Generation and Cyclotrimerization of 1,4-Dioxacyclohexyne (*p*-Dioxyne)

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1,4-Dioxacyclohexyne (*p*-dioxyne) has been generated at low temperature in tetrahydrofuran solution from 2,3-dibromo-1,4-dioxacyclohexene, *via* 2-bromo-3-lithio-1,4-dioxacyclohexene, and isolated as the corresponding cyclotrimer tris(ethylenedioxy)benzene (1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-1,4,5,8,9,12-hexaoxatriphenylene).

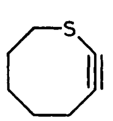
The chemistry of small-ring cyclic alkynes has recently received considerable attention from both the theoretical and the experimental points of view.[1,2] However, little is known on cycloalkynes incorporating heteroatoms directly bonded to the acetylenic group. Only recently have the synthesis of thiacyclo-oct-2-yne (**1**)[3] and the generation in an argon matrix of azacyclohex-2-yne (**2**)[4] been reported, and an *ab initio* MO study of 1,4-dioxacyclohexyne (**3**) at the GVB (Generalised Valence Bond) level of theory has been published predicting for this compound a singlet ground state of acetylenic nature, but with a significant diradical character (29%), and a small (13 kcal/mol; cal = 4.184 J) singlet–triplet separation.[5]

We now report on experiments that have led to the generation and isolation as a cyclotrimer of compound (**3**), which has the characteristics of both an acetylene diether[6] and a strained cycloalkyne.

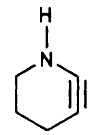
Since stable bis(triphenylphosphine)platinum(0) complexes of small-ring cycloalkynes (cyclohexyne and cycloheptyne) have been obtained by reduction of the corresponding dibromocycloalkenes in the presence of platinum(0) species,[7] we directed our efforts along these lines. However, when 2,3-dibromo-1,4-dioxacyclohexene (**4**)†‡ was treated with sodium amalgam [tetrahydrofuran (THF) −15 °C] in the presence of (ethene)bis(triphenylphosphine)platinum(0), the product was complex (**5**). The ease with which platinum insertion into the carbon–halogen bond occurs, which parallels that of halogeno substituted bicyclo[2.2.1]hept-2-ene derivatives,[8] could not be overcome by the use of chloro derivatives as cycloalkyne precursors. Thus, successive treatment of 2-chloro-1,4-dioxacyclohexene (**6**) with Bu^{t}Li (THF, −78 °C) and Pt(C_2H_4)(PPh_3)$_2$ afforded complex (**7**).

Alternatively, the generation of (**3**) by base-promoted elimination from suitable precursors and subsequent cyclotrimerization to a hexasubstituted benzene derivative, a strategy which has been applied to other strained cycloalkynes,[9] was attempted (Scheme 1). 2-Chloro-3-lithio-1,4-dioxacyclohexene (**8**), generated from (**6**) (Bu^{t}Li, THF, −78 °C), turned out to be stable in THF solution at room temperature affording, on treatment with D_2O, the deuteriodioxycyclohexene (**9**). Even after boiling under reflux for 1 h a THF solution of (**8**) followed by treatment with water, (**6**) was recovered in high yield. On the other hand, when compound (**10**), generated from (**4**) at low temperature (Bu^{n}Li, THF, −78 °C), was allowed to warm to room temperature, elimination of lithium bromide took place. Aqueous work-up and column chromatography of the crude reaction mixture (neutral Al_2O_3; light petroleum–dichloromethane mixtures of increasing polarity) allowed the isolation in low yield (2.4%) of the hexaoxatriphenylene (**11**), the cyclotrimer of 1,4-dioxacyclohexyne.

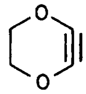
Since nickel catalysts have proved to be effective in the cyclotrimerization of cycloalkynes[9d] and acetylene diethers,[10]



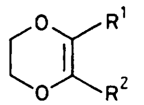
(1)



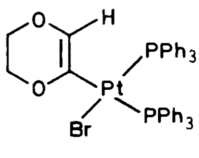
(2)



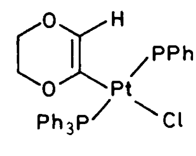
(3)



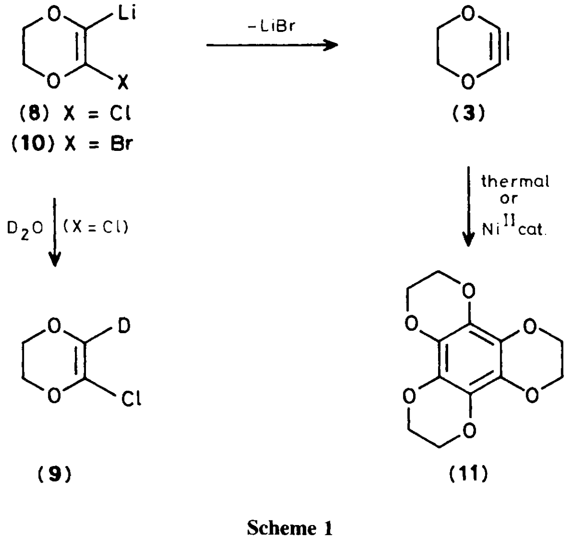
(4) $R^1 = R^2 = Br$
(6) $R^1 = H$, $R^2 = Cl$



(5)



(7)



Scheme 1

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† Prepared by bromination of 2-bromo-1,4-dioxacyclohexene at −78 °C in hexane solution followed by dehydrobromination at low temperature with potassium t-butoxide (71% yield).

‡ All new compounds gave satisfactory microanalytical and spectral data consistent with their assigned structures. *Spectral data*: (**4**), $\nu_{max.}$ (CCl_4) 1635 cm^{-1}; ^1H n.m.r. ($CDCl_3$): δ 4.30 (s); ^{13}C n.m.r. ($CDCl_3$): δ 118.10 (s), 66.99 (t); *m/z* 242 (M^+); (**5**), $\nu_{max.}$ (CCl_4) 1595 cm^{-1}; ^1H n.m.r. (C_6D_6): δ 6.6—6.3 (m, 30H), 4.6 (s, 1H), 2.1 (m, 4H); ^{31}P n.m.r. [THF, P(OMe)$_3$] δ P_A 124.4 (d), δ P_B 142.5 (d), $^2J(P_AP_B)$ 16 Hz, ^1J (P_APt) 3036 Hz, ^1J (P_BPt) 2969 Hz; (**7**), $\nu_{max.}$ (CCl_4) 1600 cm^{-1}; ^1H n.m.r. (C_6D_6): δ 6.5—6.1 (m, 30H), 4.6 (s, 1H), 2.7 (m, 4H); ^{31}P n.m.r. [THF, P(OMe)$_3$] δ 117.7 (s), ^1J (PtP) 3072 Hz; (**11**) white needles (from chloroform–hexane), sublimation at 392.3 °C (differential scanning calorimetry); $\nu_{max.}$ 3000, 2940, 2890, 1630, 1490, 1270, 1245, 1140, 1115, 955 cm^{-1}; ^1H n.m.r. ($CDCl_3$): δ 4.30 (s); $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$): δ 127.31, 64.70; *m/z* 252 (41%, M^+), 225 (15%), 224 (16%), 195 (19%), 139 (46%), 112 (45%); *m/z* 252.0648 (calc. 252.0634).

the effect of some of them in the present reaction was studied. Thus, performing the decomposition of (**10**) in the presence of catalytic amounts of biscyclopentadienylnickel and acetylacetonatonickel(II) led to a slight increase in the yield of (**11**) (3.3 and 7%, respectively). On the other hand, neither $Ni(CO)_4$ nor $Ni(CO)_2(Ph_2PCH_2CH_2PPh_2)$ showed a beneficial effect on the cyclotrimerization process.

Whereas the trapping of a cycloalkyne in the form of a transition metal complex does not necessarily imply the generation of the free compound at some stage of the reaction, the formation of the corresponding cyclotrimer is considered as a compelling evidence of the transient existence of the free cycloalkyne.[9d] Consequently, the formation of (**11**) from (**10**) provides solid evidence in favour of the transient formation and the acetylenic nature of *p*-dioxyne (**3**). To the best of our knowledge, this is the first example of a small ring cycloalkyne incorporating two heteroatoms directly bonded to the sp carbons to be reported.

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