Quantitative Preparation of Long Chain Thioethers from an Oxo-*trans*-2-Enoic Ester and a 9,12-Dioxo-*trans*-10-Enoic Acid

J. Mustafa, M.S. Ahmad Jr., A. Rauf[1] **and S.M. Osman***
Section of Oils and Fats, Department of Chemistry, Aligarh Muslim University, Aligarh-202 002, India

Branched-chain thioethers have been prepared from methyl 4-oxo- *trans*-2-hexadecenoate and 9,12-dioxo-*trans*-10-octadecenoic acid. The reagents involved in these preparations were mercaptoacetic and mercaptopropionic acids. The yields of these thioethers are almost quantitative.

KEY WORDS: 9,12-Dioxo-*trans*-10-octadecenoic acid, mercaptoacetic acid, mercaptopropionic acid, methyl 4-oxo-*trans*-2-hexadecenoate, thioethers.

Sulfur bearing fatty materials attract both industrial and academic interest. Free radical addition of mercaptans to olefin is too voluminous to revise again (1-3). However, literature on the addition of mercaptans and mercaptides to unsaturated fatty moieties are sporadic (4-6). Thioethers have been described as lubricants, additives, coatings, rubber substituents (5-7) and as an intermediate for the preparation of wetting agents and detergents (8). Thioethers have been tested for neurotropic, bactericidal, anti-inflammatory, fungicidal, anticholesteremic, hypolipemic activities (9-11). Some thioethers have also been shown as tranquilizers (12). Thioethers are also capable of increasing thermal stability of polymers and rubber (13). In view of the ever increasing industrial utility and increasing use of γ-rays for free radical reactions in industry, the preparation of thioethers is noteworthy. Recently in our laboratory, some sulfurated ethers of olefinic fatty acids were reported (14). Here, the preparation of thioethers derived from α,β-unsaturated carbonyl (I) and dioxoenoic (II) fatty compounds are discussed. This work is an extension of our interest in the derivatization of α,β-unsaturated carbonyl long chain fatty compounds (15,16).

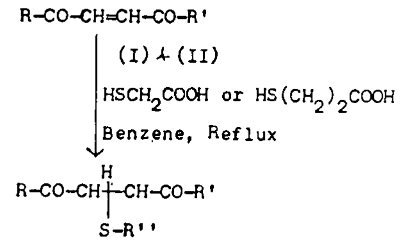
EXPERIMENTAL PROCEDURES

All the methods were the same as detailed in our earlier publications (15,16). Compounds I and II were prepared by known procedures (15-17).

Reaction of mercaptoacetic and mercaptopropionic acids with I and II (Scheme 1). In our different experiments mercaptoacetic acid/mercaptopropionic acid (1.2 M) was added to a benzene solution of I/II (1 M), and the reaction mixture was refluxed at the boiling temperature of benzene. Reactions were completed during 1 hr, as revealed by thin-layer chromatography (TLC) plates.

The following are the details of the products obtained:

Compound (III). Reaction mixture on work-up gave a solid product which, on crystallization in petroleum ether/ether (4:1 v/v), gave III as a solid in 93% yield, m.p. 73°C. Analysis: Found.C, 60.88; H, 9.1 for $C_{19}H_{34}O_5S$: Calcd. C, 60.93; H, 9.15%; IR (Nujol, cm^{-1}) : 3400 (COOH), 1735 (COOCH$_3$), 1720(-CO-), 1710 (COOH), 1440(S-CH$_2$ deformation), 1260(S-CH$_2$, wagging), 1170, 1060(C-0). NMR (CDCl$_3$, δ) : 3.23 m(3H, CO-CH-S-CH$_2$-COOH), 2.4 m(4H, 2 × CH$_2$-CO-) and other signals of fatty ester chain. Mass : M^{+} m/z 374 (27%); 113 (64%), 128 (Principal ion), 163 (65%), 177 (20%), 197 (25%), 282 (40%).



(III),(IV),(V),(VI)

(I) R = $CH_3(CH_2)_{11}$; R' = OCH_3
(II) R = $CH_3(CH_2)_5$; R' = $(CH_2)_7$-COOH
(III) R = $CH_3(CH_2)_{11}$; R' = OCH_3; R'' = CH_2-COOH
(IV) R = $CH_3(CH_2)_{11}$; R' = OCH_3; R'' = CH_2-CH_2COOH
(V) R = $CH_3(CH_2)_5$; R' = $(CH_2)_7$-COOH; R'' = CH_2COOH
(VI) R = CH3$(CH_2)_5$; R' = $(CH_2)_7$-COOH; R'' = CH_2-CH_2CC

SCHEME 1. Synthetic approach for the preparation of fatty thioethers.

Compound (IV). Reaction mixture on crystallization with petroleum ether/ether (4:1, v/v) produced a solid in 98% yield, m.p. 76°C. Analysis: Found.C, 61.8; H, 9.2 for $C_{20}H_{36}O_5S$; Calcd. C., 61.82; H, 9.32%; IR(Nujol, cm^{-1}) : 3400(COOH), 1740 (COOCH$_3$), 1720(-CO-), 1715(COOH), 1435, 1260(S-CH$_2$), 1160, 1120(C-0). NMR (CDCl$_3$, δ) : 3.22 m(1H, COCH-S-), 2.75 m(2H,-S-CH$_2$-CH$_2$), 2.38 m(6H, 3 × CH$_2$-CO-), 8.5 br,s(1H, COOH, disappeared on D$_2$0 shake) and other long chain fatty ester signals. Mass : M^{+} m/z 388 (27%) 113 (42%), 128 (Principal ion), 177 (30%), 191 (20%), 197 (30%), 282 (25%).

Compound (V). Reaction mixture gave a solid product which was purified by silica gel column chromatography by using petroleum ether/ether (80:20 v/v) as eluent. Yield of V was 95% as a semisolid product. Analysis: Found.C, 60.5; H, 8.6 for $C_{20}H_{34}O_6S$: Calcd. C, 60.55; H, 8.7%; IR (CCl$_4$; cm^{-1}):3400(COOH), 1720(-CO-), 1710(COOH), 1445, 1260(S-CH$_2$), 1160, 1065(C-O). NMR (CCl$_4$, δ) : 3.21 m(3H, CO-CH-S-CH$_2$-COOH), 3.3m (2H, -S-CH$_2$-), 2.45 m (6H, 3 × CH$_2$-CO-), 9.6 br,s (2H, 2 × COOH, D$_2$0 exchangeable) and other usual fatty acid signals. Mass : M^{+} m/z 402 (7.9%), 113 (48%), 167 (57%), 171 (50%), 182 (46%), 225 (66%), 240 (19%), 274 (18%), 275 (29%), 289 (34%), 310 (22%), 332 (5%).

Compound (VI). Semisolid reaction mixture was chromatographed over a column of silica gel by using petroleum ether/ether (80:20 v/v) as eluent. Yield of the semisolid product was 92%. Analysis: Found.C, 60.44; H, 8.68 for

---

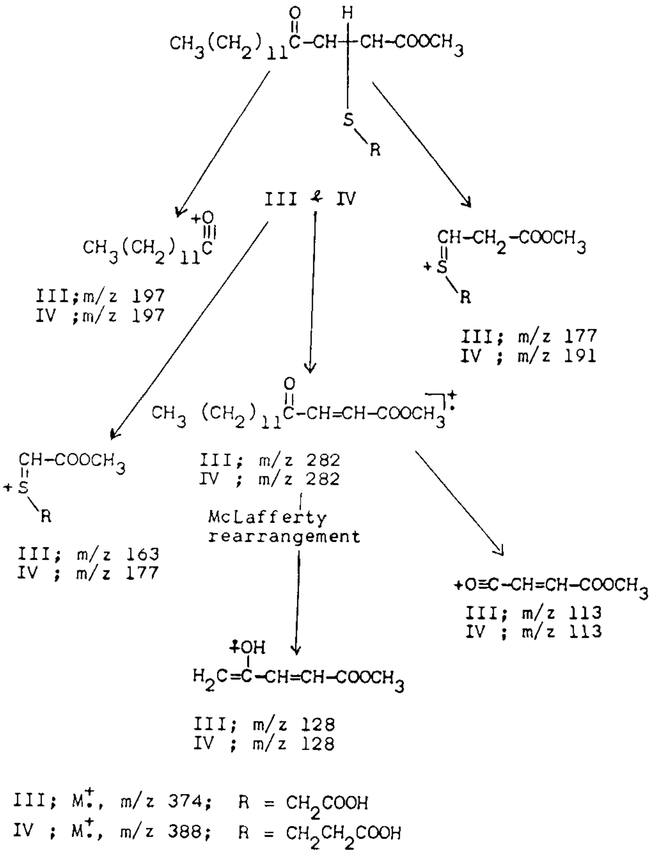
*To whom correspondence should be addressed.

[1] Present address: Applied Sciences, University Polytechnic, Aligarh Muslim University, Aligarh-202 002, India.

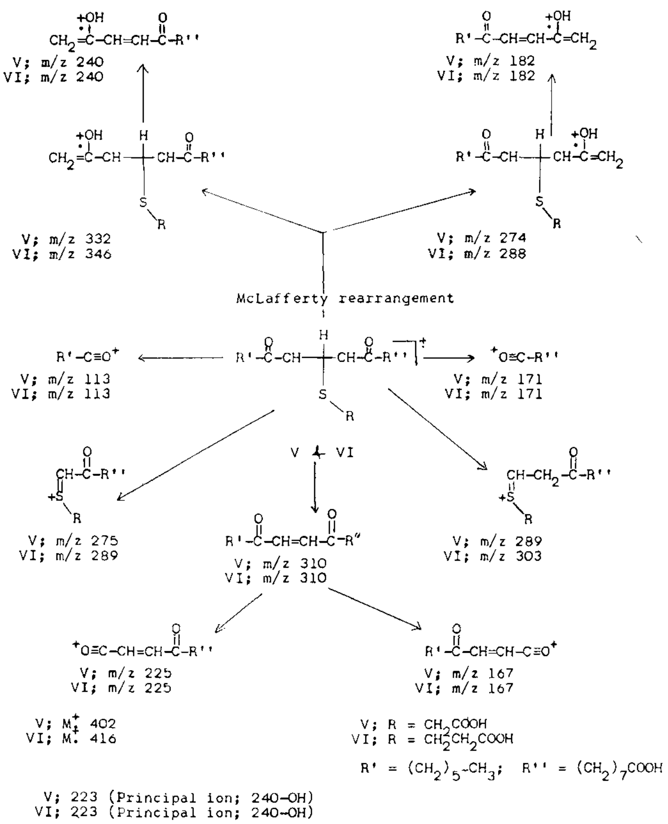
$C_{21}H_{36}O_6S$; Calcd. C, 60.54; H, 8.71%; IR(CCl_4, cm^{-1}) : 3400(COO$\underline{H}$), 1715(-CO-), 1710($\underline{CO}$OH), 1440, 1265 (S-CH_2), 1160, 1060(C-O). NMR(CCl_4, δ) : 3.26 m(1H, CO-C$\underline{H}$-S-), 2.7 m(2H, S-C$\underline{H}_2$-), 2.3 m(10H, 5 × C$\underline{H}_2$-CO-), 9.3 br,s(2H, 2 × COOH, D_2O exchangeable) and normal fatty acid signals. Mass : M^{+} *m/z* 416, (6.3%), 113 (53%), 167 (50%), 171 (52%), 182 (49%), 225 (54%), 240 (16%), 288 (13%), 289 (23%), 303 (23%), 310 (20%), 346 (7%).

DISCUSSION

When methyl 4-oxo-*trans*-2-hexadecenoate (I) in benzene was heated under reflux with mercaptoacetic and mercaptropropionic acids separately for 1 hr to get isomeric type of addition products, it gave methyl 4-oxo-2(3)-(*S*-mercaptoacetic acid) hexadecanoate (III) and methyl 4-oxo-2(3)-(*S*-mercaptopropionic acid) hexadecanoate (IV) in quantitative yields (Scheme 1). The IR spectrum of III showed diagnostic bands at 3400 (COO$\underline{H}$), 1720 (-CO-), 1710($\underline{CO}$OH), 1440 (S-CH_2 deformation), and 1260 (S-CH_2 wagging). IR spectrum of compound (IV) also exhibited absorption bands in the same region. The nuclear magnetic resonance (NMR) spectrum (III) displayed structure revealing multiplets at δ3.23 (3H, -COC$\underline{H}$-S-C$\underline{H}_2$-COOH), 2.4 (4H, protons α to carbonyl functions), and a D_2O exchangeable signal at 9.6 br, s (1H, COO$\underline{H}$). The NMR peaks of significance for compound (IV) were observed at δ3.22 m(1H, COC$\underline{H}$-S-), 2.75 m (2H, S-C$\underline{H}_2$-CH_2-), 2.38 m (6H, 3 × C$\underline{H}_2$CO-), and 8.5 br, s (1H, COOH, disappeared on D_2O shake). Mass spectra of thioethers III (M^{+}, 374) and IV (M^{+}, 388) revealed the composition as indicated by elemental analysis. Emergence of α-cleavage ions at *m/z* 197 and 113 and McLafferty ion at 128 (principal ion) fixed the position of an oxo group at C_4 in both the compounds. Mass ions at *m/z* 163 and 177 (III) and 177 and 191 (IV) indicated the isomeric nature of III and of IV (Scheme 2).



SCHEME 2. MS fragmentation pattern for compounds (III & IV).



SCHEME 3. MS fragmentation pattern for compounds (V & VI).

A similar treatment of mercaptoacetic and mercaptopropionic acids with 9,12-dioxo-*trans*-10-octadecenoic acid (II) gave the additional products of the isomeric nature—9,12-dioxo-10(11)-(*S*-mercaptoacetic acid) octadecanoic acid (V) and 9,12-dioxo-10(11)-(*S*-mercaptopropionic acid) octadecanoic acid (VI)—in quantitative yields. IR spectra of these thioethers displayed bands in the same regions as given for compound (III) and (IV). NMR for compound (V) showed characteristic peaks at δ3.21 m(3H, COC$\underline{H}$-S-C$\underline{H}_2$COOH), 2.45 m(6H, protons α to carbonyl functions) and a D_2O exchangeable signal at δ9.6 br, s(2H, 2 × COOH). Important NMR signals for compound (VI) were noted at δ3.26 m(1H, CO-C$\underline{H}$-S-), 2.7 m(2H, -S-C$\underline{H}_2$-CH_2-), 2.3 m(10H, 5 × CH_2-CO-), and 9.3 br, s(2H, 2 × COO$\underline{H}$, D_2O exchangeable). The structures of V and VI were further substantiated by their mass spectra. The molecular ion peaks are quite consistent with the elemental analyses of compound (V) and (VI). Mass ions at 275 and 289 (V) and 289 and 303 (VI) were observed due to the isomeric type of addition of mercaptans to olefinic carbons. The presence of oxo groups in these two compounds were fixed by the fragment ions at 113, 225 and 240 (C_{12}), and 171, 167 and 182 (C_9) (Scheme 3).

ACKNOWLEDGMENTS

The work was financed by a grant from USDA under PL-480. The chair of the Department of Chemistry provided the facilities.

REFERENCES

1. Kharasch, M.S., W. Nudenberg and F. Kawahara, *J. Org. Chem. 20*:1550 (1955).
2. Griesbaum, K., *Angew. Chem. Int. Ed. Engl. 9*:273 (1970).
3. March, J., *Advanced Organic Chemistry*, 2nd edn., McGraw-Hill, Kogakusha, 1977, p. 703.
4. Schwah, A.W., and L.E. Gast, *J. Am. Oil Chem. Soc. 47*:371 (1970).
5. Schwab, A.W., W.K. Rohwedder, L.W. Tjarks and L.E. Gast, *Ibid. 50*:365 (1973).
6. Schwab, A.W., L.E. Gast and W.K. Rohwedder, *Ibid. 53*:762 (1976).
7. Koenig, N.H. and D. Swern, *J. Am. Chem. Soc. 79*:4235 (1957).
8. Imperial Chemical Industries Ltd., French Patent, 786,625 (1935).
9. Bogoslovskii, N.V., N.M. Kolbina, L.M. Obvintseva and Pidemskii, *Khim.-Farm. Zh. 13*:53 (1979).
10. Brandman, H.A., J.E. Freudewald, M. Manowitz, E.J. Nikawitz and F.H. Sharpell, Jr., *Chem. Abstr. 92*:41776a (1980).
11. Ludwig, Z., F. Johanna and T. Kurt, *Ibid. 88*:89673j (1978).
12. Hirsch, A.F., *Ibid. 89*:108112q (1978).
13. James, B., and S. Richard, *Ibid. 70*:107339q (1969).
14. Khan, M., M. Hashmi, F. Ahmad and S.M. Osman, *J. Oil Tech. Assn., India, 16*:55 (1984).
15. Mustafa, J., M.S. Ahmad, Jr., A. Rauf and S.M. Osman, *J. Am. Oil Chem. Soc. 61*:555 (1984).
16. Mustafa, J., M.S. Ahmad, Jr., A. Rauf and S.M. Osman, *Ibid. 61*:941 (1984).
17. Abbot, G.G., F.D. Gunstone and S.D. Hoyes, *Chem. Phys. Lipids 4*:351 (1970).

[Received April 10, 1989; accepted July 22, 1990]