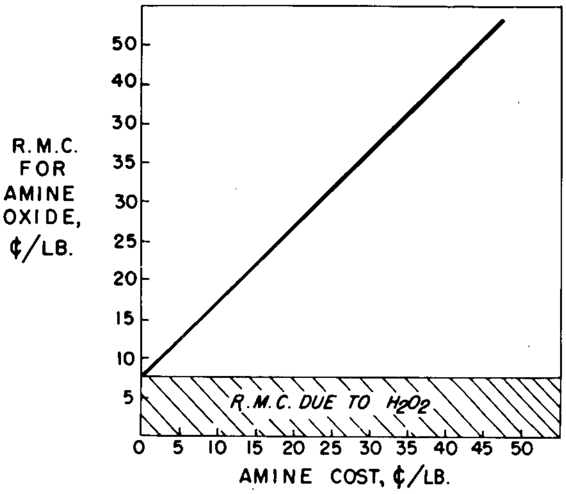

FIG. 3. Raw materials cost for dimethyldodecylamine oxide. (10% molar excess of H_2O_2; 98% conversion).

tion that thermal degradation occurs in the chromatograph column. If Cope elimination is quantitative under chromatograph conditions the peak for the olefin formed should afford a measure of amine oxide content.

Some difficulty in determining the amine oxide content of formulated detergents has been reported. The alkaline builders commonly included in detergent formulations interfere with the acidimetric procedure described above. However, the reductometric method of Brooks and Sternglanz has been found to give reliable results if the sample is first neutralized with concentrated hydrochloric acid.

Economics

The economics of fatty amine oxides depend primarily on cost of the parent amines. Figure 3 shows the raw materials cost per pound of dimethyldodecylamine oxide as a function of dimethyldodecylamine cost. With hydrogen peroxide available at 45.7¢ lb (100% basis), peroxide cost is 7.5¢ per pound of amine oxide assuming use of the recommended 10% molar excess. To realize a total raw materials cost of around 30¢/lb for the oxide, dimethyldodecylamine must be charged in at 20–25¢/lb. A raw materials cost of 30¢/lb for amine oxide should permit a selling price below 50¢/lb (100% basis). At this price level, fatty amine oxides should find broad market acceptance.

REFERENCES

1. Engelmann, M., (E. I. du Pont de Nemours & Co.), U. S. 2,159,967 (1939).
2. Guenther, F., and K. Saftien (I. G. Farbenindustrie A. -G.), U. S. 2,169,976 (1939).
3. Hay, R. J., and S. M. Richardson (The Firestone Tire & Rubber Co.), U. S. 2,755,258 (1956).
4. Moore, C. D., and R. B. Hardwick, Mfg. Chemist *29*, 194–8 (1958).
5. Pilcher, W., and S. L. Eaton (The Procter & Gamble Co.), U. S. 2,999,068 (1961).
6. Drew, H. F., and R. E. Zimmerer (The Procter & Gamble Co.), U. S. 3,001,945 (1961).
7. Kenyon, R. L., D. V. Stingley, and H. P. Young, Ind. Eng. Chem. *42*, 202–13 (1950).
8. Kirk, R. E., and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 5, Interscience, New York, 1950, p. 835.
9. Atwood, M. T., JAOCS *40*, 64–6 (1963).
10. Wieland, H., Ber. *54B*, 2368 (1921).
11. Oswald, A. A., and D. L. Guertin, J. Org. Chem. *28*, 651–7 (1963).
12. Hoh, G. L. K., D. O. Barlow, A. F. Chadwick, D. B. Lake, and S. R. Sheeran, JAOCS, *40*, 268–271 (1963).
13. Cram, D. J., M. R. V. Sahyun, and G. R. Knox, J. Am. Chem. Soc. *84*, 1734–5 (1962).
14. Linton, E. P., J. Am. Chem. Soc. *62*, 1945–8 (1940).
15. Cope, A. C., and E. R. Trumbull, Org. Reactions *11*, 317–493 (1960).
16. Brooks, R. T., and P. D. Sternglaúz, Anal. Chem. *31*, 561–5 (1959).
17. Metcalfe, L. D., Anal. Chem. *34*, 1849 (1962).

Alpha-Olefins in the Surfactant Industry

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RELATIVELY SMALL SCALE commercial quantities of straight chain α-olefins have been available from animal fats and vegetable oils for many years. However, large scale production from this source is hindered by the relatively high cost of the natural starting materials and the expense of the saponification, reduction, and dehydration processes required. Therefore, up to the present α-olefins have not found extensive favor in the surfactant industry, except for low-volume, high-cost specialty products.

Recently, however, large scale production from petroleum of high-quality, low-cost α-olefins was announced. Thus, the surfactant industry now has the incentive to investigate present and potential uses of these reactive compounds. α-Olefins not only provide opportunities for commercial development of entirely new surfactants, but in addition, these new raw materials may give improved properties in many types of products and processes now based on highly branched olefins. For instance, surfactants prepared from α-olefins undergo much more rapid biodegradation than the analogous branched-chain products.

Of particular interest for surfactants are the higher molecular weight α-olefins (C_{11}–C_{20} carbons atoms) because these materials are easily convertible into surface-active products. However, the lower molecular weight olefins (C_6–C_{11}) offer potential advantages in plastics, polymers, hydrotropes, and many types of specialty products related to the detergent industry.

Some of these new large-volume α-olefins from petroleum are available in development quantities as single carbon number cuts at a permium price. However, of much greater interest to the surfactant industry are various blends of higher molecular weight olefins. In most detergent applications, these blends offer satisfactory properties and equivalent or superior performance as compared to single molecular weight material, as well as being more economical. Some of these blends are analogous to the fat-based olefins in that only even-numbered carbon chains are present. On the other hand, some large volume petroleum-based olefins contain both even- and odd-numbered carbon chains in approximately equal amounts. The optimum blend type and molecular weight split should be considered individually for each application, based on performance and availability.

In view of the foregoing, it appears worthwhile to present the chemistry of some of the most interesting surface active agents which may be derived from α-olefins. Properties and performance characteristics of some of these surfactants are also discussed.

Reactivity

Many types of reactants, both organic and inorganic, easily add across the terminal double bond of long-chain α-olefins. Addition reactions may be of either the ionic or free radical-type, depending on the particular reactants and conditions. For purposes of illustrating these types of addition (ionic and free

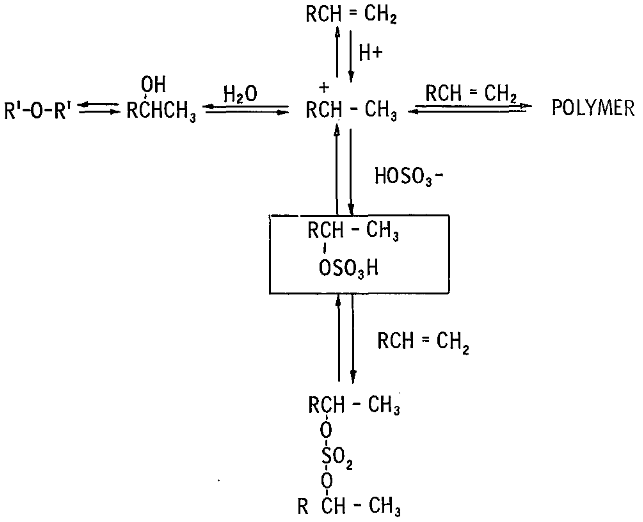


FIG. 1. Equilibrium reactions of secondary alkyl sulfates.

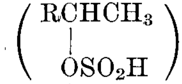
radical), hydrogen bromide addition will be used as an example. Depending on reaction conditions, hydrogen bromide may add to give a secondary bromide (ionic, "normal addition") or a primary bromide (free radical, "abnormal addition") (38,47,65). The formation of the secondary bromide ($\mathrm{RCHBr{-}CH_3}$) is favored by: high concentration of hydrogen bromide, presence of polar solvent, ferric bromide or aluminum bromide catalyst, antioxidants, darkness, and elevated temperatures. Conditions tending to give the primary bromide ($\mathrm{RCH_2{-}CH_2Br}$) are: presence of oxygen or peroxides; light; inert nonpolar solvent; and lower temperatures. Yields and proportions of the isomers can vary greatly, depending on the exact experimental conditions and the particular reactants used. By choosing favorable conditions, almost exclusive formation of either isomer is possible. In the α-olefin molecular weight range most suitable for surfactant use (C_{11}–C_{20}) hydrogen bromide addition is easily controlled to give more than 95% 1-isomer (12). At 0C and lower temperatures in the presence of peroxide, the high molecular weight α-olefins, diluted with pentane to prevent freezing, form no measurable amounts of secondary bromo compounds. Thus, under these conditions, less than 1% ionic-type hydrogen bromide addition accompanies the predominant free radical-type addition. Even at 20C and using no pentane solvent, hexadecene-1 gives about 95% of the 1-bromide and only about 5% secondary bromide.

Addition of hydrogen chloride to α-olefins, although slightly more difficult than hydrogen bromide addition, is easily accomplished. Only the ionic reaction occurs and the secondary chloride is the only product. For example, reaction of hydrogen chloride with dodecene-1 in benzene solvent at 0C using a small amount of stannic chloride catalyst gives about 98% yield of essentially pure 2-chlorododecane.

Aside from addition reactions, α-olefins may also undergo substitution and oxidation. At the present time substitution reactions, such as allylic bromination with N-bromosuccinimide, do not appear to be of much potential commercial significance in surfactants. This is true also of oxidation, although the resulting carboxylic acids may be of interest in specialty soaps or as precursors for ethylene oxide condensates. Oxidation of α-olefins with chromic acid gives a mixture of carboxylic acids composed predominantly of an acid containing one less carbon than the starting olefin (28,55).

Anionic Surfactants

Several different anionic surfactants of present or potential use in the detergent industry may be produced from α-olefins. Some of these may be made directly from the olefin in one step while others require a longer sequence of reactions to prepare the desired product. In general, these anionics include either a sulfate or a sulfonate group in the molecule; however, the reactants and conditions required for their production differ widely and the potential use properties are also extremely varied.

Preparation of Secondary Alkyl Sulfates. α-Olefins react with concentrated sulfuric acid by an ionic-type mechanism to give good yields of secondary alkyl sulfuric acids  $\left(\begin{array}{c}\mathrm{RCHCH_3}\\ | \\ \mathrm{OSO_2H}\end{array}\right)$ (6,10,12,41). Upon neutralization, the desired secondary alkyl sulfate surfactants are produced. Such surfactants are presently produced commercially on a large scale in Europe, but they have never been used extensively in the United States. In the past, these secondary sulfates were usually considered to be of poor quality and inherently poor chemical stability, probably because of the marginal quality of the olefin raw materials. However, the present availability of high-quality α-olefins should revive commercial interest in these surface-active materials. The stability of secondary alkyl sulfates produced from these α-olefins in the C_{11}–C_{20} carbon range is, in fact, comparable to that of primary alcohol sulfates. In addition, these products are excellent detergents and good foamers and wetting agents.

More details of the reaction equilibria involved in the sulfation reaction are shown in Figure 1. In order to optimize yields of monoalkyl sulfuric acid it is necessary to reduce formation of all three byproducts: ethers, polymers, and dialkyl sulfates. Kooijman (41) reported maximum yields of hexadecyl sulfate with 90% H_2SO_4 at 20C. However, recent work of Clippinger (12) indicates that for maximum product yields the reaction temperature should be maintained at 5C or lower. Higher temperatures form polymers and colored byproducts. The best yields are realized at temperatures as low as −15C, which requires the use of a solvent as a freezing point depressant. In actual practice, it is found that one volume of n-pentane per volume of olefin is satisfactory.

The equilibrium mixture always contains significant quantities of dialkyl sulfate, but its formation is suppressed by using a 1.5/1.0 or greater mole ratio of sulfuric acid to olefin (12). Even under these conditions 15–20% of the alkyl groups are always combined as dialkyl sulfate, but on neutralization each mole hydrolyzes to form one mole of monoalkyl sulfate and one mole of alcohol.

Under favorable laboratory conditions (2.0/1.0 mole ratio of sulfuric acid to olefin, −15C, and one volume n-pentane), a total monoalkyl sulfate yield of 90% may be obtained. This sulfate contains about 90% of the 2-isomer with little migration of the functional group along the chain. However, actual commercial operations might be more easily carried out at nearer room temperature. Such an increase in temperature will give slightly lower yields and greater amounts of the other secondary isomers. In no case is the 1-isomer formed.

Performancewise, secondary alkyl sulfates in the C_{11}–C_{20} carbon number range are versatile surfactants with good all-around properties (11). In typical heavy-duty formulations, a C_{11}–C_{20} sulfate blend (containing both even and odd carbon numbers) shows both washing machine foam and cotton detergency superior to commercial branched-chain dodecylbenzene sulfonates. Dishwashing foam performance is only moderate, but the high washing machine foams suggest that dishwashing foams could be optimized by formulation changes. This excellent performance together with unique solubility properties indicates that these sulfates should be of interest in liquid detergent products. A C_{11}–C_{20} sodium secondary alkyl sulfate is more soluble than a commerical sodium dodecylbenzene sulfonate and shows little effect of concentration on clear point (approximately 13C) from 3% concentration up to nearly 40%. In addition, blends of secondary alkyl sulfate with primary alkyl sulfonates (discussed below) show promise in the synthetic toilet bar field.

Preparation of Primary Alkyl Sulfonates. Primary alkyl sulfonates prepared by the free radical catalyzed addition of bisulfite (12,19,25) to α-olefins [Equation 1] are surfactants of great interest in the detergent industry.

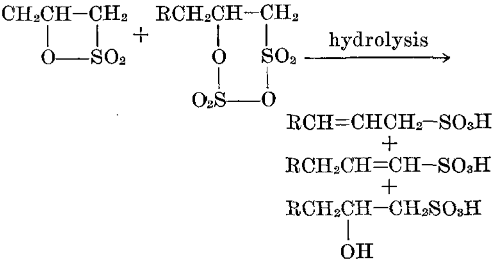
$$RCH{=}CH_2 + HSO_3^- \xrightarrow[\text{or oxygen}]{\text{peroxide}} RCH_2CH_2SO_3^- \qquad [1]$$

Primary alkyl sulfonates may also be obtained by treating a 1-bromide with sodium sulfite (16) or by oxidizing a mercaptan (3,20). Although the reaction of the 1-bromide and sodium sulfite gives satisfactory yields with lower molecular weight alkylbromides, it does not proceed readily with higher molecular weight compounds. Therefore, it is not considered to be a satisfactory method for preparation of detergent-range (C_{11}–C_{20}) alkyl sulfonates. The direct addition of bisulfite [Equation 1] is considered to be the most practical route from a commercial standpoint. This addition may be accompanied by at least two side reactions: oxidation of sulfite to sulfate; and formation of a surface-active product containing a sulfinate group as well as the sulfonate group.

The reaction of bisulfite with α-olefin is advantageously carried out in aqueous propanol as a solvent (12). Aqueous ethanol may also be used, but a 20% lower reaction rate is observed. Optimum yields of primary alkyl sulfonate are obtained by continuous addition of aqueous bisulfite so that the concentration of inorganic bisulfite remains at about 0.1 molar and is never enough to salt out a separate aqueous phase. Either air or an appropriate organic peroxide may be used as a free radical initiator. Using the above conditions and maintaining a pH of 7–8 during the reaction results in 90–100% conversion of olefin to sulfonate. Running the reaction under acid conditions gives greatly increased proportions of sulfinate-sulfonate material. This product is surface active, but its surfactant properties and performance have not been thoroughly investigated.

Primary alkyl sulfonates are of great interest because of their outstanding physical and performance characteristics in toilet bars and household detergents (11). A wide molecular weight blend of mixed sodium and ammonium primary alkyl sulfonates has good bar-forming properties. Primary alkyl sulfonates are also compatible with soap and other detergent actives, such as alkylbenzene sulfonates, alkyl sulfates, and various nonionics. In toilet bar use, foam is produced copiously and rapidly in both soft and hard water whether warm or cold. Furthermore, it produces a truly stabilized lather. It also leaves the skin with a pleasant afterfeel, and no stickiness or irritation are observed. Primary sulfonates are also good detergents for washing soiled fabric. The foam produced in formulations containing fatty alcohol additives is as dense and stable as that given by similar tallow sulfate formulations. The unusual stability of primary alkyl sulfonates (including resistance to boiling concentrated phosphoric acid) could be of importance in spray drying operations and in shelf life of formulated products.

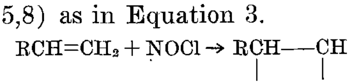
Reaction with Sulfur Trioxide. Either 1 or 2 moles of sulfur trioxide may add across the terminal double bond of α-olefins (2,6,7,17,60). In order to moderate the extreme reactivity of sulfur trioxide, the reaction is normally carried out in a solvent (liquid sulfur dioxide or ethylene dichloride), and the sulfur trioxide is often used in the form of a complex with either dioxane or pyridine. Hydrolysis and workup of either of the above initial addition products gives largely a mixture of hydroxysulfonic acid and unsaturated sulfonic acids [Equation 2]. Neutralization of these sulfonic acids gives sulfonates which possess excellent foaming and detergency properties and are quite stable under a wide range of conditions.



[2]

Reaction with Chlorosulfonic Acid. Chlorosulfonic acid may also be used as an agent for sulfonating α-olefins (17). The reaction is carried out at about 0C in an inert solvent, such as carbon tetrachloride. A small quantity of halogenation catalyst, such as iodine or ferric chloride, may be added in order to improve yield and product quality. Yields of about 85% surface-active product may be obtained in this reaction. The reaction product after nuetralization is believed to be a mixture of hydroxysulfonate, unsaturated sulfonates, and chlorosulfonate. The sulfonate mixture is highly surface active and gives solutions of excellent detergent and wetting power.

Reaction with Nitrosyl Chloride. In the presence of 4–8% nitrogen trioxide or dinitrogen tetroxide, nitrosyl chloride adds across the terminal unsaturation of α-olefins (4,5,8) as in Equation 3.

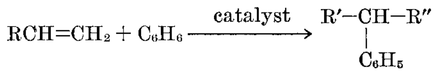


$$RCH{=}CH_2 + NOCl \rightarrow \underset{NO}{RCH}\text{—}\underset{Cl}{CH_2} \qquad [3]$$

The actual product is believed to be of a considerably more complex nature. Treatment of this addition compound with sodium sulfite and sodium bisulfite in aqueous isopropanol at 85C gives a complex surfactant mixture corresponding to an olefin conversion of about 70%. This type of surfactant has been sold commercially in the past, and laboratory tests indicate that it has excellent wool detergency and good foam and emulsifying qualities. The product is considered to be a mixture of sulfonated amines, sulfonated ketones, unsaturated and saturated sulfamate-sulfonates, and adducts of the unsaturated compounds with sodium bisulfite.

Reaction with Dinitrogen Tetroxide. Dinitrogen tetroxide in the presence of oxygen adds to α-olefins to give a mixture of nitro derivatives (56,57). Elimination of nitrous and nitric acids from the crude adduct with triethylamine results in 1-nitroolefins in good yields. Addition of alcohols or sodium bisulfite to these nitroolefins followed by reduction of the intermediate products to aminoethers (42) or aminosulfonates (27) may lead to specialty surfactants of interest.

Preparation of Secondary Phenylalkanes. Alkylation of benzene with α-olefins in an ionic type reaction catalyzed by aluminum chloride, sulfuric acid, or hydrofluoric acid yields a mixture of isomeric straight-chain secondary phenylalkanes [Equation 4] (44,49).



$$RCH{=}CH_2 + C_6H_6 \xrightarrow{\text{catalyst}} R'{-}\underset{\underset{C_6H_5}{|}}{CH}{-}R'' \qquad [4]$$

By choice of catalyst and other reaction conditions, the isomeric distribution can be varied somewhat; however, contrary to the results found with secondary alkyl sulfates, nearly exclusive production of the 2-isomer is not possible in this alkylation. Only highly isomerized mixtures of secondary alkylbenzenes are formed, and no primary phenylalkane is produced. Sulfonation of the phenylalkane gives a surfactant with excellent quality and good detergency and foaming properties. In potential usefulness and performance versatility, such straight-chain alkylbenzene sulfonates approach present day commercial branched-chain alkylbenzene sulfonates.

Preparation of Primary Phenylalkane. Primary alkyl bromides prepared from α-olefins react with benzene in the presence of an aluminum bromide catalyst to give a phenylalkane with up to 50% primary attachment of the alkyl group to the benzene (58). The derived sulfonate shows promise as a foam stabilizer in detergent formulations containing either straight-chain or branched-chain alkylbenzene sulfonate together with long-chain primary alcohols or 1,2-glycols as foam additives (45).

Cationic Surfactants

Surface-active quaternary ammonium-type cationics may be produced from α-olefins in the C_{11}–C_{20} molecular weight range. However, before discussing preparation of these cationics it is well to consider the preparation of the precursor amines. The amines, of course, can then be easily converted to quaternaries.

Preparation of Amines. Long-chain amines are of interest in themselves as corrosion inhibitors and ore flotation agents. However, they are probably more important to the surfactant industry as intermediates in the production of quaternaries and amine oxides. Amines may be conveniently prepared by reaction of 1-bromides with ammonia or other amines [Equations 5,6,7].

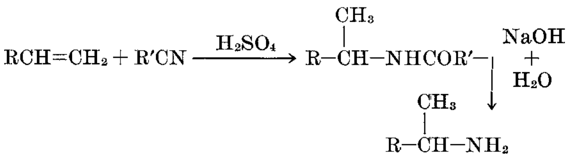
$$R{-}Br + NH_3 \longrightarrow R_2NH + RNH_2 \qquad [5]$$

$$R{-}Br + R'NH_2 \rightarrow R_2NR' + RNHR' \qquad [6]$$

$$R{-}Br + R_2'NH \rightarrow RNR_2' \qquad [7]$$

These ionic reactions may be carried out in aqueous solution at slightly above room temperatures or without solvent at about 150C and under moderate pressures (23,29,68). Alkyl bromides will also react with sodium amide in liquid ammonia at −50C to give primary amines (59).

Primary amines in which the nitrogen is attached to the number two carbon atom of a long straight chain may be prepared directly from α-olefins by addition of hydrogen cyanide or low molecular weight organic nitrile followed by basic hydrolysis [Equation 8] (52,57).



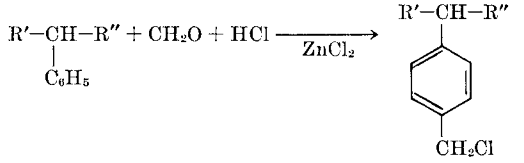
$$RCH{=}CH_2 + R'CN \xrightarrow{H_2SO_4} R{-}\overset{\overset{CH_3}{|}}{CH}{-}NHCOR' \xrightarrow{NaOH\ +\ H_2O} R{-}\overset{\overset{CH_3}{|}}{CH}{-}NH_2 \qquad [8]$$

Amines may also be obtained from α-olefins by reduction (35) of the nitroolefins.

Preparation of Quaternary Ammonium Compounds

Quaternary ammonium compounds may be produced directly from alkyl bromides using certain tertiary amines (67). Reaction of methyl chloride or benzyl chloride with a primary or secondary amine also may give quaternary salts (29).

Alkylaromatic quaternaries may be obtained by chloromethylation [Equation 9] of secondary phenylalkanes followed by reaction with a tertiary amine (15).



[9]

Quaternary ammonium compounds are useful as corrosion inhibitors, bactericides, algaecides, antistatic agents, emulsifiers, and textile softening agents.

Nonionic Surfactants

The two major types of nonionic surfactants which may be produced from α-olefins are ethylene oxide condensates and amine oxides.

Preparation of Ethylene Oxide Condensates. Ethylene oxide condensates are presently the most important type of nonionic in the surfactant industry. Alcohols, alkylphenols, carboxylic acids, and mercaptans are the active hydrogen compounds most commonly condensed with ethylene oxide to prepare surface-active agents. All of these precursors may be obtained from α-olefins.

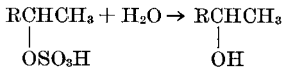
Long-chain primary alcohols may be produced from alkyl bromides by ionic hydrolysis in solvents such as water, alcohol, or acetone using insoluble basic buffers such as calcium oxide (30,48). Olefin formation often occurs as a side reaction, but may be decreased significantly by first forming the acetate using potassium acetate and then saponifying the ester with caustic.

Primary alcohols may also be formed directly from α-olefins by the Oxo reaction [Equation 10] (26,33, 53).

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\text{heat, pressure}]{\text{Co catalyst}} \begin{array}{c} RCH_2CH_2CH_2OH \\ + \\ RCH(CH_3)CH_2OH \end{array} \qquad [10]$$

This reaction gives a mixture (approximately 1:1 ratio) of primary alcohols with a $-CH_2OH$ group attached to either the 1- or 2-position of the carbon chain.

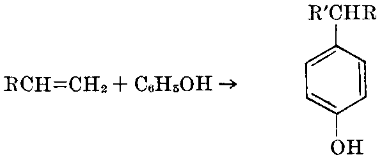
Secondary alcohols may be obtained by hydrolysis [Equation 11] (31,62) of secondary alkyl sulfuric acids.



$$\underset{\underset{OSO_3H}{|}}{RCHCH_3} + H_2O \rightarrow \underset{\underset{OH}{|}}{RCHCH_3} \qquad [11]$$

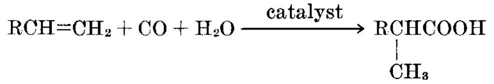
The monoalkyl sulfuric acid-olefin equilibrium is displaced to the right in Equation 11 by the use of a large excess of water (dilute acid). Just as in the formation of the monoalkyl sulfuric acids, possible side reactions during hydrolysis are ether formation and polymerization.

Alkylphenols may be prepared directly from α-olefins by alkylation of phenol (24) in the presence of an acidic catalyst [Equation 12]. This ionic reaction is similar to that of Equation 4, but the activating influence of the −OH group allows the alkylation to occur with a much milder catalyst and conditions. The product is a blend of all possible secondary alkylphenols, but there is no addition of phenol to the end carbon of the olefin to form primary alkylphenol.



[12]

Carboxylic acids are obtained from α-olefins by treatment with carbon monoxide and water [Equation 13] (1,39,40).



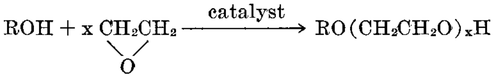
$$RCH{=}CH_2 + CO + H_2O \xrightarrow{\text{catalyst}} \underset{\displaystyle CH_3}{RCHCOOH} \qquad [13]$$

Catalysts which may be used include nickel carbonyl, boron trifluoride, and sulfuric acid. The carboxylic acid function is attached to a secondary carbon atom of the α-olefin chain. Carboxylic acids may also be prepared by direct oxidation with chromic acid.

Mercaptans may be produced by the ionic reaction of alkyl bromides with alkali hydrosulfides (3,21). α-Olefins themselves will react with hydrogen sulfide in the presence of peroxides (free radical-type reaction) to give primary mercaptans as the main product (37,63,66). In the absence of peroxides the "normal" 2-mercaptan product may be obtained (22,37). Mercaptans may also be obtained by treatment of α-olefins with thioacetic acid followed by hydrolysis [Equation 14] (9,14).

$$\begin{aligned} &RCH{=}CH_2 + CH_3COSH \xrightarrow{\text{peroxide}} \\ &\quad RCH_2CH_2SOCCH_3 \xrightarrow{\text{hydrolysis}} \\ &\quad RCH_2CH_2{-}SH \qquad [14] \end{aligned}$$

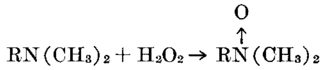
Condensation of ethylene oxide with the above active hydrogen compounds (36,46) is normally carried out at temperatures of 120–200C and pressures of 30–60 psig. Usually, a basic catalyst (sodium hydroxide) is used. The ethylene oxide condensation reaction is illustrated in Equation 15 using an alcohol as an example.



$$ROH + x\,\underset{\displaystyle \diagdown O \diagup}{CH_2CH_2} \xrightarrow{\text{catalyst}} RO(CH_2CH_2O)_xH \qquad [15]$$

Due to the various active hydrogen compounds which may be used and the widely differing degree of ethylene-oxide condensation which may be achieved, a vast number of nonionics of this type are possible. In general, condensates with only a few ethylene oxide units tend to be water insoluble and oil soluble. As the number of ethylene oxide units is increased, water solubility increases and oil solubility decreases. In the surfactant industry, the higher ethylene oxide mole ratio products are used extensively as low foamers in detergent formulations. The lower mole ratio condensates are widely used as intermediates for the production of high foaming anionic surfactants by sulfation of the hydroxyl group.

Preparation of Amine Oxides. Amine oxides may be produced in high yield by the oxidation of long-chain dimethylamines [Equation 16] (13,34,54).



$$RN(CH_3)_2 + H_2O_2 \rightarrow R\overset{\displaystyle O \atop \uparrow}{N}(CH_3)_2 \qquad [16]$$

Amine oxides are relatively new materials presently of great commercial interest. They are high quality surfactants used primarily as foam boosters and emollients in liquid detergent formulations (18,50,51).

Other Derivatives

Other long-chain derivatives of interest to the surfactant industry may be produced from α-olefins. For instance, long-chain alcohols used in certain heavy-duty formulations are valuable as foam additives. Such alcohols are also important as starting materials for primary alkyl sulfates used in both solid and liquid detergents. Preparations of alcohols from α-olefins have been previously discussed in connection with Equations 10 and 11 above.

Also of commercial interest as intermediate raw materials are long-chain 1,2-glycols. Lower molecular weight 1,2-glycols may be obtained in good yield by the direct reaction of hydrogen peroxide with α-olefins; however, the higher molecular weight products (C_{12} and above), are prepared much more conveniently by the reaction of peracetic acid with α-olefins (61,64). In reality, an intermediate monoacyl glycol is formed which is then saponified with sodium hydroxide to give the free glycol.

Long-chain 1,2-glycols may also be prepared by halogen addition (32) to α-olefins followed by hydrolysis (43). Chlorination is carried out in aqueous acetic acid at 10–30C and gives the 1,2-dichloride. The glycol is obtained by hydrolysis at 200–250C with sodium acetate.

ACKNOWLEDGMENTS

Contributions from associates at California Research Corp.; interest and support of this work by California Chemical Co.

REFERENCES

1. Adkins, H., and R. W. Rosenthal, J. Am. Chem. Soc. *72*, 4550 (1950).
2. Allied Chemical Corporation, "Reactions of Sulfur Trioxide and Its Organic Complexes," New York, 1959.
3. Beanblossom, J. E., and R. H. Kimball (Hooker Electrochemical), U.S. 2,404,425 (1946).
4. Beckham, L. J. (Solvay Process), U.S. 2,265,993; 2,336,387; 2,343,362; 2,354,359; 2,371,418; 2,373,643 (1942–1945); (Allied Chemical); U.S. 2,435,570 (1948).
5. Beekhuis, H. A. (Solvay Process), U.S. 2,370,518 (1945).
6. Birch, S. F., J. Inst. Petroleum *38*, 69 (1952).
7. Bordwell, F. G., and M. L. Peterson, J. Am. Chem. Soc. *76*, 3952 (1954).
8. Brown, J. F. (General Electric), U.S. 2,837,578 (1958).
9. Brown, R., W. E. Jones, and A. R. Pender, J. Chem. Soc. *1951*, 2123.
10. Butcher, K. L., and G. M. Dickson, J. Appl. Chem. *10*, 65 (1960).
11. California Chemical Company, Oronite Division, "Alpha Olefins Technical Bulletin," San Francisco, 1963.
12. Clippinger, E., Preprints of the Division of Petroleum Chemistry, American Chemical Society, 144 Meeting, Los Angeles, March 31–April 5, 1963.
13. Culvenor, C. C. J., Revs. Pure and Appl. Chem. (Australia) *3*, 83–114 (1953).
14. Cunneen, J. I., J. Chem. Soc. *1947*, 135.
15. Darragh, J. L., and R. D. Stayner, Ind. Eng. Chem. *46*, 254 (1954).
16. Davidson, A. (Imperial Chemical Industries), U.S. 2,053,424 (1936).
17. Downing, F. B., and R. G. Clarkson (E. I. du Pont), U.S. 2,061,617 and 2,061,620 (1936).
18. Drew, H. F., and R. E. Zimmer (Procter and Gamble), U.S. 3,001,945 (1961).
19. Fessler, W. A. (Allied Chemical), U.S. 2,653,970.
20. Fincke, J. K. (Monsanto Chemical), U.S. 2,594,411 (1952).
21. Fore, D., and R. W. Bost, J. Am. Chem. Soc. *59*, 2557 (1937).
22. Franz, R. D., and P. F. Warner (Phillips Petroleum), U.S. 3,051,758 (1962).
23. Groggins, P. H., and A. J. Stirton, Ind. Eng. Chem. *29*, 1353 (1937).
24. Groves, W. W. (Monsanto Chemical), Brit. 452,335 (1935).
25. Harman, D. (Shell Development), U.S. 2,504,411 (1950).
26. Hatch, L. F., "Higher Oxo Alcohols," Wiley, New York, 1957, Chapter 1.
27. Heath, R. L., and H. A. Piggott, J. Chem. Soc. *1947*, 1481.
28. Hickinbottom, W. J., D. Peters, and D. G. M. Wood, *Ibid.*, *1955*, 1360.
29. Hickinbottom, W. J., "Reactions of Organic Compounds," Longmans, Green and Company, New York, 1948, p. 403.
30. Hickinbottom, *Ibid.*, p. 401.
31. Hickinbottom, *Ibid.*, p. 14.
32. Hickinbottom, *Ibid.*, p. 23.

33. Hoag, H., "Proceedings of the Third World Petroleum Congress," E. J. Brill, Leiden, *1951*, p. 21.
34. Hoh, G. L. K., D. O. Barlow, A. F. Chadwick, D. B. Lake, and S. R. Sheeran, JAOCS, *40*, 268 (1963).
35. Houben-Weyl, "Methoden Der Organischen Chemie," George Thieme Verlag, Stuttgart, Vol. XI/1, 1957, pp. 382–394.
36. Jefferson Chemical Company, "Ethylene Oxide Technical Bulletin," New York, 1956.
37. Jones, S. O., and E. E. Reid, J. Am. Chem. Soc. *60*, 2452 (1938).
38. Kharasch, M. S. and W. M. Potts, J. Org. Chem. *2*, 195 (1937).
39. Koch, H. (Studiengesellschaft Kohle), Ger. 1,064,941 (1959).
40. Koch, H., Fette Seifen Anstrichmittel *59*, 493–498 (1957).
41. Kooijman, P. L., "Proc. of XI Int. Cong. of Pure and Applied Chem.," Vol. I, London, p. 499.
42. Lambert, A., C. W. Scaife, and A. E. Wilder-Smith, J. Chem. Soc. *1947*, 1474.
43. Lapporte, S. J., and W. A. Sweeney (California Research Corporation), U.S. 2,971,989 (1961).
44. Lenneman, W. L., R. D. Hites, and V. I. Komerewsky, J. Org. Chem. *19*, 463 (1954).
45. Lew, H. Y. (California Research Corporation), U.S. 2,956,025 (1960).
46. Loeffeler, K. (I. G. Farenindustrie), PB L 70248.
47. Mayo, F. R., and C. Walling, Chem. Rev. *27*, 351 (1940).
48. Olivier, S. C. J., Rec. Trav. Chim. *55*, 1027 (1936).
49. Olson, A. C., Ind. Eng. Chem. *52*, 833 (1960).
50. Pilcher, W., and S. L. Eaton (Procter and Gamble), U.S. 2,999,068 (1961).
51. Procter and Gamble, South African 60/5076 (1960).
52. Ritter, J. J., and P. P. Minieri, J. Am. Chem. Soc., *70*, 4045 (1948); J. J. Ritter, and J. Kalish, *Ibid.*, *70*, 4048 (1948); H. Plout, and J. J. Ritter, *Ibid.*, *73*, 4076 (1951).
53. Roelen, O. (Alien Property Custodian), U.S. 2,327,066 (1943).
54. Ruppert, W. (Badische Anilin und Soda-Fabrik), Ger. 1,080,112 (1960).
55. Sager, W. F., J. Am. Chem. Soc. *78*, 4970 (1956).
56. Seifert, W. K., J. Org. Chem. *28*, 125 (1963).
57. Seifert, W. K., and L. L. Ferstandig (California Research Corporation), U.S. 3,035,101 (1962).
58. Sharman, S. H., J. Am. Chem Soc. *84*, 2945, 2951 (1962).
59. Shreve, R. N., and D. R. Burtsfield, Ind. Eng. Chem. *33*, 218 (1941).
60. Suter, C. M., P. B. Evans, J. M. Kiefer, *Ibid.*, *60*, 538 (1938).
61. Swern, D., Chem. Rev. *45*, 1 (1949).
62. Tulleners, A. J. (Shell Development), Canadian 414,609 (1943).
63. Vaughn, W. E., and F. F. Rust, J. Org. Chem. *7*, 472 (1942).
64. Wallace, J. G., "Hydrogen Peroxide in Organic Chemistry," E. I. du Pont, Wilmington, Del.
65. Walling, C., "Free Radicals in Solution," Wiley, New York, 1957, p. 273.
66. Walsh, W. (Gulf Research and Development), U.S. 2,925,443 (1960).
67. Weil, I., R. G. Goebel, E. R. Tulp, A. Cahn, J. Am. Chem. Soc. Div. Petrol. Chem., Preprints *8*, No. 2, B-95 (1963).
68. Westphal, O., and D. Jerchel, Ber., *73B*, 1002 (1940); Chem. Abs., *35*, 3599 (1941).

Use Evaluation of Alcohol Derivatives in Detergent Formulations

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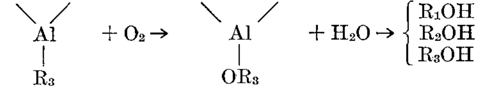
LONG CHAIN ALCOHOLS as raw materials for the detergent industry have been of significant commercial importance for many years. Due to the emphasis on biodegradability properties in today's market, the discussion here will be confined to the straight-chain primary alcohols.

These alcohols have traditionally been prepared by saponification of natural waxes, such as sperm oil, or by reduction of fatty acids obtained from oils and fats, such as coconut oil, palm kernel oil, and tallow (1). However, within the last year and one-half, straight chain primary alcohols have become available from petrochemical sources. The process for the production of these petroleum-derived alcohols (2) is briefly as follows: metallic aluminum reacts with hydrogen gas and aluminum triethyl to yield diethylaluminum hydride; the hydride is reacted with ethylene to give aluminum triethyl; the aluminum triethyl reacts with more ethylene to give a mixture of aluminum alkyls ("growth" product) containing randomly distributed alkyl groups; and this "growth" product is oxidized with air and then hydrolyzed to form even-numbered straight chain primary alcohols.



$$\overset{R_1\quad R_2}{\underset{R_3}{Al}} + O_2 \rightarrow \overset{R_2O\quad OR_2}{\underset{OR_3}{Al}} + H_2O \rightarrow \left\{\begin{array}{l}R_1OH\\ R_2OH\\ R_3OH\end{array}\right.$$

The petroleum-based alcohols and the fat and oil derived alcohols have identical physical and chemical properties when comparing the same carbon chain distributions. However, since the distribution of the petroleum-derived straight chain alcohols is governed by a Poisson distribution, proper adjustment of reaction conditions easily shifts the carbon chain length to peak at a higher or lower molecular weight. This process, therefore, can produce blends of commercial straight-chain alcohols not economically attractive in the past. Therefore, it is important to re-evaluate the effect of the carbon chain length of the alcohols upon the use properties of the major alcohol derivatives used in detergent formulations. The derivatives discussed here will be alcohol sulfates, alcohol ethoxylates and alcohol ether sulfates.

Alcohol Sulfates

The alcohol sulfates are prepared for the alcohols by typical sulfation techniques using typical sulfating agents: SO_3, cholorsulfonic acid, sulfamic acid, etc. (3). The greatest potential for alcohol sulfates in household detergent formulations appears to be in heavy duty powders. Detergency and foam stability of individual alcohol sulfates were evaluated in the following heavy duty formulation:

20%	active	15%	sodium sulfate
50%	sodium tripolyphophate	0.8%	CMC
5%	sodium silicate (meta)	9.2%	water

Foam stability tests were run in a typical plate washing test at 115F, 0.22% solids concentration, at 50 ppm hardness. In this test uniformly soiled plates are washed to obtain an end point of a permanent break in the foam covering the dishpans. One plate difference is significant below 10 plates washed. When

TABLE I
Effect of Free Alcohol on Foam Stability of Individual Alcohol Sulfates

Alcohol sulfate	Plates washed at 115F, 50 ppm hardness, 0.22% solids concentration												
	(a) As is (no free alcohol)	(b) C_{12} Alcohol per cent/active			(c) C_{14} Alcohol per cent/active			(d) C_{16} Alcohol per cent/active			(e) C_{18} Alcohol per cent/active		
		5	10	15	5	10	15	5	10	15	5	10	15
C_{12}	3	9	..	14	3	3	3	2	..	1	2	1	1
C_{14}	13	>30	..	>30*	>30	>30	>30	..	20	..	16	..	..
C_{16}	16	30	>30	>30	..	30	30	17	..	13	..	..	..
C_{18}	8–9	16	19	20	11	..	..	..	11	..	11	..	6

Note: Greater than (>) thirty plates is indicated above the 30 plate range. Due to the copious nature of the alcohol sulfate foam, it is difficult to detect an end point of this magnitude. The condition marked with an asterisk subjectively was noted to have considerable amounts of foam above the level of any others marked >30.