Tetrahedron Letters No.35, pp. 3383-3388, 1967. Pergamon Press Ltd. Printed in Great Britain.

BICYCLONONATRIENE REARRANGEMENTS

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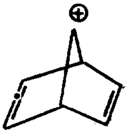
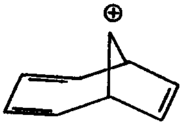
(Received in USA 23 April 1967)

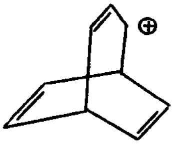
Simple vinylogs of the widely investigated norbornadienyl cation (I) include the bicyclo-[4.2.1]nona-2,4,7-trienyl (II) and bicyclo[3.2.2]nona-2,6,8-trienyl (III) cations.



I

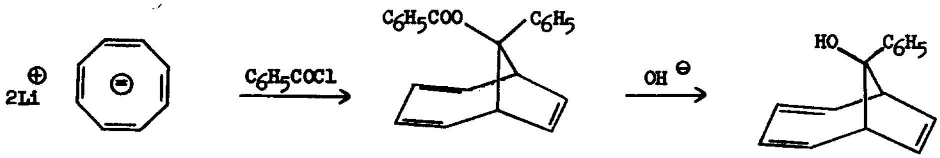


II



III

As a potential precursor of a system of type II we have prepared the tertiary alcohol V, m.p. 106°.[*] The latter is available by vigorous alkaline hydrolysis of the benzoate IV obtained by Cantrell and Shechter (1) from the reaction of dilithium cyclooctatetraenide with benzoyl chloride; the stereochemistry of IV and hence of V is based on chemical evidence advanced by these workers.



IV

V

Reaction of Alcohol V with Thionyl Chloride. Treatment of alcohol V with two equivalents of thionyl chloride and one equivalent of pyridine at room temperature in ether gave a high yield of a crystalline chloride, m.p. 46-47°. The n.m.r. spectrum of this chloride [Fig. 1] exhibited two magnetically dissimilar aliphatic protons which are strongly coupled to each other, thus excluding any symmetrical structure such as VI. The fact that the ultraviolet spectrum of this chloride resembled that of the starting alcohol V, but was also consistent

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[*] Satisfactory data have been obtained for all new compounds for which melting points are cited. We are indebted to L. Brancone and his associates for microanalyses and to W. Fulmor and his associates for spectral data.

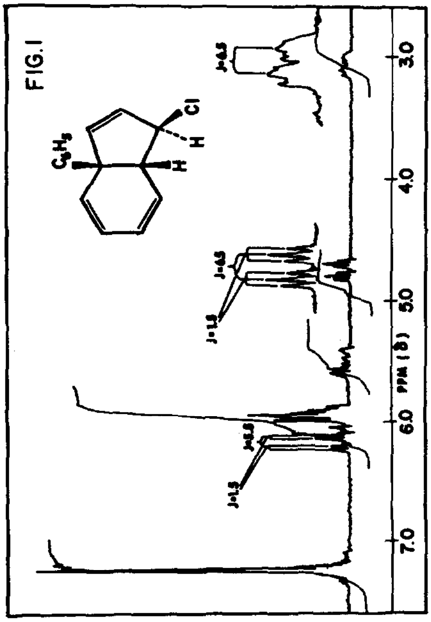


FIG.1

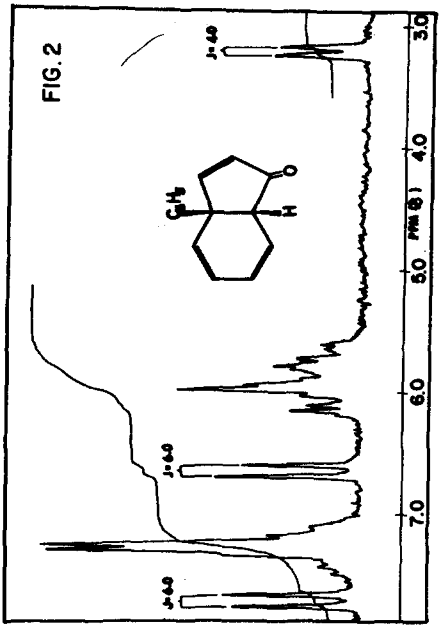


FIG. 2

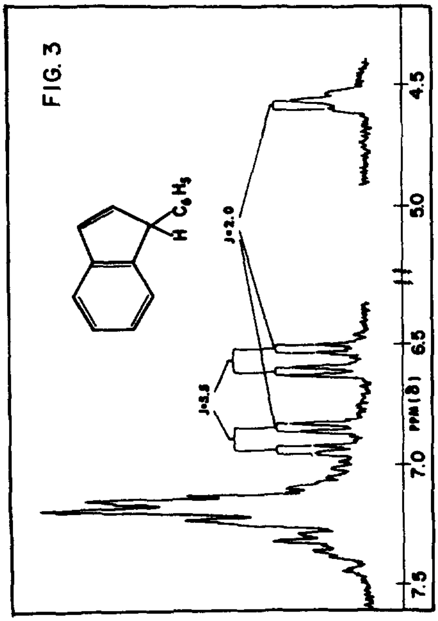


FIG. 3

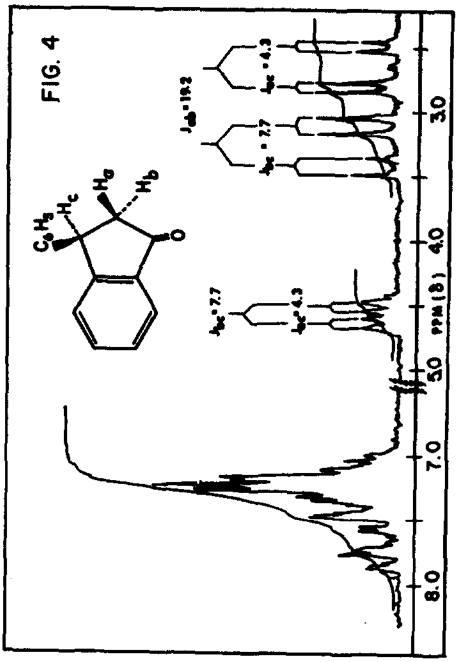
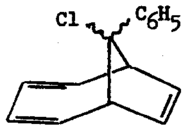
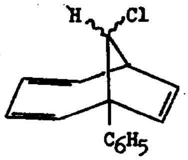


FIG. 4

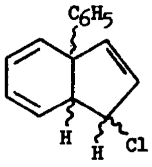
with that of the 8,9-dihydroindene system (2), led to consideration of the mechanistically plausible gross structures VII and VIII.



VI

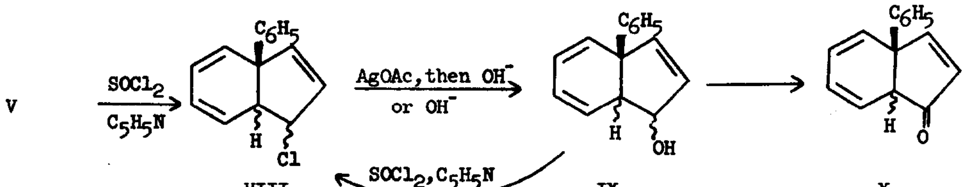


VII



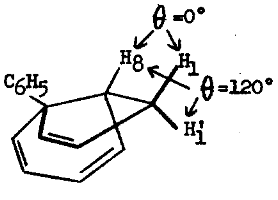
VIII

The chloride reacted rapidly with silver acetate in acetic acid to give in high yield a single acetoxy compound, m.p. 67°, which on mild hydrolysis gave an alcohol, m.p. 74°. The same alcohol could be prepared by reaction of the chloride with cold aqueous base, and the alcohol could be reconverted to the 47° chloride with thionyl chloride and pyridine in ether. The n.m.r. and u.v. spectra of the alcohol and chloride were parallel (vide infra). To distinguish between alternatives VII and VIII, the alcohol was oxidized with chromium trioxide-pyridine complex to give the corresponding ketone which in chloroform solution showed one sharp carbonyl maximum at 5.85 μ. This wavelength indicated that the ketone could not be derived from a bridged alcohol corresponding to system VII since such bridged ketones show maxima between 5.60 and 5.75 μ. Structure X for the ketone was, however, consistent with the infrared data and was unambiguously demonstrated by the n.m.r. spectrum [Fig. 2] which clearly possesses the requisite signals and parallels that of cis-8,9-dihydroindenone itself (2j).

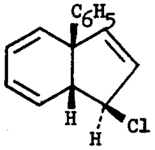


VIII IX X

If the transformations of the thionyl chloride product VIII are correctly formulated above, there remains a question as to the stereochemistry of these compounds. While the ultraviolet spectrum of ketone X is quite complex, that of VIII ($\lambda_{max}^{CH_3OH}$ 272, 266, 259 mμ; ϵ_{max} 2750, 2980, 2860) and of IX ($\lambda_{max}^{CH_3OH}$ 272, 267, 260 mμ; ϵ_{max} 2945, 3050, 2945) is typical of cis-fused 8,9-dihydroindenes and differs somewhat from trans-fused 8,9-dihydroindenes (2i,k) which typically show slightly higher extinction coefficients. A more compelling argument favoring a cis-fusion stems from the fact that the high yield conversion of chloride VIII to alcohol IX is *stereoselective*, as is the reverse reaction. Comparison of n.m.r. spectra of VIII and IX showed that both compounds had essentially the same coupling constant (6.5 Hz. for VIII, 5.5 Hz. for IX) between the vicinal "aliphatic" hydrogens. This suggests that the stereoselectivity in each direction arises by *retention of configuration*, a result which is the expected consequence of the folded *cis*-fused system but is not readily rationalized for the nearly planar *trans*-fused case.* Indeed, Dreiding models for the *cis*-fused triene show that the possible dihedral angles θ between H(1) and H(8) are ca. 0° and 120° (cf. XI), and on the basis of the modified Karplus relationship (3) only the latter seems compatible with the observed 6 ± 0.5 Hz. couplings. Thus the observed solvolytic stereoselectivity as well as the n.m.r. data both point to stereoformula XII for the 47° chloride.



XI



XII

Phenyl Migrations in the Dihydroindene Series. The gross structural assignments for alcohol IX and ketone X are supported by the observation that each compound undergoes exceptionally facile Wagner-Meerwein phenyl migration upon mild acid treatment. Reaction of alcohol IX with a catalytic amount of p-toluenesulfonic acid in refluxing alcohol-free chloroform produced as the principal product a colorless, distillable oil identified by its ultraviolet absorption

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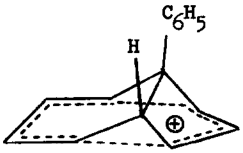
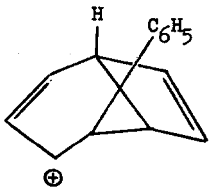
* Preliminary results show that unimolecular solvolysis of chloride XII in aqueous methanol has a slightly slower rate than solvolysis of the allylic 3-chlorocyclopentene. There is apparently no rate enhancement in this particular case from participation of the theoretically possible bis-homotropylium cation A, which could also be considered as the very interesting phenylhomosemibullvalenium cation B.

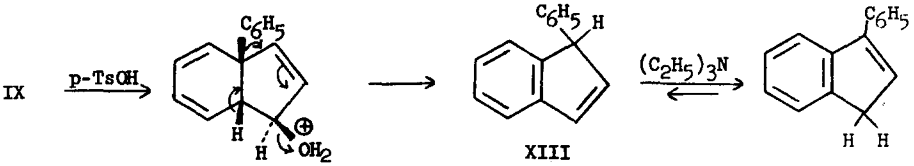


A

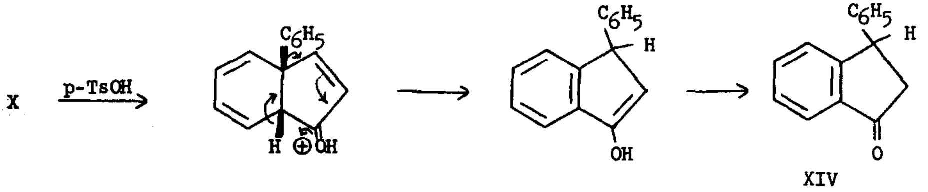


B

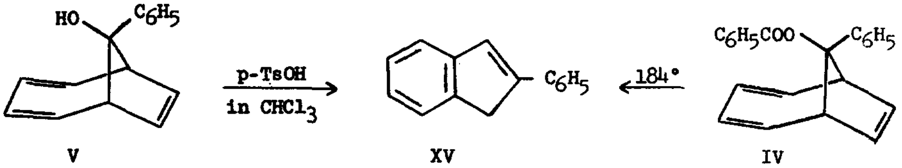
($\lambda_{max}^{CH_3OH}$ = 265, 258 mμ; ϵ = 7100, 8060) and n.m.r. spectrum [Fig. 3] as the hitherto unreported 1-phenylindene (XIII). The stability of this compound under acidic conditions is noteworthy and was taken to represent a kinetic rather than thermodynamic phenomenon in view of the known equilibrium between 1-methylindene and 3-methylindene under basic conditions (4). A dramatic demonstration of the equilibrium existing here consisted of the very rapid and complete conversion of the n.m.r. spectrum of 1-phenylindene to that of 3-phenylindene (2H doublet at δ = 3.43, J = 2 Hz.; 1 H triplet at δ = 6.50, J = 2 Hz.; 9 H aromatic multiplet centered at δ = 7.40) upon addition of a drop of triethylamine to the former in $CDCl_3$ in an n.m.r. tube.



Acid treatment of ketone X under the conditions employed for alcohol IX proceeded in a comparable fashion to give as the rearrangement product the known 3-phenyl-1-indanone (XIV) (m.p. 82-82.5°; lit. m.p. 78-9°) (5). This product showed the definitive n.m.r. spectrum of Fig. 4, and its identity was confirmed by preparation of the 2,4-dinitrophenylhydrazone, m.p. 207-209° (lit. m.p. 209-210°) (5).



Formation of 2-Phenylindene from Alcohol V. In striking contrast to the reaction of the bridged alcohol V with thionyl chloride, the action of p-toluenesulfonic acid in chloroform upon V led quantitatively to the known 2-phenylindene XV, identified by m.p., ultraviolet and n.m.r. spectra. The same olefin is reported to form upon thermolysis of the benzoate IV in boiling o-dichlorobenzene (1b).



This 2-phenylindene can not arise by way of an 8,9-dihydroindene intermediate related to X because neither the Wagner-Meerwein rearrangements discussed in the preceeding section, nor control experiments such as thermolyses of chloride VIII or of the benzoate ester of IX produced any detectable amounts of 2-phenylindene. Thus there must be entirely different mechanisms in operation for the thionyl chloride reaction of V on the one hand, and the acid-catalyzed conversion of V to XV on the other. Studies leading to a definition of these mechanisms are in progress.

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