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# One-pot Synthesis of α,α-Dichloroketones from Alkynes Using the N,N-Dimethylformamide/HCl/Potassium Monoperoxysulfate System

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The reaction of alkynes with N,N-dimethylformamide (DMF)/HCl/potassium monoperoxysulfate (Oxone, Aldrich) afforded the corresponding α,α-dichloroketones in good yields.

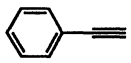
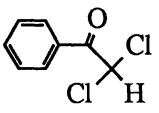
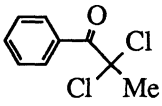
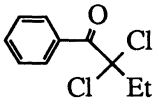
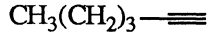
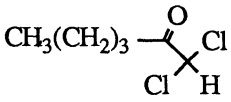
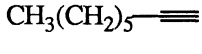
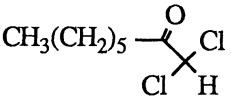
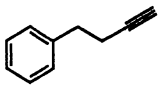
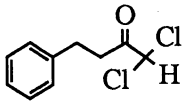
We have recently reported that the DMF/HCl/m-CPBA system served as an effective reagent not only for oxidation of alcohols,[1] but also for chlorination of ketones[2] and aromatic compounds.[3] In connection with our work, we were interested in employing this reagent system for terminal chlorination of alkynes but we could exclusively obtain the corresponding α,α-dichloroketones.

Goldschmidt et al.[4] reported that reaction of phenylacetylene with ethyl hypochlorite gave 2,2-dichloroacetophenone in low yield, whereas Jackson[5] obtained the dimethylketal of 2,2-dichloroacetophenone from the reaction of phenylacetylene with methyl hypochlorite. The reaction of alkynes with N-chlorosuccinimde[6] in methanol or chlorine[7] in methanol afforded mainly α,α-dichlorodimethyl ketals along with α,α-dichloroketones as the minor products. Treatment of 1-hexyne with chlorine in various solvents gave a mixture of 1,2-dichloro-1-hexenes, 1,2-polychlorohexanes, and 1,1-dichloro-2-hexanone (0-43%).[8] In general, the synthesis of α,α-dichloroketones seems to be hardly achieved by direct chlorination of ketones[9] because it is difficult to control regiospecific dichlorination at the same α-position.

In a typical example, phenylacetylene was treated with 2.2 equiv. of Oxone in HCl/DMF solution (2.2 equiv. of 1 M HCl solution in DMF) at 20-25 ℃ for 2 h. The reaction mixture was poured into cold water and extracted with ether. 2,2-Dichloroacetophenone was isolated by column chromatography on silica gel (hexane/EtOAc, 10/1) and identified by $^1$H NMR,[10] IR,[11] and GC/MS. In this reaction, we could identify 2-chlorophenylacetylene (7%) by GC in comparison with the authentic sample from the reaction mixture, but we could not control the reaction conditions to increase the yield of 2-chlorophenylacetylene. We also have attempted to apply other oxidants such as hydrogen peroxide and m-CPBA. We have found that Oxone gave the best results. The major impurities proved to be α-monochloroketones (5-10%). When we used m-CPBA as an oxidant the formation of the α-monochloroketones were increased. Not only was Oxone an oxidant more convenient to handle during workup than m-CPBA, but it also gave the α,α-dichloroketones in better yields. The representative results are summarized in Table 1.

In summary, the terminal alkynes gave terminal dichloroketones (entries 1, 4, 5, and 6) regardless of the substituents, and 2-alkyl-1-phenylacetylenes gave 2-alkyl-2,2-dichloracetophenones (entries 2 and 3)

Table 1. Synthesis of α,α-Dichloroketones

| Entry | Alkyne | Product | Oxidant | Yield/ %[a] |
|---|---|---|---|---|
| 1 |  |  | Oxone<br>m-CPBA | 85 (80)[b]<br>40 |
| 2 |  |  | Oxone<br>m-CPBA | 94 (88)[b]<br>35 |
| 3 |  |  | Oxone | 85 (81)[b] |
| 4 |  |  | Oxone<br>m-CPBA | 73 (67)[b]<br>41 |
| 5 |  |  | Oxone | 75 (71)[b] |
| 6 |  |  | Oxone<br>m-CPBA | 78 (73)[b]<br>69 |

a) Yields by GC. b) Isolated yields.

respectively. We believe that our procedure is a method of choice for the synthesis of α,α-dichloroketones owing to its facile and mild conditions, and good yields with high regioselectivity.

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10) Representative chemical shifts of α-protons are (δ, ppm) : 6.7 (entry 1), 5.8 (entry 4), 5.8 (entry 5), and 6.2 (entry 6).
11) Representative bands of carbonyl groups are ($cm^{-1}$) : 1700 (entry 1), 1684 (entry 2), 1684 (entry 3), 1730 (entry 4), 1725 (entry 5), and 1725 (entry 6).

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