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Reduction of Aldehydes and Ketones by Sodium Dithionite

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Conditions have been developed for the effective reduction of aldehydes and ketones by sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$. Complete reduction of simple aldehydes and ketones can be achieved with excess $\text{Na}_2\text{S}_2\text{O}_4$ in H_2O /dioxane mixtures at reflux temperature. Some aliphatic ketones, for example, pentanone and 4-heptanone, are reduced only sluggishly under these conditions. Good conversions can be achieved, however, by adding dimethylformamide to the reaction mixture, again held at reflux. The reductions of 17 compounds are described and the scope of the reaction is discussed. α -Hydroxy sulfinates are suggested as probable intermediates in these reductions.

In 1870 Schützenberger described the reducing powers of a solution of sodium bisulfite in which zinc turnings had been dissolved.¹ The reducing substance, which Schützenberger named sodium hydrosulfite, was isolated and was assigned the erroneous formula $\text{NaHSO}_2\cdot\text{H}_2\text{O}$. This substance, later obtained pure by others,^{2a} was shown in fact to be $\text{Na}_2\text{S}_2\text{O}_4$,^{2a-c} commonly known as sodium dithionite.

Over the years sodium dithionite has found many applications. It has achieved commercial importance as a reductant in vat dyeing and as a bleaching agent.³ In biochemistry sodium dithionite is used to prepare the reduced forms of several enzymes, coenzymes, and electron-transfer proteins.⁴ It can serve as an electron source for the nitrogenase system⁵ and models thereof.⁶ Organic chemical applications of sodium dithionite include reductions of azo,⁷ diazo,⁸ diazonium,⁹ nitroso,⁹ *N*-nitroso,¹⁰ and nitro compounds,^{7,11} imines,^{12,13} pyridinium salts,¹⁴ oximes (to the amines¹⁵⁻¹⁷ as well as hydrolysis to the parent carbonyl compound¹³), and nitroxides.¹⁸ Quinones are reduced to the hydroquinones,^{7,19,20} and vicinal dihalides can be dehalogenated to the corresponding alkenes.²¹ Under proper circumstances certain aromatic

aldehydes can be converted to α -hydroxy sulfinates.²² Symmetrical sulfones can sometimes be obtained by starting from halogenides^{23,24} or activated alkenes.²⁵

In view of these many applications the scarcity of reports on the reduction of carbonyl groups by sodium dithionite becomes all the more striking. Schützenberger claimed the reduction of acetone and benzaldehyde with sodium dithionite but gave no experimental details.¹ The reduction of benzil to benzoin has been twice reported^{11,18b} and the reduction of cyclohexanone to cyclohexanol in up to 10% yield has been observed as an undesired side reaction in an NADH recycling experiment.²⁶

Owing to considerations arising from other work²⁷ we have reexamined the reduction of carbonyl compounds with sodium dithionite and have developed conditions for the effective reduction of various aldehydes and ketones.²⁸

Results and Discussions

A. Synthetic Results. The results of reduction of a variety of carbonyl compounds (eq 1) are summarized in

$\text{R}^1 = \text{alkyl, aryl}; \text{R}^2 = \text{alkyl, aryl or H}$

Table I. For satisfactory yields to be obtained, the aqueous reaction medium must be mildly basic to prevent too rapid decomposition of $\text{Na}_2\text{S}_2\text{O}_4$, which is sensitive to acid (see below). Sodium bicarbonate works best. The reaction temperature must not be lower than 85 °C; for the solvents used reflux temperature is most convenient. At lower temperature little or no reaction occurs. A cosolvent such as dioxane can be used to increase the solubility of the organic compound. It is advisable to work under nitrogen to prevent air oxidation of $\text{Na}_2\text{S}_2\text{O}_4$ ²⁹ and to add the $\text{Na}_2\text{S}_2\text{O}_4$ in portions to minimize its spontaneous decomposition in aqueous solution to chiefly thiosulfate and sulfite.^{30,31}

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Table I. Reductions of Aldehydes and Ketones to Alcohols with Na₂S₂O₄

entry no.	substrate	product	solvent	yield, % ^a
1	<i>n</i> -hexanal	<i>n</i> -hexanol	H ₂ O	63
2	benzaldehyde	benzyl alcohol	H ₂ O-dioxane	84
3	2-furyl aldehyde	2-furyl alcohol	H ₂ O	90
4	cyclohexanone	cyclohexanol	H ₂ O	80
5	4- <i>tert</i> -butylcyclohexanone	4- <i>tert</i> -butylcyclohexanol (<i>cis/trans</i> = 13/87)	H ₂ O-dioxane	94 ^b
6	adamantanone	2-adamantanol	H ₂ O-dioxane	97 ^c
7	camphor	no reaction owing to sublimation	H ₂ O-dioxane	
8a	4-heptanone	4-heptanol	H ₂ O-dioxane	25 ^d
b			H ₂ O-DMF	69 ^d
9a	2-pentanone	2-pentanol	H ₂ O-dioxane	33 ^d
b			H ₂ O-DMF	85 ^e
10	2-octanone	2-octanol	H ₂ O-DMF	75 ^f
11a	cyclopentanone	cyclopentanol	H ₂ O-dioxane	52 ^d
b			H ₂ O-DMF	52 ^g
12a	2-norbornanone	2-norbornanol (<i>exo/endo</i> = 17/83)	H ₂ O-dioxane	44 ^d
b		2-norbornanol (<i>exo/endo</i> = 31/79)	H ₂ O-DMF	100 ^h
13a	cycloheptanone	cycloheptanol	H ₂ O-dioxane	35 ^d
b			H ₂ O-DMF	97 ^d
14	levulinic acid (4-oxopentanoic acid)	(4-hydroxypentanoic 1,4-lactone)	H ₂ O	54 ⁱ
15a	acetophenone	1-phenylethanol	H ₂ O-dioxane	30 ^d
b			H ₂ O-DMF	94
16a	benzophenone	diphenylmethanol	H ₂ O-dioxane	50 ^d
b			H ₂ O-DMF	94 ^j
17	4-bromobenzophenone	(4-bromophenyl)phenylmethanol	H ₂ O-DMF	92
18	ethyl phenylglyoxalate	ethyl mandelate	H ₂ O ^k	24

^a Isolated yields of pure product unless otherwise indicated; purity was at least 99% as determined by GLC. ^b Isolated as a mixture of *cis* and *trans* isomers. The major isomer was obtained in pure form by crystallization from *n*-heptane and identified as the *trans* isomer by means of ¹H NMR. ^c mp 296–300 °C (authentic sample, mp 296–297.7 °C). ^d Conversions determined by GLC. ^e An acid-soluble impurity, likely 2-(dimethylamino)pentane, was also formed in 13% yield and was removed by acid washing. ^f 2-(Dimethylamino)octane isolated as byproduct in 14% yield. ^g Dimethylcyclopentylamine isolated as byproduct in 48% yield. ^h Isolated as a mixture of *exo/endo* isomers. Stereochemistry assigned by GLC comparison with product mixture obtained from reduction of 2-norbornanone with LiAlH₄.⁴² ⁱ Isolated by continuous extraction with ether. ^j mp 65.5–66.5 °C (authentic sample, mp 69 °C). ^k Reaction carried out at room temperature; complete after 6 h. Apparently considerable hydrolysis occurs.

In hot aqueous solution aldehydes are reduced smoothly to the corresponding alcohols (entries 1–3 in Table I) and the carbonyl group of levulinic acid is also readily reduced (entry 14) as are also the carbonyl groups of cyclohexanone, 4-*tert*-butylcyclohexanone, and adamantanone (entries 4–6). These conditions are not adequate, however, for conversion of other aliphatic and aromatic ketones (Table I, entries 8a, 9a, 11a–13a, 15a, 16a).

We finally found that the problem of incomplete conversion could be abated by using dimethylformamide (DMF) as a 1:1 cosolvent with H₂O. Conversions of aromatic ketones under these conditions are virtually complete and the degree of conversion of other ketones is raised considerably. On the other hand the use of cosolvents such as chlorinated hydrocarbons, ethers, alcohols (ethanol, *n*-propanol, or *n*-butanol), or tetramethylurea, each as a 1:1 mixture with H₂O, led only to decreased yields.

With DMF as cosolvent some reductive amination reminiscent of that seen in the Leuckart reaction³² occurs, especially with methyl ketones and cyclopentanone (footnotes e–g, Table I). Apparently, Na₂S₂O₄ serves also a reductant in this reaction (eq 2). These amines formed as side products are easily removed, however, by extraction with acid.

The reactions of Na₂S₂O₄ with either benzonitrile or ethyl benzoate led only to hydrolysis of these substrates: diphenylacetylene, *N*-methylpyrrolidone, and benzoic acid

were not reduced. Both phenacyl bromide and phenacylphenylmethylsulfonium tetrafluoroborate were reduced to acetophenone at room temperature in H₂O with Na₂S₂O₄, but phenacyl benzoate was unaffected under these conditions.

B. Mechanism of Reduction. It has long been known that the reaction of Na₂S₂O₄ with some aldehydes and ketones under aqueous basic conditions at room or lower temperature can lead to α-hydroxy sulfinates (1) as shown in eq 3.

For examination of the possibility that α-hydroxy sulfinates could be intermediates in the reductions reported here, 1a derived from benzaldehyde was synthesized.^{22b} This was added to a refluxing mixture of dioxane–H₂O. The reaction product consisted of a 65/35 mixture of benzyl alcohol and benzaldehyde (eq 4). The formation

of 1a is known to be reversible,³³ explaining the presence of benzaldehyde. The results of the above experiment

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provide in our opinion good suggestive evidence for α -hydroxy sulfinates in the reactions examined by us. The absence of detectable amounts of pinacolic products in this or other reductions argues against direct transfer of a hydrogen atom to an α -hydroxyalkyl radical formed by one electron transfer steps.

The reductive decomposition of an α -hydroxy sulfinate (eq 5) involves (possibly concerted) loss of SO_2 . There is

little known of the thermal chemistry of α -hydroxy sulfinates, but precedent for the postulated loss of SO_2 can be found in the reported thermal decompositions with loss of SO_2 of several allylic sulfinic acid derivatives.³⁴⁻³⁷

There is abundant evidence that $\text{S}_2\text{O}_4^{2-}$ rapidly fragments in aqueous solution; the kinetic schemes are complicated and the product balances are often not complete.^{30,31} In neutral or mildly acidic solution eq 6 and 7 have been suggested as important contributors to the overall decomposition. The sulfoxylate anion, HSO_2^- , should be sufficiently nucleophilic to lead to the α -hydroxy sulfinate (eq 8) in a manner analogous to bisulfite (HSO_3^-)

addition. Decomposition as shown in eq 7 could account for the need of roughly 5 equiv of $\text{Na}_2\text{S}_2\text{O}_4$ necessary for complete reduction of a carbonyl compound.

The importance of the reactions of eq 6 and 7 has been questioned, however, chiefly on kinetic grounds.³⁸ Rate expressions for $\text{S}_2\text{O}_4^{2-}$ decomposition usually contain terms one-half order in $\text{S}_2\text{O}_4^{2-}$. Moreover, the SO_2^- radical anion (**2**) is readily detected by electron spin resonance in solutions of decomposing $\text{S}_2\text{O}_4^{2-}$.³⁹⁻⁴¹ These observations are in accord with eq 9 being an important (reversible) step. The radical anion **2** has also been convincingly implicated as the reductant of various biological materials.⁴

The reaction steps given in eq 9-11 represent another sequence for the formation of α -hydroxy sulfinates with **2** as the reductant. Decomposition as illustrated in eq 5 affords alcohol obtained as end product.

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Conclusions

Sodium dithionite, used under the proper conditions, is an effective reagent for the reduction of aldehydes and ketones. The reagent is safe, especially with regard to explosions. Also, water can be used as solvent or cosolvent. These two properties represent advantages over metal hydride reductants. On the other hand, more than stoichiometric amounts are needed for effective reduction and dithionite compares poorly with metal hydrides in hydride equivalents per mole. It may well be, however, that for many carbonyl reductions both on an industrial scale as well as in the laboratory the use of sodium dithionite should be seriously considered.

Experimental Section

Melting points were determined on a Mettler FP-2 melting-point apparatus equipped with a Mettler FP-21 microscope. Elemental analyses were performed in the microanalytical department of this laboratory. Infrared spectra were recorded on a Unicam SP-2000 infrared spectrophotometer or a Perkin-Elmer 257 grating infrared spectrophotometer. ^1H NMR spectra were recorded on a Varian A-60, a JEOL C-60HL, or a Hitachi Perkin-Elmer R24B spectrometer. Tetramethylsilane (Me_4Si) was used as an internal standard. A Varian XL-100 was used for recording the ^{13}C NMR and 100-MHz ^1H NMR spectra. Mass spectra were obtained on an AEI MS-902 instrument.

General Procedure for Reduction of Aldehydes and Ketones with $\text{Na}_2\text{S}_2\text{O}_4$. A solution of substrate (50 mmol) in dioxane (175 mL) or DMF for more difficultly reducible substrates is added to water (175 mL) containing NaHCO_3 (27.5 g). (When DMF was used as cosolvent, in some cases it was necessary to add some more water during the reduction to prevent gel formation.) When no cosolvent is used, the substrate is added neat. Sodium dithionite (12.5 g) is added and the reaction mixture refluxed for 4 h during which time three additional 12.5-g portions of $\text{Na}_2\text{S}_2\text{O}_4$ are added. (A total of three 12.5-g portions of $\text{Na}_2\text{S}_2\text{O}_4$ sufficed for the reductions of benzaldehyde, furfuraldehyde, 4-*tert*-butylcyclohexanone, adamantanone, and norbornanone.) The reaction is carried out under an atmosphere of nitrogen. After the mixture cooled to room temperature, water is added until the solution becomes clear and thereafter the solution is extracted with ether (furfuryl alcohol and γ -valerolactone were isolated by continuous extraction with ether for 7 and 72 h, respectively). When DMF is used as cosolvent the ether extracts are back-washed twice with water to remove traces of DMF.

After the solution is dried (MgSO_4) and the ether is removed, the products are isolated by either distillation or recrystallization. Identification is based on melting or boiling points, infrared and ^1H NMR spectra, and comparison with authentic materials. All reductions were carried out on a 2-mmol scale and for purposes of isolation were also done on a 50-mmol scale. When products were not isolated GLC was used to determine the degree of conversion and/or product ratio. In all those cases a 6 ft $\times$ 1/8 in. Carbowax 20 M on Chromosorb WAW 80-100-mesh column was used.

Reduction of 2-Octanone. 2-Octanone (6.41 g, 50 mmol) was subjected to the conditions described above for the reduction of aldehydes and ketones; DMF was used as cosolvent. After workup by the usual procedure, the combined ethereal layers were extracted with two 50-mL portions of 2 N HCl followed by washings with water and saturated NaHCO_3 . The ethereal extract was dried (MgSO_4) and ether was removed. The residue was subjected to kugelrohr distillation to give 4.90 g (37.6 mmol, 75% yield) of 2-octanol. The combined acid layers were washed once with ether and then neutralized with a 2 N NaOH solution. The aqueous solution was extracted twice with ether and the combined ethereal layers were washed with water. After the solution was dried

(Na_2SO_4) and solvent was removed, the residue was subjected to kugelrohr distillation to give 1.11 g (7.0 mmol, 14% yield) of 2-(dimethylamino)octane: IR (neat) 1050, 1110, 1160, 1275, 1385, 1470, 2770, 2870, 2960 cm^{-1} ; ^1H NMR (CCl_4) δ 2.13–2.70 (m, 1 H), 2.09 (s, 6 H), 1.24 (br s, 10 H), 0.63–1.20 (m, 6 H); methiodide, mp 232.3–233.1 $^\circ\text{C}$ (lit.⁴³ mp 240 $^\circ\text{C}$).

Anal. Calcd for $\text{C}_{10}\text{H}_{23}\text{N}$: C, 76.36; H, 14.74; N, 8.90. Found: C, 76.18; H, 14.75; N, 8.94.

Synthesis and Decomposition of Sodium Benzylhydroxysulfinate (1a). Compound 1a was synthesized by following Bazlen's method;^{22b} IR (KBr pellet) 655, 690, 955, 1030, 2600–3700 cm^{-1} (no absorption due to benzaldehyde carbonyl could be detected). To 40 mL of a refluxing dioxane– H_2O (1:1) mixture was added 1a (1.5 g, 8.7 mmol). After the mixture was refluxed for 1 h under nitrogen, a sample of the mixture was analyzed by GLC (Carbowax, vide supra) and ^1H NMR. Both benzyl alcohol and benzaldehyde were present in a 65:35 ratio. A solution of 1a in cold dioxane–water did not contain benzyl alcohol, though a marked amount of benzaldehyde was found to be present in the solution upon GLC analysis; this comes from reversible formation of the α -hydroxy sulfinate.

Reduction of Phenacyl Bromide with $\text{Na}_2\text{S}_2\text{O}_4$. A solution of phenacyl bromide (400 mg, 2 mmol) in 7 mL of ether was added to a solution of 1.10 g of NaHCO_3 in 7 mL of H_2O ; 2.00 g of $\text{Na}_2\text{S}_2\text{O}_4$ was added and the mixture was stirred under nitrogen for 6 h. The layers were separated and the aqueous layer was extracted with ether. The combined ethereal extracts were dried (MgSO_4) and the ether was evaporated. The residue was subjected to kugelrohr distillation to give acetophenone (108 mg, 0.9 mmol, 45% yield).

Reduction of methylphenacylphenylsulfonium tetrafluoroborate⁴⁴ was carried out as described above for phenacyl bromide. The sulfonium salt was added neat to the mixture because of its insolubility in ether. After 1.5 h the mixture was worked up as usual. The sulfonium salt (666 mg, 2.0 mmol) gave 486 mg of liquid residue, the sole constituents of which were acetophenone and thioanisole in a 1:1 ratio (maximum theoretical yield 488 mg). The products were identified by ^1H NMR and GLC (Carbowax, vide supra).

Attempted Reduction of Phenacyl Benzoate. Phenacyl benzoate (485 mg, 2.0 mmol) was subjected to the conditions described for the reduction of phenacyl bromide. After 6 h the reaction mixture was worked up as usual. Starting material was recovered (432 mg, 89%).

Attempted Reduction of Benzonitrile. Benzonitrile (200 mg, 2.0 mmol) was subjected to the conditions described for the

reduction of aldehydes and ketones, except that the amount of $\text{Na}_2\text{S}_2\text{O}_4$ was doubled. Dioxane was used as cosolvent. After the usual workup benzamide (178 mg, 75% yield) was isolated. The identity of the product was verified by IR, ^1H NMR, melting point, and mixture melting point with an authentic sample.

Attempted Reduction of Benzoic Acid. Benzoic acid (245 mg, 1.9 mmol) was subjected to the conditions described for reduction of aldehydes and ketones. Extra NaHCO_3 was added to allow for neutralization of benzoic acid. Dioxane was used as cosolvent. After termination of the reaction the mixture was acidified by addition of sulfuric acid and was worked up as usual. Benzoic acid was recovered (232 mg, 95% yield); no benzyl alcohol could be detected in the reaction mixture by GLC (Carbowax, vide supra).

Attempted Reduction of N-Methylpyrrolidone. N-Methylpyrrolidone (200 mg, 2 mmol) was subjected to the conditions described for reduction of aldehydes and ketones. When the reaction was terminated the mixture was subjected to continuous extraction with ether. N-Methylpyrrolidone was recovered quantitatively.

Attempted Reduction of Diphenylacetylene. Diphenylacetylene (365 mg, 2.0 mmol) was subjected to the conditions described for the reduction of aldehydes and ketones with dioxane as cosolvent; thereafter the reaction mixture was analyzed by GLC (Carbowax, vide supra). The only peak present could be attributed to diphenylacetylene. Neither stilbene nor 1,2-diphenylethane was detected in the reaction mixture.

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Registry No. 1a, 14339-77-6; $\text{Na}_2\text{S}_2\text{O}_4$, 7775-14-6; 2-(dimethylamino)octane, 7378-97-4; phenacyl bromide, 70-11-1; methylphenacylphenylsulfonium tetrafluoroborate, 34881-63-5; thioanisole, 100-68-5; benzonitrile, 100-47-0; benzamide, 55-21-0; n-hexanal, 66-25-1; benzaldehyde, 100-52-7; 2-furyl aldehyde, 98-01-1; cyclohexanone, 108-94-1; 4-tert-butylcyclohexanone, 98-53-3; adamantanone, 700-58-3; camphor, 76-22-2; 4-heptanone, 123-19-3; 2-pentanone, 107-87-9; 2-octanone, 111-13-7; cyclopentanone, 120-92-3; 2-norbornanone, 497-38-1; cycloheptanone, 502-42-1; levulinic acid, 123-76-2; acetophenone, 98-86-2; benzophenone, 119-61-9; 4-bromobenzophenone, 90-90-4; ethyl phenylglyoxalate, 1603-79-8; n-hexanol, 111-27-3; benzyl alcohol, 100-51-6; 2-furyl alcohol, 22125-63-9; cyclohexanol, 108-93-0; cis-4-tert-butylcyclohexanol, 937-05-3; trans-4-tert-butylcyclohexanol, 21862-63-5; 2-adamantanol, 700-57-2; 4-heptanol, 589-55-9; 2-pentanol, 6032-29-7; 2-octanol, 123-96-6; cyclopentanol, 96-41-3; exo-2-norbornanol, 497-37-0; endo-2-norbornanol, 497-36-9; cycloheptanol, 502-41-0; 4-hydroxypentanoic 1,4-lactone, 108-29-2; 1-phenylethanol, 98-85-1; diphenylmethanol, 91-01-0; (4-bromophenyl)phenylmethanol, 29334-16-5; ethyl mandelate, 774-40-3; 2-(dimethylamino)pentane, 57303-85-2; dimethylcyclopentylamine, 18636-91-4.

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Reactions of the Cyclopropanone Hemiketal Magnesium Salt with Some Nucleophilic Reagents¹

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Cyclopropanol (5), 1-(arylethynyl)cyclopropanol (7), 1-(3-hydroxypropyl)cyclopropanol derivative 10, 1-(2-propynyl)cyclopropanol (14), cyclopropanone cyanohydrin (19), 1-(aminomethyl)cyclopropanol (21) derivatives, benzylidenecyclopropanes 32, and ethyl cyclopropylideneacetate (38) have been prepared from the magnesium salt of cyclopropanone hemiketal 3. 3-Cyclopropylidene-1-propanol (12) and 3-cyclopropylidene-1-propyne (16) have been obtained from the cyclopropanols 10 and 14, respectively. Some reactions of this new synthon were specific. On the other hand, 3 did not undergo the nucleophilic addition of sulfur and nitrogen ylides; it underwent oxidizing ring opening with $\text{BrZnCH}_2\text{COOEt}$ and induced the decomposition of diazomethane.

The formation of cyclopropanone from ketene and diazomethane in inert solvent at -78°C has been proven

spectroscopically.^{2,3} But, in spite of its considerable interest, this three-membered-ring ketone is not sufficiently