

Soap-Based Detergent Formulations: XI. Alternate Synthesis and Structural Assignment of Sodium Methyl Alkylbenzoylsulfopropionates¹

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ABSTRACT

Sodium methyl alkylbenzoylsulfopropionates, derived from detergent alkylates, previously were reported to be good lime soap dispersing agents and beneficial additives in tallow soap based, sodium silicate built laundry detergents. Their synthesis from β -aroylacrylic acid intermediates has been facilitated by sulfonation with sodium bisulfite before esterification. This single phase process occurs rapidly at room temperature, whereas in the previously reported process, the sulfonation of the methyl ester requires a two-phase, high temperature, closed system procedure. Final esterification is mandatory for producing a useful lime soap dispersing agent, because the sulfonated disodium salt is a poor lime soap dispersing agent and not compatible with a soap-silicate mixture. Deoiling improves the detergency of the final products from either procedure; this is especially apparent when polyester-cotton permanent press fabric is laundered. Data from NMR spectra, base-induced decompositions, hydrolysis studies, and detergency screening tests suggest that the sulfopropionate product derived from the new procedure is structurally the same as that from the old one, and that these products have been sulfonated regiospecifically α to the carboxy group.

INTRODUCTION

As part of a study to develop new lime soap dispersing agents (LSDA) for use in tallow soap based laundry detergents, sodium methyl alkylbenzoylsulfopropionates (IV) were prepared from long chain alkylbenzenes as shown in Figure 1, and their detergent properties were investigated. An initial report by Marmer, et al., (1) discussed such properties of sulfopropionates (IV) prepared by modification of the method of Hedrick, et al., (2), and Linfield, et al. (3). In that procedure, intermediate aroylacrylic acids (I) are converted into product sulfopropionates (IV) by esterification and then sulfonation (I \rightarrow II \rightarrow IV). However, problems in both steps led us to examine an alternate route from I to IV, namely, sulfonation of the aroylacrylic acid I followed by esterification of the disodium salt III. Once a

product was obtained via the new route, it then became necessary to establish that this product was identical to the old product. Finally, it was desirable to determine which carbon atom of the double bond of I was being sulfonated.

EXPERIMENTAL PROCEDURES

Synthesis of the Surfactant and Intermediate

Aroylacrylic acids (I): These were prepared by the Friedel-Crafts procedure (1,3) from maleic anhydride and detergent alkylate (Nalkylene 500, avg mol wt 236, Continental Oil Co., Ponca City, Ok.; Alkylate series, Monsanto Co., St. Louis, Mo.: Alkylate 215, avg mol wt 236, and Alkylate 225, avg mol wt 243; also 1-phenylacetone, Aldrich Chemical Co., Milwaukee).

Sulfonation of I: Typically, 20 g of 86% pure aroylacrylic acid I (mw 334, 52 mmol) was dissolved in 40 ml isopropanol. The solution then was stirred in a beaker while a solution of 8.3 g sodium sulfite (66 mmol) in 60 ml water was added dropwise at a slow rate at room temperature. Too rapid an addition caused decomposition, perhaps due to the high pH of the unreacted aqueous sodium sulfite. After addition of the aqueous solution had been completed, the mixture was stirred for 20 min. At this point, an optional deoiling step could be carried out, whereby the aqueous alcohol solution is extracted with 100 ml petroleum ether to remove traces of alkylbenzene that are carried over from the synthesis of the acrylic acid I. The alcohol and most of the water then were evaporated under an air stream at room temperature to give a wet paste of the crude disodium salt, $\text{ArCOCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2\text{Na}$ (III). The product was checked for absence of I by NMR analysis by ascertaining the absence of vinyl proton signals in the δ 7 to 8 region. The equivalent wt was obtained by potentiometric titration. An aqueous solution of a weighed sample was acidified with a few drops of concentrated sulfuric acid and then titrated with standard sodium hydroxide; the equivalent wt then was obtained from the volume of titrant used between the strong acid endpoint (pH 4) and the carboxylic acid endpoint (pH 8).

Esterification of the disodium salt (III): The crude disodium salt (III) paste from the previous procedure was suspended in 200 ml 1,2-dichloroethane in a 3-neck 1 liter round bottom flask equipped with a Dean-Stark trap and condenser and a mechanical stirrer. (Magnetic stirrers were not powerful enough to stir the solids; cessation of spinning often led to the contents boiling over.) The stirring shaft was held by a lubricated sleeve that was situated above the level of the condenser, so that the lubricant would not be extracted subsequently by the boiling solvent. Concentrated sulfuric acid (3.4 ml; 66 mmol) was added dropwise. Then the water (ca. 5 ml) left over in the paste was removed by azeotropic distillation. The resulting product mixture would begin to char at this point if too large an excess of sulfuric acid was present. Then 5 ml methanol (120 mmol) was introduced, and the mixture heated for 30 min at reflux without the Dean-Stark trap. The trap then was reinstalled and the water generated in the reaction as well as unconsumed methanol was drawn off with some solvent. A fresh charge of 5 ml methanol was added and the

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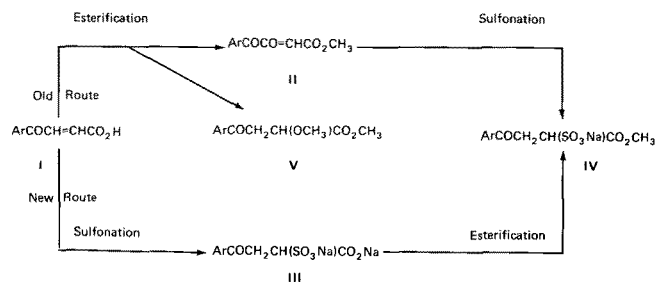


FIG. 1. Synthetic routes. Ar = long chain alkylphenyl group.

TABLE I
NMR Data of p-R-C₆H₄COCH₂CH(OMe)CO₂CH₃
(V) in CCl₄

Assignment	R = H ^a	R = Et ^b	Nalkylene 500 derived R
CH ₂	δ 3.38	δ 3.37	δ 3.32
CH	δ 4.42	δ 4.43	δ 4.42
^J CH-CH ₂ (in hz)	6.0	6.0	6.0
α OCH ₃	δ 3.47	δ 3.44	δ 3.40
ester OCH ₃	δ 3.76	δ 3.74	δ 3.67

^aReference 10.

^bReference 11.

reaction process repeated three times. Next the mixture was cooled and, while being stirred rapidly, neutralized with 11 g sodium bicarbonate (130 mmol) moistened with 2 ml water. Removal of solvent at 50 C, 5 torr, left 41.6 g solid residue of esterified product IV and some inorganic salt. The organic content was analyzed and found to contain, on a wt basis, 4% disodium salt III (by potentiometric titration), 85% anionic surfactant (by titration with Hyamine 1622 at pH 10), and 11% water-insoluble material (by deoiling). The overall yield, based on the amount of starting aroylacrylic acid, was product ester (IV), 91.1% and unesterified disodium salt (III), 3.8%.

Deoiling: Traces of oil-soluble impurities present in sulfopropionates III and IV could not be removed by trituration because of the good oil-solubility of the dry products as well. Deoiling was achieved, however, by extraction of an aqueous isopropanol solution of the crude product with petroleum ether (30-60 C). Isopropanol (30-50%) sufficed to suppress emulsion formation. The reader will note that such a solution of disodium salt III exists immediately upon completion of the addition of aqueous sodium sulfite to the alcoholic solution of aroylacrylic acid I. Therefore, such a deoiling would be carried out most sensibly at that time. NMR analysis of the removed impurities showed them to be alkylbenzene and, from product derived via the old procedure, the methanol adduct byproduct of esterifications, ArCOCH₂CH(OCH₃)CO₂CH₃ (V) (Table I).

Acetophenone generation: The sulfopropionates derived from 1-phenyloctane via the old and the new procedures were subjected to decomposition in 3 N sodium hydroxide for 10 min at 90 C to generate p-octylacetophenone, according to the procedure of Bogert and Ritter (4). The crude acetophenone was isolated from the acidified reaction mixture by extraction with ether and then evaporation of this solvent. The ether-soluble material was treated overnight with a slight excess of 2,4-dinitrophenylhydrazine in phosphoric acid and ethanol. Water was added and the crude 2,4-dinitrophenylhydrazone (DNP) removed by extraction with chloroform. The DNP then was eluted with chloroform from a short Florisil column to remove some 2,4-dinitrophenylhydrazine and finally recrystallized from a mixture of chloroform and Skellysolve B. The recrystallized product, mp 123-123.5 C, was obtained in about 20-25% yield from starting material (III or IV) prepared in either the old or new manner. Analysis: Calculated for C₂₂H₂₈N₄O₄: C, 64.06; H, 6.84. Found: C, 63.29; H, 6.81. NMR (in CDCl₃): δ 9.05, d, 1H, Ar H with 2 vicinal NO₂ groups; δ 7.9-8.5, m, 2H, remaining Ar H on dinitrophenyl ring; δ 11.33, s, 1H, N-H; δ 2.40, s, 3H, N=C-CH₃; δ 7.75, d, 2H, Ar H ortho to C(CH₃)=N; δ 7.23, d, 2H, Ar H ortho to alkyl chain; δ 2.65, t, 2H, benzylic; δ 1.3, m, 12.8 H (theor. 12 H), other methylene; δ 0.91, t, 3H, alkyl CH₃.

Spectral Analyses

IR spectra were recorded on a Perkin-Elmer 237B

ΔR_{RELATIVE}
BRAND=100

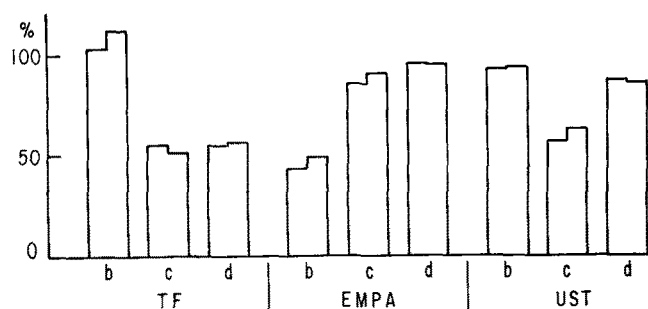


FIG. 2. Relative detergency (ΔR_{rel} ; BRAND = 100). LSDA derived from old procedure (left) vs LSDA derived from new procedure (right). LSDA = sulfopropionate ester IV derived from Nalkylene 500. Conditions: 300 ppm hardness; 120 F; 0.002% CMC; formulation b = 0.2% LSDA; c = 0.05% LSDA and 0.15% tallo soap; d = 0.17% formulation c and 0.03% sodium silicate (SiO₂:Na₂O = 1.6:1.0); BRAND = a commercial phosphate-built detergent; standard soiled fabrics TF (Testfabric cotton-polyester with permanent press finish), EMPA (EMPA 101 cotton), and UST (U.S. Testing Co. cotton).

spectrophotometer. NMR spectra were obtained on a Jeolco C60H instrument; chemical shifts are reported in ppm from internal tetramethylsilane (δ values).

Hydrolysis Study

Samples of product IV derived from both the old and the new procedures were subjected to simultaneous alkaline hydrolysis at 60 C, according to the method of Weil, et al., (5). Initial concentrations were 0.05 molar in both ester and sodium hydroxide. Individual solutions of the reactants were warmed to 60 C prior to mixing, and the ester solutions adjusted to pH 8. After combination, the extent of hydrolysis was measured by the titration of 10 ml aliquots with 0.1 N hydrochloric acid at fixed time intervals. The following rate constants and half lives were calculated: IV from old procedure: $k=0.48$ 1/mol-min, $t-1/2 = 47$ min; IV from new procedure: $k=0.47$ 1/mol-min, $t-1/2 = 48$ min.

Surface Active Properties

Lime soap dispersant requirements: LSDR were determined by the Borghetty-Bergman procedure (6).

Detergency evaluations: Detergency screening tests were obtained with the aid of a Tergotometer. All washings were run for 20 min at 120 F in 1 liter water of 300 ppm hardness with an agitation speed of 100 cpm. Five circular swatches each (4 in. diameter) of 101 cotton (EMPA), U.S. Testing cotton (UST) and Testfabric cotton-polyester with permanent press finish (TF) were washed together in each beaker. Detergency was measured in terms of increased reflectance ΔR of the washed cloth over the soiled cloth. Results are shown in Figures 2-4. Sodium carboxymethylcellulose (CMC) was added to all formulations as a standard antiredeposition agent.

RESULTS AND DISCUSSION

Synthesis

Any process change that substitutes a high temperature, long period, sealed system, two phase procedure with a room temperature, instantaneous, open system, single phase procedure must be viewed favorably. That exactly describes the advantages of the new sulfonation step over its predecessor. Furthermore, a significant side reaction of the old procedure, methanol addition across the double bond of the acrylic acid I (especially of I derived from the Monsanto Alkylates) during esterification, was avoided

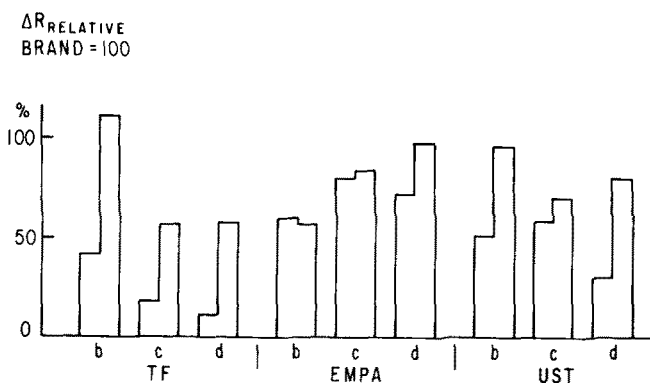
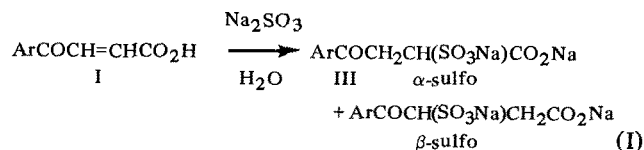


FIG. 3. Relative detergency. Disodium salt III (left) vs sulfopropionate ester IV (right) derived via new procedure from Nalkylene 500. Abbreviations and conditions as per Fig. 2.

because the sensitive double bond was eliminated by reaction with the potentially nucleophilic sulfite ion prior to esterification. The only nuisance of the new procedure is the necessity to dry the intermediate disodium salt (III) thoroughly prior to esterification.

Structural Assignment

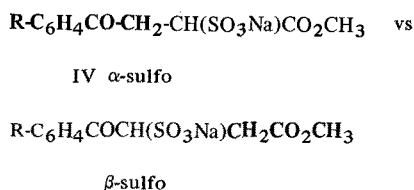
It has been established that sulfite and bisulfite add to α, β -unsaturated compounds (7,8) via an ionic mechanism. β -Sulfo compounds, for example, result from such Michael-type additions to sodium acrylate, methyl acrylate, and acrylonitrile. In the present work, however, both carbons of the active double bond in the β -aroylacrylic acid (I) or its ester (II) bear carbonyl groups. Nucleophilic addition thus could occur theoretically at each such carbon (equation 1):



We drew on literature reports and our own data to establish whether the sulfopropionate IV derived by the new procedure was the same as the one from the old procedure, whether such additions occurred regiospecifically, i.e. at one position only, and if so, at which position.

The data suggest that the products from both procedures are the same. They give the same alkaline hydrolysis rates, LSDR values, and detergency (Fig. 2). Their NMR and IR spectra are identical.

Examination of the NMR spectra of both products shows only one set of CH-CH₂ absorptions. The CH gives rise to a triplet at δ 4.9 and the CH₂ to a doublet at δ 4.1 (splitting is 6.75 hz). If both isomers were present, two such sets of signals would be expected, and they would not be overlapping. Consider, for example, the CH₂ absorption. The environment of one positional isomer differs from that of the other isomer by the type of adjacent carbonyl functionality:



The difference in chemical shift of $\text{CH}_3\text{COC}_6\text{H}_5$ (δ 2.55) and $\text{CH}_3\text{CO}_2\text{CH}_3$ (δ 2.01) (9) amounts to 0.5 ppm. Yet, no other CH₂ doublet from a second isomer is seen, and

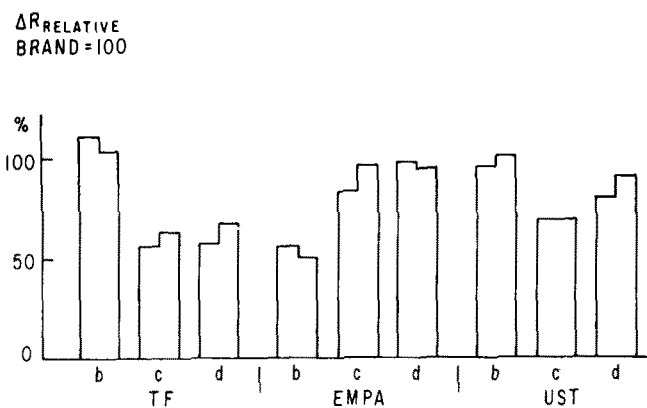


FIG. 4. Relative detergency. Sulfopropionate ester IV derived via new procedure from Nalkylene 500 (left) vs IV derived from Alkylate 215 (right). Abbreviations and conditions as per Fig. 2.

certainly not 0.5 ppm upfield or downfield from the observed CH₂ signal.

Hence, only one and the same isomer is present, regardless of synthetic route. There is evidence supporting an assignment of the sulfo group α to the carbomethoxy group. Sugiyama, et al., (10) studied the reactivity of nucleophiles toward $\text{C}_6\text{H}_5\text{COCH}=\text{CHCO}_2\text{CH}_3$ and concluded from Hückel method frontier electron density calculations that the double bond should be polarized toward the aroyl group and thus susceptible to nucleophilic attack at the carbon adjacent to the carbomethoxy group. This was substantiated for the addition of methanol to the β -benzoylacrylate (10) and to the *p*-ethylbenzoylacrylate (11). Comparison of the NMR spectra of these methanol adducts with the spectrum of our byproduct methanol adduct V (Table I) showed ours also to be the α -methoxy compound.

Bogert and Ritter (4) concluded that the sulfonation of $\text{C}_6\text{H}_5\text{COCH}=\text{CHCO}_2\text{H}$ with sodium sulfite gives the α -sulfo disodium salt adduct on the basis of their isolation of acetophenone from the strong base-induced decomposition of the adduct. We have been able to isolate *p*-octylacetophenone (as its DNP derivative) by similarly decomposing the model compound *p*-C₈H₁₇-C₆H₄COCH₂CH(SO₃Na)CO₂Na derived from the new procedure and the related methyl ester from the old procedure.

Thus, the overwhelming evidence shows that products IV derived from either procedure are the α -sulfo isomers.

Detergency Studies

Figure 2, as already discussed, shows that products derived from either route perform equally. A slight increase in soil removal from the polyester-cotton fabric was also noticed when deoiled products were used. Figure 3 shows the need for complete esterification in the new procedure and the detrimental effect of hydrolysis. It is readily apparent that the disodium salt is a poor performer relative to the ester. The poor performance of formulation b when the LSDA is the disodium salt reflects the high LSDR (>40) for the unesterified compound. Figure 4 shows a comparison of products IV synthesized via the new procedure from detergent alkylates of the same average molecular wt but from different sources. Their performances are virtually identical. We had been unable to produce an effective product from the Monsanto detergent alkylates in a previous study (1) due to problems in the esterification step.

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REFERENCES

1. Marmer, W.N., D.E. Van Horn, and W.M. Linfield, *JAACS* 51:174 (1974).
2. Hedrick, G.W., W.M. Linfield, and J.T. Eaton, *Ind. Eng. Chem.* 44:314 (1952).
3. Linfield, W.M., K.A. Roseman, H.G. Reilich, P.C. Adlaf, and C.C. Harlin, Jr., *JAACS* 49:254 (1972).
4. Bogert, M.T., and J.J. Ritter, *J. Amer. Chem. Soc.* 47:526 (1925).
5. Weil, J.K., R.G. Bistline, Jr., and A.J. Stirton, *JAACS* 32:370 (1955).
6. Borghetty, H.C., and C.A. Bergman, *JAACS* 27:88 (1950).
7. Schenk, R.T.E., and I. Danishefsky, *J. Org. Chem.* 16:1683 (1951).
8. Morton, M., and H. Landfield, *J. Amer. Chem. Soc.* 74:3523 (1952).
9. Bovey, F.A., "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N.Y., 1969, Appendix B.
10. Sugiyama, N., T. Gasha, H. Kataoka, and C. Kashima, *J. Chem. Soc. (B)* 1060 (1969).
11. Sugiyama, N., C. Kashima, H. Kataoka, and K. Tanaka, *Bull. Chem. Soc. Jap.* 43:1473 (1970).

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