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RUTHENIUM TETROXIDE OXIDATION OF ALKYNES. A NEW ONE STEP SYNTHESIS OF α-DIKETONES

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The oxidation of organic compounds with a carbon tetrachloride solution of ruthenium tetroxide (RuO_4) was first introduced by Djerassi and Engle[1] in 1953; only recently have the advantages of this powerful oxidizing agent been used in synthesis[2]. It is conveniently generated <u>in situ</u> in low concentration from a catalytic amount of ruthenium dioxide by action of an oxygen donor, like sodium meta-periodate or sodium hypochlorite; these oxidants regenerate RuO_4 from any RuO_2 produced during the oxidation. This procedure has recently been successfully employed for the otherwise difficult synthesis of strained bicyclic ketolactones and for the conversion of lactones to the corresponding ketoacids[3]. Although RuO_4 has been used with a variety of functional groups, no studies of alkynes have been reported. The products of <u>alkene</u> oxidation are usually similar to those of ozonolysis. However, the RuO_2 reoxidation procedure is far superior in certain cases where ozone or other reagents, such as chromic acid or osmium tetroxide-periodate, either reacted poorly or were completely ineffective[4]. Berkowitz and Rylander[5] in their attempted RuO_4 oxidative degradation of an aromatic nucleus, used phenylacetylene and tolan. Reaction was immediate in both cases; however, they could not isolate any oxidation products, in contrast with the successful results on simpler alkyl benzenes reported by others[2,6].

We now wish to report the use of RuO_4 for the facile and rapid oxidation of alkynes (RCCR') to the corresponding α-diketones (RCOCOR') or carboxylic acids (RCO_2H, $R'CO_2H$). Using the RuO_2-hypochlorite reoxidation procedure, the results shown in the table were obtained (yields in mole % based on reactant alkyne). Unlike the ozonolysis of similar alkynes[7,8] this method permits the recovery in good yields of α-diketones. However, the oxidation of terminal alkynes (reactions 4 and 5) gave only the corresponding acid; no

Ruthenium Tetroxide Oxidation of Acetylenic Compounds

$$R{-}C{\equiv}C{-}R' \xrightarrow[\substack{CCl_4{-}H_2O \\ 0°C}]{RuO_2/NaOCl} R{-}CO{-}CO{-}R' \; + \; RCO_2H$$

1.	R = R' = Ph	83.0%	7.5%
2.	R = R' = Bu*	70.0%	19.4%
3.	R = R' = Pr	58.5%	40.0%
4.	R = Ph, R' = H	---	66.0%
5.	R = t-Bu, R' = H	---	60.0%

* Use of periodate in place of hypochlorite gave essentially the same results.

α-keto acid (or aldehyde) was detected. The formation of diketone and acid are formally 4-electron and 6-electron changes respectively, and should require 2 and 3 moles, respectively, of hypochlorite. The reaction with highly purified 4-octyne gave this expected stoichiometry[9].

In separate experiments, both benzil and 9,10-phenanthraquinone were recovered in 90-98% yield (purified) after 24 hr at rt under the oxidation conditions. In a similar reaction with 5,6-decanedione, oxidation was very slow, and no significant reaction could be detected after three hours[10]. α-Diketones can be cleaved with hypochlorite[11] or periodate[12] alone, but under our conditions, all the diketones studied reacted too slowly to account for the amounts of acid observed. The alkynes are totally inert toward hypochlorite alone, but react instantaneously in the presence of RuO_4. Based on the above observations, benzil is definitely not a precursor to benzoic acid; it also appears that even in the aliphatic cases (reactions 2 and 3), diketone plays a very small role, if any, in cleavage product formation.

In a typical procedure, to the stirred, ice cooled black mass of RuO_2 (0.01 equiv.) was added 0.5069 M aq solution of sodium hypochlorite (∿3 equiv.) or a 10% solution of sodium metaperiodate (∿3 equiv.) until the reaction mixture became yellow. Then alkyne (1.0 equiv.; usually on a 3-4 gr scale) in a carbon tetrachloride solution (∿1 mmol/4 ml CCl_4) and hypochlorite (or periodate) solutions were added dropwise, simultaneously. The reaction was instantaneous, as indicated by the color change from yellow to black. This addition procedure was carried out over a period of about an hour. In some cases, the reaction mixture became emulsified and remained black during the entire reaction. However, the reaction progress could be followed by a starch-potassium iodide indicator test for hypochlorite. After all OCl^- was consumed the lower greenish-yellow carbon tetrachloride layer was separated from the upper aqueous layer. The latter was gravity filtered, followed by thorough extraction with ether until the ether layer was colorless. The ethereal solution was combined with the carbon tetrachloride layer and washed with bicarbonate solution; after drying ($MgSO_4$), the solvent was evaporated in vacuo. The remaining yellow product was purified either by vacuum distillation or crystallization to yield α-diketone as a yellow liquid or crystals.

The water layer and bicarbonate washings were combined, acidified (dil H_2SO_4), and thoroughly extracted with ether. The ethereal extracts were combined, dried ($MgSO_4$) and the solvent was removed in vacuo. The remaining colorless product was either vacuum distilled or crystallized to yield a pure sample of carboxylic acid.

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References and Footnotes

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