Products from the Reaction of Fatty Acids with Ketones and Their Characteristic Properties as Cutting Fluids Additives

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ABSTRACT

Hydroxy acids were synthesized in good yields from ketones and fatty acids by the use of lithium naphthalene in the presence of diethylamine. For example, from cyclohexanone and undecylenic acid (I), 2-(1-hydroxy-1-cyclohexyl)-10-undecenoic acid (III) was obtained in 92% yield. Hydroxy acids were treated with *p*-toluenesulphonic acid to give corresponding unsaturated fatty acids. From the reaction of (III), 2-(1-cyclohexenyl)-10-undecenoic acid (IV), a 3,4-unsaturated acid was obtained (yield 59%). Corrosion and lubricity tests for these products as water-based cutting fluid additives were carried out. We have found that triethanolamine salts of 2-cyclohexenyl and 2-hydroxycyclohexyl fatty acids showed effective rust-inhibiting and antiwear properties for water-based cutting fluids.

INTRODUCTION

Recently, we reported the preparation of 3-hydroxy acids from lower carboxylic acids and ketones by the action of lithium naphthalene in the presence of diethylamine (1). The reactions of fatty acids with ketones are not well known. Upon reexamination of this reaction, we found that hydroxy acids are obtained in high yields from fatty acids and ketones. When these hydroxy acids were treated with *p*-toluenesulphonic acid, corresponding unsaturated fatty acids derivatives were obtained.

The relationship of properties for water-soluble cutting fluids and chemical structures of various organic compounds has not been reported in detail. We examined antirust properties and lubricity characteristics of those 2-substituted fatty acids. This paper will describe our evaluation of new additives for water-soluble cutting fluids.

EXPERIMENTAL

Reaction of Undecylenic Acid (I) with Cyclohexanone (II)

To 0.05 mol (6.4 g) of naphthalene in 150 mL of tetrahydrofuran, 0.1 mol (0.7 g) of metallic lithium cuttings was added and the mixture was agitated at room temperature in an atmosphere of dry nitrogen. After 1 hr, 0.1 mol (7.3 g) of diethylamine was added dropwise. After agitation for 1 hr, 0.05 mol (9.2 g) of undecylenic acid (I) in tetrahydrofuran (50 mL) was added. After 2 hr, 0.1 mol (9.8 g) of cyclohexanone (II) was added to the reaction solution, which was left overnight. The mixture was refluxed for an additional 4 hr. This reflux is essential to increase the yield of compound (III). The acidic materials were separated in the usual fashion to give 13 g of crude hydroxy acid (yield 92%). Molecular distillation of this acid (3 g) with a pot still gave the following fractions: (i) 100-120 C (bath temperature)/0.1-0.01 mmHg, 0.5 g; (ii) 120-125 C/0.1-0.01 mmHg, 2.0 g. Fraction (ii) [2-(1-hydroxy-1-cyclohexyl)-10-undecenoic acid (III)] showed the following spectral data: IR (cm^{-1}): 3400 (OH), 3300 (-COOH), 1700 (-COOH), 990, 910 ($-CH=CH_2$). NMR (δ, ppm): 7.50 (3H, bs, $-\underset{|}{COOH}$, -OH), 4.8-5.1 (3H, m, $-C\underline{H}=C\underline{H}_2$), 2.20 (1H, bs, $-\overset{|}{C\underline{H}}-COOH$), 2.0 (2H, m, $-C=C-C\underline{H}_2-$), 1.51 (10H, bs ring CH_2), 1.31 [12H, bs, $-(CH_2)_6-$].

Reaction of 2-(1-Hydroxy-1-Cyclohexyl)-10-Undecenoic Acid (III) with *p*-Toluenesulphonic Acid

A mixture of the hydroxy acid (III) (10 g), and *p*-toluenesulphonic acid (1 g) was refluxed in 200 mL of benzene for 8 hr. The benzene solution was washed with water and dried over anhydrous sodium sulfate. After benzene was removed, the residue was molecular distilled with a pot still to give the following fractions; (i) 80-90 C (bath temperature)/0.01 mmHg, yield 1.0 g; (ii) 90-100 C/0.01 mmHg yield 2.5 g; (iii) 110-120 C/0.01 mmHg, yield 3.0 g. Total yield of (IV) was 59%. Fraction (iii) [2-(1-cyclohexenyl)-10-undecenoic acid (IV)] showed the following spectral data. IR (cm^{-1}): 3300 ($-\underset{|}{CO}OH$), 1700 (-COOH), 1635 ($-\overset{|}{C}=C-$), 910 and 990 ($-CH=CH_2$), 790 ($-\underset{|}{C}=CH-$); NMR (δ, ppm): 11.98 (1H, s, -COOH), 5.63 (1H, t, $-\overset{|}{C}=C\underline{H}-$), 4.79-5.03 (3H, m, $-C\underline{H}=C\underline{H}_2$), 2.73 (1H, bt, $\overset{\substack{R\\|}}{}-CH_2-C\underline{H}-COOH$), 2.02 (6H, bs, $CH=\overset{|}{CH}-C\underline{H}_2-$, $\overset{|}{C\underline{H}_2}-\underset{|}{C}=CH-C\underline{H}_2$), 1.62 (4H, bs ring $-CH_2-$), 1.34 (12H, s, $-(CH_2)_6-$).

The same technique was used to prepare a series of hydroxy acids and unsaturated acids. The results are listed in Table I.

Test Method

Aqueous solutions (0.5%) of triethanolamine salts of the acids listed in Table II were used. Distilled and deionized water was used for corrosion tests.

Method A Corrosion test with cast iron chips: Two grams of cast-iron chips (JIS G 5501, FC-20) (in Japanese JIS) which had been washed with benzene, were immersed in 0.5% aqueous solution (5 mL) of cutting fluids in a watch glass. The container was covered. After 10 min, the solution was removed by filtration. The rust-preventative effect (the amount of rust on the cast-iron chips) was ob-

TABLE I

Reaction of Fatty Acids with Ketones

Fatty acid	Ketone	Hydroxy acid: yield (%)[a] and b.p. (C/mmHg)[b]	Unsaturated acid: yield (%)[a] and b.p. (C/mmHg)[b]
Octanoic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-octanoic acid (82%) 80-82/0.1	2-(1-Cyclohexenyl)-octanoic acid (60%) 75-80/0.1
Nonanoic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-nonanoic acid (81%) 90/0.1	2-(1-Cyclohexenyl)-nonanoic acid (65%) 85-88/0.1
3,7-Dimethyl-6-octenoic acid	Cyclohexanone	3,7-Dimethyl-2-(1-hydroxy-1-cyclohexyl)-6-octenoic acid (70%) 100/0.1-0.01	3,7-Dimethyl-2-(1-cyclohexenyl)-6-octenoic acid (63%) 90-95/0.1-0.01
Decanoic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-decanoic acid (82%) 110/0.1-0.01	2-(1-Cyclohexenyl)-decanoic acid (62%) 120/0.1
Undecylenic acid	Methylisopropyl ketone	2-(2-Hydroxy-3-methyl-2-butyl)-10-undecenoic acid (45%) 135-145/2-3	–
Undecylenic acid	Cyclopentanone	2-(1-Hydroxy-1-cyclopentyl)-10-undecenoic acid (50%) 140-145/2-3	–
Undecylenic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-10-undecenoic acid (92%) 120-125/0.1-0.01	2-(1-Cyclohexenyl)-10-undecenoic acid (59%) 100-110/0.01
Undecylenic acid	Acetophenone	2-(1-Hydroxy-1-phenyl-1-ethyl)-10-undecenoic acid (68%) 125-128/0.1-0.01	–
Lauric acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-dodecanoic acid (80%) 130-140/0.1-0.01	2-(1-Cyclohexenyl)-dodecanoic acid (60%) 140-143/0.1
Myristic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-tetradecanoic acid (85%) mp 59°C	2-(1-Cyclohexenyl)-tetradecanoic acid (58%) mp 39°C
Palmitic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-hexadecanoic acid (84%) mp 69-70°C	2-(1-Cyclohexenyl)-hexadecanoic acid (57%) mp 49-50°C
Stearic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-octadecanoic acid (83%) mp 84-85°C	2-(1-Cyclohexenyl)-octadecanoic acid (67%) mp 59.5-60.5°C
Oleic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-9-octadecenoic acid (70%) 150-160/0.01	2-(1-Cyclohexenyl)-9-octadecenoic acid (65%) 140-150/0.01
Oleic acid	Acetophenone	2-(1-Hydroxy-1-phenylethyl)-9-octadecenoic acid (81%) 160-165/0.1-0.01	–
Linoleic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-9,12-octadecadienoic acid (74%) 150-160/0.01-0.001	2-(1-Cyclohexenyl)-9,12-octadecadienoic acid (83%)[c] 140-150/0.001
Naphthenic acid	Cyclohexanone	Hydroxycyclohexyl naphthenic acid (83%) 90-100/0.1	Cyclohexenyl naphthenic acid (50%) 85-90/0.1
Ricinoleic acid	Cyclohexanone	2-(1-Hydroxy-1-cyclohexyl)-12-hydroxy-9-octadecenoic acid (75%) 170-175/0.01-0.001	–

[a] The structures of the products were confirmed by IR, NMR and microanalyses. The microanalyses of the products were in satisfactory agreement with the calculated values (C, ± 0.33; H, ± 0.05).

[b] These products were distilled with a pot still. Bath temperatures of distillation are shown.

[c] A little double bond isomerization may occur during treatment with *p*-toluenesulphonic acid. We have not investigated on the absence or presence of conjugated diene systems.

TABLE II

Cutting Fluids Characterization of Various New Additives

Sample[a]	Welding load (kg cm^{-2})	Coefficient of friction	Surface tension (dyne cm^{-1})	Corrosion test	
				Method A	Method B
2-(1-Hydroxy-1-cyclohexyl)-octanoic acid	7	0.16	40	7	8
2-(1-Hydroxy-1-cyclohexyl)-nonanoic acid	10	0.15	38	8	9
2-(1-Hydroxy-1-cyclohexyl)-decanoic acid	14	0.14	36	10	10
2-(1-Cyclohexenyl)-decanoic acid	13	0.13	37	10	10
2-(2-Hydroxy-3-methyl-2-butyl)-10-undecenoic acid	17	0.11	37	10	10
2-(1-Hydroxy-1-cyclopentyl)-10-undecenoic acid	10	0.13	37	7	8
2-(1-Hydroxy-1-cyclohexyl)-10-undecenoic acid	16	0.13	38	10	10
2-(1-Cyclohexenyl)-10-undecenoic acid	16	0.12	37	10	10
2-(1-Hydroxy-1-phenyl-1-ethyl)-10-undecenoic acid	12	0.13	38	10	10
2-(1-Hydroxy-1-cyclohexyl)-dodecanoic acid	14	0.14	38	10	10
2-(1-Cyclohexenyl)-dodecanoic acid	12	0.12	36	10	10
2-(1-Hydroxy-1-cyclohexyl)-tetradecanoic acid	16	0.13	38	10	10
2-(1-Cyclohexenyl)-tetradecanoic acid	15	0.12	37	10	10
2-(1-Hydroxy-1-cyclohexyl)-hexadecanoic acid	18	0.12	35	10	10
2-(1-Cyclohexenyl)-hexadecanoic acid	17	0.11	33	10	10
2-(1-Hydroxy-1-cyclohexyl)-octadecanoic acid	15	0.12	37	10	10
2-(1-Cyclohexenyl)-octadecanoic acid	13	0.11	34	9	10
2-(1-Hydroxy-1-cyclohexyl)-9-octadecenoic acid	15	0.13	34	10	10
2-(1-Cyclohexenyl)-9-octadecenoic acid	13	0.12	33	10	10
2-(1-Hydroxy-1-phenyl-1-ethyl)-9-octadecenoic acid	14	0.09	32	10	10
2-(1-Hydroxy-1-cyclohexyl)-9-octadecenoic acid	11	0.12	32	9	10
2-(1-Cyclohexenyl)-9,12-octadecadienoic acid	12	0.12	38	9	10
2-(1-Hydroxy-1-cyclohexyl)-12-hydroxy-9-octadecenoic acid	13	0.11	37	7	9
Hydroxy cyclohexyl naphthenic acid	14	0.13	36	9	10
Cyclohexenyl naphthenic acid	14	0.14	39	10	10
Sodium nitrite	3	0.48	72	7	10
Oleic acid	9	0.15	40	6	6
10-Undecylenic acid	8	0.14	41	7	8

[a] Aqueous solutions (0.5%) of triethanol amine salts were used.

served after 24 hr. Ten points show no appearance of rust. Seven points show a little appearance of rust.

Method B Corrosion test with steel panels: Two panels (JIS G 3141, SPCC-B) (in Japanese JIS) which had been polished with emery paper (no. 610) followed by benzene rinse, and were immersed in a 0.5% aqueous solution of cutting fluids. After 10 min, the panels were removed from the solution and allowed to remain in the air at room temperature. After 74 hr, the amount of rust on the steel panels were observed. Ten points show no rust. Seven points show a small amount of rust. These methods are based on the I.P. Corrosion Test 125/63T (aqueous cutting fluids corrosion of cast-iron chips and steel panels, JIS G 3310) (2).

Welding load (kg/cm^2): The antiwear tests of the desired solution were run on a Soda-type four-ball lubricating-oil testing machine at 200 rpm. This testing machine has been officially authorized by Agency of Industrial Science and Technology of Japan as JIS K 2519 and JIS K 2219. Main particulars: test ball diameter, 3/4 in. steel ball (JIS B 1501) (high class, 1 μm tolerance); revolution of spindle, 150-1500 rpm; temperature of test oil, room temperature to 200 C; hydraulic cyclinder diameter, 80 mm; maximum load on the test ball, max. 1000 kg; pressure of the hydraulic pump, 0-20 kg/cm^2; overall dimensions, 1700 mm(d) × 650 mm(w) × 1600 mm(h); weight 450 kg. The machine is obtained from Shinko Engineering Co., Ltd. (Tokyo).

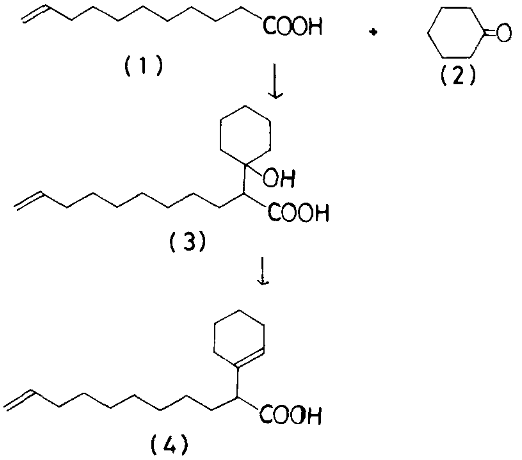
The coefficients of friction were measured at 25 C by Soda-type II oiliness pendulum apparatus, which is obtained from Shinko Engineering Co. Ltd. (Tokyo). Main particulars: test ball, 3/16 in. (4.75 mm) JIS B 1501 high class; test roller pin, diameter × length: 2.0ϕ(+0 to -0.012) × 30 mm material, SK3 (JIS G 4401); hardness, HRC 60-66; cycle of pendulum swing, ca. 4 sec; maximum pendulum swing, 0.7 radian; test road (maximum Herz/stress), 15000 kg/cm^2; temperature of test oil, room temperature to 300 C.

The surface tensions (dyne/cm) were measured at 25 C by Du Nouy Tensiometer.

RESULTS AND DISCUSSION

Convenient preparative methods of 3-hydroxy acids from ketones and lower carboxylic acids using alkali metal are well known. Pfeffer prepared α-anions of carboxylic acids in high yields by treating carboxylic acids with lithium diisopropylamine and hexamethyl phosphoramide (3). Creger prepared lithium α-lithio isobutyrate with lithium diisopropylamine (4). The method by lithium *bis*(trimethylsilyl) amide is reported (5). In these papers, the reaction of lower carboxylic acids are reported, but the reaction of fatty acids with ketones is not well examined.

Recently, we reported that lithium naphthalene in tetrahydrofuran solution is an excellent reagent for the various organic synthetic reactions (6). In connection with our studies of lithium naphthalene, this article concerns a convenient procedure for the preparation of α-substituted fatty acids using lithium naphthalene, fatty acids and ketones. For example, 2-(1-hydroxy-1-cyclohexyl)-10-undecenoic acid (III) was obtained in 90% yield from the reaction of undecylenic acid (I) and cyclohexanone (II) as shown in the Experimental section. Lithium naphthalene reagent has the following merits: (a) the reagent can be prepared without difficulty from metallic lithium and naphthalene at room temperature; (b) the reaction can be carried out at room temperature; and (c) lithium naphthalene is highly reactive and stable, since the lithium cation and the naphthalene anion are an ion pair. Furthermore, the reaction of (III) with *p*-toluenesulphonic acid gave an unsaturated acid, 2-(1-cyclohexenyl)-10-undecenoic acid (IV) selectively. Similarly, other 3-hydroxy acids and corresponding unsaturated acids were prepared and the results are listed in Table I.



Application of these fatty acid derivatives as surface active agents has been a subject of some interest. Sodium nitrite has been used in popular water-based cutting fluids. However, cutting fluids which do not contain toxic sodium nitrite are now desired by many industrial shops. Recently, the various derivatives have been considered for use as water-based cutting fluids. For water-soluble cutting fluids, antirust and antiwear properties are essential. Interestingly, we have found that triethanolamine salts of those α-substituted fatty acids derivatives have excellent antirust and antiwear properties. For example, aqueous solution (0.5%) of triethanolamine salt of compound (IV) showed excellent properties in corrosion tests with cast iron chips (method A) and steel panels (method B). Interestingly, antiwear load of this aqueous solution was about 16 kg/cm^2 at 200 rpm with a four-ball type lubricating-oil testing machine. Similarly, adducts of cyclohexanone with undecylenic acid, myristic acid, stearic acid, palmitic acid and oleic acid, and their dehydrated products have excellent properties, and their characteristics are shown in Table II. These compounds are superior to the sodium nitrite commercially used. 2-(1-Hydroxy-1-cyclohexyl)-10-undecenoic acid (III) was the best one from the viewpoint of solubility to water. The cyclohexenyl derivatives give somewhat less satisfactory results than the 1-hydroxycyclohexyl derivatives. These new additives for water-based cutting fluids were not previously known. Practical tests of these water-based cutting fluids are now in progress and show good results.

REFERENCES

1. Fujita, T., K. Suga, S. Watanabe and R. Yanagi, J. Appl. Chem. Biotechnol. 27:593 (1977).
2. Morton, I.S., Ind. Lubr. Tribol. 24:163,221,224,267 (1972); 25:141,185 (1973); (CA 82:173263 (1975)).
3. Pfeffer, P.E., and L.S. Silbert, J. Org. Chem. 35:262 (1970).
4. Creger, P.L., J. Am. Chem. Soc. 89:2500 (1967).
5. Rathke, M.W., Ibid. 92:3222 (1970).
6. Fieser, M., and L. Fieser, Reagents for Organic Synthesis, Vol 4, Wiley-Interscience, 1974, p. 348.

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