Tetrahedron Letters No. 7, pp 507 - 510, 1973, Pergamon Press. Printed in Great Britain.

THE SYNTHESIS OF PADDLANES: COMPOUNDS IN WHICH QUATERNARY BRIDGEHEAD CARBONS ARE JOINED BY FOUR CHAINS

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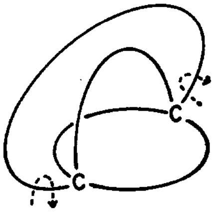
(Received in UK 21 December 1972; accepted for publication 8 January 1973)

It is hardly surprising in view of our interest in propellanes that we considered the synthesis of hubless propellanes[1] in which the hub would be replaced by a fourth chain of atoms connecting the bridgehead positions. There is no reason why such compounds should not be capable of existence albeit no concerted effort has heretofore been made to synthesize them and study their properties. We believed a priori that in such compounds, reminiscent of paddles on the Mississippi steamers of yore,* one might find interesting "in-out" type of isomerism in the sense that certain atoms might find themselves within the larger cavity of the molecule, relative to other atoms even if free rotation is possible as shown by the dotted arrow in 1.



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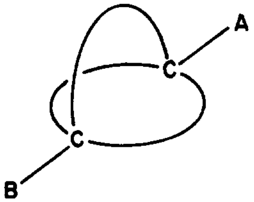

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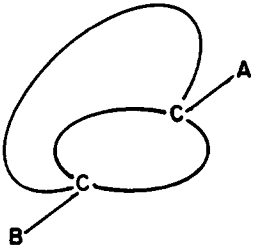

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B = A OR B ≠ A

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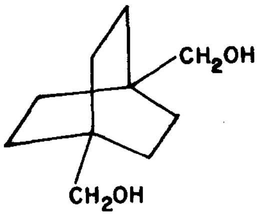
* The credit for this trivial name is due to Dr. J.J. Bloomfield who, as a resident of St. Louis, invokes nostalgic memories of the era of the paddleboats which plied the waters of that majestic river. (Cf. H.T. Kane, in Encyclopedia Brittanica, 1972 Edition, Vol. 15, p. 588).

Clearly one of the four chains must be much longer than the three others, the extent of this also being a matter for investigation. Other points of obvious interest would be the relationship between the relative length of the long chain and the shorter chains. For example, connecting the bridgehead positions of (the still unknown) bicyclo[1.1.1]butane does not require the same chain length as that required for bridging the analogous positions of, say, manxane.

It would be politic in the synthesis of such compounds to begin with a suitably substituted bicyclo-system in which each bridgehead carbon, already joined to the other by three shorter chains, would carry in addition a fourth chain, e.g. 2. This does not mean that one could not approach the synthesis of paddlanes from an intermediate such as 3 where the long chain and two shorter chains already exist leaving a short third chain to be constructed last.

Such chains can be completely carbocyclic but could also contain hetero-atoms. A synthesis of paddlanes can of course be designed from simpler starting materials than 2 or 3 but since certain compounds which are easily obtainable already exist, why not use them? In so deciding it may be that we have ourselves to thank for not yet observing "in-out" isomerism in our paddlane products. Yet one must start somewhere and the writing of our present letter is prompted at this stage by two interesting communications which though not identical to ours in the sense of their use of "in-out", are by no means unrelated.

Our first experiments have led to double paddlanes despite our awareness of the existence of high dilution experimental techniques, and our having employed them. Thus condensation of the diol 4 with sebacoyl chloride in acetonitrile solution in the presence of pyridine afforded 5, m.p. 50-52°. No trace of the simpler paddlane 6 could be detected.



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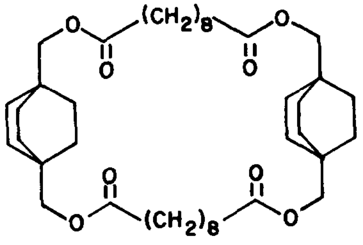

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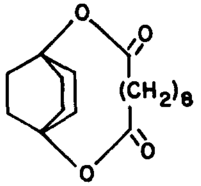

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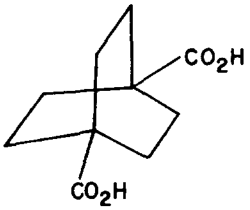
Similarly, condensation of 7 with 1,10-decanediol in benzene solution in the presence of *p*-toluenesulfonic acid afforded a mixture of oligomers from which 8, m.p. 57.5-58°, was isolated in low yield. A better method for preparing 8 was through condensation of the *bis*-acid chloride of 7 with the same diol in benzene solution, in the presence of pyridine. Here also, none of the simpler paddlane 9, which could have formed by the acid-catalyzed procedure, could be detected.



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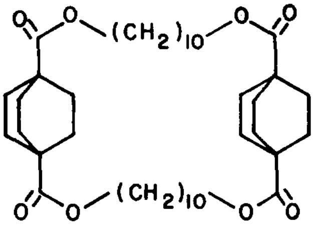

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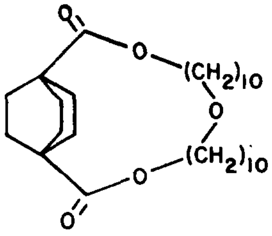

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No extraordinary behavior of protons was observed in the room temperature nmr spectra of the compounds described above. A number of other more and less obvious synthetic approaches have been used in order to obtain additional members of the paddlane series. Details will be published elsewhere. All compounds recorded herein have been characterized analytically and spectroscopically.

REFERENCES

1. J.C. Coll, DeL. R. Crist, M. Del C.G. Barrio and N.J. Leonard, *J. Amer. Chem. Soc.*, *94*, 7092 (1972), footnote 6.
2. P.G. Gassman and R.P. Thummel, *Ibid.*, *94*, 7183 (1972).
3. C.H. Park and H.E. Simmons, *Ibid.*, *94*, 7184 (1972).