

Cyclopropanation *Versus* Deoxygenation in the Reactions of Halocarbenes with pre-Aromatic Ketones

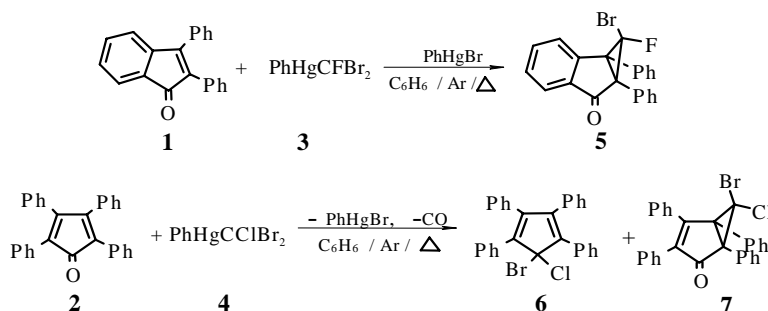
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Abstract: The reactions of halocarbenes with pre-aromatic ketones **1**, **2** resulted in cyclopropanation and deoxygenation products. The varying product ratio could be accounted for by a mechanism involving the carbonyl ylide intermediate.

Keywords: Halocarbene, deoxygenation, cyclopropanation, mechanism.

Cyclopropanes are very useful intermediates in organic synthesis¹. Our previous studies showed that the reactions of 2,4,6-triphenylcycloheptatrienone with halocarbenes gave almost no cyclopropane product². On the other hand, when another pre-aromatic ketone **1** was used as substrate, the only isolated product was found to contain cyclopropane (**eq. 1**). Furthermore, when the substrate was tetraphenylcycloheptatrienone (TPCP, **2**), both cyclopropanation and deoxygenation products were obtained (**eq. 2**). Now we wish to report these recent findings and elucidate the possible factors which were responsible for the varying product distribution.



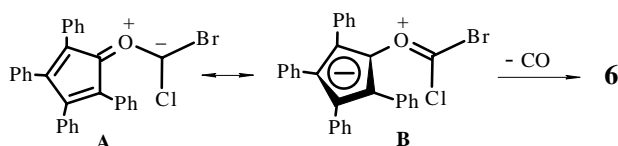
All reactions were carried out by the procedure as previously described². The yield of CO in **eq. 2** was 49.6%. The structures of products **5-7** were identified by elemental and spectral analysis³.

It is obvious that **5** and **7** arose from addition of halocarbenes to the C=C bond of substrates. X-ray crystallographic data showed that the four phenyl rings in TCPCP **2** are all

severely twisted with respect to the central cyclopentadienyl ring. This structural feature should at least be partially responsible for the much diminished addition of halocarbenes to the C=C bond. On the other hand, because the steric repulsion in the much more planar structure **1** is largely reduced, the electron-requiring carbene would certainly favor the more electron-rich C=C double bond to form compound **5** (eq. 1).

According to the ylide mechanism⁴, in the reaction of TPCP with :CBrCl, the initially generated carbonyl ylide intermediate **A** (Scheme 1) would most likely take the form **B** through resonance due to the effect of push-pull stabilization and an avoidance of steric repulsion in **A**. This conformation would strongly disfavor the other two competitive reaction paths of the carbonyl ylide intermediate⁵ and thus explains the “abnormal” high yield of CO and **6** resulted from deoxygenation.

Scheme 1. Possible mechanism for the formation of **6**



The different outcome in eq. 1 and eq. 2 clearly indicates that the pre-aromatic character and steric hindrance in the substrates were the major factors that govern the varying deoxygenation vs. cyclopropanation product ratio.

Acknowledgments

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References and Notes

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3. **5**, yellow crystal, 60.5%, mp 169-171°C. Calcd. for C₂₂H₁₄BrFO: C, 67.19; H, 3.59. Found: C, 66.94; H, 3.49. ¹HNMR: 6.86-7.99 (m). IR: 3045.3, 1715.0, 1440.1, 1150.0, 700.0. MS: *m/z* 392 (M⁺), 313, 294, 135, 77.
6, brown crystal, 40.0%, mp 150-152°C. Calcd. for C₂₉H₂₀BrCl: C, 71.99; H, 4.17. Found: C, 71.72; H, 4.30. ¹HNMR, 6.95-7.80 (m), IR, 3057.8, 1491.0, 1441.8, 769.14, 695.31, 580.47. MS: *m/z* 482 (M⁺), 447, 403, 368, 326, 289, 175, 77.
7, yellow crystal, 38.0%, mp 175-176°C. Calcd. for C₃₀H₂₀BrClO: C, 70.40; H, 3.94. Found: C, 70.09; H, 3.87. ¹HNMR: 6.95-7.80 (m), IR: 3049.6, 1712.5, 1597.7, 769.31, 728.72, 695.31. MS: *m/z* 510 (M⁺), 475, 432, 431, 319, 289, 181, 77.
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