

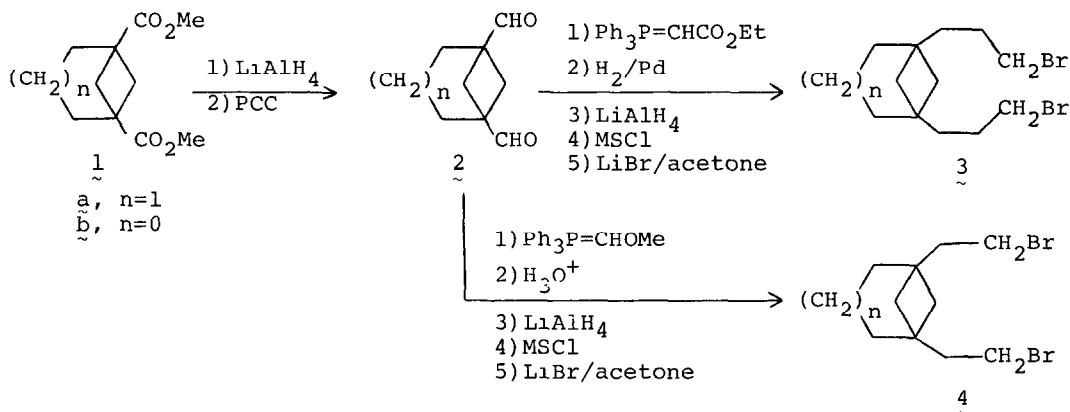
SYNTHESIS OF SOME [n.1.3.1]- AND [n.1.2.1]PADDLANES¹

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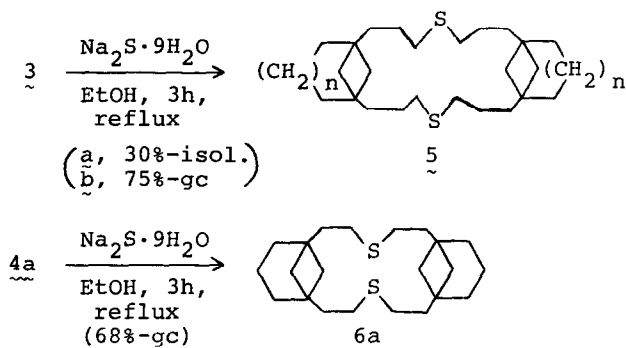
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Abstract: The synthesis of 3 dithiapaddlanes is described.

The construction of paddlanes,⁴ i.e. tricyclic compounds in which two bridgehead carbons are linked by four non-zero bridges, is a challenging problem, particularly when all the bridges are reasonably short. Our approach has been to construct bridgehead-bridgehead difunctionalized [m.1.1]bicyclic compounds,⁵ whereafter we hoped to close the fourth bridge. We now report the first results of this general approach.



An examination of models indicated that a 5-7 atom bridge should be long enough to span the bridgehead positions of a bicyclo[3.1.1]heptane or bicyclo[2.1.1]hexane. We thus converted previously prepared⁵ 1a into 3a and 4a and 1b into 3b via the straightforward sequences shown. Treatment of 3 and 4 with Na₂S resulted in the formation of dimers 5 and 6, respectively. Their general structure was indicated by their relatively long gc retention times (OV101, 250°: 5a, 17.5 min.; 5b, 9 min.; 6a, 7 min.) and mass spectra. A single crystal (mp 127-8°) X-ray analysis⁶ of 5a (Fig. 1) confirmed its structure; it is formally a [17.1.3.1]paddlane, while 6a is a [13.1.3.1]-paddlane. Clearly, however, the presence of 2 paddlane moieties/molecule makes for greater steric constraint than would be indicated by the length of the fourth bridge. Nonetheless, these molecules exhibit no obvious special properties; all bond distances and angles for 5a are normal.



Experiments aimed at desulfurization and transannular closure across the big rings of ~ 5 and ~ 6 are underway.

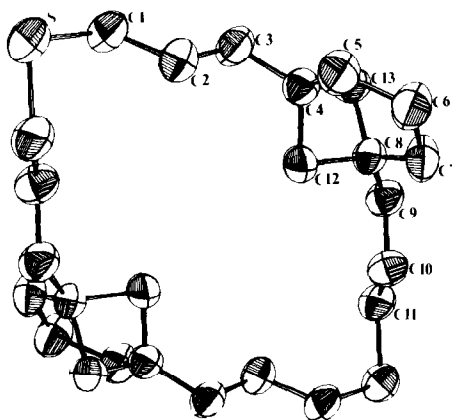


Figure 1. Computer generated perspective drawing of $\sim 5a$.

REFERENCES AND NOTES

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2. Alfred P. Sloan Foundation Fellow, 1976-80.
3. Ames Lab Summer Trainee, 1980.
4. K. B. Wiberg and M. J. O'Donnell, *J. Am. Chem. Soc.*, 101, 6660 (1979), and references therein.
5. P. Warner, B.-L. Chen and E. Wada, *J. Org. Chem.*, submitted.
6. X-ray data: crystals of $\sim 5a$ were triclinic; space group $P\bar{1}$; $Z = 1$; cell constants: $a = 9.497(4)\text{\AA}$, $b = 11.003(4)\text{\AA}$, $c = 6.433(2)\text{\AA}$, $\alpha = 101.48(3)^\circ$, $\beta = 94.95(6)^\circ$, $\gamma = 106.08(6)^\circ$; 2733 reflections measured with $\text{Mo } K\alpha$ radiation ($\lambda = 0.71034\text{\AA}$); 1765 reflections observed ($F_o > 3\sigma_{F_o}$); 1385 reflections ($2\theta < 45^\circ$) used in final refinement; present $R = 8.6\%$; $R_w = 10.8\%$; structure solved using MULTAN 76.

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