene[*4] may play a major role for the conversion.

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[*3] Absence of 2-(1-indenyl)ethyl acetate was demonstrated by vpc.

[*4] It has been suggested that isoindene has a Hückel delocalization energy (D.E.) of 1.95β (4,5).