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FORMOLYSIS OF PROTOILLUDYL CATION EQUIVALENTS
A NEW MODE OF REARRANGEMENT OF BICYCLO[4.2.0]OCT-2-YL CATION

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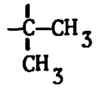
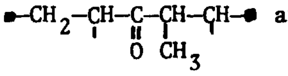
Illudoid sesquiterpenes[1] are suggested to be biosynthetically derived from humulene through protoilludyl cation A. It seemed therefore interesting for us to examine the fate of the chemically generated cation A. We wish to describe here solvolyses of the cation A equivalents 1, 2 and 3, which have been already synthesized by us[2].

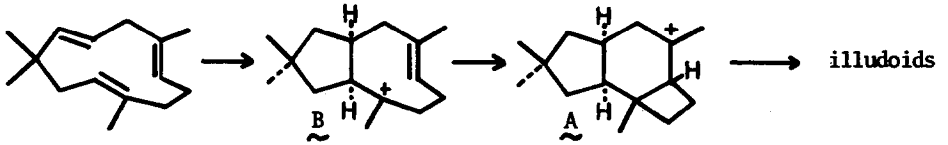
Treatment of the compounds 1, 2 and 3 in refluxing formic acid (30min) gave in 92% yield a mixture of rearranged products, i.e., tricyclic bridged formate 4 and tricyclic olefin 5, regardless the kind of the starting materials, in the same ratio (4/5 = 7/3)[3].

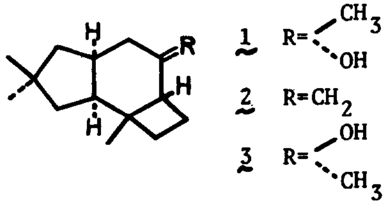
<u>Tricyclic bridged formate</u> 4[4]; m.p 48°~ 49°; nmr(CCl_4) δ0.88, 0.94, 0.99, 1.09 (each 3H, s), 4.64 (1H, d, J=1Hz), 8.10 (1H, d, J=1Hz); ir(nujol) 1750cm^{-1}; mass 250 (M^+), 204 (M^+-HCO_2H). Hydrolysis of the formate 4 with K_2CO_3 in MeOH and H_2O (3/1, r.t, 24hr) gave rise to the corresponding alcohol 6[4,5,6], which in turn was oxidized to a cyclopentanone 7[4,5,6] [ir(neat) 1740cm^{-1}] with the Jones reagent. Reduction of 7 with $NaBH_4$ in EtOH (0°, 2hr) afforded stereoselectively the original alcohol 6[7]. Therefore the endo configuration was assigned for the hydroxy group of 6.

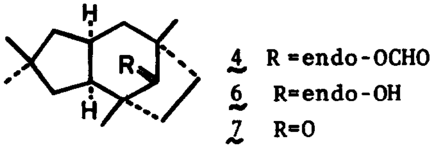
<u>Tricyclic olefin</u> 5[4,5]; nmr(CCl_4) δ0.90 (3H, d, J=6Hz), 0.99 (6H, s), 1.62 (3H, broad s, long range coupling with an olefinic proton at δ5.07), 5.07 (1H, m) ; ir(neat) 1653, 830cm^{-1}; mass 204 (M^+), 189 (M^+-CH_3). These spectral data showed

that partial structures $H-\overset{|}{\underset{|}{C}}-CH_3$, $H-\underset{|}{C}=\underset{|}{C}-CH_3$ and  $-\overset{|}{\underset{\underset{CH_3}{|}}{C}}-CH_3$ were contained in a tricyclic system and accordingly structure **5** was suggested. The structure **5** was confirmed by LIS nmr studies of a cyclopentanone **8** [ir(neat) 1742cm^{-1}], obtained from **5** by hydroboration-oxidation (aq. NaOH-H_2O_2) and subsequent Jones oxidation (75% from **5**). **8**; nmr(CCl_4) δ0.84 (3H, s), 0.99 (3H, d, J=6.5Hz), 1.02 (3H, s), 1.05 (3H, d, J=6.5Hz); mass 220 (M^+). The LIS nmr spectrum [$Eu(fod)_3$/**8** = 0.36, CCl_4] of **8** exhibited peaks[8] at δ1.72 (S[9]=1.4, 3H, s, 15Me), 1.82 (S=1.8, 3H, d, J=6.5Hz, 12Me), 2.45 (S=2.3, 1H, m, 4βH), 2.74 (S=4.3, 3H, s, 14Me), 2.85 (1H, m, 5βH), 3.04 (S=5.1, 1H, d, $J_{1\alpha-1\beta}$=12Hz, 1βH), 3.16 (S=8.0, 1H, d, $J_{1\alpha-1\beta}$=12Hz, 1αH), 3.34 (1H, m, 5αH), 3.60 (1H, m, 4αH), 3.93 (S=4.4, 1H, m, 3-H), 4.00 (S=5.8 1H, q, $J_{9-10\beta}$=10Hz, $J_{10\alpha-10\beta}$=13Hz, 10βH), 5.05 (S=8.9, 3H, d, J=6.5Hz, 13Me), 5.20 (S=7.4, 1H, m, 6-H), 6.74 (S=13.0, 1H, q, $J_{9-10\alpha}$=5Hz, $J_{10\alpha-10\beta}$=13Hz, 10αH), 8.00 (S=13.4, 1H, m, 7-H), 8.20 (S=13.0, 1H, q, $J_{9-10\alpha}$=5Hz, $J_{9-10\beta}$=10Hz, 9-H). Extensive spin decoupling experiments on the above LIS spectra revealed the presence of partial structures  $\bullet-CH_2-\underset{|}{CH}-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-\underset{|}{CH}-\bullet$ and $\bullet-CH_2-\bullet$ (the • sign means a quarternary carbon atom). Moreover, the large S values of 10α, 3α and 4α protons indicated an A/B cis, B/C cis and 3βMe structure with an approximate conformation **9** for the skeleton[10].

The structures **4** and **5** suggested that the reactions proceeded through the same intermediate protoilludyl cation **A**. Models show that this species can take two conformation **A-1** and **A-2**. Since in the former conformation the vacant orbital at C-7 and the C-5-C-6 bond are parallel, the transformation to the bridged compound[11] **4** is readily understood. The latter conformation contains parallel C-2-H, C-3-C-6 bonds and 2pz orbital at C-7. Therefore, the conformer **A-2** is expected to undergo fragmentation at C-3-C-6[12] and concomitant hydride shift from C-2 to C-3. The trans-cyclooctenyl cation **C** thus produced would then be readily cyclized to the observed product[13,14] **5**, since C-2 and C-6 are close in **C**. Similar cyclization process from a cyclooctenyl cation to a bicyclo[3.3.0]octane has been proposed as a biosynthetic step for a sesterterpene retigeranic acid[15]. The above results show that under standard solvolytic conditions the simple protoilludyl cation is not transformed to either illudane or hirsutane, although it does yield the other two naturally occuring ring skeletons, probably on the conformational grounds. Solvolyses of conformationally perturbed protoilludane derivatives are under investigation.

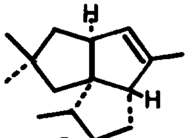






Hβ δ4.00 S=5.8 6-H δ5.2 S=7.4

Hα δ6.74 S=13



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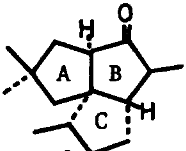

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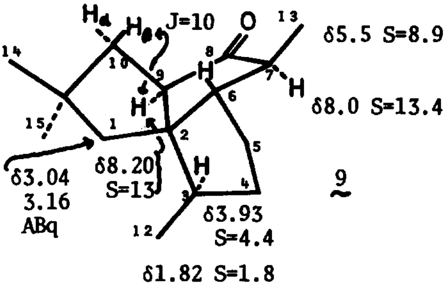

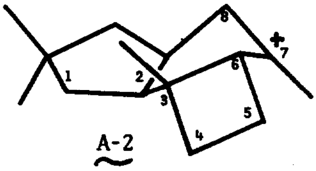

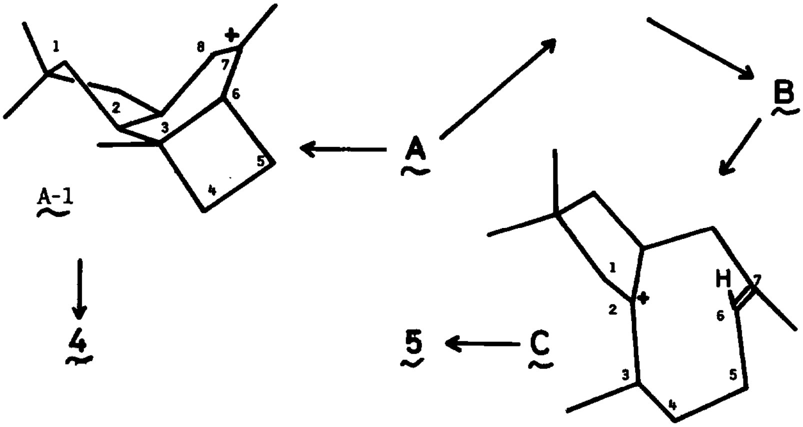

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2. Y.Ohfune, H.Shirahama and T.Matsumoto, Tetrahedron Lett., 4377 (1975).
3. Similar treatment at r.t(3hr) of **1**, **2** and **3** increased the **4**/**5** ratio to 9/1.
4. Satisfactory elementary analytical data were obtained.
5. Obtained as an oil.
6. Reasonable nmr, ir and mass spectral data have been obtained for this compound.
7. Reduction of bicyclo[4.2.0]octan-2-one with hydride reagents gave endo-alcohol as the major component; a) A.C.Cope, J.M.Grisar and P.E.Peterson, J.Amer.Chem.Soc., **82**, 4299 (1960); b) A.C.Cope, S.Moon, C.Ho.Park and G.L.Woo, ibid., **84**, 4865 (1962).
8. The peaks were assigned as shown in the parentheses by extensive decoupling experiments.
9. A.F.Cockerill and D.M.Rackham, Tetrahedron Lett., 5149 (1970).
10. The configuration of C-13 was assigned as β by taking into consideration the thermodynamic stability.
11. Solvolysis of bicyclo[4.2.0]oct-2-yl derivatives has been shown to give endo-bicyclo[3.2.1]oct-8-yl derivatives; a) Y.Yamada, Dissertation, Tohoku Univ., (1966); b) D.Do.Khac.Manh, M.Fetizon and J.P.Flement, Tetrahedron, **31**, 1897 (1975); c) In the rearrangement of manool into hibane skeleton, the intervention of cyclooctenyl and bicyclo[4.2.0]octyl cation intermediates has been demonstrated. J.L.Fourrey, J.Polonsky and E.Wenkert, Chem.Commun., 714 (1969) and other references therein.
12. The trans-cyclooctenyl cation **B** has been suggested to be a biogenetic precursor for the protoilludyl cation **A**. T.C.Feline and G.Mellows, Chem. Commun., 64 (1974).
13. Examples for the formation of cis-bicyclo[3.3.0]octyl derivatives from trans[a]- and cis[b]-cyclooctenyl cations have been recorded; a) H.Hart and M.Suzuki, Tetrahedron Lett., 4327 (1975); b) A.C.Cope, M.Martin and M.A.McKervey, Quart.Rev., **20**, 119 (1966).
14. Force field calculations of the strain energy of isomeric tricycloundecanes show that the skeleton of **5** has a comparable energy to the most stable isomer homoadamantane (E.Osawa, private communication). Formation of **5** is therefore an energetically reasonable process. We thank Dr.Osawa of this Department for informing us his results prior to publication.
15. M.Kanda, R.Takahashi, Y.Iitaka and S.Shibata, Tetrahedron Lett., 4610 (1972)