according to its ^{1}H NMR spectrum. This was followed by the elution of the main product **3** (30 mg, 25 % yield, 45 % based on C_{60} reacted). The ^{1}H NMR data are reported in the above text and in Figs. 1, *a, b*.

B. The reaction mixture obtained after the interaction of C_{60} (50 mg, 0.07 mmol) with diazomethane **2** prepared from **1** (60 mg, 0.17 mmol) was subjected to chromatography on silica gel to afford small amounts of the unreacted C_{60}, adduct $C_{60} \cdot CPh_2$ (23 mg, 32 %), **3**, and three more Cr-containing fullerenes.

Though the elemental analyses of the adducts are not always satisfactory for all of the elements, the presence or the absence of chromium is determined reliably enough by both X-ray-fluorescence and combustion analyses. For example, here is the analysis of one of the adducts obtained from the reaction with excess diazomethane **2**. Found (%): C, 78.07; H, 3.09; Cr, 9.16. $C_{108}H_{30}Cr_3O_9$. Calculated (%): C, 79.65; H, 1.84; Cr, 9.58.

Decomplexation of compound 3. A solution of iodine (20 mg) in toluene was added to a solution of **3** (20 mg) in toluene and stirred for 1 h. The solvent was removed *in vacuo*. The residue was washed with ether to remove the remaining iodine and dried *in vacuo*. The ^{1}H NMR spectrum of product **4** is given in Fig. 1, *c*.

Authors are thankful to D. V. Zagorevskii for recording the FAB-MS spectrum.

The present work was carried out with financial support from the Russian Foundation for Basic Research (Project No. 93-03-18725) and the Intellectual Cooperation Foundation.

References

1. V. I. Sokolov, *Dokl. Akad. Nauk*, 1992, **326**, 647 [*Dokl. Chem.*, 1992, **326** (Engl. Transl.)].
2. P. J. Fagan, J. C. Calabrese, and B. Malone, *Acc. Chem. Res.*, 1992, **25**, 134.
3. M. Rasinkangas, T. T. Pakkanen, T. A. Pakkanen, M. Ahlgren, and J. Rowinen, *J. Am. Chem. Soc.*, 1993, **115**, 4901.
4. F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157.
5. M. Eiermann and F. Wudl, *J. Am. Chem. Soc.*, 1994, **116**, 8364.

Received December 6, 1994;
in revised form December 29, 1994

An unusual pathway of the oxidation of diethyl ether by bismuth(v) derivatives

V. A. Dodonov,* T. I. Zinov'eva, and N. V. Dolganova

N. I. Lobachevsky State University, Nizhnii Novgorod,
23 prosp. Gagarina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 658 592

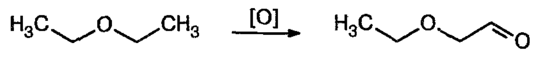
Di(*tert*-butylperoxy)triphenylbismuth and the triphenylbismuth—*tert*-butyl hydroperoxide system transform diethyl ether into ethoxyacetic aldehyde. The latter undergoes further conversions under these reaction conditions to give the corresponding hydroxyperoxide, ethoxyacetic acid, and bismuth(III) acylates.

Key words: diethyl ether, ethoxyacetic aldehyde, triphenylbismuth, *tert*-butyl hydroperoxide, oxidation.

We have established previously that di(*tert*-butylperoxy)triphenylbismuth (**1**) and the triphenylbismuth—*tert*-butyl hydroperoxide system are capable of direct ketonization of methylene groups in aliphatic[1] and alkylaromatic[2] hydrocarbons. We assume that ketonization occurs under the action of singlet oxygen, like in the oxidation of hydrocarbons by the aluminum tri(*tert*-butoxide)—hydroperoxide and *tert*-butylperoxydibutoxyaluminum—hydroperoxide systems.[3,4]

The reaction of peroxide **1** or the $Ph_3Bi—Bu^tOOH$ oxidizing system (at 1 : 2, 1 : 3, or 1 : 4 reagent ratios) with diethyl ether at temperatures not exceeding 15 °C did not result in direct ketonization of the methylene groups. Instead, oxidation of the methyl group occurred.

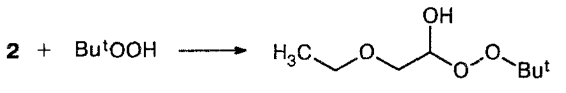
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 783—784, April, 1995.



2

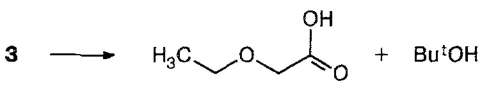
The content of ethoxyacetic aldehyde (**2**) in the reaction products was 0.40—0.60 mol per one mol of the starting organobismuth compound. We did not isolate pure aldehyde **2** from the reaction mixture. The IR spectrum of the reaction solution contained an absorption band at about 1725 cm^{-1}. When in solution, the resulting aldehyde underwent all reactions typical of aldehydes: the "silver mirror" reaction and the reactions with fuchsin-sulfurous acid and with Fehling's solution. We also obtained the 2,4-dinitrophenylhydrazone (m.p. 148—150 °C) and the dimedone derivative (m.p. 177 °C) of this aldehyde. Mixtures of this compound with authentic samples of the respective derivatives of compound **2** showed no depression of the melting point.

It should be noted that the above oxidizing systems always contained free hydroperoxide. The latter is known to be capable of nucleophilic addition to carbonyl compounds to give hydroxyperoxide **3**.



3

For example, when the solvent and volatile reaction products were removed after 20 h, the resulting hydroxyperoxide underwent spontaneous decomposition accompanied by heating while the color of the nonvolatile residue changed from light-yellow to brown. When the reaction mixture was kept for 80 h, the reaction products contained no hydroxyperoxide **3**. On the other hand, the yield of *tert*-butanol increased from 1.06 (in the case of the reaction performed for 20 h) to 2.06 mol and ethoxyacetic acid was additionally formed.



The content of the acid is not high because it, like acetic acid,[5] dephenylates triphenylbismuth. In fact, the yield of benzene increased from 0.20 to 0.50 mol in the reactions conducted for 80 h. In addition, the IR spectra of the solid residue insoluble in organic solvents contained an absorption band in the 1620 cm^{-1} region typical of the carboxylic group.

Experimental

IR spectra of solutions in CCl_4 and in vaseline oil were recorded on a UR-20 spectrophotometer. GLC analyses were carried out on a Tsvet 265 chromatograph equipped with a flame ionization detector using a 3 m × 3 mm column and 15 % REOPLEX-400 mobile phase on a Chromaton N-AW-DMCS carrier; the temperature was 90 °C.

The oxidation of diethyl ether with the $Ph_3Bi—Bu^tOOH$ system was performed at component ratios of 1 : 2, 1 : 3, and 1 : 4. A mixture of Ph_3Bi (5 mmol) and the corresponding amount of Bu^tOOH in Et_2O was kept at 10—15 °C for 20 or 80 h. After a specified period of time, the precipitate that formed in the reaction mixture was filtered off. The amount of bismuth in the precipitate was determined (58.12 %), and its IR spectroscopic analysis was carried out. The solvent and the volatile reaction products were recondensed from the filtrate under reduced pressure. Bu^tOOH was virtually absent in the filtrate even after 20 h. The yields of C_6H_6 and Bu^tOOH were determined by GLC, that of $EtOCH_2C(O)OH$ was found by titration, and that of compound **2** was determined by analyzing the amount of the dimedone derivative. The non-volatile residue consisted of a mixture of Ph_3Bi and unidentified resinous products.

The oxidation of Et_2O by peroxide **1** was carried out in a similar way.

Aldehyde **2** was obtained by the oxidation of ethylcellosolve by the $Ph_3Bi—Bu^tOOH$ (1 : 3) system under the conditions used for oxidizing primary and secondary alcohols.[6]

This work was financially supported by the Competition Center for Fundamental Natural Studies at Saint-Petersburg University (Grant No. 94-9.4-219).

References

1. V. A. Dodonov and T. I. Zinov'eva, *Metalloorg. Khim.*, 1993, **3**, 375 [*Organomet. Chem. USSR*, 1993, **3** (Engl. Transl.)].
2. V. A. Dodonov, T. I. Zinov'eva, and N. N. Osadchaya, *Zh. Obshch. Khim.*, 1988, **58**, 712 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
3. V. A. Dodonov, L. P. Stepovik, and S. M. Sofronova, *Zh. Obshch. Khim.*, 1990, **60**, 1839 [*J. Gen. Chem. USSR*, 1990, **60** (Engl. Transl.)].
4. V. A. Dodonov, L. P. Stepovik, S. M. Sofronova, and V. V. Shereshovets, *V Vsesoyuz. konf. po metalloorganicheskoi khimii. Tez. dokl.* [*V All-Union Conf. on Organomet. Chemistry. Abstracts*], Riga, 1991, 107 (in Russian).
5. H. Gilman and H. L. Yale, *J. Am. Chem. Soc.*, 1951, **73**, 2880.
6. V. A. Dodonov and T. I. Zinov'eva, *IX Vsesoyuz. konf. po peroksidam. Tez. dokl.* [*V All-Union Conf. on Peroxides. Abstracts*], Gor'kii, 1990, 105 (in Russian).

Received January 10, 1995