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# OXIDATIVE DECARBOXYLATION OF [n.2.2]PROPELLANE CARBOXYLIC ACIDS WITH LEAD TETRAACETATE. REARRANGEMENT APPROACH TO BICYCLO[n.2.2]BRIDGEHEAD ALKENES.

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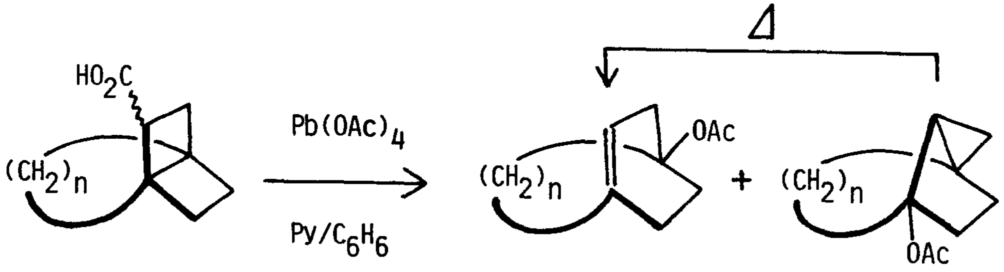
Summary: Oxidative decarboxylation of [n.2.2]propellane carboxylic acids (1a-c) with lead tetraacetate gave the bicyclic acetates (2b, c) having a bridgehead double bond and/or the tricyclic acetates (3a, b) in good yields. Vapor phase thermolysis of 3a or 3b afforded the bridgehead olefin 2a or 2b quantitatively.

Bridgehead olefins have attracted rapidly increasing attention in view of their significance concerning the stereochemistry of alkenes,[1] and, especially, recent interest has continued to be focused on development of new efficient methods providing an entry to highly strained bridgehead olefins.[2] In a continuation of the study on the transformation of readily available [n.3.2]-propellanes into other important carbocyclic ring systems,[3] we wish to report here a novel rearrangement approach to the bridgehead-substituted bicyclo-[n.2.2]bridgehead alkenes (2a-c) based on oxidative decarboxylation of [n.2.2]-propellane carboxylic acids (1a-c) with lead tetraacetate or followed by vapor phase thermolysis of the above reaction products (3a, b).

[n.2.2]Propellane carboxylic acids 1a-c[4,6] were prepared from [n.3.2]-propellanones[3] in 37-50% overall yields by the following sequence of reactions; 1) condensation with ethyl formate, 2) diazo-group transfer by tosyl azide, 3) photochemical Wolff rearrangement in methanol, 4) alkaline hydrolysis.



1 a, b, c
n = 4, 5, 6

2 a-c

3 a-c

Reaction of 1a-c with lead tetraacetate was carried out in the presence of pyridine in benzene solution at 80 °C for 1 h. The [6.2.2]propellane 1a gave the desired 8-acetoxybicyclo[6.2.2]dodec-1(10)-ene 2c[6] in 81% yield presumably via rearrangement of initially formed cyclobutyl cation to an allylcarbinyl one. In the case of the [5.2.2]propellane 1b, cyclopropylcarbinyl type tricyclic acetate 3b,[6] however, was obtained as the major product (60%) along with 13% of bicyclo[5.2.2]undecene derivative 2b.[7] Moreover, the [4.2.2]-propellane 1a afforded only the tricyclic acetate 3a[6] (68%) without any formation of the bridgehead alkene 2a.[7] Significantly, vapor phase thermolysis (250 °C, 30 sec, under nitrogen stream) of the tricyclic acetates 3a and 3b gave the corresponding bicyclic olefins 2a[6,8] and 2b in quantitative yields. Thus, an efficient synthetic route to bicyclo[n.2.2]bridgehead alkenes with functionality at the opposite bridgehead position was exploited.

## References and Notes

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4) 1a-c thus prepared were mixtures of exo and endo epimers. However, the mixtures were used without separation for oxidation with $Pb(OAc)_4$, because it has been well known that the primary process of the reaction with $Pb(OAc)_4$ is the formation of alkyl radicals followed by oxidation by $Pb^{IV}$ or $Pb^{III}$ species to classical cation intermediates and, therefore, the stereochemistry of starting acids may be disregarded in the present case.[5]
5) R.A.Scheldon and J.K.Kochi, Org.React., 19, 279(1972).
6) All new compounds gave satisfactory spectral and analytical data.
7) Small amounts (3-5%) of [n.2.2]propellenes were also detected.
8) The parent bicyclo[4.2.2]dec-1(8)-ene was synthesized quite recently; J.R.Wiseman, and J.J.Vanderbilt, J.Am.Chem.Soc., 100, 7730(1978).

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