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SOME HIGHLY SHIELDED METHYL GROUPS IN BICYCLIC HYDROCARBONS[1,2]

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A new family of bicyclic compounds have recently been prepared in these laboratories, and the present preliminary report deals with the synthesis and unusual proton NMR spectra of a selection of these Bicyclic Hydrocarbons.

Fig. I illustrates the synthetic routes used in the preparation of the Bicyclic Hydrocarbons. Ketone I was prepared by the conjugate addition of α-naphthylmagnesium bromide to isophorone (1), and other tetrasubstituted ketones were prepared in an analogous manner (2). Although formation of the desired bicyclic hydrocarbon (such as V) was effected by acid-catalyzed cyclization of any or all of the olefins II, IVa and IVb, the simplest route utilizes acid treatment of carbinols such as IIIa and IIIb. The use of concentrated sulfuric acid in the cyclization step gave the desired hydrocarbon in 10 to 30% yields. Use of trifluoroacetic acid (TFA) sometimes afforded substantially better yields (in favorable cases, in the range 50-60%) of cleaner products. The structures of the hydrocarbons prepared by this scheme are shown in Fig. II, and the methyl proton chemical shifts are summarized in Table I.

The structures of the hydrocarbons follow from an analysis of the proton and carbon-13 NMR spectra of the compounds, together with combustion analysis and mass spectrometric data. Compound X, arising from cyclization to form a new 6-membered ring, is produced in small amounts in the reaction leading highly predominantly to VI, despite the considerably greater strain in

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[2] Taken in part from the Ph.D. dissertation of M.J.G., Texas A&M University, 1970.

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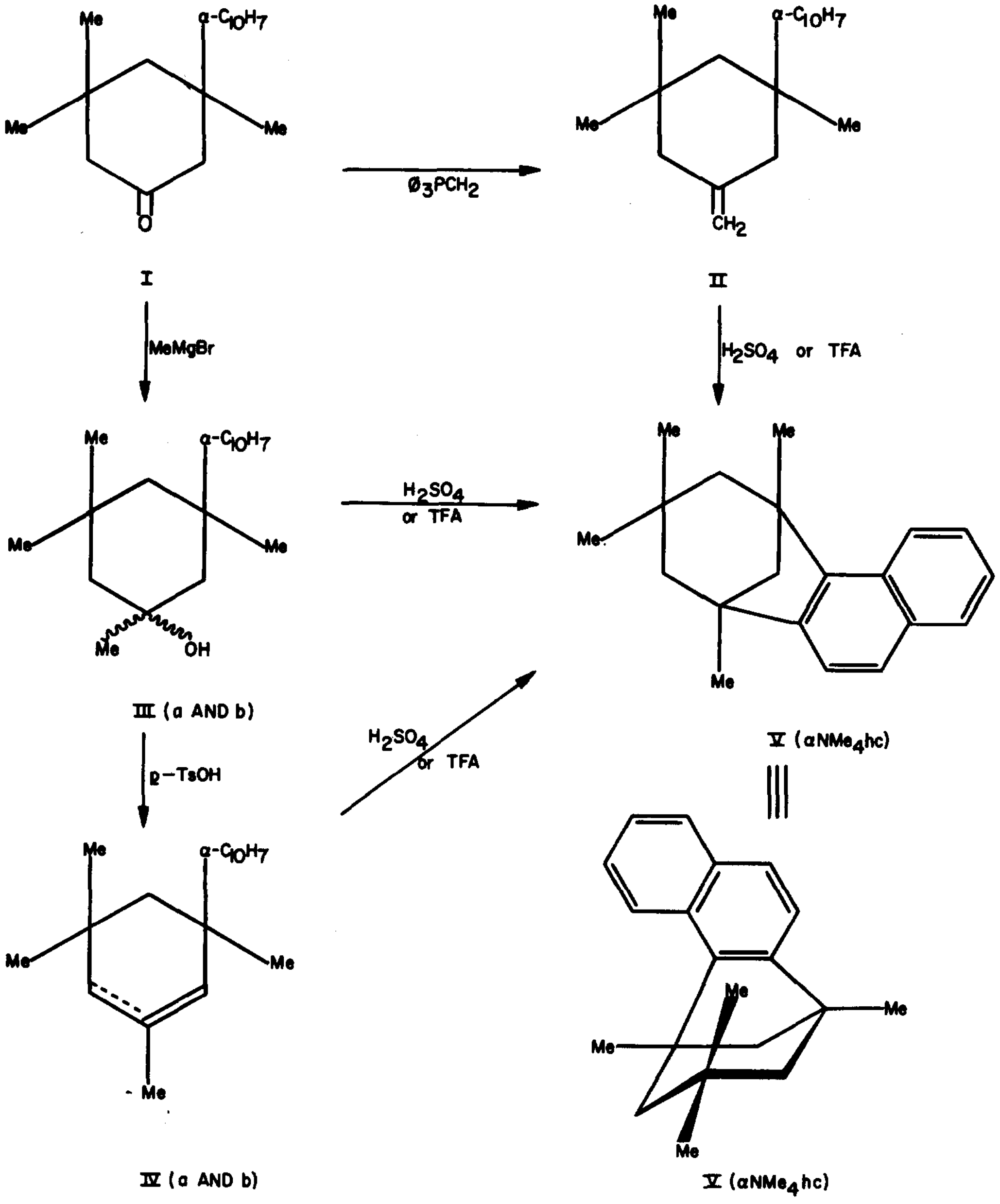
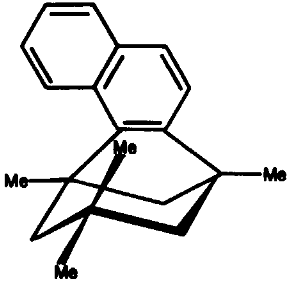
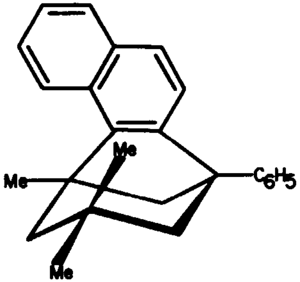


FIGURE I. SYNTHETIC ROUTES TO BICYCLIC HYDROCARBONS



V (αNMe$_4$hc)



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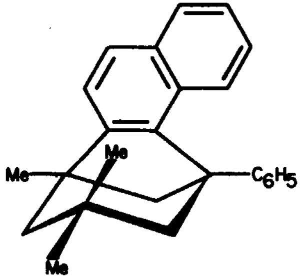
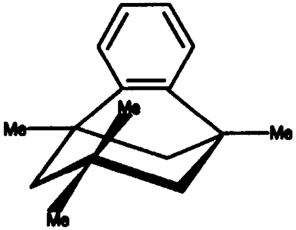
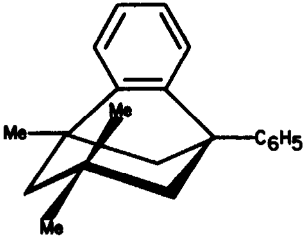


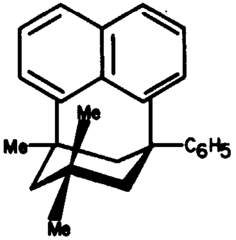
VII (βNØMe$_3$hc)



VIII (ØMe$_4$hc)



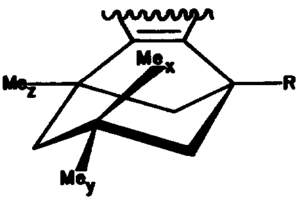
IX (ØØMe$_3$hc)



X (1,8αNØMe$_3$hc)

FIGURE II. STRUCTURES OF BICYCLIC HYDROCARBONS

Table I. Methyl Proton NMR Chemical Shifts (10% w/w in $CDCl_3$) of Bicyclic Hydrocarbons



(for compounds V and VIII, R = Me_q)

	Compound	δ_{Me_x}	δ_{Me_y}	δ_{Me_z}	δ_{Me_q}
V	(αNMe_4hc)	-0.38	0.86	1.71	1.39
VI	($\alpha NØMe_3hc$)	-0.32	0.99	1.80	--
VII	($\beta NØMe_3hc$)	-0.41	1.00	1.48	--
VIII	($ØMe_4hc$)	-0.15	0.84	1.30	1.30
IX	($ØØMe_3hc$)	-0.07	0.95	1.36	--
X	($1,8\alpha NØMe_3hc$)	-0.23	0.96	1.53	--

the latter. Both electronic and steric factors are very probably involved in the large VI:X ratio of products. Elucidation of these factors, as well as other details of the acid-catalyzed cyclization reactions are currently under investigation.

These new Bicyclic Hydrocarbons are of particular interest for their methyl proton NMR shift data. Large ring-current induced shifts have been very extensively investigated only for protons lying in or near simple aromatic and heteroaromatic ring planes (the well-known down-field shifts) or for protons subject to ring current effects arising from rather large π-systems (3). Data on out-of-plane, upfield ring current shifts arising from simpler aromatic systems of well defined geometry, hitherto somewhat lacking, has important theoretical and practical implications (4). The data now reported should complement that obtained on the larger π-systems, to aid in our general understanding and utilization of diamagnetic ring current shifts. Work in progress is directed toward the synthesis of analogous molecular types having methyl and other groups held rigidly in close proximity to the face of an aromatic ring system, as well as an evaluation of the relations between chemical shifts and spin couplings observed and both substitution type and bond angle strain effects.

Acknowledgement

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References

1. (a) B. L. Shapiro and co-workers, to be published; (b) complete details of the preparation and characterization of all compounds are contained in the Ph.D. dissertation of M.J.G., Texas A&M University, 1970.
2. Proton NMR studies of these ketones are described in the immediately preceding paper.
3. e.g., see (a) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969, pp. 64-71, 79-82, and references cited therein; (b) R. H. Mitchell and V. Boekelheide, J. Amer. Chem. Soc., 92, 3510 (1970).
4. e.g., (a) C. C. McDonald and W. D. Phillips, Ibid., 89, 6332 (1967), (b) J. T. Gerig and J. D. Reinheimer, Ibid., 92, 3146 (1970).