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N-BRIDGED HETEROCYCLES. PART III. A NEW SIMPLE SYNTHESIS OF 1,3-POLYMETHYLENEBENZIMIDAZOLONES, THEIR CROWN ETHER ANALOGUES AND RELATED SYSTEMS†

By M.M. Htay and O. Meth-Cohn*

The Ramage Laboratories, University of Salford, Salford M5 4WT, England.
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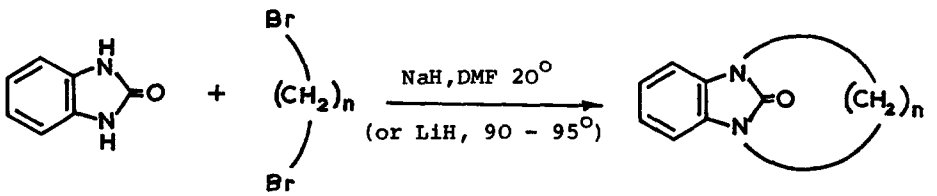
We have reported previously on the synthesis and aromaticity of the series of bridged benzimidazolones[1](3). We now disclose a versatile and simple approach of wide application to these and related systems exemplified in Scheme 1 and Table 1.

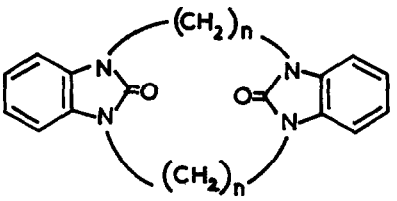


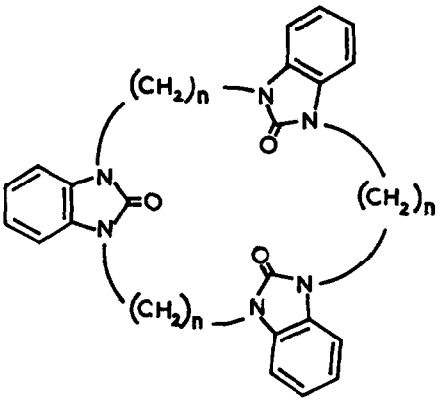
(1) (2) (3) a; n = 12
b; n = 10

Scheme 1

The method involves the slow, dropwise addition of a mixture of benzimidazolone (1) and an α,ω-dibromoalkane (2) in DMF, to a stirred suspension of sodium hydride, followed by filtration, evaporation and chromatography (alumina) of the residue. It will be seen that good yields of the monomer (3) are obtained with high values of n (10 or 12) but that reduction of the chain length results in increasing amounts of the dimer, no monomer being formed with n = 5, 6, 7 or 8 only the dimers (4) and trimers (5b).

† Dedicated to Prof. Hans Suschitzky on his 60th birthday.

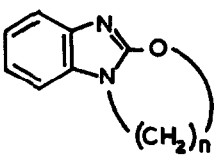


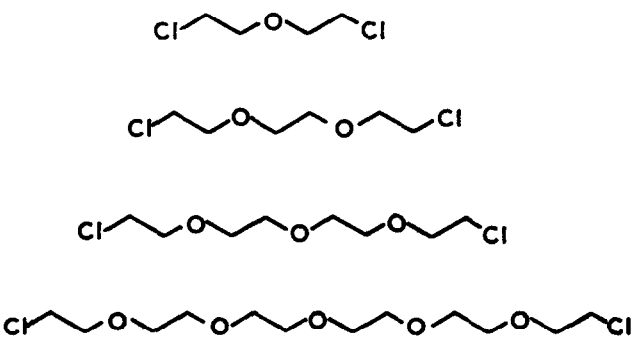


(4) a; n = 5
b; n = 6
c; n = 7
d; n = 8
e; n = 10

(5) a; n = 4
b; n = 6

Further contraction (n = 4) results in formation of the trimers (5a) and the N,O - bridged system (6b), while solely the latter type of product is isolated with n = 3 (6a).

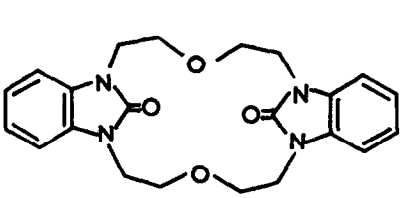




(6) a; n = 3
b; n = 4

(7)

By use of the α,ω-dichloro ethers (7) in the above synthesis, a series of crown ether analogues (8 - 11) were similarly isolated.



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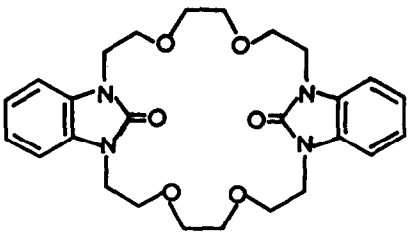

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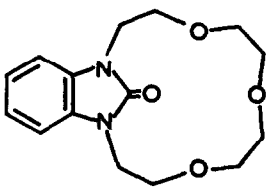
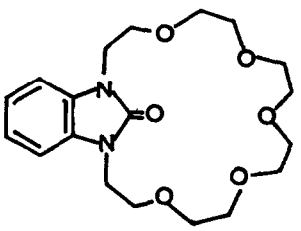


(10)

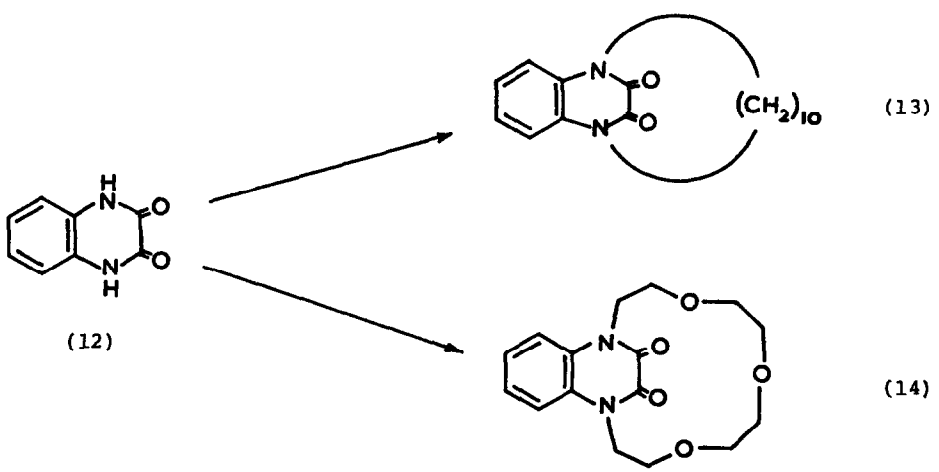


(11)

Furthermore, replacement of benzimidazolone by, for example quinoxaline - 2,3 -dione (12) or 6-methyluracil (15), similarly gave corresponding products (Scheme 2 and 3 and Table).

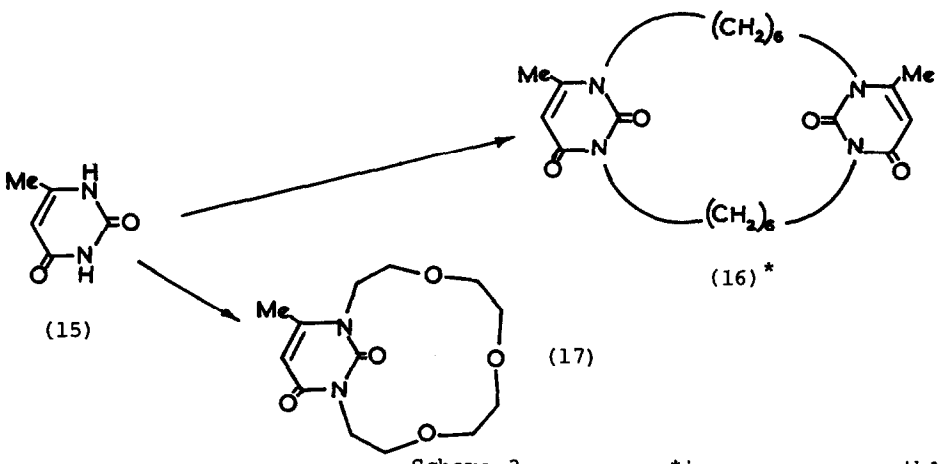
Many of the above compounds form complexes with cations, particularly group I and II metal ions. Some of these have been isolated as stable crystalline compounds and their properties will be discussed elsewhere.

We thank the British Council for a grant to M.M.H.



(12) (13) (14)

Scheme 2



Scheme 3 *isomers are possible

Table

Compound	3a	3b	4a	4b	4c	4d	4e	5a	5b	6a
Yield (%)	60	38.2	10.2	8.4	1.7	5.7	0.6	5.5	2.8	29.4
M.p (°C)	129-30	107-8	173	211	102-5	189-90	139-40	218-19	151-52	116-17

Compound	6b	8	9	10	11	13	14	16	17
Yield (%)	5.9	14.8	12.4	13.7	78.5	5.3	7.2	4.3	0.2
M.p (°C)	138-40	197-99	114	117-18	95-100 at 0.05 mm	172-4	184	160-64	92-94

References

1. R. J. Hayward and O. Meth-Cohn, J. Chem. Soc. Perkin I, 1975, 212 and 219.