Solvolytic Cyclization of 1-Allylindenes

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1-ALLYLINDENES can be used in formolytic diene cyclizations to provide benzobicyclo-octyl formates in good yields by more economical pathways than previous routes[1] which begin with benzonorbornadiene, *etc.*

In the preceding Communication, formolysis of *exo*-6,7-benzobicyclo[3,2,1]octen-3-yl toluene-*p*-sulphonate was shown to proceed without aryl$_1$-4 participation[2] to give thermodynamically controlled products with rearranged carbon skeletons. The same initial intermediate could be expected from cyclization of 1-allylindene (I), and this might provide a similar spectrum of products. Addition of (I) to formic acid[3] under reflux and analysis of samples at various times (by v.p.c. on a Carbowax 1500 column operating at *ca.* 175—200°) revealed that within 20 min. (I) was consumed and a 3 : 1 mixture of (II) and (V) resulted. Formate (IV) was detected only when toluene-*p*-sulphonic acid was present in the formolysis and then only after several hours and at the expense of (II) and (V).

The above data are consistent with initial diene cyclization to give the 6,7-benzobicyclo[3,2,1]-octen-3-yl cation, which reacts with solvent predominantly from the equatorial direction. 1,2-Hydride rearrangement of ion (A) gives (B),† which rapidly isomerizes to (C) by a 1,2-phenyl shift (or two 1,2-alkyl shifts); the solvent reacts with (C) to provide mainly the *exo*-formate (V) under kinetic control.

According to the arguments presented in the

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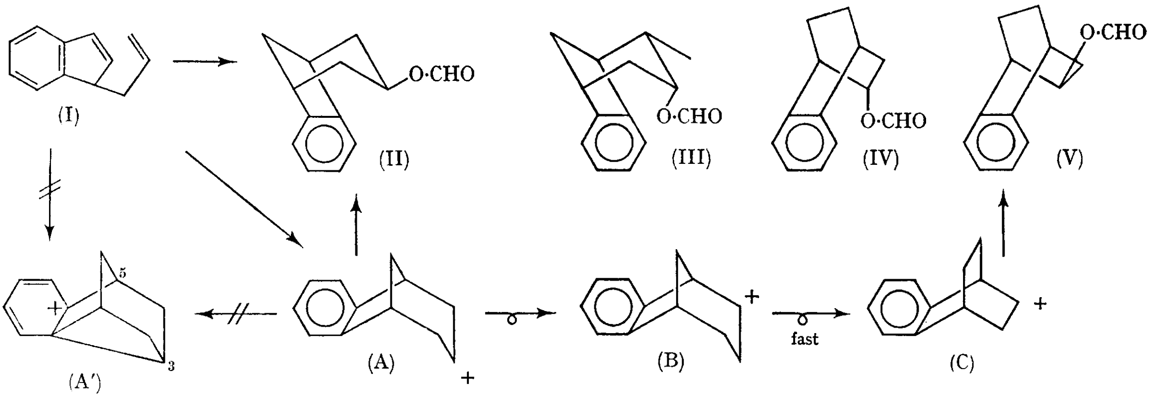
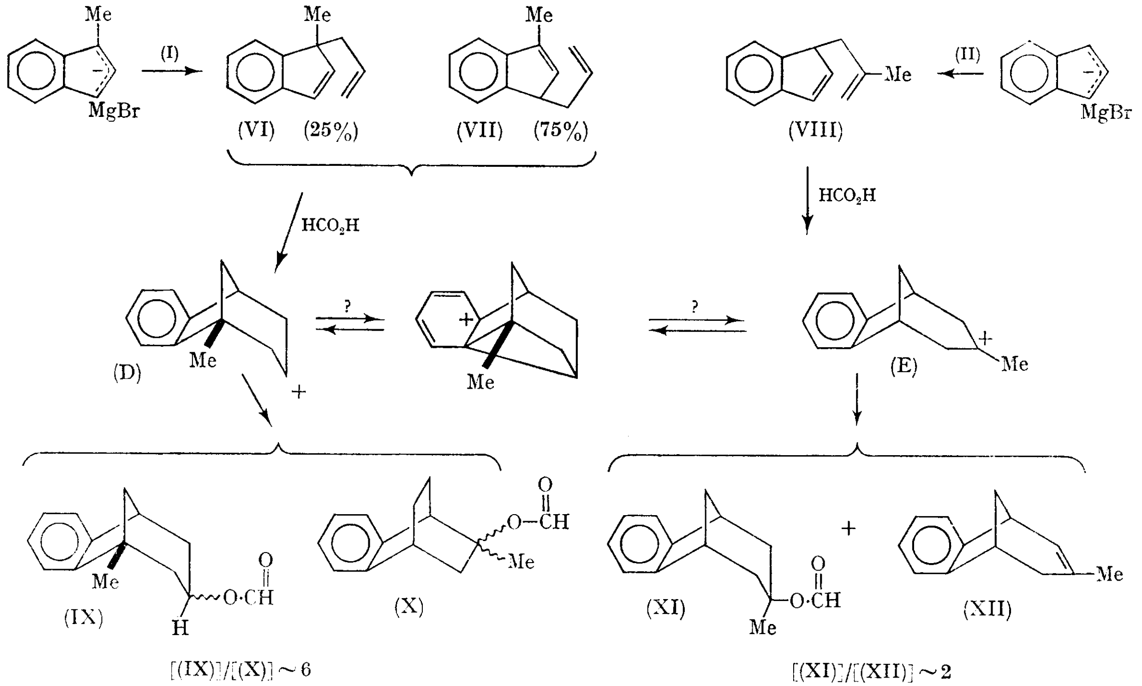
† For an alternative path from (A) to (B), see footnote 4 in the preceding note.



preceding Communication, *if* 1,3-aryl bridging occurs, substituents or isotopic labels can move between positions 1, 3, and 5 in cation (A′). No indication of such a process appears in the toluene sulphonate solvolyses reported earlier and we probed further into this possibility by generating 1-methyl- and 3-methyl-6,7-benzobicyclo[3,2,1]-octen-3-yl cations by diene cyclizations in order to ascertain whether common products arose from both ions.‡ The ions were generated from



Reagents: (i) $CH_2{:}CH{\cdot}CH_2Br$; (ii) $CH_2{:}CMe{\cdot}CH_2Br$.

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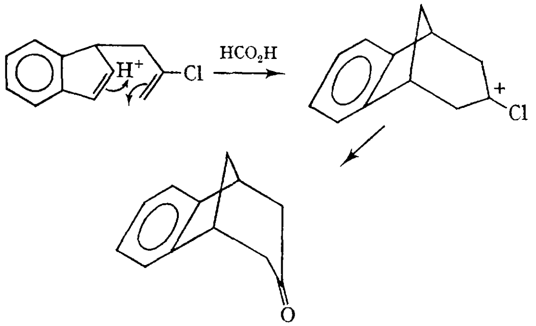
‡ In the absence of detailed mechanistic information, we do not wish to infer that discrete ions, as opposed to concerted cyclizations, are involved; the ionic formulations are used essentially to follow the closures and rearrangements formally.

suitable allylindenes,§ as outlined in the chart. The products¶ arising from each ion‡ are distinct and different, there being no indication that any equilibration by 1,3-phenyl migration occurred. It is noteworthy that ion (E) did *not* rearrange to the more stable bicyclo[2,2,2]-structure (see the preceding Communication), presumably because the tertiary ion is reluctant to isomerize to a secondary one. The latter observation, concerning stabilization of the bicyclo[3,2,1]-structure by the methyl group, ultimately led us to use β-chloroallyl groups as nucleophilic substrates in intramolecular electrophilic cyclization, thus opening up a general synthesis of novel cycloalkanones,[3] *e.g.*,



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§ Compounds (VI–(VIII) were prepared from indenylmagnesium bromide or 1-methylindenylmagnesium bromide in tetrahydrofuran, by reaction with the appropriate allyl bromide at *ca.* 0°, using inverse addition to prevent indene isomerization and polyalkylation. The structures were established by elemental analysis and n.m.r. spectroscopy using data on methylindenes for comparison (A. Bosch and R. K. Brown, *Canad. J. Chem.*, 1964, **42**, 1718.

¶ Compounds (IX—(XII) were obtained in pure form by preparative v.p.c. on a Tide column at 175°, using a Wilkins Auto-prep instrument, and characterized by elemental analysis, infrared, and n.m.r. spectroscopy. Although final confirmation of structure and stereochemistry by independent synthesis has not yet been completed, the major point of no cross-over between ions (D) and (E) is clearly established.

[1] H. Tanida, K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, 1967, **89**, 3212, and references therein.
[2] B. Capon, *Quart. Rev.*, 1964, **18**, 45.
[3] P. T. Lansbury and E. J. Nienhouse, *J. Amer. Chem. Soc.*, 1966, **88**, 4290.