

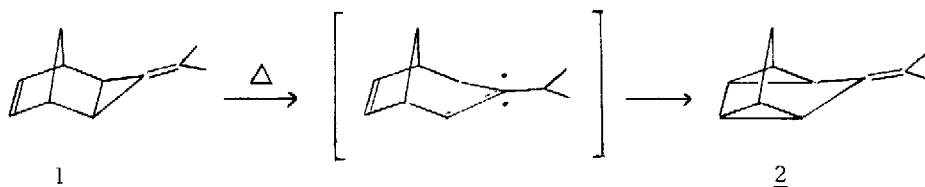
FLASH THERMOLYSIS OF 3,7-DIISOPROPYLIDENETETRACYCLO [3.3.1.0^{2,4}.0^{6,8}] NONANE. AN ACCESS TO THE PENTACYCLO [4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]NONANE SYSTEM

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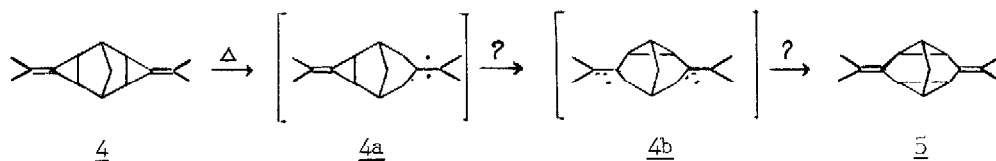
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The thermal valence isomerisation of 3-isopropylidenetetracyclo [3.2.1.0^{2,4}] oct-6-ene 1 to 3-isopropylidenetetracyclo [3.3.0.0^{4,6}.0^{2,8}] octane 2 was recently reported (1).



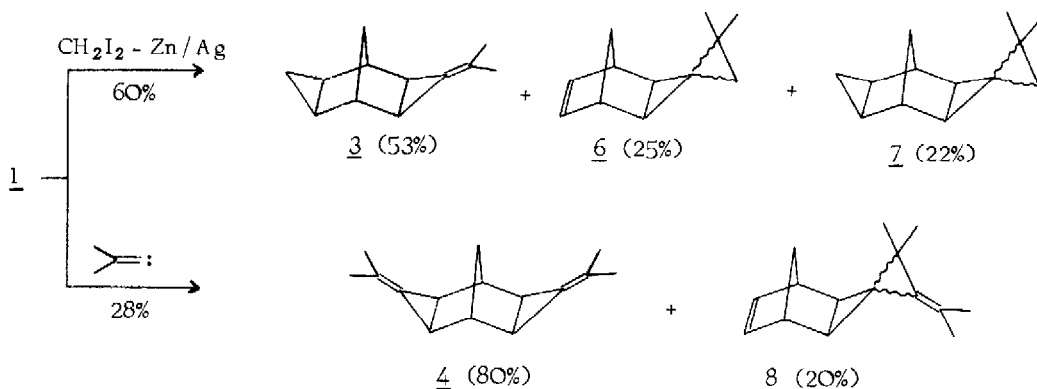
It was worthwhile to try to extend this reaction to hydrocarbons in which the endo double bond is replaced by a cyclopropane ring, since it would involve an intramolecular trapping of a trimethylene methane by a σ bond (2). The hydrocarbon 4 seemed particularly attractive since the stabilisation by allylic resonance of the intermediate biradicals 4a and 4b might provide a driving force for the expected rearrangement to the triasterane 5.



In the present paper, we report the synthesis and the thermal behaviour of 3-isopropylidene- and 3,7-diisopropylidene-tetracyclo [3.3.1.0^{2,4}.0^{6,8}] nonanes 3 and 4.

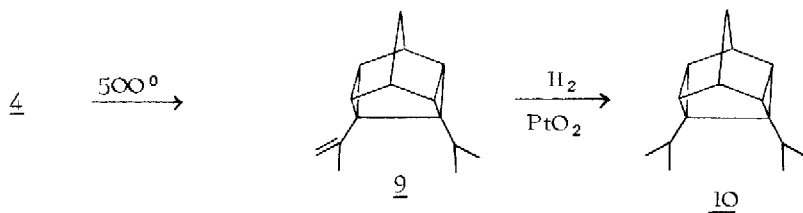
Compounds 3 and 4 were prepared from the diene 1 respectively by cyclopropanation with the Simmons-Smith reagent (3) and by reaction with isopropylidene carbene prepared in situ from 1,1-dibromo-2-methyl-propene and methyllithium (4).

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The hydrocarbons formed (5) were easily separated by vapor phase chromatography and identified from spectroscopic data. The exo, exo configurations of the cyclopropane rings in 3, 4 and 7 is strongly supported by their N.M.R. spectra, particularly by the highfield signals ($\delta_{\text{CCl}_4}^{\text{TMS}} = 0.41, 0.43$ and 0.46 ppm respectively) of the bridge methylene protons shielded by the proximate cyclopropane rings (2^c), and for 4 by the symmetrical pattern of the spectrum ($\delta_{\text{CCl}_4}^{\text{TMS}} = 2.45$ (b.s., 2H), 1.72 (s., 12H), 1.45 (b.s., 4H) and 0.43 ppm (b.s., 2H).

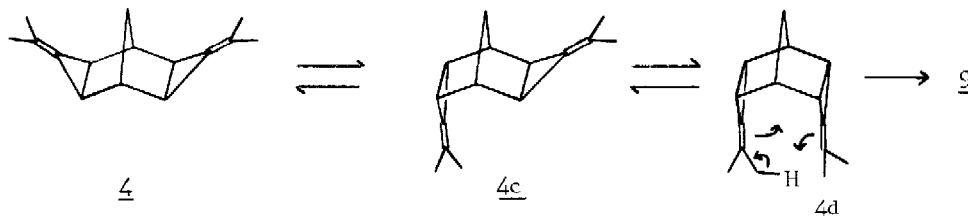
Flash thermolysis of hydrocarbons 3 and 4 were carried out at various temperatures (6). 3, unchanged until 550° , gave several decomposition products at higher temperatures (no isomer of 3 could be detected among these substances). In contrast, compound 4 rearranged at 500° to give a new hydrocarbon 9 in almost quantitative yield.



The M.S. data proved that 9 is an isomer of the starting material 4. The ^1H -N.M.R. spectrum showed the presence of an isopropyl- ($\delta_{\text{CCl}_4}^{\text{TMS}} 2.15$, septuplet, $J = 7$ Hz, 1H and 0.70 ppm, d, $J = 7$ Hz, 6H) and an isopropenyl- ($\delta_{\text{CCl}_4}^{\text{TMS}} 4.77$, m, 2H and 1.78 ppm, m, 3H) groups. The other protons signals (2.48 , m, 2H, $1.70 - 1.94$ ppm, m, 6H) suggested a pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}] nonane system. The structure was easily confirmed by comparing the N.M.R. spectra of the saturated hydrocarbon 10 (obtained by catalytic hydrogenation of the olefin 9) and of the known corresponding dimethyl pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}] nonane (7) ^1H -N.M.R. spectrum of 10 ($\delta_{\text{C}_1\text{Cl}_3}^{\text{TMS}} 0.77$ (d, $J = 7$ Hz, 12H); $1.70 - 1.94$ (m, 6H), 2.28 (septuplet,

J = 7 Hz, 2H) and 2.46 ppm (b.s., 2H).

A plausible mechanism for the rearrangement $\underline{4} \rightarrow \underline{9}$ is depicted in scheme I.



Successive flap inversions of the cyclopropane rings of $\underline{4}$ give rise respectively to the exo, endo- and the endo, endo-isomers $\underline{4c}$ and $\underline{4d}$ ⁽⁸⁾. Such flaps occur via well stabilised trimethylenemethane intermediates, allowing the facile rupture of the cyclopropane bonds. In the configuration $\underline{4d}$, the allylic hydrogens of the methyl groups are in good position to promote an ene reaction leading exclusively to the alkene $\underline{9}$.

Finally, the absence of triasterane $\underline{5}$ among the thermolysis products is consistent with the results reported by Berson et al. ⁽⁹⁾ as this work was in process. According to the suggestion of these authors, a rearrangement like $\underline{4} \rightarrow \underline{5}$ might imply the combination of two triplet diradicals, i.e. the simultaneous breaking of the two cyclopropane bonds to give a quadriradical, the formation of which being highly improbable.

We are grateful to Professor J.M. Conia for his encouragement and interest in the course of this work.

REFERENCES AND NOTES

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- (5) The stereoselectivity of the reaction with isopropylidene carbene has to be noted, the bulky carbene adding preferentially to the less substituted double bond - See R.A. Moss in "Carbenes", Vol. I, p. 257, John Wiley and Sons (1973).
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- (7) L.A. Paquette, J.S. Ward, R.A. Boggs and W.B. Farnham, J. amer. chem. Soc. **97**, 1101 (1975). We thank Professor Paquette for kindly sending us the NMR spectra of some substituted pentacyclo [4.3.0.0^{2,4}.0^{3,8}.0^{5,7}] nonanes.
- (8) The exo, exo configuration 4 is thermodynamically favored over 4c and 4d, but, here, the equilibria are displaced by subsequent rearrangement of the latter.
- (9) J.A. Berson, L.R. Corwin and J.M. Davis, J. amer. chem. Soc., **96**, 6177 (1974).