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## Bifunctional Detergents as Novel Catalysts (*Final Report*)

BY:

Dr. R.S. Brown  
University of Alberta

SUBMITTED TO:  
SCIENTIFIC AUTHORITY

R.G. Clewley  
Defence Research Establishment Suffield  
Box 4000, Medicine Hat, Alberta, T1A 8K6

September 1994

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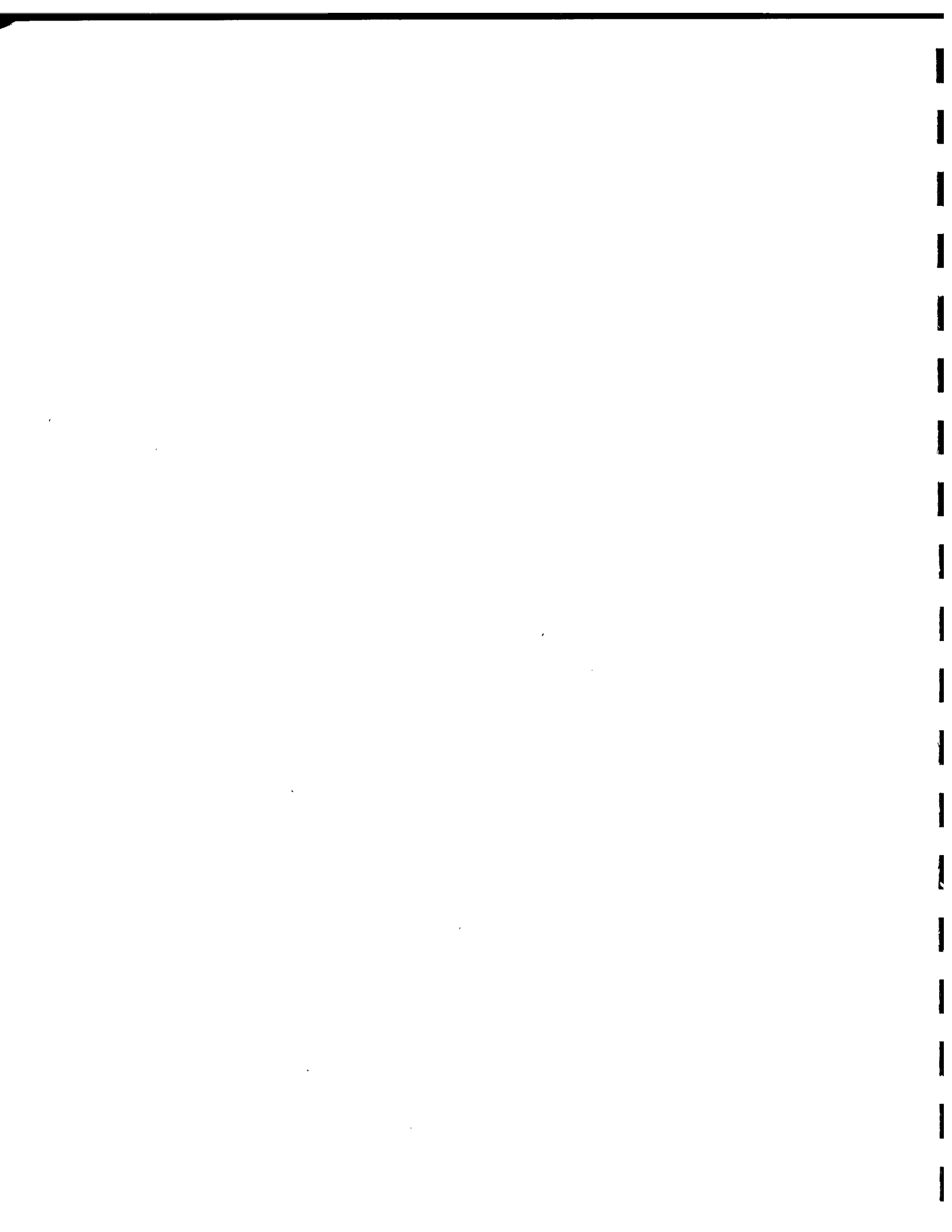
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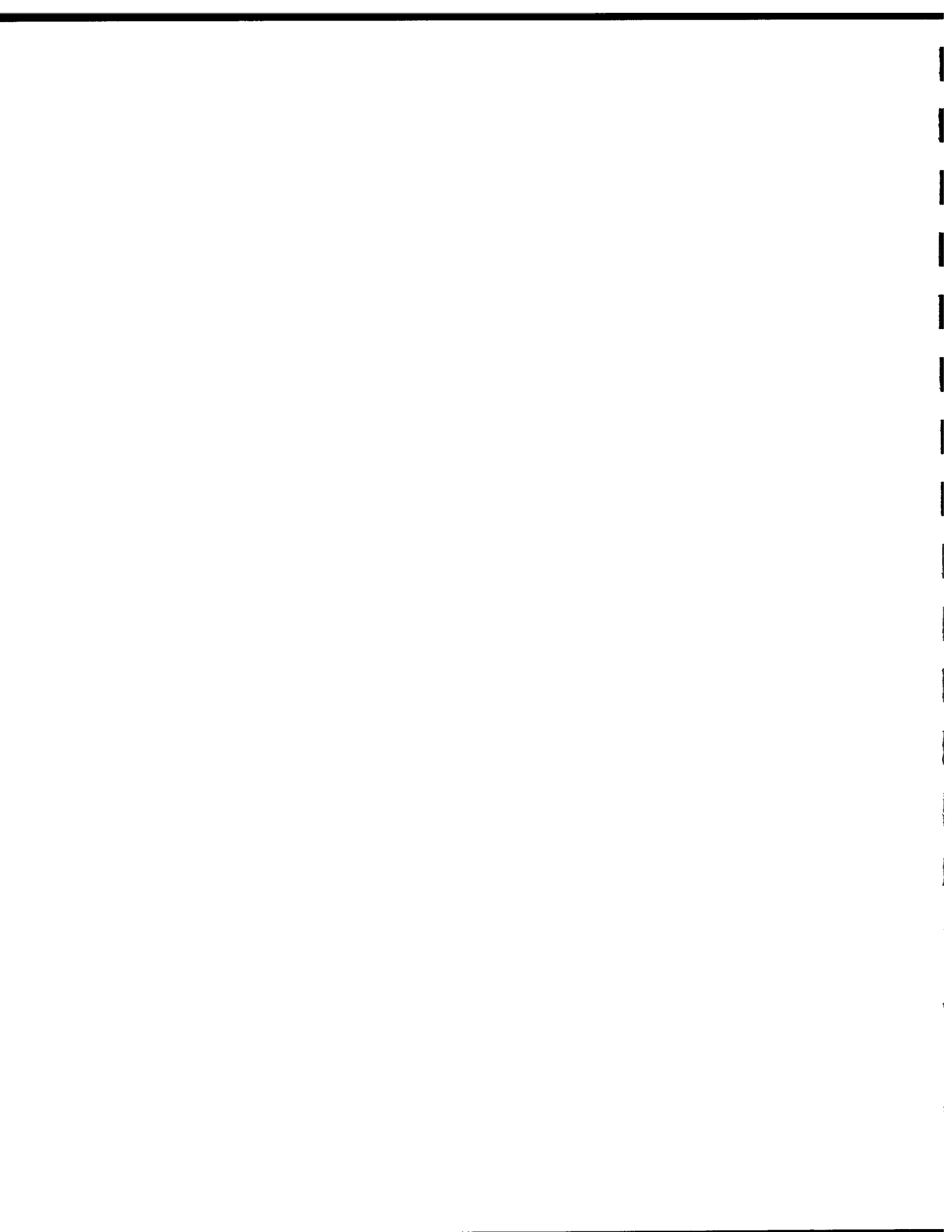
BIFUNCTIONAL DETERGENTS AS  
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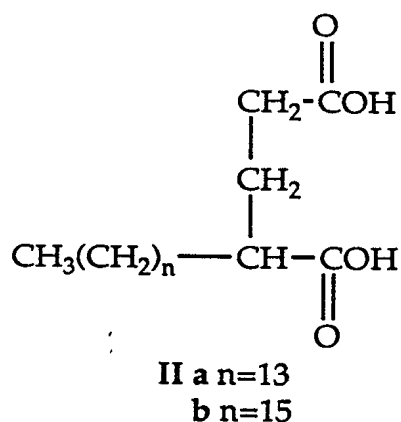
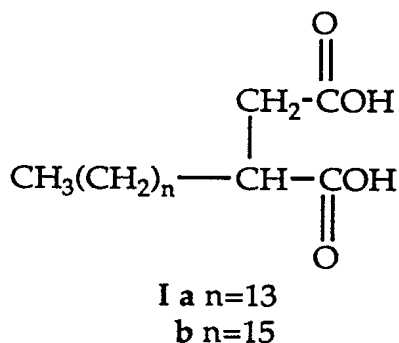
Dr R.S. Brown  
Department of Chemistry  
University of Alberta  
Edmonton, Alberta  
T6G 2G2

Contract No. W7702-1-R260  
Final Report

September 1994



The oxidation of phenyl ethylsulfide (Ph-S-Et) and ClCH<sub>2</sub>CH<sub>2</sub>SEt, as models for the oxidation of sulfur mustard, were investigated in the presence of 2-*n*-alkyl succinic (I) and 2-*n*-alkylglutaric (II) acids at 25°C in aqueous media containing added co-solvents and I<sub>2</sub>. As specified in the Report covering work October 1, 1992 - February 28, 1993 (preparation date April 15, 1993), this system is plagued with problems and is unfeasible for the oxidation of mustard simulants. The main problems that detract from this methodology are: 1) purification of the organic co-solvents to eliminate long term spontaneous reduction of I<sub>2</sub>; 2) solubility of the decarboxylic acids that precludes formulation at high concentration.



In subsequent work we investigated the kinetics of cleavage of the acyl halide benzoylchloride in the presence of Ia or acetic acid/acetate, and succinic acid/succinate in dry acetonitrile. In these studies, the acidity of the medium was adjusted by setting the ratio of [carboxylic acid]/[carboxylate] at 3:1, 1:1, and 1:3. The carboxylate salts were prepared as their tetra-*n*-butyl ammonium salts by mixing equimolar amounts of the acid and *n*-Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup> (40% in H<sub>2</sub>O). The salts were isolated after removal of H<sub>2</sub>O.

The kinetics were monitored at 25°C at 240 nm using a Cary 210 uv/visible spectrophotometer. Reactions were initiated by injecting 30 μL of a stock solution of benzoyl chloride (9.4 × 10<sup>-3</sup> M) in CH<sub>3</sub>CN into 3.0 mL of CH<sub>3</sub>CN containing the

buffering acid/carboxylate species. The comparison data are given in Tables 1 and 2. Note here that satisfactory solutions of Ia in CH<sub>3</sub>CN could not be obtained for reasons of solubility. However, given the fact that the succinic acid reacts at rates that are comparable, or in some cases slower than acetic acid, this study was discontinued.

Table 1 Pseudo-first order rate constants for reaction of benzoyl chloride in CH<sub>3</sub>CN/acetate buffer at 25°C

#	[buffer] <sub>total</sub>	[AcOM:AcOH]*	k <sub>obs</sub> (s <sup>-1</sup> )
1	0.01	3 : 1	(3.38±0.03) × 10 <sup>-1</sup>
2	0.01	1 : 1	(1.10±0.01) × 10 <sup>-2</sup>
3	0.01	1 : 3	(2.55±0.05) × 10 <sup>-3</sup>

M = *n*-Bu<sub>4</sub> N<sup>⊕</sup>

Table 2 Pseudo-first order rate constants for reaction of benzoyl chloride in CH<sub>3</sub>CN/succinate buffer at 25°C

#	[buffer] <sub>total</sub>	MOOC(CH <sub>2</sub> ) <sub>2</sub> COOM: HOOC(CH <sub>2</sub> )COOH	k <sub>obs</sub> (s <sup>-1</sup> )
1	0.01	3 : 1	(4.41±0.04) × 10 <sup>-1</sup>
2	0.01	1 : 1	(1.37±0.01) × 10 <sup>-2</sup>
3	0.01	1 : 3	(0.71±0.01) × 10 <sup>-3</sup>

M = *n*-Bu<sub>4</sub> N<sup>⊕</sup>



Report Covering Work February 1992 - October 1992

"Bifunctional Detergents as Novel Catalysts"

Supply and Services Canada

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for

Defence Research Establishment Suffield

National Defence

RALSTON, Alberta

T0J 2N0

Prepared by: Robert S. Brown

Department of Chemistry

University of Alberta

EDMONTON, Alberta

T6G 2G2

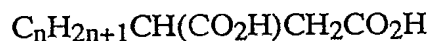
Preparation Date: October 26, 1992

Over the reporting period we have prepared and characterized six examples of long chain dicarboxylic acids.



1 n=12

2 n=14



3 n=12

4 n=14



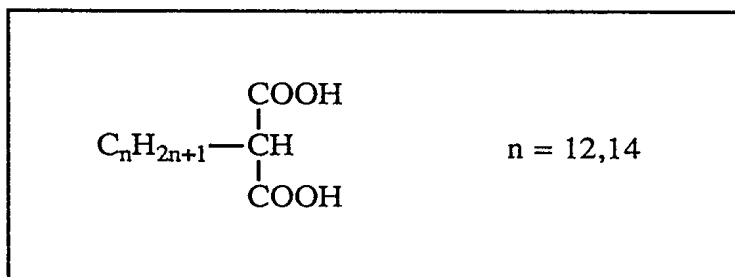
5 n=12

6 n=14

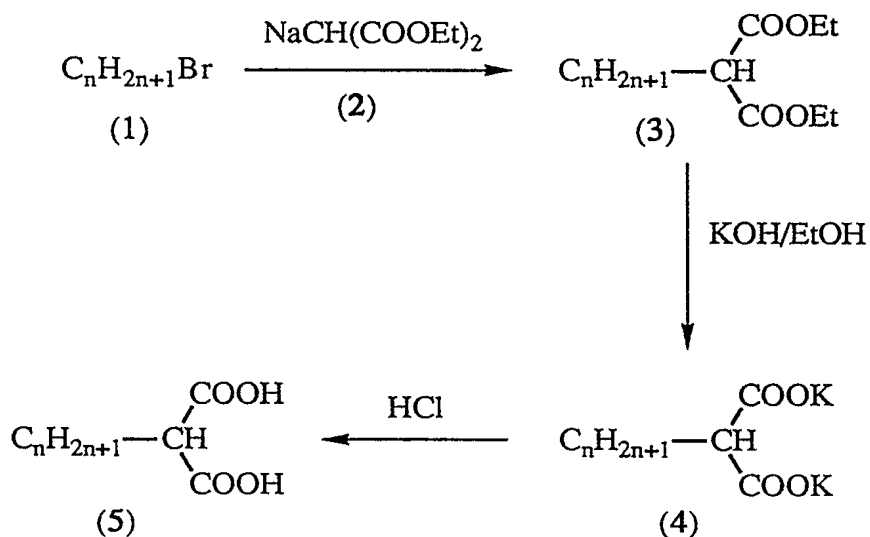
These have been prepared in quantities that are sufficient to allow evaluation of their efficacy to promote the oxidation of thioethers by  $I_2$  in the presence of  $I^-$ . We have encountered several difficulties in the kinetic work due to solubility problems that require organic cosolvents, and a spontaneous reaction that proceeds in the absence of thioether. After close to two months of work, we have traced the origins of the spontaneous reaction to some impurities in the commercial LiI we used to keep the ionic strength constant. The use of KI circumvents this problem. Currently we are undertaking detailed kinetic measurements that will be the subject of the next report.

## Experimental Syntheses

### i) Malonic acid series



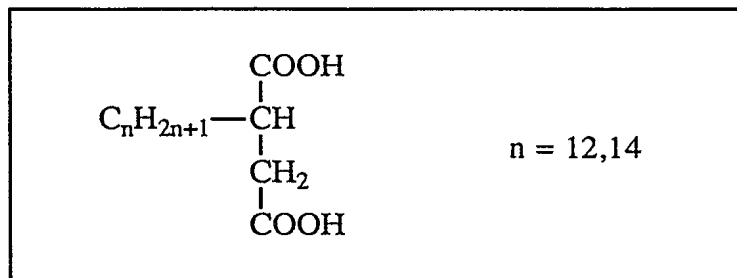
The acids were synthesized from the normal primary long-chain alkyl bromides (Aldrich) according to the following scheme:



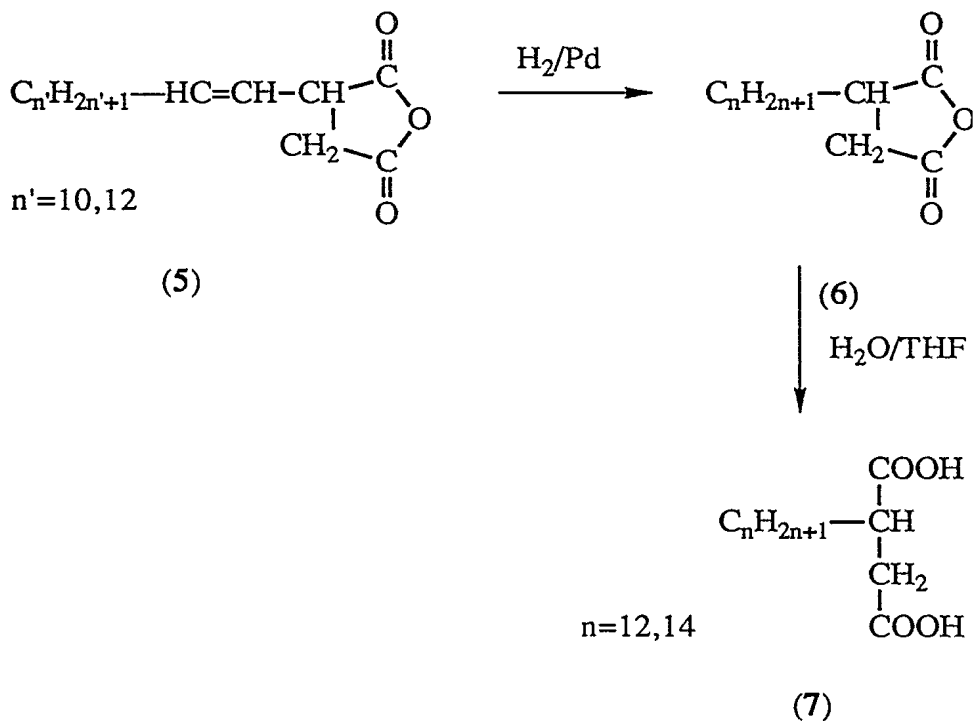
The condensation of the bromide (1) with sodio-ethyl malonic ester (2), freshly prepared from fractionally distilled malonic ester (Aldrich) was carried out<sup>1,2</sup> in purified (dried and distilled) refluxing n-butanol (Anachemia) for 24-36 h. The product (3) was then hydrolyzed<sup>3</sup> with KOH (25%) / EtOH solution (5h, reflux). The potassium salt (4) was neutralized with hydrochloric acid to liberate the free acid, and the free acid was then extracted from the aqueous solution with ether. The extracted acids were recrystallized 2-3 times from acetonitrile. Overall yields were 72% (n=12)

and 85% (n=14). The melting points of the compounds were within good agreement with literature values: mp 120-121°C (n=12) lit.<sup>2</sup> 120.0°C; mp 120-121°C (n=14), lit.<sup>2</sup> 120.6°C, lit.<sup>4</sup> 118-120°C. Analysis: n=12 (on hand, 11.8 g pure, ~ 20 g to purify). <sup>1</sup>H NMR (400 MHz) (MeOH-d<sub>4</sub>) δ 3.26 (t, 1 H), 1.82 (m, 2 H), 1.30 (m, 20 H), 0.89 (t, 3 H). Anal. Calc. for C<sub>15</sub>H<sub>28</sub>O<sub>4</sub>: C, 66.14; H, 10.36. Found: C, 66.25; H, 10.58; M.S. Calc. for C<sub>15</sub>H<sub>26</sub>O<sub>3</sub> (M-18) 255.191; found: 255.196. For n=14 (on hand, 35.8 g) <sup>1</sup>H NMR (400 MHz) (MeOH-d<sub>4</sub>) δ 3.26 (t, 1 H), 1.81 (m, 2 H), 1.31 (m, 24 H), 0.89 (t, 3 H). Anal. Calc. for C<sub>17</sub>H<sub>32</sub>O<sub>4</sub>: C, 67.96; H, 10.73. Found: C, 68.19; H, 10.58; M.S. Calc. for C<sub>17</sub>H<sub>30</sub>O<sub>3</sub> (M-18) 282.219; found: 282.219.

## ii) Succinic Acid Series



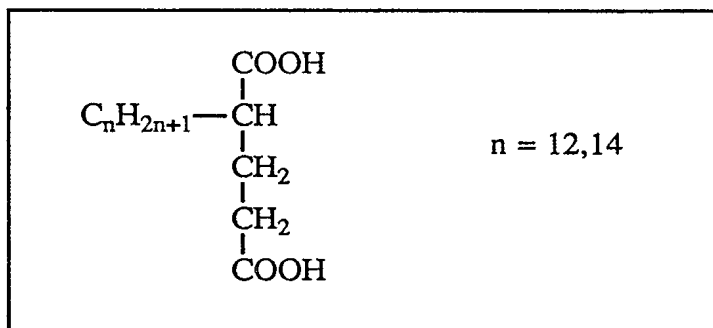
N-alkyl succinic acids were made from the corresponding commercially available long chain N-alkyl unsaturated anhydrides according to the following scheme:



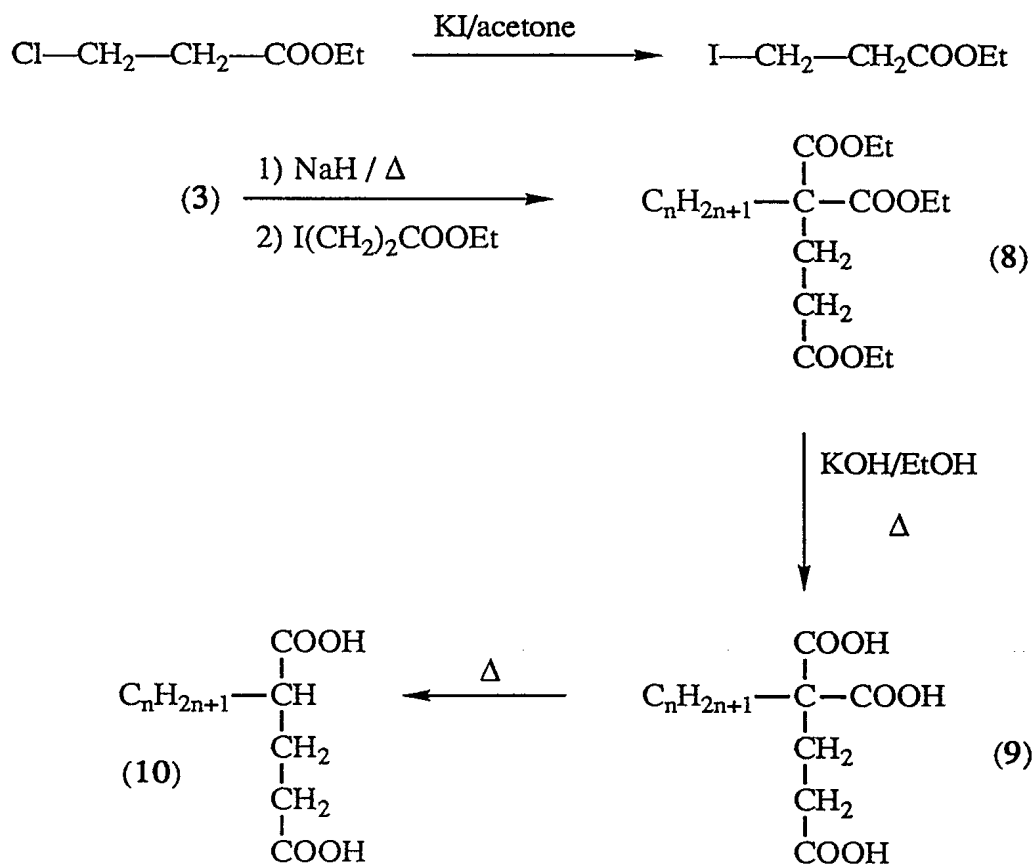
The commercially available 2-dodecen-1-yl succinic anhydride (Sigma) or 2-tetradecen-1-yl succinic anhydride (Pfaltz and Bauer, Inc.) were hydrogenated in dry THF using Pd/C catalyst in a Parr hydrogenation apparatus (60 PSI, 3 h, RT). The saturated anhydrides (6) were hydrolyzed in H<sub>2</sub>O/THF solution (overnight reflux). THF was removed by rotevaporation and the acids were

crystallized from acetonitrile. Overall yields were 85% (n=12) and 48% (n=14). Analysis: n=12 (on hand 9.0 g; 20 g left to purify).  $^1\text{H}$  NMR (400 MHz)  $\text{CDCl}_3$ :  $\delta$  2.78 (m, 1 H), 2.65 (m, 1 H), 2.45 (m, 1 H), 1.62 (m, 1 H), 1.48 (m, 1 H), 1.30 (m, 20 H), 0.80 (t, 3 H), offset 2 H; mp 102-103°C. Anal. Calc. for  $\text{C}_{16}\text{H}_{30}\text{O}_4$ : C, 67.10; H, 10.56. Found:  $\text{C}_{16}\text{H}_{30}\text{O}_4$ : C, 67.26; H, 10.62; M.S. Calc. for  $\text{C}_{16}\text{H}_{28}\text{O}_3$  (M-18) 268.203; found: 268.203. For n=14 (on hand 20.5 g).  $^1\text{H}$  NMR (400 MHz)  $\text{CDCl}_3$ :  $\delta$  2.84 (m, 1 H), 2.71 (m, 1 H), 1.69 (m, 1 H), 1.53 (m, 1 H), 1.25 (m, 24), 0.87 (t, 3 H). mp 103-104°C. Anal. Calc. for  $\text{C}_{18}\text{H}_{34}\text{O}_4$ : C, 68.75; H, 10.90. Found:  $\text{C}_{18}\text{H}_{34}\text{O}_4$ : C, 69.03; H, 11.16; M.S. Calc. for  $\text{C}_{18}\text{H}_{32}\text{O}_3$  (M-18) 296.235; found: 296.234.

## iii) Glutaric Acid Series



The acids were synthesized<sup>1,2,3</sup> from n-dodecyl bromide (Aldrich) and n-tetradecyl bromide (Aldrich) according to the following scheme:



Ethyl- $\beta$ -iodopropionate was made<sup>5</sup> from commercially available ethyl- $\beta$ -chloropropionate (Aldrich). The general procedure<sup>3</sup> for the preparation of 1:3:3-tricarbethoxyalkanes (8) was improved. Instead of sodium metal,<sup>3</sup> (reaction is too slow), sodium hydride was used. Distillation *in vacuo* yielded 1:3:3-tricarbethoxyalkanes at bp 205°C / 1.0 mm Hg (45%) (n=12) and bp 220°C / 0.7 mm Hg (57%) (n=14). Hydrolysis and decarboxylation yielded the crude dicarboxylic acids which were purified by crystallization from benzene (n=12) or Skelly B (n=14). The overall yields were 25% (n=12) and 36% (n=14) m.p. 71-72°C (lit.<sup>2</sup> 71.5°C) (n=12) and 76-77°C (lit.<sup>2</sup> 77.5°C). Analysis: n=12 (on hand 19 g) <sup>1</sup>H NMR (400 MHz) CDCl<sub>3</sub>  $\delta$  2.51 (m, 1 H), 2.37 (1 m 2 H), 2.01 (m, 1 H), 1.89 (m, 1 H), 1.70 (m, 1 H), 1.38 (m, 1 H), 1.25 (m, 20 H), 0.85 (t, 3 H), offset ~ 2 H. Anal. Calc. for C<sub>17</sub>H<sub>32</sub>O<sub>4</sub>: C, 67.96; H, 10.73. Found: C<sub>17</sub>H<sub>32</sub>O<sub>4</sub>: C, 68.19; H, 10.58; M.S. Calc. for C<sub>17</sub>H<sub>30</sub>O<sub>3</sub> (M-18) 282.219; found: 282.219. For n=14 (on hand 22 g) <sup>1</sup>H NMR (400 MHz) CDCl<sub>3</sub>  $\delta$  2.46 (m, 1 H), 2.32 (m, 2 H), 1.98 (m, 1 H), 1.85 (m, 1 H), 1.65 (m, 1 H), 1.32 (m, 1 H), 1.20 (m, 24 H), 0.80 (t, 3 H). Anal. Calc. for C<sub>19</sub>H<sub>36</sub>O<sub>4</sub>: C, 69.47; H, 11.05. Found: C<sub>19</sub>H<sub>36</sub>O<sub>4</sub>: C, 69.68; H, 11.18; M.S. Calc. for C<sub>19</sub>H<sub>34</sub>O<sub>3</sub> (M-18) 310.250; found: 310.250.

## References

1. *Organic Synthesis Coll.* v. II, p. 474.
2. B.D. Sharma, A.B. Biswas, *Anal. Chem.* **1958**, *30*, 1356-1361.
3. J.G. Buchanan, A.W. Johnson, J.A. Mills and A.R. Todd, *J. Chem. Soc.* **1950**, 2845.
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Report Covering Work October 1, 1992 - February 28, 1993

"Bifunctional Detergents as Novel Catalysts"

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Prepared by: Robert S. Brown

Department of Chemistry

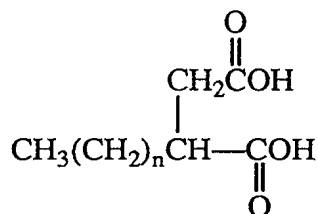
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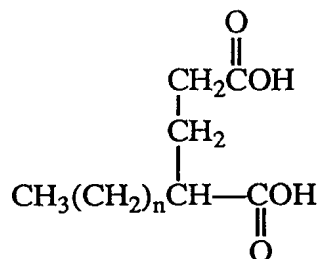
CANADA T6G 2G2

Preparation Date: April 15, 1993

The oxidation of phenyl ethyl sulfide (Ph-S-Et) and Cl-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>3</sub>, as models for the oxidation of sulfur mustard, was investigated in the presence of 2-*n*-alkylsuccinic (I) and 2-

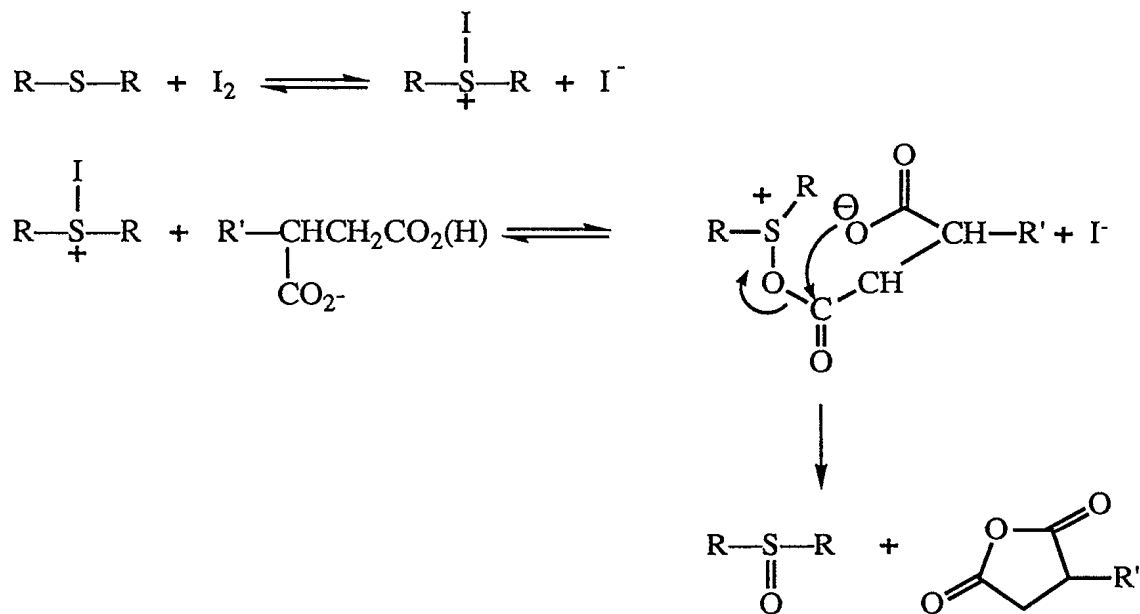


**Ia** *n*=13  
**b** *n*=15



**IIa** *n*=13  
**b** *n*=15

*n*-alkylglutaric (II) acids at 25°C in aqueous media containing added cosolvents. The ultimate oxidizing agent was molecular I<sub>2</sub> according to the following scheme.



The kinetics of loss of I<sub>2</sub> was monitored as the rate of disappearance of [I<sub>2</sub>]<sub>T</sub> (T=total), at 353 nm at constant pH.

Conditions:	[sulfide] = $1.5 \times 10^{-3}$ M	
	[M <sup>+</sup> I <sup>-</sup> ] = 0.02-0.05 M	(M <sup>+</sup> =Li, Ka, Me <sub>4</sub> N <sup>+</sup> , nBu <sub>4</sub> N <sup>+</sup> )
	[I <sub>2</sub> ] = $5 \times 10^{-5}$ - $1 \times 10^{-4}$ M	
	[buffer] = $2 \times 10^{-3}$ - $5 \times 10^{-3}$ M	(buffered with I or II)

In solutions containing iodine and iodide ion, the concentration of free I<sub>2</sub> relative to the total [I<sub>2</sub>]<sub>T</sub> is given as:

$$[I_2] = [I_2]_T / (1 + K_I [I^-])$$

where K<sub>I</sub> is given as the triiodide equilibrium constant:



and:  $[I_2]_T = [I_2] + [I_3^-]$

It was found that commercial grade LiI contained some impurities that caused the blank reaction in the absence of R-S-R to be too fast. KI and Me<sub>4</sub>N<sup>+</sup>I<sup>-</sup> had limited solubility in the solvent systems studied. Overall the best choice for a source of iodide in terms of solubility and lack of impurities was nBu<sub>4</sub>N<sup>+</sup>I<sup>-</sup>.

Cosolvents tried:

- |    |                                      |                     |
|----|--------------------------------------|---------------------|
| 1. | EtOH                                 | 33%, 50%, 80% (V:V) |
| 2. | HOCH <sub>2</sub> CH <sub>2</sub> OH | 33%, 50%, 80% (V:V) |
| 3. | glycerol                             | 50% (V:V)           |
| 4. | dimethoxyethane (DME)                | 50% (V:V)           |

- |    |         |   |
|----|---------|---|
| 5. | PEG-400 | 20%, 50% (V:V)                                      |
| 6. | PEG-400 | 50% with 5% and 10% (V:V) added 2-methylpyrrolidine |
| 7. | diglyme | 50% (V:V)   |

All hydroxyl containing cosolvents gave very fast blank reactions ( $\sim 10^{-3} \text{ s}^{-1}$ ) for the apparent reduction of  $\text{I}_2$ . Careful purification of these by distillation helped to stabilize the blank reaction, but did not eliminate it. Even so, observation of the kinetics of  $\text{I}_2$  reduction promoted by the long chain dicarboxylic acids could not be undertaken due to limits of solubility ( $\geq 0.001 \text{ M}$ ) in all media investigated except 50% DME in which the tetraethylammonium disalts of the dicarboxylic acids were soluble to the extent of  $0.005 \text{ M}$ .

Given in Tables I and II are the pseudo-first order rate constants for disappearance of  $\text{I}_2$  at  $25^\circ\text{C}$  in 50% DME solutions containing Ph-S-Et or  $\text{ClCH}_2\text{CH}_2\text{SEt}$ , and various concentrations of the disodium and ditetraethylammonium dicarboxylates. In all cases investigated, the rate of the reaction depended on the [dicarboxylic acid], but it did not depend upon the presence of added sulfide. To confirm whether the techniques used could reproduce the reactions reported by Higuchi et al<sup>1</sup> the oxidation of the two disulfides (Ph-S-Et,  $\text{ClCH}_2\text{CH}_2\text{SEt}$ ) by  $\text{I}_2$  in purely aqueous conditions in the presence of succinic acid was monitored.

Conditions: 0.01 and 0.02 M succinic acid  
0.01 M KI  
pH = 6.95 (adjusted by addition of KOH in purified  $\text{H}_2\text{O}$ ).  
 $8 \times 10^{-5} \text{ M I}_2$

Two sets of kinetic runs were performed, one with all components present except thioether, and the other with all components including  $1 \times 10^{-3} \text{ M}$  thioether. The results, given in Table III, indicate that the oxidation of Ph-S-Et is a slower process than the blank decomposition of  $\text{I}_2$ . Indeed, increasing the [succinic acid] for oxidation of PhSEt seems to produce a drop in  $k_{\text{obsd}}$ , so

Table I Observed Pseudo First Order Rate Constants for the Reduction of I<sub>2</sub> at 25°C in 50% DME Solutions.<sup>a</sup>

Run #	[disodium dicarboxylate] (M)	[Ph-S-Et] (M)	k <sub>obsd</sub> (s <sup>-1</sup> )	
1	<b>Ia</b>	0.002	1 x 10 <sup>-3</sup>	(5.81±0.06) x 10 <sup>-5</sup>
2	<b>Ia</b>	0.004	1 x 10 <sup>-3</sup>	(7.71±0.07) x 10 <sup>-5</sup>
3	<b>Ia</b>	0.004	---	(6.85±0.07) x 10 <sup>-5</sup>
4	<b>Ib</b>	0.002	1 x 10 <sup>-3</sup>	(6.65±0.06) x 10 <sup>-5</sup>
5	<b>Ib</b>	0.002	---	(6.41±0.08) x 10 <sup>-5</sup>
6	<b>IIa</b>	0.002	1 x 10 <sup>-3</sup>	(6.37±0.06) x 10 <sup>-5</sup>
7	<b>IIa</b>	0.002	---	(6.57±0.07) x 10 <sup>-5</sup>

<sup>a</sup>pH 7.3; [nBu<sub>4</sub>NI] = 0.05 M; [I<sub>2</sub>]<sub>T</sub> = 5 x 10<sup>-5</sup> M

Table II Observed Pseudo First Order Rate Constants for the Reduction of I<sub>2</sub> at 25°C in 50% DME Solutions.<sup>a</sup>

Run #		[ditetraethylammonium dicarboxylate] (M)	[ClCH <sub>2</sub> CH <sub>2</sub> -SEt] (M)	k <sub>obsd</sub> (s <sup>-1</sup> )
1	<b>Ia</b>	0.004	1 x 10 <sup>-3</sup>	(8.02±0.18) x 10 <sup>-5</sup>
2	<b>Ia</b>	0.004	---	(8.43±0.13) x 10 <sup>-5</sup>
3	<b>Ib</b>	0.005	1 x 10 <sup>-3</sup>	(9.61±0.28) x 10 <sup>-5</sup>
4	<b>Ib</b>	0.005	---	(9.26±0.31) x 10 <sup>-5</sup>
5	<b>IIa</b>	0.005	1 x 10 <sup>-3</sup>	(7.46±0.17) x 10 <sup>-5</sup>
6	<b>IIa</b>	0.005	---	(7.08±0.15) x 10 <sup>-5</sup>

<sup>a</sup>pH 8.45; [nBu<sub>4</sub>NI] = 0.05 M; [I<sub>2</sub>]<sub>T</sub> = 5 x 10<sup>-5</sup> M

Table III Observed Pseudo First Order Rate Constants for the Reduction of I<sub>2</sub> in H<sub>2</sub>O, pH 6.95, T = 25°C.<sup>a</sup>

Run #	[succinic acid] (M)	[Thioether] (M)		k <sub>obsd</sub> (s <sup>-1</sup> )
1	0.01	1 x 10 <sup>-3</sup>	(PhSEt)	(8.20±0.17) x 10 <sup>-6</sup>
2	0.01	---	---	(8.48±0.26) x 10 <sup>-6</sup>
3	0.02	1 x 10 <sup>-3</sup>	(PhSEt)	(6.88±0.14) x 10 <sup>-6</sup>
4	0.02	---	---	(7.04±0.26) x 10 <sup>-6</sup>
5	0.01	1 x 10 <sup>-3</sup>	(ClCH <sub>2</sub> CH <sub>2</sub> SEt)	(7.03±0.08) x 10 <sup>-4</sup>
6	0.01	---	---	(8.26±0.28) x 10 <sup>-6</sup>

<sup>a</sup>[KI] = 0.01 M; [I<sub>2</sub>] = 8 x 10<sup>-5</sup>M. see reference 1 for conditions.

the process clearly is not catalytic. However, in the case of oxidation of  $1 \times 10^{-3}$  M ClCH<sub>2</sub>CH<sub>2</sub>SEt, a 100-fold increase in the observed rate of disappearance of I<sub>2</sub> was apparent. This experiment indicates that the reduction of I<sub>2</sub> depends markedly on the structure of the thioether.

To determine whether our *n*-alkylsuccinic or glutaric acids were capable of facilitating the oxidation of ClCH<sub>2</sub>CH<sub>2</sub>SEt, 50% DME solutions containing the same components and concentrations of **Ia,b,IIa** cited in Table I were investigated. No acceleration of the reduction of I<sub>2</sub> over that of the blank reaction was observed.

### Conclusions and Recommendations

The use of long chain alkylsuccinic and glutaric acids for the I<sub>2</sub> promoted oxidation of mustard simulants in mixed solvent/aqueous solutions has proven to be unfeasible in our hands. The main problems that detract from this methodology are: 1) purification of organic cosolvents to eliminate a long term spontaneous reduction of I<sub>2</sub>; 2) solubility of the dicarboxylic acids that preclude formulation at high concentrations.

### References

1. Gensch, K.-H.; Pitman, I.H.; Higuchi, T. *J. Am. Chem. Soc.* 1968, *90*, 2096.





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