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DEHYDROHALOGENATION OF THE BIS-DICHLOROCARBENE ADDUCTS OF SOME CYCLOHEXA-1,4-DIENES: A REGIOSPECIFIC ROUTE TO HOMOTROPILIDENES.[1]

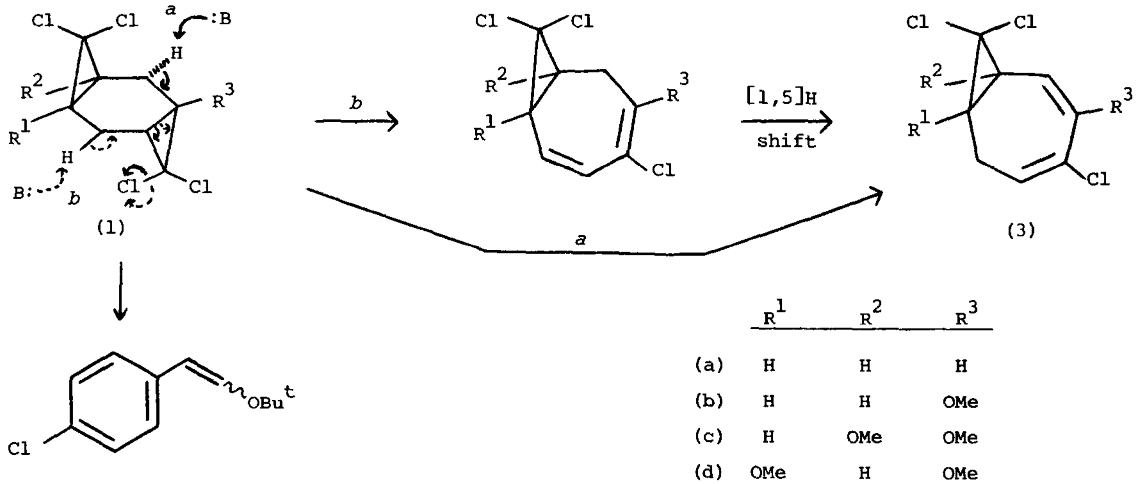
Martin G. Banwell and Brian Halton*

Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand.

Summary: *Dehydrochlorination of the methoxytricyclooctanes (1b-d) affords the homotropilidenes (3b-d) regiospecifically by 1,4-elimination in strongly basic media.*

The dehydrohalogenation of mono-dichlorocarbene adducts of medium and large ring cycloalkanes and -alkadienes has provided a route to compounds not easily accessible by other methods. In the presence of a strong base such compounds undergo 1,2-elimination to give a ring fused cyclopropene which suffers further dehydrochlorination and rearrangement to give product(s) by a pathway which is dependent on the size of the fused ring.[2,3] By comparison, little is known of the behaviour of the bis-dihalogenocarbene adducts of the cycloalkadienes under comparable conditions; the tetrachlorotricyclooctane (1a) has been studied previously and was found to yield an *E/Z* mixture of the *p*-chlorostyrene (2).[4] We now report on the behaviour of the mono- and di-methoxytetrachlorotricyclooctanes (1b-e) in the presence of strong base.

The *anti*-tricyclooctanes (1b-e) were obtained in excellent yield from the appropriate aromatic ether by Birch reduction and subsequent bis-addition of dichlorocarbene.[5,6] When (1b-e) are added to an excess of t-BuOK in THF[2-4] severe decomposition occurs and a multitude of products are formed. The sole isolable compound (4%) results from (1d) and, while it has been identified as a $C_{10}H_{11}O_2Cl_3$ species, its structure remains in doubt. However, by reversing the mode of addition and adding the filtered base to the substrate each of (1b-d) undergoes smooth



(1)

(3)

(2)

	R^1	R^2	R^3
(a)	H	H	H
(b)	H	H	OMe
(c)	H	OMe	OMe
(d)	OMe	H	OMe
(e)	OMe	OMe	H

dehydrochlorination to yield the homotropilidenes (3b-d) (59, 18 and 54%) respectively, as the sole isolable products in a regiospecific manner.[7,8] Whereas the reactions of (1b,d) proceed readily, that of (1c) is markedly slower and product (3c) is contaminated with inseparable starting material. Surprisingly, the 1,7-dimethoxy derivative (1e) is resistant to reaction and is recovered unchanged.

The regiospecific formation of the homotropilidenes (3b-d) must involve 1,4-elimination. Although we favour abstraction of H-2 (path *a*, Scheme) as has been reported for the mild thermolysis of analogues in weakly basic media,[9] and is consistent with the increased steric demand of (1c), we cannot distinguish between this and removal of H-6 (path *b*, Scheme) followed by rapid [1,5]H shift. The failure of (1b-d) to suffer 1,2-elimination to yield a tricyclooct-1(8)-ene by analogy with all other ring fused *gem*-dichlorocyclopropanes in the presence of strong base is unusual. When the non-methoxylated compound (1a) is subjected to the same conditions the same styrenes (2) are produced and, while the yield is low, no evidence was obtained for homotropilidene formation. Surprisingly, re-subjection of the homotropilidenes (1b-d) to base (either mode of addition) shows the compounds to be remarkably resistant to further dehydrochlorination; only slight decomposition occurs and the compounds are recovered in high yield.

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References and Footnotes:

1. Studies in the Tricyclooctane Series II. For Part I see reference 4.
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3. W.E. Billups, *Accounts Chem. Res.*, 1978, 11, 245; M.G. Banwell, R. Blattner, A.R. Browne, J.T. Craig, and B. Halton, *J.C.S. Perkin I*, 1977, 2165 and references cited.
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6. Compounds (1c,d) have been obtained previously: A.J. Birch, J.M. Brown, and F. Stansfield, *J. Chem. Soc.*, 1974, 5343.
7. ^{1}H and ^{13}C data (in $CDCl_3$) are:
    (3b) δ 1.75-2.4, complex m, 2H; 2.7-2.95, m, 2H; 3.53, s, 3H; 4.94, d *J* 6 Hz, 1H; 6.44, t *J* 3 Hz, 1H. 22.4, 25.8, 28.8, 54.7, 66.6, 91.9, 117.8, 128.0, 153.2.
    (3c) δ 1.94, broad t *J* 6 Hz, 1H; 2.89, overlapping d of d, 2H; 3.45, s, 3H; 3.62, s, 3H; 5.02, s, 1H; 6.56, t *J* 3 Hz, 1H. 22.8, 31.1, 55.0, 55.4, 67.2, 69.5, 92.4, 118.8, 127.8, 154.6.
    (3d) δ 2.23, d *J* 6 Hz, 1H; 2.90, d of d *J* 18 and 3 Hz, 1H; 3.29, d of d *J* 18 and 3 Hz, 1H; 3.42, s, 3H; 3.54, s, 3H; 4.88, d *J* 6 Hz, 1H; 6.47, t *J* 3 Hz, 1H. 26.9, 35.4, 54.8, 55.0, 64.8, 69.2, 91.8, 118.2, 128.5, 153.3.
8. Compounds (3b-d) decompose in a matter of hours when exposed to air at room temperature.
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