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SYNTHESES, NMR SPECTRA, AND C-H ACIDITIES OF HYDROCARBONS IN THE TRICYCLO[2.1.1.$0^{5,6}$]HEXANE AND TRICYCLO[1.1.1.$0^{4,5}$]PENTANE SERIES.

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As part of a research program designed to study reactivity changes resulting from bond deformations in small ring compounds we have been interested in effects caused by altering the geometry of the bicyclobutane system. Some time ago, one of us reported on the unusually high degree of s-character in the C-H bonds at positions 6 and 7 in tricyclo[3.1.1.$0^{6,7}$]heptane (I) as evidenced by the very high C^{13}-H coupling constant (200c.p.s.) and the occurence of deuterium-hydrogen exchange under relatively mildly basic conditions.[1] In this communication we wish to report the extension of these studies to hydrocarbons of the tricyclo-[2.1.1.$0^{5,6}$]hexane and tricyclo[1.1.1.$0^{4,5}$]pentane series (II and III).[2,3]

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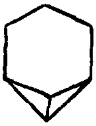
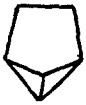


I



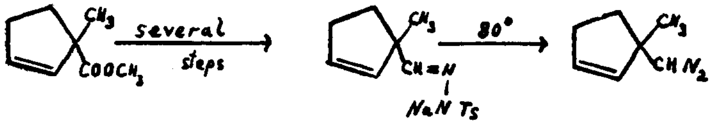
II

III

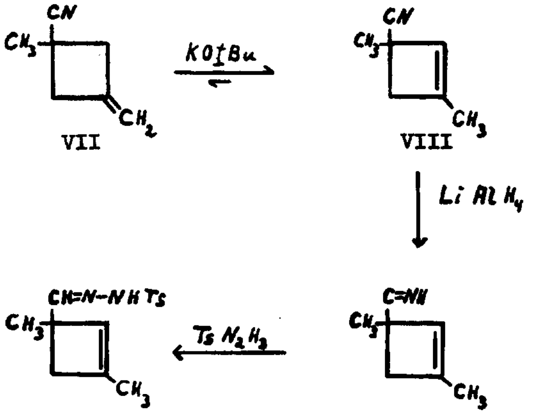
Intramolecular cyclizations of suitable cyclopentenyl- and cyclobutenylcarbenes appeared to be the most promising route to hydrocarbons of structures II and III. The diazoalkene VI and the tosylhydrazone X were chosen as carbene precursors and were synthesized as follows:

The methyl cyclopentenylcarboxylate IV was converted through the acid chloride to its N-methylanilide, which on lithium aluminum hydride reduction gave the carboxaldehyde. The sodium salt of the carboxaldehyde tosylhydrazone (V) was decomposed at 80° in triglyme under vacuum. Under these conditions the diazoalkene VI distilled into a cold trap as soon as it was formed, and was protected from thermal decomposition.

The methylenecyclobutyl nitrile VII[4] was equilibrated with the cyclobutene derivative VIII by treatment with potassium *t*.-butoxide in dimethylsulfoxide (K = 5 in favor of VIII).[5] Lithium aluminum hydride reduction gave the imine IX which was converted to the tosylhydrazone X.

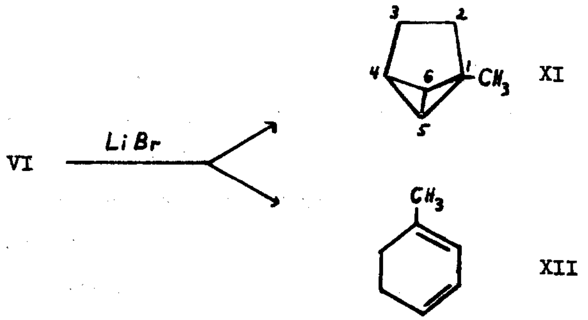


IV V VI



Although pyrolysis of both the tosylhydrazone sodium salt (V) and of the diazoalkene VI gave the desired methyltricyclohexane XI in modest yield, a large number of other hydrocarbons resulted from intramolecular insertions and rearrangements.[6] It was found advantageous to effect nitrogen elimination from VI by treatment with anhydrous lithium bromide solution in ether at 0°.

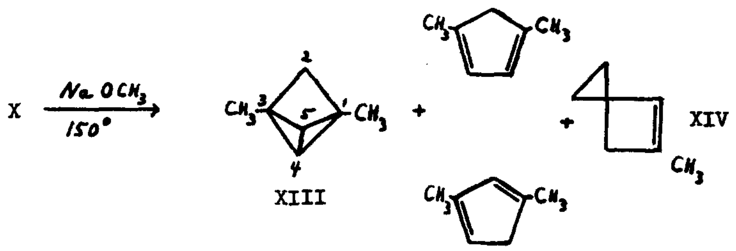
Under these conditions only two hydrocarbons were formed in equimolar quantities (yield based on tosylhydrazone: 50°/o). 1-Methylcyclohexadiene (XII) was identified at its Diels-Alder adduct with maleic anhydride. The assignment of structure XI to the other hydrocarbon follows unambiguously from the elemental analysis (found: C, 89.26; H, 10.87), molecular weight by mass spectrum (parent peak at mass 94), and from spectral data. Whereas the infrared spectrum shows C-H vibrations with high force constants (3070 cm^{-1}), but otherwise indicates the absence of unsaturation, the n.m.r. spectrum was found highly characteristic for structure XI. Signals were centered at 8.14 (m), 8.43 (m) 8.65 (m), and 8.79 τ (s). Combining the areas of the partially overlapping high field resonances, the relative signal strengths were 1:2:7. This leads to the assignment of the signals to protons at positions 4, 5 - 6, 2 - 3, and the methyl group, in a sequence of increasing shielding. The highly complex and poorly resolved pattern of the two low field signals indi-



cated mutual coupling of all ring protons. With the aid of double resonance it was possible to determine the coupling between proton 4 and 5 as $|J_{4,5}| = 1.95$ c.p.s. $J_{C^{13}-H}$ at positions 5 and 6 was found to be 206±1 c.p.s. The same measurement yielded 10.0±0.5 c.p.s. for $|J_{5,6}|$.

Shortly before this manuscript was submitted for publication Lemal and Shim published the synthesis of tricyclo[2.1.1.0^{5,6}]-hexane by a similar method.[3] The n.m.r. spectrum reported for this hydrocarbon is generally compatible with that of XI; however, it appears that Lemal and Shim have misassigned the chemical shifts of protons 1, 4 and 5, 6, respectively.

The dimethyltricyclopentane XIII was obtained in 10% yield from the base-catalyzed decomposition of tosylhydrazone X under conditions where the product was immediately swept from the reaction mixture into a cold trap. The major fraction of the reaction product was a mixture of dimethylcyclopentadienes and of a small fraction of the methylspirohexene XIV. The structure of XIII is confirmed by elemental analysis (found: C, 89.07; H, 10.55), by the absence of evidence for unsatura-



XIII

XIV

tion in the infrared and ultraviolet spectra, and most convincingly, by a detailed analysis of the n.m.r. spectrum. Signals were centered at 7.02 (m), 7.91 (m) and 8.96 τ (s) with relative intensities of 1:1:3. The spin-spin interactions between protons at positions 2, 4, and 5 were analyzed as A_2B_2 system giving the following constants: $|J_{AA}| = 7.66$, $|J_{BB}|$ 3.13, $|J_{AB}| = 5,80$, and $|J'_{AB}| = 0.90$ c.p.s. Furthermore, the C^{13}-H coupling constant associated with the low-field signal, measured at 60 and 100 mc gave the value of 212 ± 2 c.p.s., necessitating the assignment of this signal to the protons at positions 4 and 5. Also from the C^{13}-H satellite spectrum, 7.5 c.p.s. was found for $|J_{4,5}|$, a value which agrees very well with J_{AA}. Consequently, 3.13 c.p.s. must be assigned to the geminal coupling constant of the methylene group. Analysis of the spectrum of the 4-deuterio derivative of XIII (as AXX' system) confirms the assignments of the spin coupling parameters. A better agreement of the calculated with the observed spectrum can be obtained when $J_{2,4}$ and $J'_{2,4}$ are assumed to have opposite signs. In analogy to similar rigid systems we suggest that the larger $J_{2,4}$ corresponds to the coupling of protons at opposite sides of the symmetry plane of the molecule.[7]

The dimethyltricyclopentane XIII was found to rearrange readily under mild acid catalysis to a mixture of dimethylcyclopentadienes.[8] Both hydrocarbons XI and XIII react with methyllithium in ether to give the stable lithium derivatives XV and XVII, which on treatment with methyl iodide and deuteriomethanol gave XVI and XVIII, respectively. The metalation sites in XI and XIII were deduced from the n.m.r. spectra of XVI and XVIII. The non-equivalence of the two methyl groups in XVI is shown by the occurence of two methyl resonances at 8.78 and 8.95 τ. The spectrum of XVIII is similar to that of XIII except that the intensity of the low field signal is reduced to one half, and that the fine structure of both signals at 7.02 and 7.91 τ is changed to that expected for an AXX' system with the coupling constants cited for XIII.

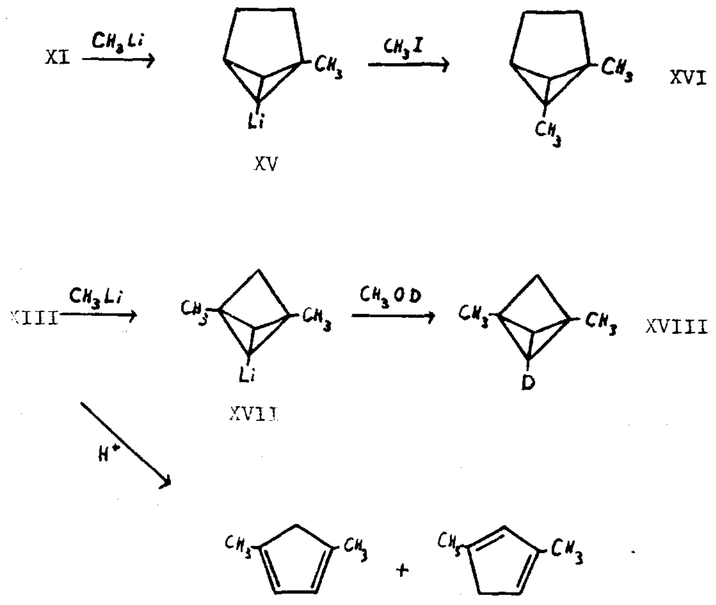


Table 1 summarizes the C^{13}-H coupling constants and the relative rates of metalation with methyllithium in ether at 25° of four highly strained hydrocarbons. Since resonance stabilization of any possible carbanionic intermediate cannot occur in these systems, the observed C-H acidity must be determined by the electronegativity of the carbon atom and by possible inductive effects of substituents. It can be seen that there exists a crude linear relationship between the logarithm of the metalation rate and the C-H coupling constant ($\log k/k_0 \simeq 0.16\ J - 32$) which serves as a measure for the s-character in the C-H bond. It is particular noteworthy that 3,3-dimethylcyclopropene seems to follow this correlation quite well despite of significant structural differences. Since the inductive effect caused by methyl substituents cannot be evaluated at present, some deviations from this correlation should be expected.[9] It remains to be seen whether this correlation is a general one, and whether the more meaningful base-catalized hydrogen exchange rates will follow such a linear relationship. Experiments along these lines are in progress.

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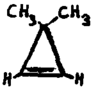
TABLE 1.

Carbon-13 Coupling Constants and Relative Metalation Rates of Strained Hydrocarbons with Methyllithium in Ether at 25°.[a]

	$J_{C^{13}-H}$	k/k_o	$\log k/k_o$
	221 ± 0.5	2,500	3.4
	212 ± 2	65	1.8
	206 ± 1	12	1.1
	200 ± 1	1	0.0

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a) The rates were followed by measuring the disappearance of the methyllithium peak by n.m.r. *vs.* an internal standard.

REFERENCES AND FOOTNOTES

1) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, 85, 2022 (1963).

2) With exception of the very recently published syntheses of tricyclo[2.1.1.$0^{5,6}$]hexane by Lemal and Shim[3], no hydrocarbons in either series have been reported. However, several derivatives of both skeletons are known. *Cf.* J. Meinwald and Swithenbamk and A. Lewis, *ibid.*, 85, 1880 (1963); A. Small, *ibid.*, 86, 2091 (1964); S. **Masamune**, *ibid.*, 86, 735 (1964); W. von E. Doering and M. Pomeranz, *Tetrahedron Letters*, No. 17, 961 (1964).

3) D. M. Lemal and K. S. Shim, *ibid.*, No. 44, 3231 (1964).

4) H. N. Cripps, J. K. Williams and W. H. Sharkey, *J. Am. Chem. Soc.*, 81, 2723 (1959).

5) Cf. A. Schriesheim, R. J. Muller and C. A. Rowe, Jr., *ibid.*, 84, 3164 (1962); E. Gil-Av and J. Shabtai, *J. Org. Chem.*, 29, 257 (1964).

6) Insertion occured into the methyl group, and into the ring C-H bond. In addition small amounts of methyl migration product was found.

7) G. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, 83, 2769 (1961); K. B. Wiberg, B. R. Lowry and B. Y. Nist, *ibid.*, 84, 1594 (1962).

8) It appears that even such mild acids as methanol and water catalize the rearrangement.

9) Judging from preliminary experiments in the tricycloheptane series, the influence of methyl substitution on the metalation rate appears to be small.