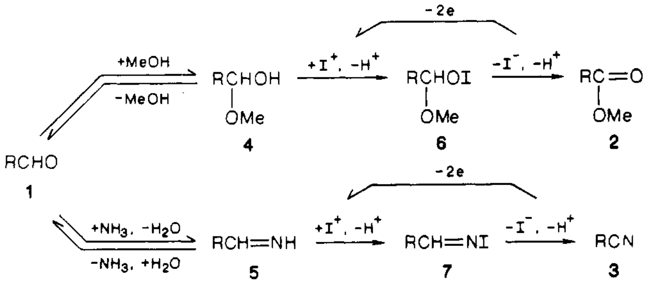
and therefore it is reasonable to assume that the actual oxidizing agent was a positive iodine species generated electrochemically, which formed a redox system with iodide anions.[6]

The analogous chemical reaction of **1** with I_2 in ammoniacal methanol has been reported to give **2** and **3**.[7] We also observed that the reaction of **1** with I_2 in NaOMe–MeOH gave **2** in contrast to a mixture of **3** and **2** in NaOMe–MeOH–NH_3,[8] in which the relative yield of **3** to **2** decreased with increasing the amount of NaOMe.[9] Moreover, at least an equimolecular amount of I_2 and sufficient base to neutralize the HI formed were required to complete these reactions.

From the above observations, the course of the present electrochemical reaction seems to resemble that of the chemical reaction with I_2. Generally, **1** and alcohols are known to form equilibrium mixtures with the hemiacetals (**4**), and the formation of **4** is catalyzed by both acid and base.[10] Also, **1** readily reacts with ammonia to give aldimines (**5**).[2b] Consequently, the reaction path may be represented as follows:



The positive iodine species generated by electrochemical oxidation of I^- attacks **4** or **5** to give an intermediate such as **6** or **7**, which then undergoes an elimination of HI by base to afford the corresponding product **2** or **3**, and the resulting I^- is reoxidized at the anode. In the electrolyte system employed for the preparation of **3**, the equilibrium must lie far to the aldimine side, since **1** were predominantly converted into **3**. In addition, **5** is presumed to be more oxidizable than **6**.

It may be concluded that the overall electrochemical reaction involves the in situ generation of positive iodine species which then gets involved in the production of **2** and **3**. By the electrochemical method, **1** could effectively be converted into **2** or **3** by using small amounts of reagents which are readily available and inexpensive, particularly aromatic aldehydes.

Experimental Section

Preparative electrolyses were carried out in a 100-mL separable flask equipped with a fine frits cup as the cathode compartment, a cylindrical platinum net anode, and a nickel coil cathode.

General Procedure for the Preparation of 2. A solution of aldehyde (50 mmol) and KI (5 mmol) in MeOH (80 mL) containing NaOMe (10 mmol) was electrooxidized under a constant current of 0.5 A (the terminal voltage was ca. 10 V). As the catholyte, the same concentration of NaOMe–MeOH was used. During the electrolysis, the anolyte was stirred with a magnetic stirring bar, and the cell was cooled with running water. The progress of the reaction was followed by GLC analyses of the anolyte.

After completion of the reaction, the solution in the anode compartment was concentrated under reduced pressure without heating. The residue was vigorously shaken with a saturated sodium hydrogen sulfite solution (10 mL), treated with water, and extracted with ether (3 × 25 mL). The combined ether extracts were washed with water (30 mL), dried over anhydrous sodium sulfate, and distilled under reduced pressure or recrystalized after removal of the solvent.

Preparation of 3. In a similar manner, the aldehyde (50 mmol) was dissolved in MeOH (80 mL) containing NaOMe (10 mmol), KI (10 mmol), and ammonia (380 mmol), and the resulting solution was subjected to electrooxidation at ice-bath temperature. After the electrolysis, the anolyte was worked up as above.

Products obtained were identified by comparison of their physical and spectral data with those of authentic samples or with the literature data.[11]

Registry No. Fe, 7439-89-6; H_2SO_4, 7664-93-9; 4-$CH_3C_6H_4CHO$, 104-87-0; 2-$CH_3OC_6H_4CHO$, 135-02-4; 4-$CH_3OC_6H_4CHO$, 123-11-5; 2-ClC_6H_4CHO, 89-98-5; 4-ClC_6H_4CHO, 104-88-1; 2-$NO_2C_6H_4CHO$, 552-89-6; 4-$NO_2C_6H_4CHO$, 555-16-8; $(CH_3)_2(HOCH_2)CCHO$, 597-31-9; *n*-C_6H_7CHO, 123-72-8; *n*-$C_5H_{11}CHO$, 66-25-1; *n*-C_7H_{15}, 124-13-0; $CH_3(CH_2)_3CH(C_2H_5)CHO$, 123-05-7; cyclo-$C_6H_{11}$, 2043-61-0; $C_6H_5CO_2Me$, 93-58-3; 2-$CH_3C_6H_4CO_2Me$, 89-71-4; 4-$CH_3C_6H_4CO_2Me$, 99-75-2; 2-$CH_3OC_6H_4CO_2Me$, 606-45-1; 4-$CH_3OC_6H_4CO_2Me$, 23676-09-7; 2-$ClC_6H_4CO_2Me$, 610-96-8; 4-$ClC_6H_4CO_2Me$, 1126-46-1; 2-$NO_2C_6H_4CO_2Me$, 606-27-9; 4-$NO_2C_6H_4CO_2Me$, 619-50-1; $(CH_3)_2(HOCH_2)CCO_2Me$, 14002-80-3; C_6H_5CN, 100-47-0; 2-$CH_3C_6H_4CN$, 529-19-1; 4-$CH_3C_6H_4CN$, 104-85-8; 2-$CH_3OC_6H_4CN$, 6609-56-9; 4-$CH_3OC_6H_4CN$, 874-90-8; 2-ClC_6H_4CN, 873-32-5; 4-ClC_6H_4CN, 623-03-0; $(CH_3)_2(HOCH_2)CCN$, 19295-57-9; *n*-C_3H_7CN, 109-74-0; *n*-$C_5H_{11}CN$, 628-73-9; *n*-$C_7H_{15}CN$, 124-12-9; $CH_3(CH_2)_3CH(C_2H_5)CN$, 4528-39-6; cyclo-$C_6H_{11}CN$, 766-05-2; KI, 7681-11-0; NaI, 7681-82-5; $(Et)_4NI$, 68-05-3; I_2, 7553-56-2; MeOH, 67-56-1; NaOMe, 124-41-4; NH_3, 7664-41-7; 2-furancarboxaldehyde, 98-01-1; 1-naphthylenecarboxaldehyde, 66-77-3; methyl 2-furancarboxylate, 611-13-2; methyl 1-naphthylenecarboxylate, 2459-24-7; methyl furimidate, 51282-48-5; 1-naphthylenenitrile, 86-53-3.

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(5) Weinberg, N. L. *Technique of Electro-Organic Synthesis*; Wiley: New York, 1975; Part II.

(6) (a) Miller, L. L.; Watkins, B. F. *Tetrahedron Lett.* **1974**, 4495. (b) Shono, T.; Matsumura, Y.; Inoue, K.; Iwasaki, F. *J. Chem. Soc., Perkin Trans. 1* **1986**, 73.

(7) Misono, A.; Osa, T.; Koda, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2875.

(8) If no NaOMe is used, the former reaction does not occur, and the latter is extreamly slow and gives very poor yields of **2** and **3**.

(9) An addition of I_2 to ammoniacal methanol sometimes resulted in a sudden explosion. Therefore, the treatment of I_2 with ammonia was deemed to highly dangerous, especially on a large scale, because of the formation of the explosive nitrogen triiodide. See: Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic: New York, 1963; P 480.

(10) Buehler, C. A.; Pearson, D. E. *Survey of Organic Syntheses*; Wiley: New York, 1970; Chapter 9.

(11) Pollack, J. R. A.; Stevens, R. *Dictionary of Organic Compounds*; Eyre and Spottiswoode Ltd: Great Britain, 1965.

Concerning the Reported Photosolvolysis of 4-Chloro-2-butanone in Alcoholic Media[1]

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In 1970, Kossanyi and Mogto[2] reported the photoreaction of 4-chloro-2-butanone (**4-CB**) in several alcoholic solvents. Two products were obtained, the anticipated alcohol resulting from carbonyl photoreduction plus the

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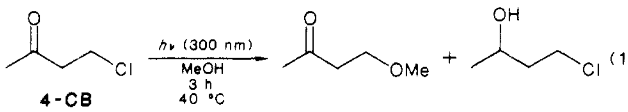
(1) Organic Photochemistry. 74. Part 72: Morrison, H. *Rev. Chem. Intermed.* **1987**, *8*, 128. Part 73: Duguid, R.; Maxwell, B. D.; Munoz-Sola, Y.; Muthuramu, K.; Rasbury, V.; Singh, T.-V.; Morrison, H.; Das, P. K.; Hug, G. L. *Chem. Phys. Lett.* **1987**, *139*, 475–478. Abstracted, in part, from the doctoral dissertation of L.D.C., Purdue University, December, 1986.

(2) Mogto, J. K.; Kossanyi, J. *Ann. Chim. (Paris)* **1970**, *5*, 481.

unexpected ether arising from C-4 substitution (eq 1).

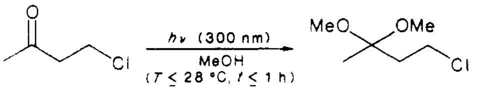


4-CB

(1)

This reaction came to our attention because of our interest in the phenomenon of σ^*/π^* LUMO mixing[3] and the potential photoinitiated cleavage of an otherwise "transparent" nucleofuge made possible by such MO mixing.[4,5] Significant mixing of this type can be demonstrated theoretically for certain conformations of **4-CB**[3] and the apparent photosubstitution reaction could therefore be an experimental indication that activation of the C–Cl linkage has occurred. In fact, we have found that the ether is *not* a primary photoproduct, but rather is formed in a dark, acid-catalyzed process.

Photolysis of a 0.1 M methanolic solution of **4-CB**, using 300-nm light at the ambient temperature of a covered Rayonet reactor (40 °C) for 4 h, lead to the previously observed ether and alcohol in a 9:1 ratio respectively (by GC). A similar photolysis of **4-CB** in the presence of 1-chlorobutane gave no evidence for formation of butyl methyl ether. However, irradiation of a **4-CB** solution at temperatures less than 28 °C for 1 h produced a new product, which has been identified by GC/MS and by ^{13}C NMR as 1-chloro-3,3-dimethoxybutane (**4-CK**; eq 2).



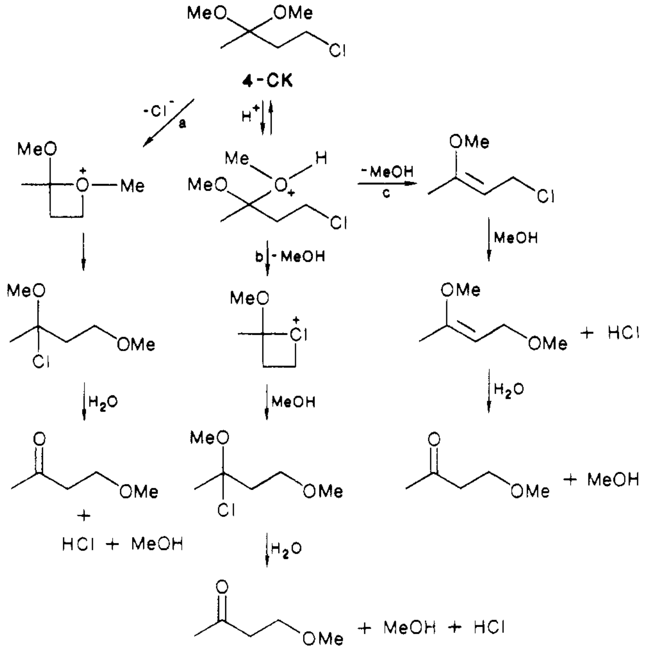
4-CK

(2)

Thus, no molecular ion could be observed, by either EI or CI, but the base peak at m/e 121 corresponds to $M^{\bullet+}$ (152) – OCH_3, with the isotope peak at m/e 123 demonstrating that Cl is still present in this fragment. The other major ion at m/e 89 corresponds to $M^{\bullet+} - CH_2CH_2Cl$. Five ^{13}C NMR signals are observed at δ 20.93 (C_1), 39.95 and 40.65 (C_3 and C_4), 46.14 (CH_3O), and 101.01 (C_2). The assignments of the CH_3 and CH_2 units were confirmed by use of the Attached Proton Test.[6]

The fact that the earlier workers had missed this product is readily understood, for the ketal transforms over to the keto ether with remarkable facility. In fact, all attempts to isolate the **4-CK** by concentration of a photolysis mixture in vacuo gave only the ether, and one could observe this conversion occurring at ambient temperature in the NMR tube (in fact, some conversion was observed to occur upon storage of the ketal in a freezer over a month's time). Likewise, an attempted independent synthesis using the reaction of **4-CB** with trimethyl orthoformate resulted in the exclusive formation of the 4-methoxy-2-butanone. Conversion of **4-CK** to the keto ether is catalyzed by acid, and methanolic solutions of the ketal were more stable when sodium bicarbonate was present. Nevertheless, even these solutions yielded only the keto ether upon evaporation of the solvent. Water, in the absence of acid, did not catalyze this conversion though it was found to accelerate formation at **4-CK** from **4-CB**.

Scheme I



Though it is therefore clear that **4-CK** is the precursor of the substitution product,[7] it appears that the ketal is itself not a primary photoproduct. Two samples of **4-CB** were irradiated for 19 h at which time both analyzed for 9% **4-CK**. One of the tubes was further irradiated for 10 h while the other was kept in the dark for an equal amount of time. Analysis now showed 24% and 26% **4-CK** in the two tubes, respectively. The formation of ketals during the photolysis of ketones in methanol has been reported[8] and apparently derives from the adventitious (and still unexplained) formation of acid when methanol solutions are irradiated.[9] Thus, irradiation of **4-CB** in methanol containing sodium bicarbonate gave no evidence for ketal formation; as expected, the addition of dry HCl gas to a methanolic solution of **4-CB** in the dark rapidly led to the formation of **4-CK**.[10]

Photolytic conversion of **4-CB** to the keto ether is not unique to methanol.[2] Irradiation in 2-propanol at 28 °C also leads to a mixture of reduction and substitution products. That acid is formed concomitantly was ascertained by dilution of the photolysis mixture with water and titration with base and phenolphthalein, and only a trace of ether formation was observed when the photolysis was conducted in the presence of sodium bicarbonate. However, by contrast with methanol, GC analyses of photolyses conducted at lowered temperatures failed to give evidence for an intermediate ketal. Photolysis in ethanol gave no detectable amounts of either ketal or ether; presumably acid formation is minimal in this solvent.

The mechanism for the unusually facile conversion of the ketal to the keto ether is of interest in its own right. Three possibilities seem worthy of consideration and are depicted in Scheme I. All of these options have their

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[3] Morrison, H.; Singh, T.-V.; de Cardenas, L.; Severance, D.; Jordan, K.; Schaefer, W. *J. Am. Chem. Soc.* **1986**, *108*, 3862.

[4] Morrison, H. *Rev. Chem. Intermed.* **1987**, *8*, 128.

[5] Morrison, H.; de Cardenas, L. *J. Org. Chem.* **1987**, *52*, 2590.

[6] LeCocq, C.; Lallemand, J. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 150.

[7] We had earlier considered methyl vinyl ketone, perhaps formed by photolytic dehydrohalogenation, as a possible precursor of the keto ether. This was ruled out by capture ratio studies in a solvent consisting of an 8:2 mixture of trifluoroethanol and methanol. In this solvent, an acidic methyl vinyl ketone solution in the dark gave a 300:1 ratio of methoxy to trifluoroethoxy ketones, whereas photolysis of 4-CB gave these products in a ratio of 1.2:1.0.

[8] Malatesta, V.; Jennings, M.; Hackett, P. *Can. J. Chem.* **1983**, *61*, 366.

[9] Cristol, S. J.; Lee, G. A.; Noreen, A. L. *Tetrahedron Lett.* **1971**, 4175. Roussi, G.; Beugelmans, R. *Tetrahedron Lett.* **1972**, 1333.

[10] This may be common to β-chloroketones; we have made a similar observation with *exo*-6-chloro-2-norbornanone (Singh, T.-V., unpublished observations).

problems. Path a involves solvolysis of a primary halide and requires that a ketal alkoxy group ends up as the ether. In fact, when photolytically generated methyl ketal in methanol was placed in a large excess of ethanol and warmed to ca. 40 °C, appreciable 4-ethoxy-2-butanone was formed, even when the ethanol contained sodium bicarbonate (so as to prevent ketal exchange). Path b would explain such incorporation of the solvent at the 4-position, but it invokes a chloronium ion within a four-membered ring, a ring size that other workers have claimed is particularly disfavored for chlorine participation.[11] Finally, path c would explain the very facile substitution of the chloride by conversion of the ketal to a highly reactive allylic halide, but this mechanism requires that a ketal to enol ether transformation occur under unusually mild conditions.[12] Further studies are clearly needed before this issue can be resolved.

Experimental Section

^{1}H NMR spectra were recorded on a Perkin-Elmer R-32 (90 MHz) or a Nicolet NT-470 (470 MHz) spectrometer. ^{13}C NMR spectra were obtained on a Varian XL-200 instrument. Mass spectra were obtained with a Finnigan automated GC EI/CI mass spectrometer. Gas chromatography utilized a Varian Model 90P instrument for preparative work and Models 1200 or 1400 FID chromatographs with a Hewlett-Packard 3380 or 3380A digital integrator for quantitiative studies. Most photolyses were carried out in a Model RPR-100 Rayonet Reactor (New England Ultraviolet Corp.) with an MGR merry-go-round and 300-nm lamps; the ambient temperature in a covered reactor is ca. 40 °C, and removal of the cover allowed for photolysis at lower temperatures (28 ± 2 °C). Some experiments used a Pyrex filtered Canrad-Hanovia 450-W medium-pressure mercury lamp (Model 679A), with a merry-go-round in a thermostatted cooling bath set to maintain temperatrures from 5 to 20 °C. All photolyses employed matched sets of 10 mm i.d. Pyrex photolysis tubes, and the solutions were degassed with argon for 15 min prior to photolysis. Quantitative experiments included tetradecane in the photolysis solution as an internal standard for GC analysis; complete experimental details for these may be found in the Ph.D. thesis of L.D.C. 4-Chloro-2-butanone (**4-CB**)[13,14] was prepared by bubbling dry HCl gas through a solution of methyl vinyl ketone in sulfur dioxide at −78 °C. The methanol was Burdick and Jackson, Distilled in Glass, Spectrograde.

Photolytic Conversion of 4-CB to 1-Chloro-3,3-dimethoxybutane (4-CK). Aliquots of a 1 M solution of **4-CB** in 3 mL of methanol that had been dried over molecular seives were photolyzed in the Rayonet Reactor with 16 300-nm lamps for 1 h at 28 °C. Gas chromatographic analysis on a 2 ft × 0.125 in. 3% FFAP on 60/80 AW-DMCS Chromosorb W column at 110 °C showed formation of **4-CK** at 6.8 min (other retention times: **4-CB**, 7.8 min; 4-methoxy-2-butanone, 4.7 min). The limiting amount of **4-CK** formation was ca. 20% (the remainder being **4-CB**) with attempts to generate higher conversions leading to diminished **4-CK** and the formation of 4-methoxy-2-butanone. The solutions were either transferred to 10-mm NMR tubes for ^{13}C NMR spectroscopy or subjected to GC/mass spectral analysis. (In general, solutions were 0.1 M in **4-CB**, and somewhat higher conversions to **4-CK** (25%–30%) could be obtained with the medium-pressure lamp and a reaction temperature of 5 °C.) All attempts to purify **4-CK** lead to the isolation of 4-methoxy-2-butanone.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8318825) for support of this research and Daniel Severance for helpful discussions. High-field NMR data were obtained through the Purdue University Biological Magnetic Resonance Laboratory (Grant NIH-RR01077), and the GC/MS data were obtained on an instrument provided by the NSF (Grant CHE-8010832).

Registry No. 4-CB, 6322-49-2; 4-CK, 111772-63-5; 4-methoxy-2-butanone, 6975-85-5.

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(11) Peterson, P. E.; Coffey, J. F. *J. Am. Chem. Soc.* **1971**, *93*, 5208 and references therein.

(12) Marsi, M.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1467 and references therein.

(13) Mogto, J. K.; Wiemann, J.; Kossanyi, J. *Ann. Chim. (Paris)* **1970**, *5*, 471.

(14) Woodward, R. B.; Sondheimer, F. *J. Am. Chem. Soc.* **1953**, *75*, 5438.

Communications

Disproportionation of (Acyloxy)borohydrides: A ^{11}B NMR Study of the Reaction between Sodium Borohydride and Isobutyric Acid

Summary: ^{11}B NMR confirms the existence of BH_4^- ions in large amounts in diglyme solutions of (acyloxy)borohydrides through disproportionation of both the mono- and bis(acyloxy) compounds. The equilibria are slow but need to be carefully examined when designing chiral reducing agents from $NaBH_4$.

Sir: In recent years some reports on the use of chirally modified $NaBH_4$ in asymmetric reductions have appeared.[1] Morrison[2] and Hirao[3] have independently studied a reagent prepared from $NaBH_4$, isobutyric acid, and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose. Optical yields as high as 83% ee were reported[3] in the reduction of propiophenone. These works raised the question whether the initially formed (acyloxy)alkoxyborohydrides disproportionate in the same way as the related lithium alkoxyaluminohydrides which we have previously studied in some detail using ^{27}Al and ^{7}Li NMR.[4] In this paper we report a similar ^{11}B NMR study of $NaBH_4$ modified with isobutyric acid in diglyme solution.

When $NaBH_4$ reacts with a carboxylic acid, hydrogen gas is evolved (eq 1). By measuring the quantity of hydrogen gas evolved we found, in line with previous work,[5,6]

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(1) Midland, M. M. *Asymmetric Synthesis*; Academic: New York 1983; Vol.2, p 45.

(2) Morrison, J. D.; Grandbois, E. R.; Howard, S. I. *J. Org. Chem.* **1980**, *45*, 4229.

(3) Hirao, A.; Itsuno, S.; Owa, M.; Nagami, S.; Mochiguki, H.; Zoorov, H. H. A.; Niakahama, S.; Yamazaki, N. *J. Chem. Soc., Perkin Trans. 1* **1981**, 900.

(4) (a) Malmvik, A.; Obenius, U.; Henriksson, U. *J. Chem. Soc.*, Perkin *Trans. 2* **1986**, 1899. (b) Malmvik, A.; Henriksson, U.; Obenius, U.; *J. Chem. Soc., Perkin Trans. 2* **1986**, 1905.

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