Tetrahedron Letters No. 27, pp 2563 - 2566.
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0040-4039/79/0701-2563$02.00/0

STUDIES IN THE SYNTHESIS OF 7,8-BENZO[5]METACYCLOPHANE

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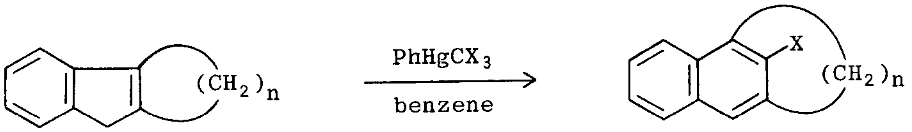
Summary. Compound *5* reacted with silver perchlorate in anhydrous benzene to give *3a* and in wet acetone to give a mixture of *9* and *10*; treatment of *9* with potassium t-butoxide in dimethyl sulphoxide gave *11*.

Parham and his coworkers have shown[1] that benzometacyclophane derivatives (*2a* and *2b*) can be made in good yields by heating the corresponding indene derivatives[2] (*1*) with phenyl (trichloromethyl)- and phenyl(tribromomethyl)-mercury, respectively, in benzene solution. Thus when *1* (n = 6) was heated, under reflux, with an excess of phenyl(trichloromethyl)-mercury in benzene solution, the benzo[6]metacyclophane derivative (*2a*, n = 6) was obtained[1b] in 74% yield. However, when *1* (n = 5) was heated with a twofold excess of phenyl(trichloromethyl)-mercury in boiling benzene solution for 41 hr, the naphthalene derivative (*3a*) was obtained[1b] in 66% yield together with *4* (8.4%). The desired benzo[5]metacyclophane derivative (*2a*, n = 5) was not detected in the products.



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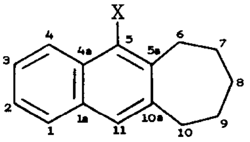
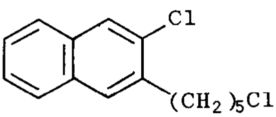
2 *a*; X = Cl
b; X = Br



3 *a*; X = Cl
b; X = H



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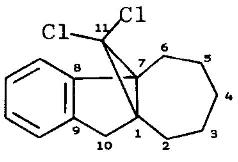

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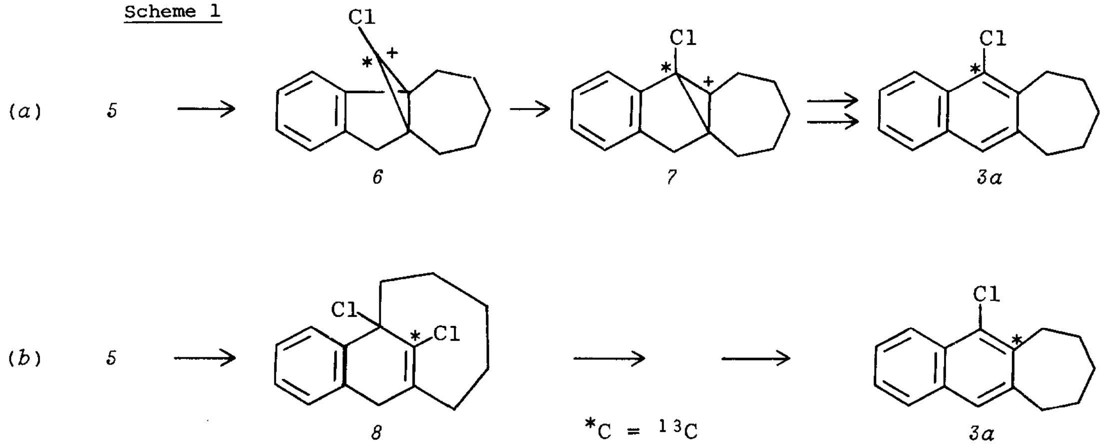
We have previously found[3] that the silver perchlorate promoted ring-expansion of halogenocarbene adducts of cyclic olefins generally proceeds more readily than the corresponding thermally promoted reaction[4]. Furthermore, as bridged *trans*-cyclo-octene derivatives, including [5]metacyclophane itself[5], have been prepared, it seemed likely that the benzo[5]metacyclophane derivative (*2a*, n = 5) would be stable enough to be isolable. We therefore decided to investigate the action of silver perchlorate on 8,9-benzo-11,11-dichlorotricyclo[5.3.1.0^{1,7}]-undec-8-ene[6] (*5*).

Treatment of *5* with an excess of *M*-silver perchlorate in anhydrous benzene solution for 12 min. at room temperature gave *3a* as the sole isolable product. The latter compound (*3a*) was obtained as a crystalline solid, m.p. 96-96.5°C (lit[1b] 99-99.5°C), in 61% yield. No evidence was obtained for the presence of the benzo[5]metacyclophane derivative (*2a*, n = 5) in the products. Structure *3a*[8] was assigned to the product on the basis of ^{1}H and ^{13}C [in CDCl$_3$, δ 27.6, 28.9, 31.5, 31.9, 36.9, 124.9, 125.7, 126.1, 127.3, 129.6, 129.9, 132.9, 139.3, 142.7] n.m.r. spectroscopic and chemical evidence. Thus when a solution of *3a* in ethanol was shaken with hydrogen in the presence of 10% palladium charcoal and magnesium oxide, *3b* [^{13}C n.m.r. (CDCl$_3$): δ 29.1, 32.4, 36.8, 125.1, 126.7, 127.0, 132.4, 142.1], m.p. 103°C, was obtained in 98% yield. As expected, when *3b* was treated with sulphuryl chloride in dichloromethane solution, it was converted back into *3a* in high yield.

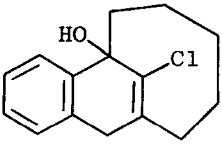
Parham *et. al.* suggested[1b] a mechanism for the conversion of *5* into *3a* which involves (Scheme 1a) initial loss of chloride ion to give the cyclopropyl cation (*6*) which then isomerizes to the cyclopropyl cation (*7*) by a process involving 1,2-aryl migration. Disrotatory ring opening of *7*, followed by proton loss leads to the observed product (*3a*). One unsatisfactory feature of this mechanism is that aryl migration is unlikely to be concerted with loss of chloride ion from *5* as cleavage of the carbon-chlorine bond *exo* to the seven-membered and *endo* to the five-membered ring would be expected[9] to be favoured[10]. With the hope of obtaining further information relating to the conversion of *5* into *3a*, we therefore prepared a sample of *5*, specifically labelled with ^{13}C at C-11, treated it with silver perchlorate in benzene solution and examined the ^{13}C n.m.r. spectrum of the product (labelled *3a*)[11].

Scheme 1



*C = ^{13}C

The ^{13}C n.m.r. spectrum of the labelled *3a* thus obtained was identical to that of the unlabelled compound (see above) except for the enhanced intensity of the signal at δ 139.3. As this signal could not be assigned with certainty, labelled *3a* was converted by catalytic hydrogenolysis (see above) into labelled *3b*. An almost quantitative yield was obtained. The ^{13}C n.m.r. spectrum of labelled *3b* was found to be identical to that of the unlabelled compound (see above) except for the enhanced intensity (by a factor of *ca.* 4) of the signal at δ 142.1. From their low intensities relative to those of the resonance signals of the other aromatic carbon atoms in the ^{13}C n.m.r. spectrum of unlabelled *3b*, it seems reasonable to assign the signals at δ 132.4 and 142.1 to the resonances of the two pairs of quaternary carbon atoms, i.e. C-1a, C-4a and C-5a, C-10a. Furthermore as the C-2 resonance is the furthest downfield signal in the ^{13}C n.m.r. spectrum of 2-methylnaphthalene[12], it is reasonable to assign the signal at δ 142.1 in the spectrum of *3b* to the resonance of C-5a (or C-10a). It may therefore be concluded that the conversion of *5* into *3a* does not involve aryl migration which would result in C-5 being labelled (Scheme 1a) but rather that it involves initial ring expansion to give a *trans*-cyclo-octene derivative (*8*, Scheme 1b) which is then converted by several steps into *3a*. Presumably the conversion of *8* into *3a* must involve a prototropic rearrangement, whereby the *trans*-cyclo-octene double bond is brought into conjugation with the benzene ring, followed by a 1,2-alkyl shift. Perhaps the most remarkable feature of this transformation (Scheme 1b) is that the original chloride ion leaving group is apparently retained, even in the presence of silver ion, and that it becomes the 1-chloro substituent in the final product (*3a*).



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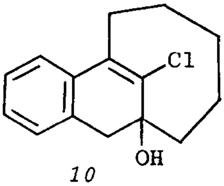

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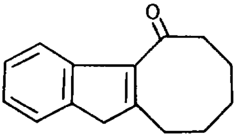

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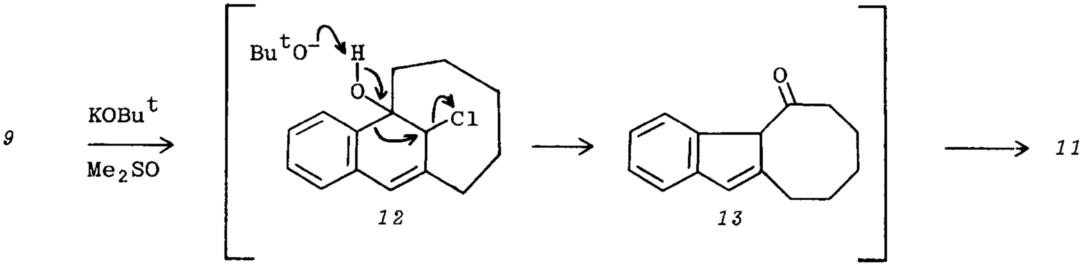
Treatment of *5* with an excess of *M*-silver perchlorate in acetone-water (44:1 v/v) for 15 min. at 20° gave two products which were separated by chromatography on silica gel. The less polar product [R_f 0.4 (CHCl$_3$-EtOH, 98:2 v/v)] was eluted first and isolated as a crystalline solid, m.p. 103°C in 35% yield; this compound was assigned the structure *9* on the basis of its ^{1}H n.m.r. spectrum [220 MHz (CDCl$_3$): δ 0.60 (1H,m), 1.5-2.0 (4H,m), 2.0-2.2 (3H,m), 2.37 (1H, t, $J \sim 12$ Hz), 2.59 (1H,s), 3.20 (1H, dt, $J \sim 12$ and 5 Hz), 3.53 (1H, d, $J = 22$ Hz), 3.79 (1H, d, $J = 22$ Hz), 7.10 (1H,m), 7.24 (2H,m), 7.63 (1H,m)] and its ready conversion (Scheme 2 and below) into *11*. The more polar product [R_f 0.3 (CHCl$_3$-EtOH, 98:2 v/v)], which was isolated in 31% yield, has not yet been obtained crystalline; it has provisionally been assigned the structure *10* on the basis of its i.r., n.m.r. (^{1}H and ^{13}C) and mass spectra.

Scheme 2



When *9* was treated with a fourfold excess of *M*-potassium t-butoxide in dimethyl sulphoxide solution for 60 sec. at 20°, *11* was obtained and isolated as a yellow crystalline solid, m.p. 101-102°C, in 73% yield. The latter compound (*11*) was characterized on the basis of its infrared ($\nu_{max}^{CHCl_3}$ 1650 cm^{-1}), ^{1}H n.m.r. [90 MHz ($CDCl_3$): δ 1.5-2.0 (6H,m), 2.87 (4H,m), 3.55 (2H,s), 7.15-7.40 (3H,m), 7.87 (1H,m)] and ^{13}C n.m.r. spectra. The probable mechanism for the base-promoted conversion of *9* into *11* is indicated in Scheme 2. The first and last steps of this transformation (i.e. the conversions of *9* → *12* and *13* → *11*, respectively) both involve prototropic rearrangements which would be expected to be thermodynamically favourable. Unlike *9*, *10* is relatively stable to treatment with potassium t-butoxide in dimethyl sulphoxide solution.

Attempts to convert *9* or *10* into the benzo[5]metacyclophane derivative (*2a*, n = 5) have so far been unsuccessful.

Acknowledgements. We thank Professor Philip Warner for a most helpful discussion. One of us (P.G.) also thanks the Science Research Council for the award of a Research Studentship.

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[3] C.B. Reese and A. Shaw, *J. Amer. Chem. Soc.* **92**, 2566 (1970); *J.C.S. Perkin I* 2422 (1975).

[4] M.S. Baird and C.B. Reese, *J. Chem. Soc.(C)* 1803, 1808 (1969).

[5] J.W. van Straten, W.H. de Wolf and F. Bickelhaupt, *Tetrahedron Letters* 4667 (1977).

[6] Compound *5* was prepared by stirring solutions of *1* (n = 5) in chloroform and sodium hydroxide in water (1:2 w/w) rapidly together in the presence of a catalytic amount of cetyltrimethylammonium bromide at room temperature; it was obtained as a pure colourless solid[7], m.p. 108-109°C, in 82% yield.

[7] Satisfactory spectroscopic and microanalytical data have been obtained for all crystalline compounds described.

[8] Parham's assignment[1b] of structure *3a* to the product obtained by heating *1* (n = 5) with $PhHgCCl_3$ was based on the observation that it could be converted into 3-chloro-1,2,4,5-benzenetetracarboxylic acid by oxidation.

[9] U. Schöllkopf, *Angew. Chem. internat. Edit.* **7**, 588 (1968).

[10] We are grateful to Professor Philip Warner for causing us to doubt the validity of this mechanism (Scheme 1a) and thus for encouraging us to carry out further studies.

[11] Compound *5*, specifically labelled with ^{13}C, was prepared as above by treating a solution of *1* (n = 5) in an approximately twofold excess of $CHCl_3$ (6.6% ^{13}C) with aqueous sodium hydroxide in the presence of cetyltrimethylammonium bromide. Only the signal at δ 77.5 was intensified in the ^{13}C n.m.r. spectrum of the *5* obtained, thus indicating that it was specifically labelled at C-11. Crystalline ^{13}C-labelled *3a* was obtained from the latter material (labelled *5*) in 54% isolated yield.

[12] L.F. Johnson and W.C. Jankowski, "Carbon-13 NMR Spectra. A Collection of Assigned, Coded, and Indexed Spectra", Wiley, New York, 1972, Spectrum No. 416.

(Received in UK 30 April 1979)