

COMMUNICATIONS TO THE EDITOR

The Syntheses of Spiro Orthocarbonates

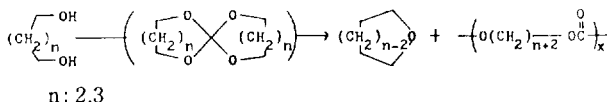
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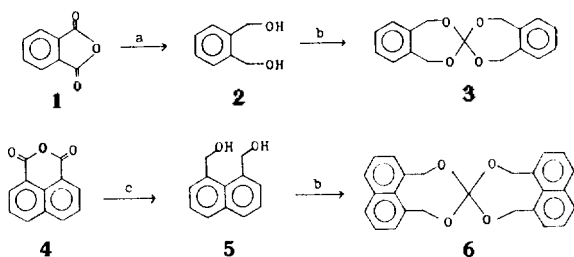
In an effort to produce monomers that would undergo polymerization with either no change in volume or slight expansion, it was found that bicyclic compounds in which two rings were opened for every new bond that was formed in the polymer chain would accomplish that object. Thus various bicyclic monomers, such as spiro orthoesters, ketal lactones, trioxabicyclooctanes and spiro orthocarbonates, were synthesized and found to indeed expand on polymerization.^{1,2} These monomers appear to be capable of many uses including high strength composites³ and dental fillings.⁴

From a study of series of bis-spiro orthoesters derived from lactones and diglycidyl ether of hydroquinone, Iwama⁵ reported that the monomer which has larger ring produces greater expansion on ring opening polymerization. With this facts, larger membered spiro orthocarbonate was tried to synthesized. Sakai and his coworkers⁶ successfully prepared the highly reactive and versatile five and six-membered spiro orthocarbonates by the reaction of diol with bis(*n*-butyl)tin oxide followed by the treatment with carbon disulfide. However, the larger membered spiro orthocarbonate was relatively unstable due to its strain in the two larger membered rings and was decomposed to cyclic ether and polycarbonate as shown on scheme 1.



Scheme 1

Here we report the successful preparation of seven- and eight-membered spiro orthocarbonates starting from phthalic anhydride and 1,8-naphthalene dicarboxylic acid anhydride as shown on scheme 2.



Reagents: a. $\text{BF}_3/\text{NaBH}_4$, b. 1) $(n\text{-Bu})_2\text{SnO}$ 2) CS_2 , c. LiAlH_4

Scheme 2

Diol **2** and **5** were prepared by the reduction of corresponding acid anhydrides **1** and **4**. 1,2-Bis(hydroxymethyl) ben-

zene **2** was prepared in 61% yield from the treatment of phthalic anhydride with $\text{BF}_3/\text{NaBH}_4$ in dried THF; mp 63-64°C (lit⁷ 63-65°C); IR (KBr) 3200 cm^{-1} (OH stretching), 760 (1,2-disubst. benzene); ¹H-NMR (acetone d_6) δ 7.50-7.20 (m, 4H, ArH), 4.75 (d, 4H, CH_2), 4.40 (t, 2H, OH). 1,8-Bis(hydroxymethyl)naphthalene **5** was obtained in 70% yield following the published procedures⁸ in which compound **4** in dried THF and dried benzene was treated with LiAlH_4 ; mp 154-156°C (lit⁸ 156-156.5°C); IR (KBr) 3340 and 3210 cm^{-1} (OH stretching); ¹H-NMR (acetone d_6) δ 8.00-7.32 (m, 6H, ArH), 5.27 (s, 4H, CH_2), 2.80 (s, 2H, OH). In this preparation, we also obtained variable amount of 2,3-dihydro-2-oxaphenylene depending on reaction conditions. When this reaction was carried with $\text{BF}_3/\text{NaBH}_4$, the oxaphenylene compound became the major product instead of diol.

Spiro orthocarbonates **3** and **6** were synthesized by Sakai's procedures. Seven-membered spiro orthocarbonate **3** was prepared in 78% yield by treatment of diol **2** with $(n\text{-Bu})_2\text{SnO}$ followed by treatment with carbon disulfide; mp 222-223°C; IR (KBr) 1130 cm^{-1} (C-O stretching), 750 (1,2-disubst. benzene); ¹H-NMR (CDCl_3) δ 7.37-7.00 (m, 8H, ArH), 5.00 (s, 8H, CH_2). The structure of compound **3** was confirmed by IR and NMR spectrum. In IR spectrum the OH stretching band of starting diol was disappeared and the intensity of C-O stretching band was greatly increased. The absence of any C=O stretching band also supports the formation of spiro compound without direct formation of polycarbonate. Eight-membered spiro orthocarbonate **6** was synthesized in 70% yield by the same method as compound **3**; mp 293-295°C(dec); IR(KBr) 1170 and 1020 cm^{-1} (C-O stretching); ¹H-NMR (CDCl_3) δ 7.50-7.30 (m, 12H, ArH), 5.37 (s, 8H, CH_2). In this preparation also there was no direct formation of polycarbonate. From a preliminary experiment, it was found that slight volume expansion (1-1.5%) was accompanied on polymerization of both spiro orthocarbonates **3** and **6**.

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Activation of C-H Bonds by Metals and Metal Oxides

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Extensive atom superposition and electron delocalization molecular orbital (ASED-MO) calculations of CH bond scission mechanisms and transition state structures on various metal and metal oxide surfaces have recently uncovered the bonding interactions governing CH activations on these surfaces. We have examined CH bond cleavage in adsorbed unsaturated molecules on iron,^{1,2} platinum,^{2,5} vanadium⁶, and α -bismuth molybdate ($\text{Bi}_2\text{Mo}_3\text{O}_{12}$).⁷ We have also examined the dehydrogenation of methane on iron⁸ and methoxy coordinated to molybdenum trioxide.⁹ The molecular orbital explanations of CH activation in all these cases show common features. In each case, the transition state is reached with a stretch of 0.4-0.6 Å in the CH bond toward the metal atom or oxygen anion which accepts the hydrogen atom. In the transition state the CH bond is significantly stabilized by forming σ -donation bond to the acceptor (A). The degree of CH activation depends on what happens to the two electrons in the CH-M or CH-O²⁻ antibonding counterpart σ^* orbital. There are four possibilities: (a) the CH-A σ^* orbital remains occupied in the transition state, in which case the barrier is high; (b) the CH-A σ^* orbital loses one electron by photoexcitation, in which case the barrier is low; (c) the CH-A σ^* orbital is stabilized by a higher-lying empty orbital, in which case the barrier is low; (d) the CH-A σ^* orbital donates one or both electrons into low-lying acceptor orbitals, in which case the barrier is low. Case (a) is envisioned in orbital correlation diagram (see Figure 1) which explains the high bond scission barrier. Case (b), (c), and (d) are illustrated in Figure 2. The first three cases are exemplified by making some general comments on optimizing the conditions for CH activation in methane and other alkanes. The last one is treated for the CH bond activations on Fe(100) and V(100) surfaces in the present study.

Case(a): Methoxy on MoO_3 ⁹ Molybdenum trioxide has a filled O²⁻ 2p band which is ~3 eV beneath the bottom of the empty Mo^{VI} 4d band.¹⁰ When surface-coordinated methoxy, OCH₃, is oriented for H transfer to a surface O²⁻ and the transition state is variationally optimized, the CH-O²⁻ σ^* orbital is found in the band gap and it is doubly occupied. The calculated activation barrier is therefore high (2.6 eV), which is reflected by the 500°C temperature required for reaction. This is a case of limited or non-activation since the CH-O²⁻ σ donation orbital and CH-O²⁻ σ^* orbital are both

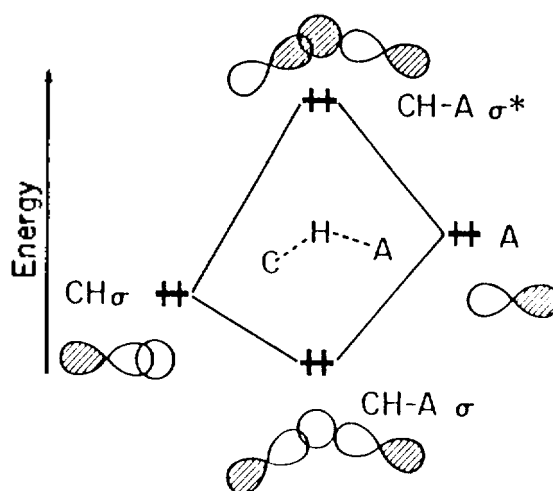


Figure 1. Schematic representation of the closed-shell repulsive interactions which afford a high activation barrier to CH bond cleavage by H acceptor.

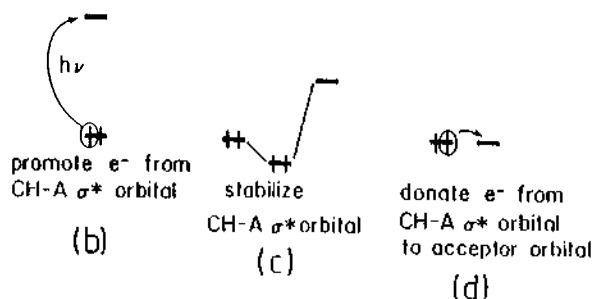


Figure 2. Various cases of CH bond activation.

doubly occupied and the resulting transition state C-H-O bond order is zero.

Case(b): Photoactivation of Methoxy on MoO_3 ⁹ Referring to Case(a) above, an O 2p \rightarrow Mo 4d charge transfer excitation creates a hole at the top of the O 2p band. Now as the CH bond is stretched toward the transition state the CH-O²⁻ σ^* orbital energy level runs up through the O 2p band and picks up the hole. In the transition state this orbital is again in the band gap but is only half-occupied. The transition state