Reaction of Cyclo-octenylidene Derivatives with Benzene and BF_3–Et_2O

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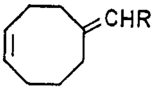
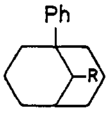
Summary The phenyl-containing bicyclo[3,3,1]nonanes, (**2**), (**3**), and (**4**), are obtained by heating the cyclo-octenylidene ester (**1**) and the methyl ketone (**5**), respectively, with boron trifluoride in benzene.

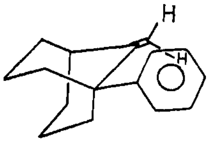
Heating the cyclo-octenylidene ester (**1**) with BF_3–Et_2O in benzene (1 : 1) under reflux for 1 h gave a mixture of the ester (**2**) (30%) together with its corresponding acid (**3**) (19%). An analogous product (**4**) (25%) was obtained from the cyclo-octenylidene methyl ketone (**5**) under the same conditions.



(1) R=CO_2Et
(5) R=Ac



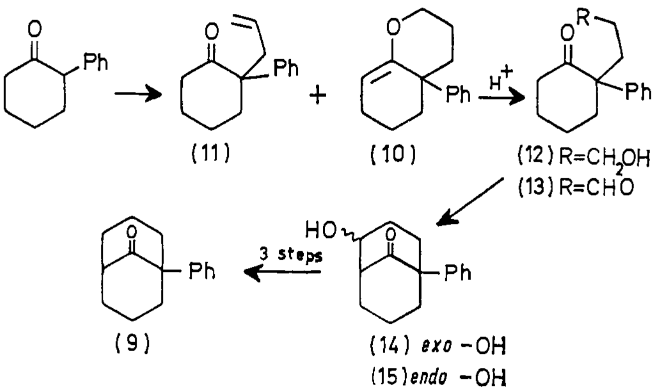
(2) R=CO_2Et
(3) R=CO_2H
(4) R=Ac
(6) R=CH_2OH
(8) R=CH_2Cl



(7)

Reduction of the ester (**2**) with lithium aluminium hydride gave the alcohol (**6**) which was converted by $POCl_3$–C_5H_5N into a mixture of the olefin (**7**) and the chloride (**8**). In the n.m.r. spectrum of (**7**) there are two olefinic protons of widely separated chemical shift (τ 5·25 and 5·95), the signal at higher field assigned to the proton which is shielded by the aromatic ring. Ozonolysis of the olefin (**7**) gave a low yield of the ketone (**9**).

To prove that the ketone (**9**) has the [3,3,1] skeleton, we have synthesised it by the route shown in Scheme 1.

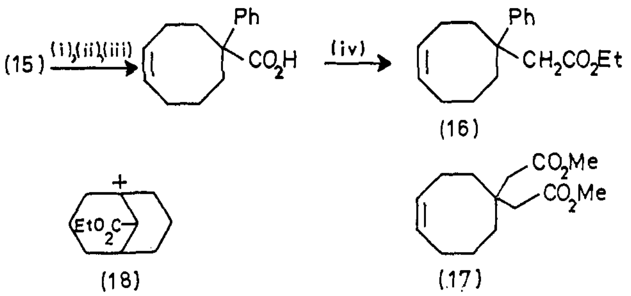


Scheme 1.

Alkylation of 2-phenylcyclohexanone with 1,3-dibromopropane and sodium hydride gave a mixture of the enol ether (**10**) and the olefin (**11**). Mild hydrolysis of the mixture converted the enol ether (**10**) into the alcohol (**12**) which was then easily separable from (**11**) by chromatography. Oxidation (CrO_3, C_5H_5N, CH_2Cl_2) of the alcohol (**12**) and cyclisation[1] (HCl–dioxan) of the aldehyde (**13**) yielded two epimeric alcohols. The *exo*-epimer (**14**) (>C*H*OH, 7 Hz width at $\frac{1}{2}$ height)[2] was dehydrated *via* solvolysis of the tosylate[1] and catalytically reduced to give a ketone identical with (**9**).† Wittig methylenation of the ketone (**9**) yielded an olefin identical with (**7**).

† After completion of this synthesis we became aware of an alternative route to this compound (L. Baiocchi, A. Gambacorta, R. Nicoletti, and V. Petrillo, *Ann. Chim.* (*Italy*), 1971, 744); comparison with an authentic sample supplied by Professor Nicoletti shows it to be identical with (**9**).

Transformation of the ester (**1**) into (**2**) and (**3**) is mechanistically unusual for a medium ring compound. An intermediate which appeared plausible was the ester (**16**) formed by a Friedel–Crafts alkylation of benzene by the ester (**1**) mediated by BF$_3$. This ester has been synthesised by the route shown in Scheme 2. Under the reaction conditions successful for conversion of (**1**) into (**2**) it gives no detectable amount of the latter. Moreover, the diester (**17**), synthesised *via* a modified Guareschi imide from cyclo-oct-4-enone, is recovered unchanged under the same conditions. An electrophilic attack on benzene is likely at some step in the reaction since replacement of benzene by toluene yielded an analogous *p*-tolyl ester (28%) and acid (21%) mixture, whereas no product was isolated using nitrobenzene.



Scheme 2. Reagents: (i) TsCl; (ii) NaOEt[3]; (iii) NaOH; (iv) SOCl$_2$, CH$_2$N$_2$ Arndt-Eistert.

Ring-closure to the carbonium ion (**18**) would be slow, more because of the lack of nucleophilicity of the $\alpha\beta$-unsaturated ester[4] than as a result of any strain at the bridgehead.‡ Subsequent rapid alkylation of benzene or toluene would account for the fact that there is little difference in the rate at which (**2**) and its *p*-tolyl analogue are formed. The bridgehead character of the carbonium ion (**18**) does mean that proton loss is inhibited since the resulting olefin is strained.[5]

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‡ The bridgehead bicyclo[3,3,1]nonane carbonium ion is believed to be relatively strain-free (W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, 1968, **33**, 1239).

[1] E. W. Colvin, J. Martin, W. Parker, R. A. Raphael, B. Shroot, and M. Doyle, *J.C.S. Perkin I*, 1972, 860.

[2] W. Kraus, W. Rothenwöhrer, and R. Chassin, *Tetrahedron Letters*, 1969, 4581.

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[5] J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, 1970, **92**, 956; J. A. Marshall and H. Faubl, *ibid.*, p. 948.