nism, but for CF_3OF they are unsupportive. For the one case (*cis*-1,4-dichloro-2-butene) in which the stereoselectivity can be observed for both CF_3OF and CF_3OCl, one would have to conclude that the mechanism of addition is rather different in this case. Quite probably, the mechanisms are different in nearly every case.

In conclusion, it is clear from this and other work with CF_3OCl that this hypohalite is an excellent source of electrophilic chlorine, and the reactions with simple alkenes are entirely consistent with this concept. The best explanation for the observed products is that CF_3OCl adds to most carbon–carbon double bonds in a highly concerted manner, giving rise to syn addition products. In contrast, our work offers little evidence in support of electrophilic fluorine in CF_3OF. The reaction products found with CF_3OF are most readily accounted for on the basis of a free-radical reaction mechanism, which would account for the observed reactivity, regioselectivity, and low stereoselectivity.

Acknowledgment. The financial support of this work by the National Science Foundation is gratefully acknowledged. Funds for the mass spectrometer were provided by the National Science Foundation and the U.S. Army Research Office. J. V. Paukstelis provided valuable assistance with NMR. D.D.D. also thanks the Alfred P. Sloan Foundation and the Alexander von Humboldt Stiftung for fellowships during part of this work.

Registry No. CF_3OCl, 22082-78-6; CF_3OF, 373-91-1; *trans*-$CHCl{=}CHCl$, 156-60-5; *erythro*-$CF_3OCHClCHClF$, 84010-97-9; *threo*-$CF_3OCHClCHClF$, 84010-98-0; $CH{=}CCl_2$, 75-35-4; $CF_3OCH_2CCl_2F$, 84010-99-1; $CH_2{=}CF_2$, 75-38-7; $CF_3OCH_2CF_3$, 20193-67-3; $CF_3OCF_2CH_2F$, 84011-00-7; $CF_2{=}CCl_2$, 79-35-6; $CF_3OCF_2CCl_2F$, 25476-71-5; $CF_3OCCl_2CF_3$, 25476-71-5; CF_3CCl_2F, 374-07-2; $CF_3{=}CBr_2$, 430-85-3; CF_3CBr_2F, 27336-23-8; $CF_3OCBr_2CF_3$, 84011-01-8; $CF_3OCF_2CBr_2F$, 84011-02-9; $CF_2{=}CHBr$, 359-08-0; CF_3OCF_2CHBrF, 84011-03-0; $CF_3OCHBrCF_3$, 84011-04-1; $CF_2{=}CFBr$, 598-73-2; $CF_3OCF_2CF_2Br$, 1561-51-9; $CF_3OCFBrCF_3$, 84011-05-2; *cis*-$CHF{=}CHF$, 1630-77-9; $CF_3OCHFCHF_2$, 84011-06-3; $CH_2{=}CHCH_3$, 115-07-1; $CF_3OCH_2CHFCH_3$, 84011-07-4; $CF_3OCH(CH_3)CH_2F$, 84011-08-5; $CH_2{=}CHCH_2Cl$, 107-05-1; $CF_3OCH_2CHFCH_2Cl$, 84011-09-6; $CF_3OCH(CH_2Cl)CH_2F$, 84011-10-9; *cis*-$ClCH_2CH{=}CHCH_2Cl$, 1476-11-5; *erythro*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$, 84011-11-0; *threo*-$CF_3OCH(CH_2Cl)CHFCH_2Cl$, 84011-12-1; $CH_2{=}CHOCOCF_3$, 433-28-3; $CF_3OCH_2CHFOCF_3$, 84011-13-2; $CF_3OCH(OCOCF_3)CH_2F$, 84011-14-3; $CH_2{=}CHF$, 75-02-5; $CF_3OCH_2CHF_2$, 84011-15-4; $CF_3OCHFCH_2F$, 84011-16-5; $CH_2{=}CHBr$, 593-60-2; CF_3OCH_2CHBrF, 84011-17-6; $CH_2{=}CHOCOCH_3$, 108-05-4; $CF_3OCH_2CHFOCOCH_3$, 84011-18-7; $CF_3OCH(OCOCH_3)CH_2F$, 84011-19-8; $FCH(OCOCH_3)CH_2F$, 3852-06-0; $CF_3CF{=}CF_2$, 116-15-4; $CF_3OCF_2CF_2CF_3$, 59426-77-6; $CF_3OCF(CF_3)_2$, 60901-74-8; $CF_3OCHClCHCl_2$, 84011-20-1; $FCHClCHCl_2$, 359-28-4; $CF_3OCCl_2CH_2Cl$, 84011-21-2; $CF_3OCF_2CH_2Cl$, 25957-33-9; CF_3CH_2Cl, 75-88-7; $CF_3OCCl_2CF_2Cl$, 84011-22-3; $CF_3OCF_2CCl_3$, 54362-34-4; $CF_3OCF_2CBr_2Cl$, 84011-23-4; $CF_3OCBr_2CF_2Cl$, 84011-24-5; $CF_3OCF_2CHBrCl$, 84011-25-6; $CF_3CHBrCl$, 151-67-7; $CF_3OCFBrCF_2Cl$, 84011-26-7; $CF_3OCF_2CFBrCl$, 84011-27-8; *erythro*-$CF_3OCHFCHFCl$, 84011-28-9; *threo*-$CF_3OCHFCHFCl$, 84011-29-0; $CF_3OCH(CH_3)CH_2Cl$, 84011-30-3; $CF_3OCH_2CHClCH_3$, 84011-31-4; $CF_3OCH(CH_2Cl)CH_2Cl$, 84011-32-5; $CF_3OCH_2CHClCH_2Cl$, 84011-33-6; *erythro*-$CF_3OCH(CH_2Cl)CHClCH_2Cl$, 84011-34-7; $CF_3OCH(OCOCF_3)CH_2Cl$, 84011-35-8; $ClCH_2CHFOCOCF_3$, 84011-36-9; $CF_3OCHFCH_2Cl$, 84011-37-0; F_2CHCH_2Cl, 338-65-8; *erhthro*-$CF_3OCH(CH_3)CHClCH_3$, 84011-38-1; *threo*-$CH_3OCH(CH_3)CHClCH_3$, 84011-39-2; $CF_3OCH(OCOCH_3)CH_2Cl$, 84011-41-6; $CF_3OCF_2CFClCF_3$, 41255-96-3; $CF_3OCF(CF_3)CF_2Cl$, 41255-97-4; norbornylene, 498-66-8; cyclohexene, 110-83-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *cis*-1-chloro–2–(trifluoromethoxy)cyclohexane, 84011-40-5; 2-chloro–3-(trifluoromethoxy)norbornane, 84011-42-7.

Notes

Desulfurization of Thiols and Thioketones by Sodium Triethylborohydride and Iron(II) Chloride on Alumina

Howard Alper,*[1] Sharon Ripley, and Trish L. Prince

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Received February 16, 1982

The extrusion of sulfur from organic compounds is relevant to the problem of the desulfurization of crude oil. Of the various organic sulfur compounds known, thiols and thioketones are the most susceptible to desulfurization. Therefore, if one is to have reasonable expectations that a process for the removal of sulfur from fuel oil will be successful, it is almost mandantory that such a method be applicable to thiols and thioketones.

One class of desulfurization agents are metal carbonyls which can convert thioketones to either alkenes [$Co_2(CO)_8$, $C_5H_5Fe(CO_2)_2$] or hydrocarbons [$Fe(CO)_5$, KOH][2]. Two of us have also recently found that mixed-metal hydride/transition-metal halide reagents are useful for the preparation of hydrocarbons from thiols. The most suitable reagent combination is sodium triethylborohydride and ferrous chloride.[3]

There has been considerable interest in the use of reagents deposited on refractory oxides for effecting organic transformations.[4,5] The principal advantages of carrying out organic synthesis by using such supported reagents include the ease of product separation at the end of the reaction and the mild conditions often used. We now report that thiols can be desulfurized by treatment with iron(II) chloride and sodium triethylborohydride on alumina. In addition, thioketones undergo desulfurization in this manner as does crude oil and Athabasca bitumen.

A variety of experimental conditions were used for the reaction of a thiol (1) with sodium triethylborohydride and $FeCl_2$ on alumina. The best results were obtained by the use of a 1:2:4 ratio of $1/FeCl_2/Na(C_2H_5)_3BH$ (eq 1) in

$$\underset{1}{RSH}\xrightarrow[FeCl_2,\ THF-C_6H_6]{Na(C_2H_5)_3BH/Al_2O_3}\underset{2}{RH}+\underset{3}{RR} \tag{1}$$

---

[1] E. W. R. Steacie Fellow, 1980–1982.

[2] Alper, H.; Paik, H. N. *J. Org. Chem.* **1977**, *42*, 3522.

[3] Alper, H.; Prince, T. L. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 315.

[4] McKillop, A.; Young, D. W. *Synthesis* **1979**, *401*, 481.

[5] Posner, G. H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 487.

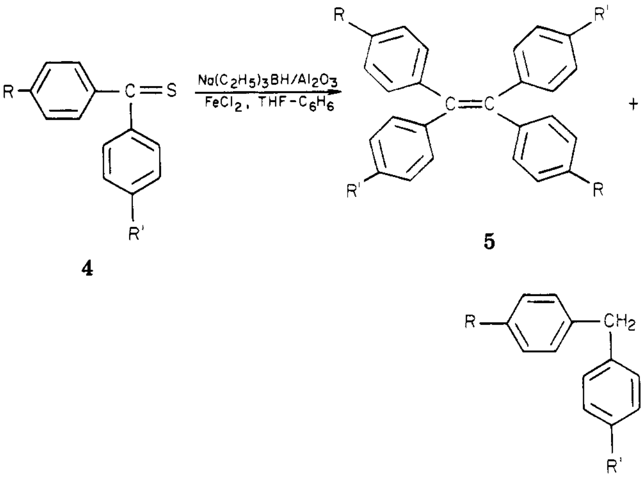
Table I. Products Obtained from the Reactions of Thiols or Thioketones with $Na(C_2H_5)_3BH$ and $FeCl_2$ on Al_2O_3

thiol or thioketone	product[a]	yield, %
1, R = Ph_3C[b]	2	48
	3	38
1, R = β-naphthyl[c]	2	39
1, R = 1-adamantyl	2	73
1, R = 2,5-dichlorobenzene	2	67
4, R = R^1 = OCH_3	5	70
	6	12
4, R = R^1 = CH_3	5	68
4, R = R^1 = $N(CH_3)_2$	5	75
4, R = H; R^1 = OCH_3	5	76

[a] The products were identified by comparison of properties (e.g., IR, NMR, and mass spectra) with those for authentic materials. [b] Use of $Li(C_2H_5)_3BH$ instead of $Na(C_2H_5)_3BH$ gave 2 in 33% yield and 3 in 39% yield. [c] Use of $CoCl_2$ instead of $FeCl_2$ afforded 2 in 15% yield and 3 in 54% yield.

benzene–tetrahydrofuran (THF) (Table I). It is important that the borohydride first interact with alumina, the subsequent steps being reaction with the thiol and $FeCl_2$. Much lower conversions result by first depositing $FeCl_2$ on alumina, followed by $Na(C_2H_5)_3BH$ and then reaction with 1. Poorer product yields also resulted on substitution of $Li(C_2H_5)_3BH$ for $Na(C_2H_5)_3BH$ or of $CoCl_2$ for $FeCl_2$. In comparison with the homogeneous method, sodium triethylborohydride on alumina gives higher total yields of desulfurized products from thiols. However, the yield of 2 is reduced. It should be emphasized that while the heterogeneous reaction occurs at room temperature (rather than at −78 °C), the reaction workup is very simple.

Use of thioketones 4 as substrates for the reaction with $FeCl_2$ and $Na(C_2H_5)_3BH$ on alumina affords olefins in good yields (eq 2), the byproduct being the hydrocarbon 6 (Table I). The results are superior to the homogeneous process, where 5 is obtained in lower yield, and disulfides [7, ((p-RC_6H_4)(p-$R^1C_6H_4$)$CHS)_2$] are also formed (Table II).



4

5

6

Having demonstrated that $Na(C_2H_5)_3BH$ and $FeCl_2$ on alumina is a useful desulfurization method, we then investigated the applicability of this process to the removal of sulfur from crude oil. A sample of Shell crude oil, containing 1.46% sulfur, was treated in the manner described for thiols and thioketones, except that the oil was used as both reactant and solvent. Analysis after the reaction indicated 0.71% sulfur. Similarly, the sulfur content (4.48%) of a sample of Athabasca bitumen was lowered to 2.53% after treatment with $Na(C_2H_5)_3BH$/$FeCl_2$/Al_2O_3. The reaction time was 6 h for both the crude oil and bitumen experiments. Longer reaction times did not improve the extent of desulfurization.

Table II. Products Obtained from the Reaction of Thioketones with $Na(C_2H_5)_3BH$ and $FeCl_2$

R and R^1 of 4	products	yield,[a] %
OCH_3, OCH_3	5	20
	6	21
	7	28
CH_3, CH_3	5	34
	6	44
	7	17
OCH_3, H	5	38
	6	13
	7	21
H, H	5	34
	6	49
	7	10
$N(CH_3)_2$, $N(CH_3)_2$	5	45
	6	28
	7	20

[a] The products were identified by comparison of properties (e.g., IR, NMR, and mass spectra) with those for authentic materials.

In conclusion, the mixed metal halide/metal hydride on alumina system described above is useful for the desulfurization of thiols, thioketones, and crude oil.

Experimental Section

General Procedure for the Reaction of Thiols and Thioketones with $Na(C_2H_5)_3BH$ and $FeCl_2$ on Alumina. A mixture of 12 mL of a 1 M THF solution of $Na(C_2H_5)_3BH$ and alumina (10 g, oven dried overnight at 400 °C) was stirred for 10 min. The thiol or thioketone (3.0 mmol) in THF (5 mL) was added to a THF solution (5 mL) of $FeCl_2$ (6.0 mmol), and the resulting solution was added to the borohydride–Al_2O_3 mixture, followed by additional benzene (30 mL). The reaction mixture was stirred for 2–8 h (reaction followed by thin-layer chromatography). The slurry was filtered, the precipitate was washed with methylene chloride, and the washings were added to the filtrate. Water (5–10 drops) was added to the latter, the solution was filtered and dried ($MgSO_4$), and rotary evaporation of the filtrate gave the crude products which were separated by recrystallization or by chromatography on silica gel with hexane/ether as the eluant.

General Procedure for the Reaction of Thioketones with $Na(C_2H_5)_3BH$ and $FeCl_2$. To 3.0 mmol of $FeCl_2$ was added THF (2.0 mL) followed by 1.5 mmol of the thioketone dissolved in the minimum amount of THF. Additional THF (6.0 mL) was added, and the reaction mixture was stirred for 15 min at room temperature and then cooled to −78 °C. Sodium triethylborohydride (6.0–6.2 mL of a 1 M solution in THF) was added, and the solution was then stirred at −78 °C for 10 min (reaction mixture turned black). The reaction mixture was allowed to warm to room temperature with stirring and then cooled to 0 °C. The reaction was quenched by the addition of moist sodium sulfate, followed by water (10 mL). The mixture was stirred for 30 min and then extracted with methylene chloride (50 mL). The CH_2Cl_2 extract was washed with water, dried ($MgSO_4$), and concentrated by rotary evaporation. Product separation was achieved by chromatography on silica gel, with the hydrocarbon (hexane or hexane-benzene), alkene (hexane–benzene or benzene), and disulfide (benzene or benzene–ether) being eluted in order of increasing polarity of eluants.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. 1 (R = Ph_3C), 3695-77-0; 1 (R = β-naphthyl), 91-60-1; 1 (R = 1-adamantyl), 34301-54-7; 1 (R = 2,5-dichlorobenzene), 5858-18-4; 2 (R = Ph_3C), 519-73-3; 2 (R = β-naphthyl), 91-20-3; 2 (R = 1-adamantyl), 281-23-2; 2 (R = 2,5-dichlorobenzene), 106-46-7; 3 (R = Ph_3C), 17854-07-8; 4 (R = R′ = OCH_3), 958-80-5; 4 (R = R′ = CH_3), 1141-08-8; 4 (R = R′ = NMe_2), 1226-46-6; **4** (R = H;R′ = OCH_3), 1141-07-7; **4** (R = R′ = H), 1450-31-3; **5** (R = R′ = OCH_3), 10019-24-6; **5** (R = R′ = CH_3), 5831-43-6; **5** (R = R′ = NMe_2), 1261-86-5; **5** (R = H;R′ = OCH_3), 68578-78-9; **5** (R = R′ = H), 632-51-9; **6** (R = R′ = OCH_3), 726-18-1; **6** (R = R′ = CH_3), 4957-14-6; **6** (R = H;R′ = OCH_3), 834-14-0; **6** (R = R′ = H), 101-81-5; **6** (R = R′ = NMe_2), 101-61-1; **7** (R = R′ = OCH_3), 42495-96-5; **7** (R = R′ = CH_3), 64725-53-7; **7** (R = H; R′ = OCH_3), 83476-34-0; **7** (R = R′ = H), 1726-02-9; **7** (R = R′ = NMe_2), 83463-89-2; $Na(C_2H_5)_3BH$, 17979-81-6; $FeCl_2$, 7758-94-3.

Paramagnetic Solvent Nuclear Magnetic Resonance Shifts in Radical Anion Solutions. 3. Kinetic Method for Measuring Molar Paramagnetic Solvent Shifts of Unstable Radical Anions

Constantinos G. Screttas* and Maria Micha-Screttas

The National Hellenic Research Foundation, Athens 501/1, Greece

Received April 30, 1982

The purpose of this paper is (1) to describe a method by which the molar paramagnetic solvent shift of an unstable, e.g., with respect to disproportionation, radical anion can be measured and (2) to show that the mode of radical anion preparation may have an effect upon the magnitude of the molar paramagnetic solvent shift.

Solvent NMR shifts in radical anion solutions, in most cases, are linearly related to the formal concentration of the radical anion. This enables one to measure kinetics[1] by observing solvent shifts with respect to time in systems involving a stable radical anion either as a reactant or as a product. If the reaction in question obeys a rate law other than first order, it is necessary to know the molar shift of the radical anion; otherwise, the rate constant will be expressed in terms of units hertz/mole instead of moles/liter. In the case of stable radical anions the molar paramagnetic solvent shift can be determined readily.[2] However, there are cases in which a radical anion has a pronounced tendency toward disproportionation. This means that during the preparation of a concentrated solution of such a radical anion, which requires prolonged reaction of quivalent quantities of the alkali metal and the substrate, the radical anion disproportionates. In this category belongs the ketyl anion of phenyl trityl ketone, benzopinacolone. Attempted direct synthesis of lithium phenyltritylketyl according to eq 1 led to a reddish solution

$$\mathrm{Ph_3CCOPh + Li \rightarrow (Ph_3CCOPh)^{-}\cdot Li^{+}} \qquad (1)$$

which was feebly paramagnetic. When, however, the ketyl anion was generated by electron transfer from lithium naphthalene radical anion (eq 2), a bluish solution was

$$\mathrm{Li^{+}C_{10}H_8^{-}\cdot + Ph_3CCOPh \rightarrow (Ph_3CCOPh)^{-}\cdot Li^{+} + C_{10}H_8} \qquad (2)$$

obtained instead, which gradually turned red within a few hours. This color change was accompanied by decay of the paramagnetism which was associated with the "blue" species, obviously the ketyl anion $(Ph_3CCOPh)^{-}\cdot Li^{+}$. In Figure 1 is given the decay curve of the solvent shift in a solution of lithium phenyltritylketyl in THF prepared according to eq 2. The electron-transfer reaction in eq 2 is instantaneous and quantitative due to the great difference[3] in the electron affinities of Ph_3CCOPh and $C_{10}H_8$, in favor of the former compound. In Figure 1 is also given a plot of the data according to the second-order rate law, which obviously is obeyed and agrees with the process (3) shown in eq 3. For further experimental evidence that

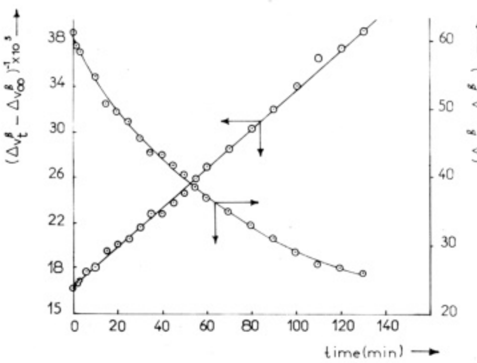


Figure 1. Decay curve of paramagnetism in an initially 0.48 M solution of lithium phenyltritylketyl in THF at 35 °C. The straight line is a plot of the same data according to the second-order rate law.

$$\mathrm{(Ph_3CCOPh)^{-}\cdot + (Ph_3CCOPh)^{-}\cdot \rightarrow (Ph_3CCOPh)^{2-} + Ph_3CCOPh} \qquad (3)$$

the decay of the paramagnetism is due to the disproportionation reaction and not due to an alternative one, see the following discussion as well as the Experimental Section. A rate constant of 0.175 L Hz^{-1} min^{-1} at 35 ± 0.5 °C was extracted from the data. In order to convert the rate constant into the appropriate units of L mol^{-1} min^{-1}, it was necessary to know the molar paramagnetic solvent shift of the lithium phenyltritylketyl. This was done by extrapolation of the kinetic line. Thus we could obtain a rather accurate estimate of the shifts at the moment of mixing the reagents and from them the molar shifts. The molar shifts referred to the two proton bands of THF were $\Delta\nu_m^{\alpha} = 178$ and $\Delta\nu_m^{\beta} = 162$ Hz/mol (at 80 MHz and after being corrected for the naphthalene ASIS). The latter molar shift was used to convert the rate constant to units of L mol^{-1} s^{-1}, which now is $k = 1.80 \times 10^{-5}$ L mol^{-1} s^{-1}. This kinetic method of measuring molar paramagnetic solvent shifts is applicable to radical anions which decay with a half-life of the order of 1 min or longer.

In the first paper of this series[2] we stated that if a radical anion tends to disproportionate, then its preparation by mixing equimolar quantities of the dianion and the neutral aromatic molecule, i.e., by inverse disproportionation, e.g., eq 4, would lead to the equilibrium mixture. On the basis

$$\mathrm{(Ph_3CCOPh)^{2-}K_2^{2+} + Ph_3CCOPh \not\rightleftharpoons 2(Ph_3CCOPh)^{-}\cdot K^{+}} \qquad (4)$$

of the above-given information, the phenyl trityl ketone dianion appeared to be an ideal system for proving or disproving the correctness of our statement. We chose to employ potassium phenyl trityl ketone dianion because of its greater chemical stability (with respect to solvent cleavage) as compared to the relevant stability of $(Ph_3CCOPh)^{2-}Li_2^{2+}$. Thus a solution prepared according to eq 4 and being 0.40 N in "active alkalinity" exhibited a shift of only 11.6 Hz at 80 MHz. This small shift remained constant throughout the period of our observations, which lasted 1 h, and it was found unchanged after

---

[1] (a) Screttas, C. G. *J. Chem. Soc., Chem Commun.* **1972**, 869. (b) Screttas, C. G. *J. Chem. Soc., Perkin Trans. 2* **1974**, 745. Screttas, C. G.; Georgiou, D. G. *Tetrahedron Lett.* **1975**, 417. Screttas, C. G.; Cazianis, C. T. *Tetrahedron* **1978**, *34*, 933.

[2] Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1981**, *46*, 993.

[3] Higashi, K.; Baba, H.; Rembaum, A. "Quantum Organic Chemistry"; Interscience: New York, 1965; p 312.

0022-3263/83/1948-0252$01.50/0