Letters to the Editor

Chlorine dioxide as a novel oxidant for organometallic compounds

A. V. Kuchin, I. A. Dvornikova, and I. Yu. Nalimova*

Institute of Chemistry, Komi Research Center, Ural Branch of the Russian Academy of Sciences,
48 ul. Pervomaiskaya, 167610 Syktyvkar, Russian Federation.
Fax: +7 (821 2) 43 6677. E-mail: chemi@ksc.komi.ru

Methods for the oxidation of organometallic compounds are rather well-developed, but these reactions are often accompanied by the formation of by-products. Thus, the search for new selective oxidants is in progress.

We have previously shown[1,2] that chlorine dioxide (ClO_2) selectively oxidizes allyl alcohols and dialkyl sulfides. The present study deals with investigation of the oxidation of organometallic compounds by ClO_2 under mild conditions.

$$(RCH_2)_3Al \xrightarrow[Et_2O,\ 20\ ^{\circ}C]{ClO_2} RCH_2OH + RCHO + RCOOH$$

$$(RCH_2O)_3Al \xrightarrow[2)\ H_2O]{1)\ ClO_2} RCH_2OH + RCHO + RCOOH$$

$$R = n\text{-}C_7H_{15},\ Pr^i$$

The oxidation of trialkylalanes with normal and branched radicals by the stoichiometric amount (0.5 mol per M—C bond) or an excess of ClO_2 results in the alcohol as the major product (90% yield) and a minor amount of the corresponding acid and aldehyde. Oxidation with a deficiency of the oxidant and subsequent hydrolysis give the corresponding alkane and alcohol in approximately equal amounts (the total yield is 98%). No organochlorine derivatives have been found. Thus, chlorine from ClO_2 adds to the metal.

The feasibility of the oxidation of aluminum alcoholates is of particular interest. CrO_3—Py complex[3] was used earlier for this purpose. Chlorine dioxide proved to be markedly less active, and the total yield of the corresponding aldehyde and acid did not exceed 15—20%.

The oxidation of *ate*-complexes is known to be accompanied by the formation of a large amount of by-products (olefins, dimers, and carbonyl compounds), and these complexes are converted into trialkyl aluminum compounds by addition of $AlCl_3$.[4] The use of ClO_2 for the oxidation of lithium tetraoctylaluminate obtained from oct-1-ene and $LiAlH_4$ results in the formation of octanol in more that 90% yield virtually without by-products.

$$LiAlH_4 + CH_2{=}CH(CH_2)_5Me \xrightarrow[THF]{TiCl_4} (C_8H_{17})_4AlLi \xrightarrow{ClO_2} n\text{-}C_8H_{17}OH$$

The oxidation of the Grignard reagents with alkyl or allyl radicals occurs in the same way.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2025—2026, October, 1999.

1066-5285/99/4810-2001 $22.00 © 1999 Kluwer Academic/Plenum Publishers

$$RCH_2MgX \xrightarrow[Et_2O,\ 20\ ^{\circ}C]{ClO_2} RCH_2OH + RCHO + RCH_2CH_2R$$

$R = n\text{-}C_6H_{13}$, Ph; X = Cl, Br

Normally, the alcohol (yield 85—90%) and a negligible amount of the aldehyde are formed in this reaction. However, in the case of benzyl Grignard reagent the reaction proceeds slower (taking 1 h, whereas $C_7H_{15}MgBr$ is oxidized in 5—10 min) and is complicated by the formation of a small amount of the dimer. The reaction was monitored by GLC following hydrolysis of the reaction mixture.

Thus, ClO_2 is a selective and convenient oxidant for organometallic compounds of nontransition metals.

GLC analysis was performed on a Khrom-5 chromatograph equipped with a steel column (300×0.4 cm) with 6% SKTF on Chromaton-NAW-GMDS (the column temperature was 50—200 °C), nitrogen as the carrier gas, and a flame-ionization detector.

A sample of an organometallic compound was dissolved in anhydrous diethyl ether, and ClO_2 as a mixture with N_2 was bubbled in at −20 °C for 5—60 min. After hydrolysis (EtOH, H_2O, 10% H_2SO_4) the reaction mixture was extracted with diethyl ether, the solvent was removed, and the residue was analyzed by GLC. The resulting products were identified by comparison with authentic compounds.

References

1. A. V. Kuchin, L. L. Frolova, and I. V. Dreval, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1871 [*Russ. Chem. Bull.*, 1996, **45**, 1781 (Engl. Transl.)].
2. A. V. Kuchin, S. A. Rubtsova, and L. P. Karmanova, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2110 [*Russ. Chem. Bull.*, 1998, **47**, 2051 (Engl. Transl.)].
3. A. V. Kuchin, R. A. Nurushev, I. P. Podlipchuk, and G. A. Tolstikov, *Metalloorgan. Khim.*, 1991, **4**, 582 [*Organomet. Chem. USSR*, 1991, **4** (Engl. Transl.)].
4. A. V. Kuchin and G. A. Tolstikov, *Preparativnyi alyuminii-organicheskii sintez* [*Preparative Organoaluminum Synthesis*], Komi Nauchn. Tsentr, Syktyvkar, 1997, 58 (in Russian).

Received April 27, 1999;
in revised form June 2, 1999