values of η produce low reactivity.

Since the lowest energy absorption band in the electronic spectrum is also related to $(I - A)$, we can also use the spectra of molecules as a guide to reactivity.[11] However care must be taken to show that the first band is indeed related to the appropriate frontier orbitals.

Judging by its spectrum, the hardest molecule appears to be CF_4. Its first adsorption band has a maximum at 110.5 kK, compared to 78.2 for CH_4.[11] Neither I nor A is accurately known, but I is about 15 eV and A about −8 eV. This makes $\eta \simeq 11.5$ eV, compared to 10.3 for CH_4.

Conclusion. In the preceding sections it has been shown that the concepts of absolute electronegativity and hardness have considerable predictive power for the reactions of typical organic molecules and radicals. The use of eq 3 seems particularly promising, even though only initial interactions are considered. However it must not be regarded as infallible, since it is no better than the results in the tables indicate.

Physical–organic chemistry over the years has explained most of the phenomena discussed in many different ways. It is not the intent of the present work to discredit any of these explanations. The intent is to show that χ and η can also be used in a novel and rational way.

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Notes

A Convenient Method for the Reduction of Ozonides to Alcohols with Borane–Dimethyl Sulfide Complex

Lee A. Flippin,* David W. Gallagher, and Keyvan Jalali-Araghi

Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, California 94132

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A versatile procedure for the direct conversion of ozonides to alcohols[1] would be a potentially valuable addition to the synthetic repertory. Several well-known reducing agents have been exploited for this purpose; however, all of these suffer from intrinsic limitations. Thus, lithium aluminum hydride efficiently reduces ozonides,[2,3] but it cannot be used in the presence of a variety of other functional groups. Sodium borohydride,[3d,4] while tolerant of a wider range of functionality than $LiAlH_4$, is generally limited to use in highly polar solvents—the usual requirement of an aqueous extraction step to remove these solvents in the workup stage of $NaBH_4$ reductions may render the procedures inconvenient for the preparation of water-soluble alcohols.[5,6] Complexes of borane with pyridine, triethylamine, and tetrahydrofuran have been carefully evaluated for direct reductions of 10-undecenoic

Table I

1-decene $\xrightarrow[2.\ BH_3\text{-DMS}]{1.\ O_3}$ 1-nonanol (1) + 1-decene ozonide (2) + nonanal (3)

entry	reaction conditions	product distribution[a]
1	2.0 equiv of BH_3–DMS, 22 °C, 24 h	1 (47%) + 2 (52%) + 3 (≤1%)
2	4.0 equiv of BH_3–DMS, 22 °C, 24 h	1 (100%)
3	2.0 equiv of BH_3–DMS, 40 °C, 3 h	1 (64%) + 2 (36%)
4	3.0 equiv of BH_3–DMS, 40 °C, 3 h	1 (95%) + 2 (4%) + 3 (1%)
5	4.0 equiv of BH_3–DMS, 40 °C, 1 h	1 (100%)

[a] Product distributions were determined on the crude reaction mixtures by ^1H NMR spectroscopy (300 MHz; $CDCl_3$) with internal TMS as a reference.

Table II

methyl 10-undecenoate $\xrightarrow[2.\ BH_3\text{-DMS}]{1.\ O_3}$ methyl 10-hydroxydecanoate (4) + methyl 10-undecenoate ozonide (5) + 1,10-decanediol (6) + methyl 10-oxodecanoate (7)

entry	reaction conditions	product distribution[a]
1	3.5 equiv of BH_3–DMS, 22 °C, 18 h	4 (95%) + 5 (3%) + 7 (2%)
2	4.0 equiv of BH_3–DMS, 22 °C, 16 h	4 (91%) + 5 (8%) + 7 (1%)
3	4.0 equiv of BH_3–DMS, 22 °C, 24 h	4 (98%) + 5 (1%) + 7 (1%)
4	4.0 equiv of BH_3–DMS, 40 °C, 2 h	4 (72%) + 6 (27%)
5	5.0 equiv of BH_3–DMS, 22 °C, 16 h	4 (35%) + 6 (65%)

[a] Product distributions were determined from the crude reaction mixtures by ^1H NMR spectroscopy (300 MHz; $CDCl_3$) with internal TMS as the reference.

(1) For an overview of currently available methods for this transformation, see: (a) Fischer, G. W.; Zimmerman, T. In *Comprehensive Heterocyclic Chemistry*; Potts, K. T., Ed.; Pergamon Press: New York, 1984; Vol. 6 p 879. (b) Bailey, P. S. In *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1, Chapter 8. (c) Bailey, P. S. In *Ozonation in Organic Chemistry*; Academic Press: New York, 1982; Vol. 2.

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(5) For a summary of procedures and leading references concerning the general use and workup of sodium borohydride reduction mixtures, see: (a) *Reagents for Organic Synthesis*; Fieser, L., Fieser, M., Eds.; Wiley: New York, 1967; Vol. 1, p 1049. (b) Gaylord, N. *Reduction with Complex Metal Hydrides*; Interscience: New York, 1957; p 1013. (c) Hudlicky, M. *Reductions in Organic Chemistry*; Horwood: Chichester, 1984; p 21.

(6) For example, Sousa and Blum reported a preparation of water-soluble 1,6-hexanediol in 63% yield via $NaBH_4$ reduction of cyclohexene ozonide (ref 3d). In our hands the procedure afforded crude 1,6-hexanediol, mp 41–42.5 °C, in 56% yield.

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Table III

substrate	method[a]	products	yield, %
methyl oleate	A	1-nonanol and methyl 10-hydroxydecanoate	96[b]
anethole	A	*p*-anisyl alcohol	78
trans-stilbene	A	benzyl alcohol	90
1-decene	A	1-nonanol	82
methyl 10-undecenoate	A	methyl 10-hydroxydecanoate	98[b]
benzyl 10-undecenoate	B	benzyl 10-hydroxydecanoate	67
diethyl fumarate	C	ethyl glycolate	75[b,c]
cyclohexene	A	1,6-hexanediol	81[c]

[a] Method A: 4.0 equiv of BH_3–DMS, 22 °C, 24 h. Method B: 3.0 equiv of BH_3–DMS, 22 °C, 21 h. Method C: 3.5 equiv of BH_3–DMS, 22 °C, 24 h. [b] Crude yield. [c] Water-soluble product.

acid ozonide and ethyl 10-undecenoate ozonide in CCl_4 solution; however, the methods appear to be of limited value—yields of the desired alcohols were low (5–55%), and contamination by aldehyde or diol side products was a substantial problem over the range of conditions employed.[6]

We report that borane–dimethyl sulfide complex (BH_3–DMS)[7] is a mild, versatile reagent for carrying out the direct reduction of ozonides. For example, 4 equiv of BH_3–DMS efficiently reduces methyl 10-undecenoate ozonide and methyl oleate ozonide (0.1 M ozonide in CH_2Cl_2, 22 °C, 24 h) to monohydric alcohols without affecting their carbomethoxy groups. Selected data from our study of BH_3–DMS reductions of 1-decene ozonide and methyl 10-undecenoate ozonide are shown in Tables I and II, respectively. Diethyl fumarate ozonide afforded a 3:1 mixture of ethyl glycolate and ethylene glycol, respectively, when 4 equiv of BH_3–DMS were employed; however, when 3.5 equiv of the reducing agent were used, we isolated ethyl glycolate as the exclusive product (75% yield). Surprisingly, benzyl 10-undecenoate ozonide suffered up to 20 mol % overreduction with as little as 3.5 equiv of BH_3–DMS under our usual conditions. Alternatively, 3.0 equiv of the reducing agent (0.1 M ozonide in CH_2Cl_2, 22 °C, 21 h) cleanly afforded benzyl 10-hydroxydecanoate (67% yield after column chromatography). Our samples of methyl 10-hydroxydecanoate, benzyl 10-hydroxydecanoate, and ethyl glycolate underwent substantial polymerization within several weeks of storage at room temperature. Bulb-to-bulb distillation of freshly prepared samples of these products at 0.1–0.5 Torr also led to unacceptable loss due to polymerization; however, the 10-hydroxydecanoate esters could be isolated in fair yield (55–67%) by column chromatography.

We found it convenient to carry out the ozonolysis, reduction, and the hydrolytic workup sequence in a one-flask operation. Thus, after ozonolysis was complete the reaction mixtures were purged with nitrogen, and a calculated amount of BH_3–DMS was added. The reaction mixtures were quenched with a minimal amount (ca. 1 mL) of aqueous 5% HCl, and the excess acid was neutralized by addition of solid $NaHCO_3$. Finally, the reaction mixtures were treated in the same flask with a drying agent, filtered, and concentrated to afford the crude alcohols. With the exception of ethylene glycolate, the crude products were uniformly obtained in near-quantitative yield, and in most cases they contained less than 2 mol % of contaminants. Typical results obtained from the ozonolysis–reduction of alkenes are summarized in Table III.

In conclusion, BH_3–DMS is a mild, efficient reagent for the direct reduction of ozonides to alcohols in methylene chloride solution. Employed at room temperature the reagent is tolerant of carboxylic ester functionality; in addition, our conservative hydrolytic workup procedure allows the easy application of this method to the preparation of water-soluble alcohols. We are currently investigating the details of the mechanism of borane reductions of ozonides vis-a-vis the apparent stoichiometry requirement (~3:1 BH_3:ozonide) and the potential use of BH_3–DMS for ozonide reductions in the presence of other functional groups.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a GE-Nicolet QE-300 spectrometer. Chemical shifts are reported in ppm relative to internal tetramethylsilane (δ 0.00) in $CDCl_3$.

Methylene chloride and all liquid alkenes were distilled prior to use. *trans*-Stilbene, mp 123–124 °C, was used without purification. Borane–dimethyl sulfide complex (BH_3–DMS), obtained from Aldrich Chemical Co., was assayed by quantitative hydrolysis[9] and used without purification. Ozone was generated by passing oxygen through a 0.3-m Berthelot tube[10] operated at a potential of 7.5 kV. The ozone concentration in the effluent stream was not monitored. All operations with BH_3–DMS were performed under a dry nitrogen atmosphere.

Ozonolysis–Reduction of Alkenes. General Procedure. A 100-mL three-neck round-bottom flask was equipped with a dry ice cold-finger condenser protected by a $CaCl_2$ drying tube, an ozone inlet tube, and a magnetic stirrer. The flask was charged with 35 mL of CH_2Cl_2 and 3.5 mmol of an alkene, and the solution was cooled to −78 °C with a dry ice–acetone bath. The effluent stream from an ozone generator was bubbled into the methylene chloride solution (ca. 30 cm^3/min) for 1 h after the blue color of unreacted ozone was noticeable. The reaction mixture was allowed to warm to room temperature, and dry nitrogen was bubbled through it for 10 min. Borane–dimethyl sulfide complex (10.5–14 mmol) was added by syringe over several minutes, and the reaction mixture was allowed to stand at room temperature for 21–24 h. One milliliter of aqueous 5% HCl was added, and the resulting mixture was vigorously stirred for 1 h. Solid $NaHCO_3$ was added until the aqueous layer tested basic to pHydrion paper, and anhydrous $MgSO_4$ was added until a small amount of the flocculent, unhydrated drying agent persisted for 30 min in the stirred suspension. The reaction mixture was filtered and concentrated with a rotary evaporator to isolate the crude products.

1-Decene. 1-Decene was ozonized according to the general procedure, and the resulting ozonide solution was treated with 4.0 equiv of BH_3–DMS. Crude 1-nonanol (≥98 mol %) was obtained in 95% yield; column chromatography of this material afforded the pure alcohol[11] in 82% yield: ^1H NMR δ 3.63 (t, J = 7 Hz, 2 H), 1.76 (s, 1 H), 1.56 (m, 2 H), 1.27 (m, 12 H), 0.88 (t, J = 7 Hz, 3 H).

Methyl 10-Undecenoate. Ozonolysis of this compound and reduction of the ozonide with 4.0 equiv of BH_3–DMS afforded methyl 10-hydroxydecanoate (98 mol %) in 98% yield. Column chromatography of the crude material always resulted in a substantial reduction in yield; however, very pure methyl 10-hydroxydecanoate[12] was obtained in 55% yield from one attempt (silica gel; 3:1 hexane–ether): ^1H NMR δ 3.66 (s, 3 H), 3.63 (t, J = 6 Hz, 2 H), 2.30 (t, J = 7 Hz, 2 H), 2.13 (s, 1 H), 1.57 (m, 4 H), 1.30 (m, 10 H).

Benzyl 10-Undecenoate. Reduction of benzyl 10-undecenoate ozonide with 3.0 equiv of BH_3–DMS afforded benzyl 10-hydroxydecanoate (94 mol %) in 89% yield. Column chroma-

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tography of the crude material (silica gel; 6:1 hexane–ether) gave the pure hydroxy ester in 67% yield: ^{1}H NMR δ 7.40–7.25 (m, 5 H), 5.16 (s, 2 H), 3.62 (t, 2 H), 2.38 (t, 2 H), 1.75–1.50 (m, 4 H), 1.30 (m, 10 H).

Diethyl Fumarate. Reduction of diethyl fumarate ozonide with 3.5 equiv of BH_3–DMS afforded ethyl glycolate (≥98 mol %) in 75% yield. No attempt was made to further purify this compound: ^{1}H NMR δ 4.25 (q, J = 7 Hz, 2 H), 4.17 (s, 2 H), 3.00 (br s, 1 H), 1.33 (t, J = 7 Hz, 3 H).

Methyl Oleate. Ozonolysis of methyl oleate and reduction of the ozonide with 4.0 equiv of BH_3–DMS gave a 1:1 mixture of 1-nonanol and methyl 10-hydroxydecanoate (≤2 mol % contaminants) in 96% yield.

Anethole. Ozonolysis of this compound and reduction of the ozonide with 4.0 equiv of BH_3–DMS gave a quantitative yield of crude *p*-methoxybenzyl alcohol. Column chromatography (silica gel; 19:1 hexane–ether) afforded 78% of the pure alcohol:[12] ^{1}H NMR δ 7.31 (d, J = 9 Hz, 2 H), 6.89 (d, J = 9 Hz, 2 H), 4.63 (s, 2 H), 3.83 (s, 3 H), 1.68 (s, 1 H).

***trans*-Stilbene.** Reduction of *trans*-stilbene ozonide with 4.0 equiv of BH_3–DMS gave pure (100 mol %) benzyl alcohol[12] in 90% yield: ^{1}H NMR δ 7.38–7.28 (m, 5 H), 4.70 (s, 2 H), 1.73 (s, 1 H).

Cyclohexene. Reduction of cyclohexene ozonide with 4.0 equiv of BH_3–DMS afforded 1,6-hexanediol (97 mol %; mp 39–41 °C) in 95% yield. Recrystallization of the crude material from ether afforded 1,6-hexanediol,[3d] mp 42.0–43.0 °C, in 81% yield: ^{1}H NMR δ 3.66 (t, J = 6.3 Hz, 4 H), 1.65 (s, 2 H), 1.63–1.51 (m, 4 H), 1.48–1.33 (m, 4 H).

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Registry No. 1, 143-08-8; 2, 20525-37-5; 3, 124-19-6; 4, 2640-94-0; 5, 96620-40-5; 6, 112-47-0; 7, 14811-73-5; BH_3-DMS, 13292-87-0; *p*-anisyl alcohol, 105-13-5; benzyl alcohol, 100-51-6; benzyl 10-hydroxydecanoate, 67853-00-3; ethyl glycolate, 623-50-7; 1,6-hexanediol, 629-11-8; 1-decene, 872-05-9; methyl 10-undecenoate, 111-81-9; methyl oleate, 112-62-9; anethole, 104-46-1; *trans*-stilbene, 103-30-0; benzyl 10-undecenoate, 106262-52-6; diethyl fumarate, 623-91-6; cyclohexene, 110-83-8.

Facile Synthesis of Trifluoro- and Hexafluoroisopropyl Halides

Michael Hanack* and Jörg Ullmann

Universität Tübingen, Institut für Organische Chemie, Lehrstuhl II, Auf der Morgenstelle 18, D-7400 Tübingen 1, Federal Republic of Germany

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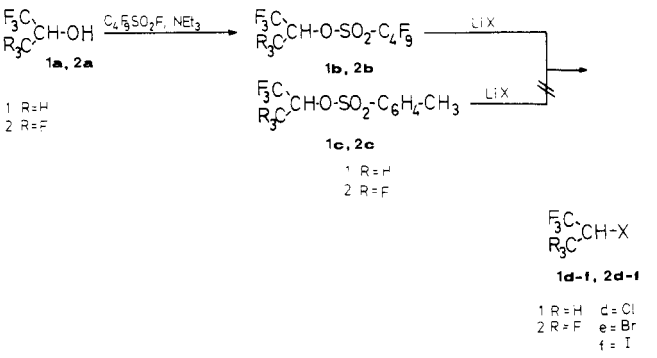
We report here about a facile synthesis of trifluoro- and hexafluoroisopropyl halides **1d–f** and **2d–f** by a simple nucleophilic substitution at the secondary carbon atom of the corresponding nonafluorobutanesulfonates (nonaflates) **1b** and **2b**.

The methods reported hitherto for the synthesis of tri- and hexafluoroisopropyl chlorides, bromides, and iodides **1d–f** and **2d–f** are summarized briefly. The general application of these methods in common laboratories is limited owing to the expenditure of the reaction conditions, the toxicity of the chemicals used, or the difficult accessibility of the starting materials.

A method for preparing **1d–f** and **2d–f** is, e.g., the direct halogenation of 1,1,1-trifluoropropane to give the halides **1d,e**, formed as a mixture of mono- and dihalotrifluoropropanes, which is difficult to separate.[1-6] **1d** is also



synthesized by treating 1,1,1,2-tetrachloropropane with HF and HgO.[2,7] **1d** and **1e** are prepared[8,9] from α-chloro(or α-bromo)propionic acid and SF_4. 1,1,1-Trifluoroisopropyl iodide (**1f**) has not been described yet. Chlorination, bromination, or iodation of the potassium salt of the hexafluoroisobutyric acid[10] yields the 1,1,1,3,3,3-hexafluoroisopropyl halides **2d–f** in good yields. The acid, however, is not commercially available and requires the application of the toxic octafluoroisobutene.[11] (Basic cleavage of an α-halohexafluoroisopropyl pentafluoroethyl ketone[12,13] and treatment of the α-bromohexafluoroisobutyramide with KCN[14] is a tedious synthetic route due to the difficult preparation of the educts). A direct synthesis of **2d,e** from 1,1,1,3,3,3-hexafluoro-2-propanol (**2a**) and phosphorus pentachloride,[15] phosphorus tribromide/bromine,[15] or dibromotriphenylphosphorane[16] respectively yields the products impure and in small quantities. **2d** is produced as one of four differently substituted chlorofluoropropanes,[17,18] from 3,3,3-trifluoro-1,1,2-trichloropropene and HF in the presence of $SbCl_5$; **2d** is formed by reacting 1,1,3,3,3-pentafluoro-2-chloropropene with KF in formamide.[19] (After HCl elimination, heptachloropropane reacts with KF to give the same product[20]). **2e** is obtained by the reaction of bromomalonic

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