N-benzoyl-N-carbamylcysteine with respect to benzoyl transfer. While the sequence of reactions from III to IV seems reasonable, kinetic data are not available for definitive conclusions. In connection with this mechanism it would also seem that the acetylation reaction proceeds by a similar sequence and that these reactions are followed by acetylation at the carbamyl nitrogen to give the isolated N′,S-diacetyl-N-carbamylcysteine. However, one would expect from this sequence the formation of, at least, S-acetyl-N-carbamylcysteine. This compound was not found even with less than stoichiometric amounts of acetic anhydride and the possibility of a concerted acetylation by the anhydride suggests itself, although no definitive conclusion can be reached.

Acknowledgment.—The authors are indebted to Mr. Robert Martin for obtaining the n.m.r. traces. Support of this work, in part, by Grant G-14368 from the National Science Foundation is gratefully acknowledged.

Acid-Catalyzed Interchange Reactions of Carboxylic Acids with Enol Esters[1b]

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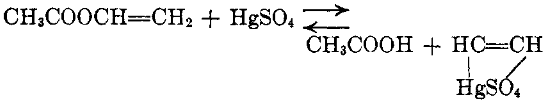
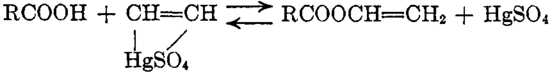
The reaction of vinyl acetate with carboxylic acids in the presence of sulfuric acid catalyst gives a mixture of the acylals ethylidene diacetate, 1-acetoxy-1-acyloxyethane, and 1,1-diacyloxyethane. By contrast, the homologous isopropenyl acetate gives the ester-acid interchange reaction as well as anhydride formation previously reported. Attempts to isolate the geminal diester, bromoisopropylidene distearate *via* the reaction of isopropenyl stearate, *N*-bromosuccinimide, and sodium stearate were not successful, although evidence for its formation includes spectral disappearance of isopropenyl unsaturation bands, hydrogenolysis to *n*-octadecyl alcohol and *n*-octadecyl stearate, ethanolysis to ethyl stearate, and hydrolytic rearrangement to hydroxyacetone stearate.

The interchange reaction of vinyl esters with carboxylic acids is described by Adelman[2] as distinctly different in nature from ordinary transesterifications or ester-acid interchanges. The former reaction is reported to be unaffected by acid[3] or basic catalysis and specifically catalyzed by metal salts, typically mercuric salts with or without added boron trifluoride,[4] capable of forming complexes with acetylene. Evidence was brought to bear that the reaction course actually involved primary formation of an acetylene–mercury salt complex which then underwent a second stage addition reaction with reagent carboxylic acid:

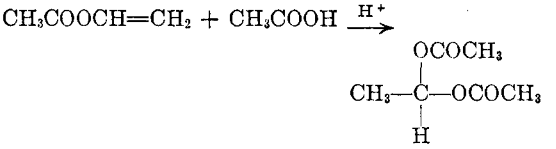


$$\mathrm{CH_3COOCH{=}CH_2 + HgSO_4 \rightleftarrows CH_3COOH + \underset{HgSO_4}{HC{=}CH}} \quad (1)$$



$$\mathrm{RCOOH + \underset{HgSO_4}{CH{=}CH} \rightleftarrows RCOOCH{=}CH_2 + HgSO_4} \quad (2)$$

On the other hand, sulfuric acid–catalyzed reaction of vinyl acetate with carboxylic acids without mercury salts catalysis is reported by other workers as giving reaction products. Thus in a German patent,[5] the reaction of vinyl acetate with acetic acid catalyzed by sulfuric acid is stated to yield an acylal, namely, ethylidene diacetate.



$$\mathrm{CH_3COOCH{=}CH_2 + CH_3COOH \xrightarrow{H^+} CH_3{-}\overset{\displaystyle OCOCH_3}{\underset{\displaystyle H}{C}}{-}OCOCH_3} \quad (3)$$

Vinyl acetate and the homologous enol ester, isopropenyl acetate, might be expected to show significant differences in reactivities. Nevertheless, Hagemeyer and Hull[6] report results paralleling those reported by Adelman[2] namely, that isopropenyl esters and carboxylic acid react in the presence of mercury salts to form isopropenyl esters of the reactant acids; that is, "vinyl interchange" is the predominant reaction. But Hagemeyer and Hull[6] also report that, using only sulfuric acid catalysis, acetic anhydride and the anhydride of the reagent carboxylic acid are formed.

In the case of sulfuric acid catalysis our own findings are at variance with this previous report and give evidence that a fairly complicated situation actually exists. We find, for example, that

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(1)(a) To be presented at 142nd National Meeting of the American Chemical Society, September 9–14, 1962, Atlantic City, New Jersey; (b) One of the laboratories of the Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

(2) R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

(3) In reaction of vinyl acetate with carboxylic acids, sulfuric acid is reported (ref. 2) to have no catalytic activity whatsoever. See also T. Asahara and M. Tomita, *J. Oil Chemists' Soc., Japan*, **1**, 76 (1952).

(4) Based on analogous examples given in U. S. Patent 2,646,437, July 21, 1953 (J. B. Dickey and T. E. Stanin), the reaction of isopropenyl acetate and stearic acid, using mercuric acetate–boron trifluoride catalyst should have given isopropenyl stearate. Under these conditions we obtained only traces of the expected product but instead isolated stearic anhydride in at least 74% yield (see Experimental).

(5) Ger. Patent 313,696, July 19, 1919.

(6) H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

reaction of five moles of isopropenyl acetate with one mole of stearic acid catalyzed by sulfuric acid gives about equimolar amounts of *two* products, isopropenyl stearate and stearic anhydride. When stearic anhydride is present initially in the reaction mixture, the yield of isopropenyl stearate (based on stearic acid converted) rises from 53% (anhydride initially absent) to 68% when half a mole of stearic anhydride is present per mole of stearic acid, and to 93% when one mole of stearic anhydride per mole of stearic acid, is present. These results are concordant with those of Phillips,[7] who reports isopropenyl ester formation from acid anhydrides and isopropenyl acetate *via* sulfuric acid catalysis.

It will be recalled that Adelman,[2] depending on titrations measuring liberated water-soluble acetic acid, believed *no reaction* occurred in the case of capric acid–vinyl acetate–sulfuric acid systems although he was aware of reported[5] acylal formation from vinyl acetate, sulfuric acid, and acetic or benzoic acid systems. In our hands the reaction of vinyl acetate, stearic acid, and sulfuric acid catalyst (with no mercury salts present) led to a mixture of the three acylals, ethylidene distearate, m.p. 62°, ethylidene monostearate monoacetate, m.p. 43°, and ethylidene diacetate, as well as a small amount of unidentified liquid acetate ester, b.p. 72°/9.6 mm., which were separated by column chromatography on Florisil.[8]

Characterization of the substance melting at 62° as ethylidene distearate is based on the following data. The infrared spectrum shows a broad ester band at 1757 cm.$^{-1}$ with a shoulder at about 1747 cm.$^{-1}$ suggesting an acylal structure.[9] Significantly absent are bands in the 1200–1300-cm.$^{-1}$ region indicating that the acetoxy group is not present in the molecule. Saponification gives 947 mg. of stearic acid per gram of ester (calculated 955 mg./g.), and the molecular weight values observed 586 g./mole (Rast) and 579 g./mole (ebullioscopic), and elemental analysis are in excellent agreement with the calculated values. The X-ray long spacing of 43.2 Å. is of the right order of magnitude for a distearate ester.

The compound is not identical with ethylene glycol distearate and could be independently prepared from the mixed diester, ethylidene monoacetate monostearate, by transesterification with stearic acid.

Ethylidene monoacetate monostearate, the second major product eluted from the Florisil[8] column, melted from 43 to 46° and showed a strong acetate absorption band at 1228 cm.$^{-1}$. Other prominent spectral bands included a carbonyl band at 1765 cm.$^{-1}$ with an inflection at about 1752 cm.$^{-1}$, a C—H stretching band inflection at about 2990 cm.$^{-1}$ probably due to unsymmetrical C—H bands and a characteristic 1010 cm.$^{-1}$ band. The structure assignment for this compound is based on the presence of the infrared ester band positions; on the X-ray long spacing of 27.5 Å. which is a value of the right order of magnitude for a monostearate; on the elemental analyses which agree well with the calculated values and separate well from the values calculated for the geminal distearate; and on the observed molecular weight determinations 345, 361 g./mole (Rast), 415 g./mole (ebullioscopic) which, on comparison with the calculated value of 371 g./mole, indicate that only one stearate grouping is present. The intense 1215-cm.$^{-1}$ band of ethylidene diacetate is not present in the spectrum of the compound melting from 43 to 46°, indicating that the substance is not simply a mechanical mixture of ethylidene diacetate and ethylidene distearate.

Ethylidene acetate stearate (1-acetoxy-1-stearoyloxyethane) is an example of a mixed acylal wherein two nonidentical ester groups are attached to the same carbon atom. This class of compounds is rarely encountered. The only previous examples reported in the literature are 1-acetoxy-1-benzoyloxyethane[5] and 1-acetoxy-1-butyroxybutane,[10] apart from some early preparations by Rübencamp[11] in 1884.

Rübencamp prepared 1-acetoxy-1-butyroxyethane, among several other related compounds, by the reaction of 1-acetoxy-1-chloroethane with silver butyrate. We obtained Rübencamp's 1-acetoxy-1-butyroxyethane in 60% yield by the reaction of vinyl acetate with butyric acid in the presence of sulfuric acid; the physical properties of our preparation closely agree with Rübencamp's values. In the Experimental some additional examples of enol ester–carboxylic acid exchange reactions are given.

In summary, then, under conditions of sulfuric acid catalysis carboxylic acids *add* to vinyl acetate and *exchange* with isopropenyl acetate, although in the latter case significant amounts of anhydride are also formed. The flowsheet (Fig. 1) summarizes previous and present results.

In an attempt to prepare a ketone acylal, isopropenyl stearate reacted with *N*-bromosuccinimide (NBS) in the presence of sodium stearate. We had hoped that this reaction might give the geminal distearate of bromoacetone hydrate (I) as the equation illustrates.

We were not able to isolate I from the reaction of isopropenyl stearate, NBS, and sodium stearate, but evidence pointing toward the actual formation of the postulated intermediate includes the disappearance of the prominent 6.0 and 11.5 μ in-

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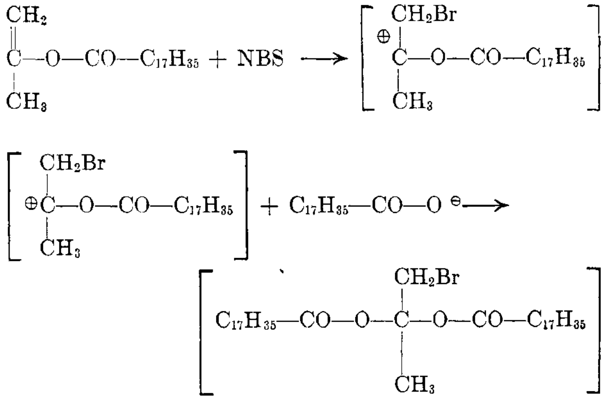
[7] B. Phillips, Jr., U. S. Patent 2,466,738, April 12, 1949.

[8] Mention of a trade name does not imply endorsement by this agency of this product over similar products.

[9] Ethylidene diacetate shows a similar band at 1762 cm.$^{-1}$ with a shoulder at 1753 cm.$^{-1}$ (Perkin-Elmer 21 instrument) resolving at higher resolution (Beckman IR-7 grating instrument) into two bands at 1765 cm.$^{-1}$ and 1753 cm.$^{-1}$. P. J. Scheuer and S. G. Cohen, *J. Am. Chem. Soc.*, **80**, 4933 (1958) have suggested that such carbonyl splitting is characteristic only of cyclic acylals.

[10] W. A. Mosher and C. L. Kehr, *ibid.*, **82**, 5342 (1960).

[11] R. Rübencamp, *Ann.*, **225**, 267 (1884).



I

frared unsaturation bands originally present, the ease of hydrolysis with rearrangement of the reaction product to hydroxyacetone stearate, ease of ethanolysis to ethyl stearate, and hydrogenolysis under fairly mild conditions to *n*-octadecyl alcohol and *n*-octadecyl stearate.

An alternative structure for I was considered and rejected involving addition of the elements of stearoyl hypobromite in the reverse direction to form 2-bromo-1,2-distearoyloxypropane. This compound, although hydrolysable to hydroxyacetone stearate, is not likely to give *n*-octadecyl alcohol or its ester on hydrogenolysis. This alternative formulation would also require the formation of a primary carbonium ion lacking the reasonance stabilization that can occur in the tertiary carbonium ion intermediate leading to I.

The hydroxyacetone stearate obtained by the hydrolytic rearrangement reduces Fehling's solution and alkaline triphenyltetrazolium reagent and is identical with the product obtained by metathetic[12] reaction of bromoacetone and triethylammonium stearate. The flowsheet (Fig. 1) summarizes previous and present results.

Experimental

Melting points were determined on the Kofler stage but are otherwise not corrected. Spectra were determined using a Perkin-Elmer double beam Model 21 spectrophotometer (NaCl prism) in carbon disulfide solution at 10 g./l. The carbonyl region values are corrected values using the 1700-cm.$^{-1}$ water vapor peak. Stearic acid, m.p. 70°, was obtained from the best commercial grade by recrystallization from acetone. Oleic acid was prepared from olive oil and was at least 98% pure by gas-liquid chromatographic analysis of the methyl ester.

Isopropenyl Stearate.—Stearic acid, 8.5 g. (0.03 mole), freshly distilled isopropenyl acetate, 15 ml. (0.15 mole), and concentrated sulfuric acid, 0.017 ml., were heated under reflux for 5 hr. The cooled mixture was diluted with pentane, treated with 2 g. of anhydrous sodium acetate, and filtered to remove salts. The volume was reduced to 250 ml. under reduced pressure and by means of cooling and further volume reduction successive crops of crystalline matter were collected. Initial crops were scales of stearic anhydride,[13] m.p. 73°, $\bar{\nu}_{\max}^{CS_2}$ 1818, 1752, and 1032 cm.$^{-1}$. Subsequent crops gave the mixed stearic acetic anhydride, m.p. 52°, $\bar{\nu}_{\max}^{CS_2}$ 1817, 1750, 1124, 1087, 1060, 1000 cm.$^{-1}$, previously reported, m.p. 54°,[14] The mixed anhydride gradually disproportionated to stearic anhydride and acetic anhydride. The total yield of stearic anhydride thus obtained was 45%.

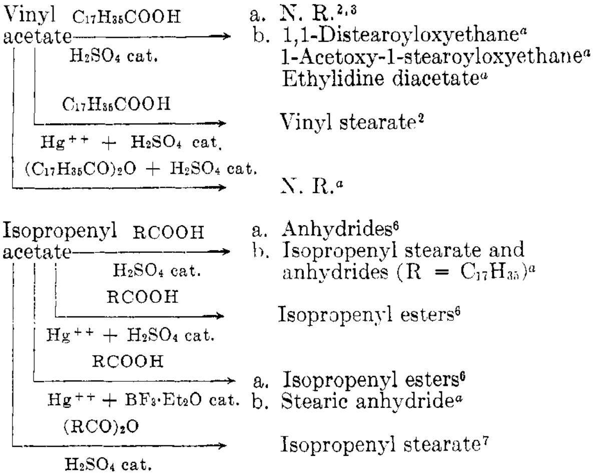


Fig. 1.—Summary of previous and present[a] results.

The mother liquors were worked up for enol ester content by two alternative methods: Distillation gave isopropenyl stearate, b.p. 184–189°/0.4 mm., which on recrystallization from pentane gave the analytical sample, m.p. 36–37°, $\bar{\nu}_{\max}^{CS_2}$ 1751, 1674, 1205, 1148, 1120, and 868 cm.$^{-1}$. Alternatively the mother liquors were freed of acid and anhydride by chromatography on Florisil with hexane. The enol ester was rapidly eluted and recovered in 54% yield.

Anal. Calcd. for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42. Found: C, 77.89; H, 12.60. Both the chromatographic and distillation isolation procedures decomposed residual stearic anhydride.

Preparation of Isopropenyl Stearate. Effect of Added Stearic Anhydride.—When the above procedure was modified by the inclusion in the initial mixture of 0.5 mole of stearic anhydride per mole of stearic acid initially present, the yield of isopropenyl stearate was 68% based only on the stearic acid present. When 1 mole of stearic anhydride per mole of stearic acid was included in the system, the yield rose to 93% on the stearic acid basis.

Isopropenyl Stearate from Stearic Anhydride.[7]—Stearic anhydride, 5.5 g. (0.01 mole), isopropenyl acetate, 10 g., (0.1 mole), and 2 drops of sulfuric acid were refluxed for 5 hr. Isolation as described above gave 4 g. of isopropenyl stearate (62%).

Acetic-Stearic Mixed Anhydride.—To confirm the identity of acetic-stearic mixed anhydride, obtained as an intermediate in the reaction of stearic acid, isopropenyl acetate, and sulfuric acid catalyst (*vide supra*), an independent preparation of this mixed anhydride was conducted. Stearic acid, 5.5 g., acetic anhydride, 10 ml., and 3 drops of sulfuric acid were heated to reflux temperature (20 min. required) and slowly distilled for 1 hr. to remove acetic acid as formed. The cooled, solidified reaction mixture was triturated with pentane and 5.5 g. of solids were collected by filtration. The material was immediately dried *in vacuo*, since it was observed that its stability was increased when no traces of solvent were present. The product, m.p. 52°, showed the spectrum previously obtained by the isopropenyl acetate–stearic acid–sulfuric acid procedure and was apparently complete free of stearic anhydride (infrared 1032-cm.$^{-1}$ band absent). On storage for 3 days, the odor of acetic anhydride

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[12] *Cf.* W. T. Moreland, *J. Org. Chem.*, **21**, 820 (1956), and ref. 16.

[13] N. O. V. Sonntag, J. R. Trowbridge, and I. J. Krems, *J. Am. Oil Chemists' Soc.*, **31**, 151 (1954), give m.p. 70.0–70.4° $\bar{\nu}_{\max}$ 1735 and 1780 cm.$^{-1}$, single beam instrument, probably neat using KBr prism.

[14] R. E. Dunbar and F. C. Garven, *J. Am. Chem. Soc.*, **77**, 4161 (1955).

was easily detectable, and recrystallization at the end of this period gave stearic anhydride m.p. 73°.

Reaction of Stearic Acid with Isopropenyl Acetate in the Presence of Boron Trifluoride Etherate and Mercuric Acetate.—The procedure of Dickey and Stanin[4] applied by them to other carboxylic acids was followed, but we obtained stearic anhydride instead of isopropenyl stearate. Isopropenyl acetate, 20 g., stearic acid, 28 g., mercuric acetate, 0.2 g., and 0.1 ml. of commercial boron trifluoride etherate were heated at 55–60° for 14 hr. The mixture was then treated with sodium acetate to neutralize the boron trifluoride. A filtered aliquot, evaporated *in vacuo* to remove excess isopropenyl acetate, showed strong carbonyl bands in the infrared characteristic of the anhydride function, and showed only weak bands where isopropenyl stearate absorbs. Dilution with hexane, decolorization with active carbon, and crystallization gave 20 g. of stearic anhydride (74% yield).

Isopropenyl Oleate.—Isopropenyl oleate was prepared from oleic acid, isopropenyl acetate, and sulfuric acid catalyst under conditions described above for the stearate. No attempt was made to isolate anhydrides. The reaction mixture was treated with sodium acetate to neutralize sulfuric acid and directly distilled. Isopropenyl oleate distilled at 174–175°/1.5 mm., d^{30}_4 0.8675, $\eta^{30}\text{D}$ 1.4522 (yield 45%). The infrared showed a peak at 3015 cm.$^{-1}$ (H—C = C), did not resolve 1120-cm.$^{-1}$ peak, but otherwise resembled the spectrum of the saturated analog. No *cis* to *trans* isomerization occurred.

Anal. Calcd. for $C_{21}H_{38}O_2$: C, 78.20; H, 11.87. Found: C, 78.12; H, 11.96.

1-Cyclohexenyl Stearate.—1-Cyclohexenyl acetate was prepared from cyclohexanone and acetic anhydride by the procedure of Machinskaya[15] using sulfuric acid catalysis. The product boiled at 50°/5 mm. (spinning band column), previously reported[15] 58–68°/5 mm., 180°/760 mm. To 62 g. (0.443 mole) of cyclohexenyl acetate and 238 g. (0.828 mole) of stearic acid was added 20 drops of sulfuric acid. The mixture was heated at 65°/20 mm. to remove acetic acid for 2.5 hr. at 65° and then at ambient pressure for an additional 3 hr. An aliquot of the mixture showed anhydride bands in the infrared. A portion of the excess stearic acid was recovered by crystallization from pentane, and the mother liquors were freed of residual acid and anhydride by passage in pentane through a Florisil column. The earliest eluates gave 37 g. of colorless, oily cyclohexenyl stearate which solidified on standing. This material showed no C—O infrared bands in the 1200–1300-cm.$^{-1}$ region indicating that acetate was absent. Recrystallization of the earliest eluates at −20° from pentane gave the analytical sample, m.p. 37.5–38.0°, irregular plates, $\bar{\nu}^{CS_2}_{max}$ 1745, 1690, 1124, 1148 cm.$^{-1}$. Later eluates gave mixtures of cyclohexenyl acetate and cyclohexenyl stearate. Cyclohexenyl stearate was recovered from these eluates by removal of the more volatile cyclohexenyl acetate by distillation: total yield of cyclohexenyl stearate, 25%.

Anal. Calcd. for $C_{24}H_{44}O_2$: C, 79.06; H, 12.16. Found: C, 78.92; H, 12.12.

1-Acetoxy-1-stearoyloxyethane and 1,1-Distearoyloxyethane.—Freshly distilled vinyl acetate, 429 g. (5 moles), stearic acid, 112 g. (0.4 mole), and 1.5 ml. of concentrated sulfuric acid were refluxed for 6 hr. The mixture was treated with 6 g. of anhydrous sodium acetate, and 345 g. of excess vinyl acetate was collected by distillation at atmospheric pressure. Further distillation *in vacuo* gave 28 g. of ethylidene diacetate. The solid residues were chromatographed on 1.25 kg. of Florisil. Elution with hexane gave a forerun containing 3 g. of vinyl stearate followed by a fraction rich in 1,1-distearoyloxyethane but containing a small proportion of 1-acetoxy-1-stearoyloxyethane. Later hexane eluates and 1:1 hexane-benzene eluates, on evaporation, gave uncontaminated 1-acetoxy-1-stearoyloxyethane. Recrystallization of the eluate fractions ultimately gave 30 g. of ethylidene distearate and 43 g. of acetate stearate.

The 1,1-distearoyloxyethane crystallized well from pentane and melted sharply at 62°.

Anal. Calcd. for $C_{38}H_{74}O_4$: C, 76.71; H, 12.54; mol. wt., 594 g./mole. Found: C, 76.70; H, 12.36, mol. wt., 586 g./mole (Rast), 579 g./mole (ebullioscopic).

The 1-acetoxy-1-stearoyloxyethane melted from 43 to 46°.

Anal. Calcd. for $C_{22}H_{42}O_4$: C, 71.30; H, 11.42; mol. wt. 371 g./mole. Found: C, 71.44; H, 11.41; mol. wt., 353 g./mole (Rast), 415 g./mole (ebullioscopic).

Conversion of 1-Acetoxy-1-stearoyloxyethane to 1,1-Distearoyloxyethane.—1-Acetoxy-1-stearoyloxyethane (4.62 g., 12.5 mmoles) and stearic acid (10 g., 35 mmoles) were heated at 100° for 0.75 hr. with 2 drops of sulfuric acid in a fine stream of nitrogen introduced by means of a capillary with tip submerged below the melt to help remove acetic acid by entrainment. After addition of 500 mg. of sodium bicarbonate, the mixture was diluted with hexane and chromatographed on a small column of Florisil to remove colored material. Elution with 25% benzene in hexane and 100% benzene gave the expected weight of 1,1-distearoyloxyethane melting at 61–62°. The infrared spectrum of this material was identical with that previously obtained from the vinyl acetate–stearic acid reaction product already described.

1-Acetoxy-1-butyroxyethane.—Freshly distilled vinyl acetate, 465 g. (5.41 moles), butyric acid 38.1 g. (0.433 mole), and 1.5 ml. of sulfuric acid were refluxed for 6 hr., cooled, and 6 g. of solid sodium bicarbonate was added. The excess vinyl acetate was removed by distillation at atmospheric pressure. Fractionation under reduced pressure gave 36 g. of ethylidene diacetate and 43.7 g. of 1-acetoxy-1-butyroxyethane, b.p. 129°/94 mm., b.p. 192°/760 mm., $\eta^{28.2}\text{D}$ 1.4062, $\eta^{30}\text{D}$ 1.4053, sp. gr.$^{15°}$ = 1.012, d^{30}_4 0.9949, molecular refractivity calcd. 42.5. Found: 42.9. Previously reported[11] sp. gr. 15° = 1.016 $\eta^{28.2}\text{D}$ 1.4065, b.p. 192.4°.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.40; H, 8.02.

A small late fraction of distillate, 3 g., showed only a weak 1225-cm.$^{-1}$ infrared absorption band and may contain some of the geminal dibutyrate. The pot residue was a water-soluble black tar (12.2 g.).

Hydroxyacetone Stearate.—Stearic acid, 20 g. (0.07 mole) in 500 ml. of tetrahydrofuran was stirred with 1.6 g. (0.07 g.-atom) of sodium metal shavings overnight until salt formation was complete. To the resulting slurry, isopropenyl stearate, 10 g. (0.031 mole), and *N*-bromosuccinimide, 8.65 g. (0.05 mole) were added and the mixture was stirred and refluxed for 3 hr. during which time blue, green, and golden yellow transient colorations were observed. The mixture was concentrated under reduced pressure, diluted with hexane, and filtered to remove excess sodium stearate. After washing with water, drying with sodium sulfate, and evaporating to dryness, the residue, 12 g., was placed on 250 g. of Florisil in hexane. Elution with hexane gave, typically, no residue on evaporation, although in one run 1.7 g. of unreacted isopropenyl stearate was recovered. Elution with benzene and with dichloromethane gave 6.2 g. of hydroxyacetone stearate in a state of high purity. The analytical sample recrystallized from pentane had m.p. 57.5–58.5°; lit. 56.5°.[16] The compound rapidly reduced Fehling's solution and triphenyl tetrazolium reagent. The compound was identical in every respect with a specimen prepared from bromoacetone and triethylammonium stearate (see below) and showed a partially resolved band pair in the infrared at 1748 and 1739 cm.$^{-1}$, other prominent bands occurring at 1375, 1360, 1270, 1233, 1195, 1152, 1120, 965, 900, and 720 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{40}O_3$: C, 74.06; H, 11.84. Found: C, 74.25; H, 11.97; Br, absent.

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[15] I. V. Machinskaya, *J. Gen. Chem. USSR*, **22**, 1205 (1952); *cf. Chem. Abstr.*, **47**, 6357 (1953).

[16] C. Paquot and P. Hiep, *Centre Natl. Recherche Sci. Labs. Bellevue*, (Paris), No. 18, **136**, (1952); *Chem. Abstr.*, **47**, 3231 (1953).

Hydroxyacetone Stearate from Bromoacetone.—Bromoacetone, 41 g. (0.3 mole), was added to a solution of triethylamine, 30 g. (0.3 mole), stearic acid, 85 g. (0.3 mole), and acetone, 100 ml., and the mixture was refluxed for 3 hr. After cooling and dilution with 2.5 l. of hexane, the solution was washed successively with water, dilute hydrochloric acid, and 1% potassium hydroxide in 40% ethanol–60% water. The organic layer was then dried with sodium sulfate and freed of traces of stearic acid by passage through a pad of Florisil. The product, recrystallized from pentane, weighed 43 g., melted at 57.5–58.5°, and was identical with the previous preparation.

Attempted Reduction of the Isopropenyl Stearate–NBS–Sodium Stearate Reaction Product (I).—A solution of 20 g. of stearic acid (0.07 mole) in 500 ml. of tetrahydrofuran (distilled from sodium under dry nitrogen) was stirred overnight with 1.6 g. of sodium shavings (0.07 g.-atom) until soap formation was complete. A solution of 10.0 g. of isopropenyl stearate (0.031 mole) in 25 ml. of dry tetrahydrofuran and 8.65 g. of NBS (0.05 mole) was simultaneously added at room temperature with stirring and the mixture was then brought to reflux temperature and held at that temperature for 3 hr. This mixture was treated with prereduced Adams' catalyst (prepared in dry THF from 5 g. of platinum oxide, discarding the supernatant solvent) and shaken overnight with hydrogen at 50 p.s.i. The mixture was filtered and the solvent removed from the filtrate under reduced pressure. The residue was dissolved in hexane and chromatographed on Florisil. Elution with hexane gave no residue. Elution with 20% benzene in hexane and 50% benzene in hexane gave 2.1 g. of *n*-octadecyl stearate m.p. 61–62°, lit.[17] m.p. 62°, identical in infrared spectrum with an authentic sample. Elution with benzene gave 0.8 g. of *n*-octadecyl alcohol, m.p. 57.5–59° (no depression with authentic sample, and identical infrared spectrum on crystal film.) Elution with 20–100% methylene chloride in benzene gave 5.7 g. of hydroxyacetone stearate, identical in melting point and infrared spectrum with an authentic sample.

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(17) J. Sauer and H. Adkins, *J. Am. Chem. Soc.*, **59**, 1 (1937).

Dissociation Constants and Ultraviolet and Infrared Spectra of Pyridinesulfonic Acids[1]

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The dissociation constants of a number of pyridinesulfonic acids have been determined spectrophotometrically in water and 42% alcohol. Changes in pK_a values and changes in infrared and ultraviolet spectra are discussed in terms of structural changes.

The dissociation constants of the dimethylpyridines[4] show that the effects of methyl groups on the pK_a value are approximately additive. To see whether a similar effect operated with the sulfonic acid grouping, a number of pyridinesulfonic acids were prepared and their dissociation constants were determined from the variation of their ultraviolet spectra with hydrogen ion concentration. It was hoped to deduce the position of the sulfonic acid group in the sulfonation product[5] of 2,6-di-*t*-butylpyridine. After this work had been completed, the sulfonation product was shown independently to be the 3-sulfonic acid.[6,7] Although our data were unable to show in which direction sulfonation had occurred in the 2,6-di-*t*-butylpyridine molecule, they are of general interest and are now reported.

TABLE I

ULTRAVIOLET SPECTRA OF THE SULFONIC ACIDS OF PYRIDINE BASES[a]

Compound	In 0.1 *N* HCl λ_{max}	In 0.1 *N* HCl ϵ_{max}	In 0.1 *N* NaOH λ_{max}	In 0.1 *N* NaOH ϵ_{max}
Pyridine	256			
2-Pyridinesulfonic acid	262	6,900	254	3,200
			260	3,800
			267	2,800
3-Pyridinesulfonic acid	261.5	5,060	254	2,490
			260	2,750
			267	1,970
4-Pyridinesulfonic acid	222	5,910	264	2,860
	263	5,050		
2,6-Lutidine	270			
2,6-Lutidine-3-sulfonic acid	218	5,740	268	4,330
	273	8,550	275	3,460
2,6-Lutidine-4-sulfonic acid	278.5	9,200	276	4,900
2,6-Di-*t*-butylpyridine	273			
2,6-Di-*t*-butylpyridine-3-sulfonic acid	220.5	6,580	220	11,200
	272.5	10,330	260.5	3,340

[a] Wave lengths are measured in mμ.

Table I contains data on the ultraviolet spectra of the sulfonic acids measured in both acid and alkaline solutions. The strong band appearing with a maximum between 260 and 280 mμ is very probably due to a transition of a π-electron from the ground state of the molecule to an excited π-

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(4) H. C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, **77**, 1723 (1955); H. C. Brown, J. Donahue, and H. E. Podall, unpublished data; R. J. L. Andon, J. D. Cox, and E. F. G. Herington, *Trans. Faraday Soc.*, **50**, 918 (1954).

(5) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953).

(6) N. Muller and W. J. Wallace, *J. Org. Chem.*, **24**, 1151 (1959).

(7) H. C. van der Plas and H. J. den Hertog, *Tetrahedron Letters*, **1**, 13–17 (1960).