1-Aza-adamantanes from Phloroglucinols

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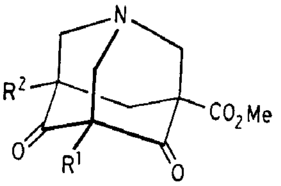
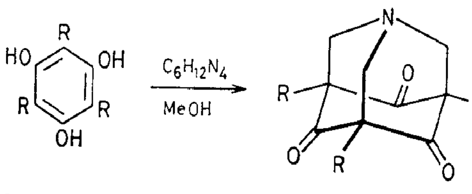
The tricyclic heterocycles of type (**4**) can be synthesised from substituted phloroglucinols in one step.

The recently synthesised 1-aza-adamantanes of type (**1**)[1] are of interest not only because of their diamond-like structure, but also because of their unusual chemical and spectroscopic properties.[2]

We have developed another approach to such compounds. Phloroglucinol is known to react not only as a phenol but also as a ketone, C-2, C-4, and C-6 acting as nucleophilic centres, and we have shown[1] that hexamethylenetetramine is an



(1) R¹, R² = alkyl.



(2) R = Me
(3) R = Et

(4) R = Me
(5) R = Et

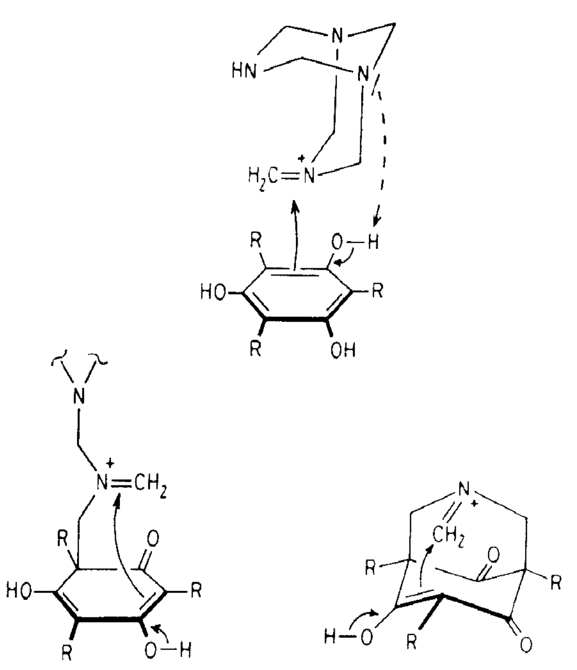
Table 1. Properties of (4) and (5).

	M.p.[a] /°C	ν_{max}/cm^{-1} (KBr)	¹H N.m.r. δ($CDCl_3$)
(4)	270—271	2987, 2975, 2934, 1736, 1688	1.25 (s, 9H, Me), 3.41 (s, 6H, CH_2)
(5)	244—245	2998, 2976, 2946, 2894, 1734, 1692, 1674	1.01 (t, 9H, Me), 1.82 (q, 6H, CH_2Me), 3.43 (s, 6H, CH_2)

[a] Sealed capillary.

appropriate electrophilic partner for addition to a number of cyclohexane-1,3-dione derivatives to yield (1). However, refluxing phloroglucinol in various solvents under a variety of conditions with hexamethylenetetramine yielded no tricyclic products; only condensation reactions were observed, possibly analogous to the formation of phenol formaldehyde resin.

However, when we chose alkylated compounds such as trimethyl- (2) or triethyl-phloroglucinol (3),[3] we obtained new derivatives of 1-aza-adamantane (4) and (5) (Table 1)† in good yields (*ca.* 80%). These compounds have unusual structures with corresponding chemical and physical properties of practical and theoretical interest.[4]



Scheme 1. Postulated intermediates.

Thus, under certain conditions the electrophilic potential of hexamethylenetetramine can be regenerated several times by protonation followed by bond cleavage, as we postulate with the mechanism in Scheme 1. In this way, all three carbon–carbon bonds are formed specifically in one step.

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† Refluxing (2) [(3)] with hexamethylenetetramine in absolute methanol for several hours led to the precipitation of the desired product (4) [(5)] as cotton-like needles, whose structure was unambiguously confirmed chemically and spectroscopically.

References

1 N. Risch and W. Saak, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 923; *Angew. Chem.*, 1982, **94**, 926.
2 Unpublished work.
3 These compounds may be synthesised by classical methods (H. Weidel and F. Wenzel, *Monatsh. Chem.*, 1898, **19**, 249) starting from the corresponding trialkylbenzenes.
4 A. W. J. D. Dekkers, J. W. Verhoeven, and W. N. Speckamp, *Tetrahedron*, 1073, **29**, 1691; C. A. Grob, M. Bolleter, and W. Kunz, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 708; *Angew. Chem.*, 1980, **92**, 734.