TABLE II

SURFACE TENSION OF SOLUTIONS OF NA-SULFONATES OF 1,4-DI-*n*-ALKOXYBENZENES AT 25°

	Compounds							
Concn., %	I	II	III	IV	V	VI	VII	VIII
1.0	67.3	67.5	58.07	47.43	33.4	29.1	—	—
0.5	69.75	69.0	63.1	53.87	37.84	29.1	27.45	—
0.25	70.0	69.75	65.7	56.94	44.46	31.6	28.2	26.4
0.125			68.7	61.82	48.7	34.32	29.1	26.8
0.0625				65.45	53.6	40.72	31.4	26.8
0.0312				67.98	58.4	46.89	35.86	28.24
0.0156					[a]	51.8	40.3	30.4
0.0078					59.5	55.5	[a]	33.5
0.0039					68.7	61.08	45.9	38.8
0.0019					69.8	64.28	50.0	44.4
0.00098							55.0	47.9
0.00049							57.1	53.0
0.000245							64.0	58.4
0.000123								64.2

[a] Solution lost.

Surface activity of the Na-sulfonates. The surface tensions of aqueous solutions of I–VIII were determined at 25° using a Du Noüy tensiometer. The surface tension of the distilled H_2O used in preparing the solutions was 71.42 dynes at 25°. In all cases except VII and VIII a 1% solution of the Na-sulfonate was used as initial concentration to be measured. In the cases of VII and VIII it was necessary to use initial concentrations of 0.5% and 0.25% on account of the lower solubility of these salts. After determining the surface tension of the initial solution it was diluted with an equal volume of water and the surface tension of the new solution determined. The process was continued until surface tension values obtained approached that for water. The values obtained are recorded in Table II and are plotted in Figure 1.

Acknowledgment. This investigation was supported by grants from funds made available to Davidson College by E. I. du Pont de Nemours & Co., Inc., and The Monsanto Chemical Co. The author is indebted to the late Dr. R. W. Bost at whose suggestion the study was initiated.

DAVIDSON, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY]

Polysoaps. II. The Preparation of Vinyl Soaps[1]

HAROLD H. FREEDMAN,[2] J. PHILIP MASON, AND A. I. MEDALIA[2a]

Received July 10, 1957

Three types of vinyl monomers, each containing a group capable of functioning as an emulsifying agent, have been prepared. An unequivocal synthesis of one of the intermediates, 10-phenylundecanoic acid, was accomplished.

In this publication we report for the first time the synthesis of vinyl monomers which also function as emulsifying agents. Although vinyl monomers which contain long chain alkyl groups are well known, there are no well defined vinyl monomers which could also be classified as good emulsifying agents. Such monomers may be called vinyl soaps. Their polymers and copolymers are thus true polysoaps, a new type of polyelectrolyte. Of particular interest is the possibility of using vinyl soaps as the sole emulsifying agent in the emulsion polymerization of conventional vinyl monomers, with the objective of preparing a latex in which the emulsifying agent is chemically bound to the polymer. This will be reported in a future publication; the present study is concerned only with the preparation of the vinyl soaps, polymerization data being included only to demonstrate the nature of these compounds.

DISCUSSION

From a structural viewpoint a vinyl soap would combine the functionalities of both a vinyl monomer and a soap; *i.e.*, an activated vinyl group attached to a salt of a long-chain carboxylic acid of

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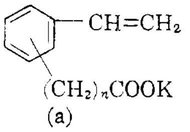
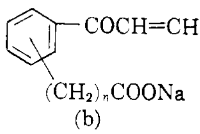
(1) For the first paper of this series, see S. K. Sinha, A. I. Medalia, and D. P. Harrington, *J. Am. Chem. Soc.*, **79**, 281 (1957). This work was supported by the General Latex and Chemical Corp., Cambridge, Mass.

(2) Abstracted from the thesis of H. H. Freedman, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School, Boston University. Present address, The Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.

(2a) Present address, Godfrey L. Cabot, Inc., 38 Memorial Drive, Cambridge, Mass.

between eight and eighteen carbon atoms.[3] Vinyl soaps are conveniently classified according to the nature of the activated vinyl group. Three general classes were investigated: (a) a styrene, (b) an acrylophenone, and (c) an acrylamido soap.


(a)

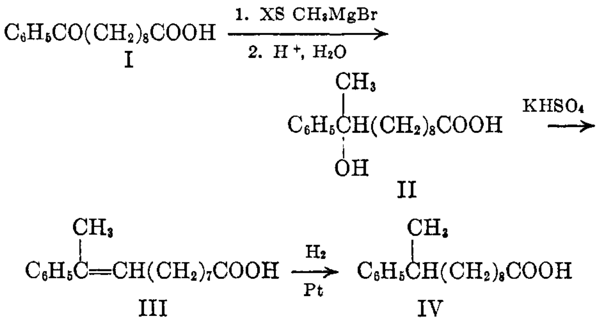

(b)

$CH_2{=}CHCONH(CH_2)_nCOOK$
(c)

A logical starting material for both the styrene and the acrylophenone monomeric soaps is a long-chain, phenyl-substituted fatty acid, commonly prepared by the Friedel-Crafts acylation or alkylation of benzene. The acylation method has been comprehensively investigated by Papa, Schwenk, and Hankin[4] who prepared a large number of ω-phenyl long-chain acids by a five-step process starting with a dicarboxylic acid. A more direct route, where applicable, is the Friedel-Crafts alkylation of benzene with one of the readily available alkene acids; provided, however, that branching in the carbon chain is not undesirable. Two possible starting materials, phenylstearic[5] and phenylundecanoic[6] acids prepared by the alkylation of benzene with oleic and undecenoic acids respectively, have been reported. The former product, originally believed to be predominantly 9-phenylstearic acid was later shown to be a mixture of approximately equal parts of the 9 and 10-isomers;[7] while the structure of phenylundecanoic acid has not been fully elucidated prior to this work.

Structure of phenylundecanoic acid. According to Fourneau and Baranger[1] the product from the Friedel-Crafts reaction of undecenoic acid or its ethyl ester with benzene leads to a separable mixture of the 10- and 11-phenyl isomers, with the former predominating. We were unable to confirm these results. Phenylundecanoic acid and its methyl ester were prepared in amounts up to a kilogram but in no case were two fractions observed which could correspond to the isomers reported; rather, there was invariably obtained, in yield of 50–60%, a single product of sharp boiling point and constant index of refraction. Since these criteria do not necessarily exclude a mixture of isomers,[8] the structure of the product was investigated.

Both C-methyl determination and quantitative analysis for methyl groups by means of infrared absorption at 7.25 μ[9] indicated that, within the rather large experimental error, the product contained one methyl group per molecule. Further, a strong band typical of mono-alkyl, α-branched phenyl[10] was present at 13.12 μ in the infrared, but there was no trace of the band at 13.4–13.6 μ associated with unbranched, monosubstituted phenyl.[10] These facts indicate that our product was predominantly 10-phenylundecanoic acid, IV.[11] Further proof of structure was obtained through unequivocal synthesis by the route outlined in (d).



$$\text{(d)}\ HOOC(CH_2)_8COOH \xrightarrow{Ac_2O} \text{polyanhydride} \xrightarrow[AlCl_3]{C_6H_6}$$

$$\underset{\text{I}}{C_6H_5CO(CH_2)_8COOH} \xrightarrow[2.\ H^+,\ H_2O]{1.\ XS\ CH_3MgBr} \underset{\text{II}}{C_6H_5\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}H(CH_2)_8COOH} \xrightarrow{KHSO_4}$$

$$\underset{\text{III}}{C_6H_5\overset{\displaystyle CH_3}{C}{=}CH(CH_2)_7COOH} \xrightarrow[Pt]{H_2} \underset{\text{IV}}{C_6H_5\overset{\displaystyle CH_3}{C}H(CH_2)_8COOH}$$

Benzoylnonanoic acid (I) was prepared from sebacic acid by the method of Hill[12] and converted to 10-phenyl-10-hydroxyundecanoic acid (II) by Grignard synthesis. Dehydration of II to 10-phenyl-9,10-undecenoic acid (III) proceeded smoothly and pure, isomer-uncontaminated 10-phenylundecanoic acid (IV) resulted from the hydrogenation of III. The infrared spectrum of IV was practically identical to that of phenylundecanoic acid prepared by the Friedel-Crafts method. However, since the refractive indices differed somewhat and it was possible to prepare a crystalline amide from the isomer-uncontaminated IV but not from the other, it would appear that our product, prepared according to the method of Fourneau and Baranger,[6] does contain a small amount (perhaps 5–10%) of the straight-chain isomer;—not enough to detect in the infrared spectrum, but enough to prevent the for-

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[3] A. M. Schwartz and J. W. Perry, *Surface Active Agents*, Interscience Publishers, New York, 1949, p. 25.

[4] D. Papa, E. Schwenk, and H. Hankin, *J. Am. Chem. Soc.*, **69,** 3018 (1947).

[5] B. H. Nicolet and C. M. DeMilt, *J. Am. Chem. Soc.*, **49,** 1103 (1927).

[6] E. Fourneau and P. M. Baranger, *Bull. soc. chim.*, (4) **49,** 1161 (1931).

[7] C. S. Marvel and J. Harmon, *J. Am. Chem. Soc.*, **54,** 2515 (1932).

(8) For example, Marvel and Harmon[7] show that for 9- and 10-phenylstearic acid, these constants are practically identical.

(9) S. H. Hastings, *et al.*, *Anal. Chem.*, **24,** 612 (1952).

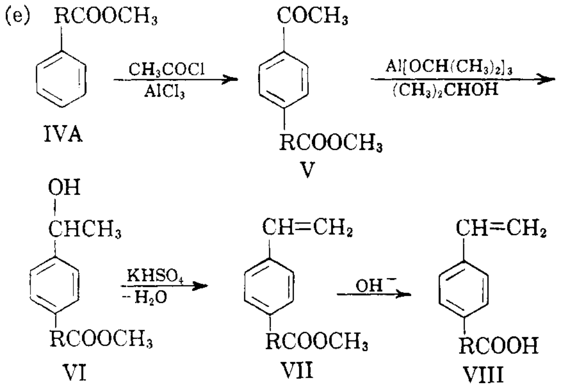
(10) H. L. McMurray and V. Thornton, *Anal. Chem.*, **24,** 318 (1952).

(11) It is noteworthy that the Distillation Products Co. lists a product (No. 5352) designated only as "Phenylundecanoic Acid," which proved to be identical to our product in all respects. An inquiry elicited the information that the acid in question was prepared by the Friedel-Crafts alkylation of benzene with undecenoic acid and the principal constituent was believed to be 10-phenylundecanoic acid.

(12) J. W. Hill, *J. Am. Chem. Soc.*, **54,** 4105 (1932).

mation of crystalline derivatives of IV and of its subsequent reaction products.

Preparation of p-styrylundecanoic acid. Methyl 10-phenylundecanoate (IVA) was converted to 10-p-styrylundecanoic acid (VIII) as shown in (e), by a procedure analogous to that of Overberger, *et al.*[13]

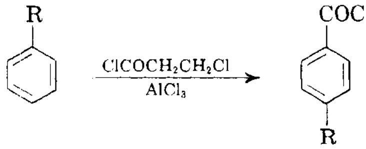


where R = CHCH$_3$(CH$_2$)$_8$—

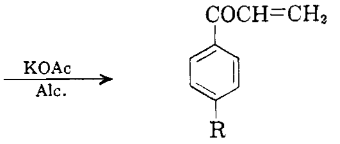
Acetylation of IVA to methyl 10-(p-acetylphenyl)undecanoate (V) was accomplished in good yield only when the complex between acetyl chloride and aluminum chloride was preformed in the absence of solvent and the ratio of ester (IVA) : acetyl chloride : aluminum chloride was in the neighborhood of 1:2.5:2.

Reduction of V with aluminum isopropoxide in isopropyl alcohol afforded methyl 10-[p-(α-hydroxyethyl)phenyl]undecanoate (VI) in nearly quantitative yield. The alcohol VI was dehydrated over fused potassium bisulfate to methyl 10-p-styrylundecanoate (VII), which in turn was saponified to the desired monomer, 10-p-styrylundecanoic acid (VIII). Both the styryl ester (VII) and acid (VIII), when stabilized with a suitable inhibitor, could be kept unchanged at ice box temperatures. At room temperature, however, they polymerized to products ranging from a viscous liquid to a glassy solid. Further details on their polymerization are given in the Experimental Section.

Preparation of p-acrylylphenylundecanoic acid. Since little information on nuclear-substituted acrylophenones was available, model compounds were prepared and their chemical and spectral properties noted. All of the acrylophenones here reported were prepared by the dehydrohalogenation with potassium acetate of the corresponding β-chloropropiophenones.

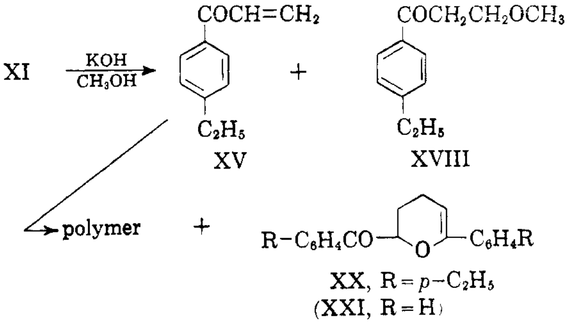


IX, R = C_2H_5
X, R = $CH_2COOC_2H_5$
IV, R = $CH(CH_3)(CH_2)_8COOH$
IVA, R = $CH(CH_3)(CH_2)_8COOCH_3$
XI, R = C_2H_5
XII, R = $CH_2COOC_2H_5$
XIII, R = $CH(CH_3)(CH_2)_8COOCH_3$
XIV, R = $CH(CH_3)(CH_2)_8COOH$



XV, R = C_2H_5
XVI, R = $CH(CH_3)(CH_2)_8COOCH_3$
XVII, R = $CH(CH_3)(CH_2)_8COOH$

When p-ethyl-β-chloropropiophenone (XI) was warmed in methanolic potassium hydroxide solution, three products were isolated. These included p-ethyl-β-methoxypropiophenone (XVIII), poly-p-ethylacrylophenone, and a condensation dimer (XX), believed to be analogous to the dimer of acrylophenone (XXI, R=H) obtained by Alder *et al.*[14] Since XX was also obtained in fair yield by exposing the vinyl ketone (XV) to the action of base, it would appear that an alkali saponification technique for the conversion of XIII to XVII would lead to a number of undesirable by-products.



The β-chloroketone ester (XIII) was obtained as a non-crystallizable oil; attempts at distillation led to loss of hydrogen chloride and its conversion to an intractable polymeric mass. Therefore, the crude oil was dehydrohalogenated directly with potassium acetate to methyl 10-(p-acrylylphenyl) undecanoate (XVI) and this was purified by distillation using a falling film molecular still. The ester (XVI) polymerized slowly at room temperature or rapidly in the presence of initiator to a hard, glassy polymer but could be kept unchanged in the cold when inhibited. This is in contrast to acrylophenone itself, which slowly dimerizes in the presence of inhibitor at −9°.[15]

As expected, the ester, XVI, could not be converted to the acid (XVII) by acid or base hydrolysis; only polymerization, dimerization, or additions across the activated vinyl group resulted.

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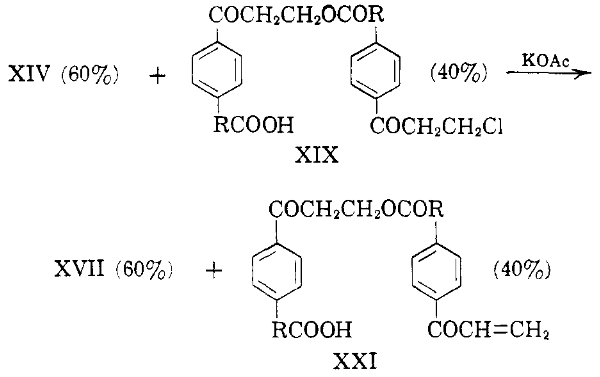
[13] C. G. Overberger, *et al.*, *J. Am. Chem. Soc.*, **75**, 3326 (1953).

[14] K. Alder, H. Offermans, and C. Ruder, *Ber.*, **74B**, 926 (1941).

[15] C. H. F. Allen, *et al.*, *J. Am. Chem. Soc.*, **62**, 656 (1940).

Therefore, attempts were made to prepare the desired compound (XVII) directly, rather than through its ester (XVI), even though preliminary experiments had shown that an additional complication was involved.

When 10-phenylundecanoic acid (IV) was acylated with β-chloropropionyl chloride there was obtained a mixture of XIV and XIX which could be dehydrohalogenated quantitatively to the mixture of XVII and XXI. Presumably the bimolecular products, XIX and XXI, were obtained either from the intermolecular condensation of the carboxyl with the active halogen, or by addition of the carboxyl across the vinyl group subsequent to partial dehydrohalogenation. They accounted for 40% of the mixture in each case. Since the mixtures could not be purified without decomposition and polymerization, the composition of each was determined by various analytical methods.



where $R = CH(CH_3)(CH_2)_8-$

Though pure 10-(*p*-acrylylphenyl)undecanoic acid (XVII) could not be prepared due to the above discussed intermolecular esterification, it may be noted that the mixture of XVII and XXI in the form of its potassium salt, served in all respects as a satisfactory polymerizable emulsifying agent. Some details on its polymerization are given in the Experimental Section.

Preparation of acrylamido fatty acids. The last class of vinyl soaps here investigated were those containing an acrylamido group in conjunction with a long chain fatty acid. These were conveniently prepared by the Ritter reaction[16] between acrylonitrile and undecenoic or 12-hydroxystearic acids, respectively. The preparation and properties of these acrylamidoundecanoic and acrylamidostearic acids, as well as various derivatives, have been previously reported by one of us[17] in conjunction with a general study of the intermolecular bonding forces in crystalline amido acids. As with the previous monomers, the acrylamido compounds could be polymerized in bulk, in organic solution, or as aqueous solutions of their alkali metal salts. However, unlike the styrene and acrylophenone vinyl soaps, these showed only poor emulsifying properties, probably due to the undesirable presence of the highly polar amide group at the end of the molecule opposite to the carboxylate anion.

EXPERIMENTAL[18]

10-Phenylundecanoic acid (IV). (a) *By Friedel-Crafts.* No substantial improvement over the method of Fourneau and Baranger[5] was discovered. The single product, a water white, fairly viscous liquid, had b.p. 187–189° (1.5 mm.), n_D^{25} 1.4959. The yield was generally 45%.[19] λ_{max}^{alc} 260 mμ, ε 265; λ_{max}^{liq} COOH 5.86, 10.65; PhCH 13.12; Ph 6.23, 6.70, 14.29 μ.

Anal. Calcd. for $C_{17}H_{26}O_2$: C, 77.9; H, 10.0; Neut. Equiv. 262.4; C-methyl, 5.7. Found: C, 77.7; H, 10.0; Neut. Equiv. 264.8; C-methyl, 4.2.

The p-bromphenacyl ester was prepared by a standard method and after three crystallizations from alcohol melted at 84–86°.

Anal. Calcd. for $C_{25}H_{31}O_3Br$: C, 66.1; H, 6.8; Br, 17.4. Found: C, 66.0; H, 6.4; Br, 17.2.

The methyl ester (IVA) was prepared by a similar Friedel-Crafts reaction. Again, fractional distillation yielded only a single product, b.p. 160–162° (2 mm.) n_D^{25} 1.4850, unchanged by refractionation through a 50-cm. heated Vigreaux column at a reflux ratio of 50:1. λ_{max}^{MeOH} 260 mμ, ε 220; λ_{max}^{liq} $COOCH_3$ 5.75; C—CH_3 7.28; Ph, 6.25, 6.70, 14.29; PhCH 13.15 μ.

(b) *By unequivocal synthesis:* (1) *9-Benzoylnonanoic acid* (I). This was prepared by the method of Hill.[12] The crude product, contaminated with sebacic acid, was purified by recrystallization from 1:1 aqueous alcohol, rather than by hot water extraction as specified by Hill.[12] The yield of white, crystalline powder, m.p. 83–84°, was 16 g. (20%). An analytical sample was obtained as large, shiny plates from ligroin, m.p. 84–85°.

Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.3; H, 8.4; Neut. Equiv. 262.3. Found: C, 73.3; H, 8.5; Neut. Equiv. 264.4.

Inasmuch as the melting point of our product differed by 5° from those previously reported (Hill[12] gives 77–78° and Papa, et al.[4] report 78–79°), the semicarbazone was prepared; white needles from acetone, m.p. 158–159°.

Anal. Calcd. for $C_{17}H_{25}O_3N_3$: C, 64.1; H, 7.9; N, 13.2. Found: C, 64.4; H, 8.1; N, 13.2.

(2) *Crude 10-phenyl-10-hydroxyundecanoic acid* (II). To 8.5 g. of I in 500 ml. of dry ether under a nitrogen blanket was added dropwise 25 ml. of a 4*N* ethereal solution of methylmagnesium bromide (Arapahoe Chemical Co., used as received) over a 30-min. period. The vigorous reaction was modified by ice bath cooling and resulted in the precipitation of a white solid which did not dissolve after 8 hr. of reflux. The mixture was decomposed with 300 ml. of ice cold 5% sulfuric acid and filtered from 1 g. of starting material. The ether solution was washed, dried, and evapo-

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[16] H. Plaut with J. J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951) and other refs. cited therein.

[17] H. H. Freedman, *J. Am. Chem. Soc.*, **77**, 6003 (1955).

[18] All melting and boiling points are uncorrected. Analyses were performed by Dr. C. K. Fitz, Needham Heights, Mass., and by Dr. K. Ritter, Basel, Switzerland. Ultraviolet spectra were obtained with a Beckman DU and infrared spectra with a Perkin-Elmer Model 12-C spectrophotometer equipped with rock salt optics and a flushing system to minimize atmospheric absorptions.

[19] The very high boiling pot residue, which accounted for an additional 40–50% of starting material, is believed to be low molecular weight polymer of 10-undecenoic acid.[20] This is inferred from its infrared spectrum which shows the complete absence of phenyl absorptions.

[20] J. R. Cann and E. D. Amstutz, *J. Am. Chem. Soc.*, 66, 839 (1944).

rated, leaving 8 g. of a viscous yellow oil whose infrared spectrum indicated that it was a mixture of about 80% of II and 20% of I. Since the oil could not be purified by other methods, the unreacted keto-acid (I) was removed *via* its insoluble semicarbazone. To a solution of the crude product in 40 ml. of dry pyridine was added 1.34 g. of semicarbazide hydrochloride in 5 ml. of water. After brief warming and dilution with water there was obtained 2 g. of the semicarbazone of I. The aqueous pyridine solution was extracted with ether, the extracts washed, dried, and the solvents evaporated. The residue consisted of 3.5 g. (40%) of a non-crystallizable oil which was used without further purification. $\lambda_{\max}^{\text{liq}}$ OH 2.94; C—CH_3 7.27; COOH 5.84; PhCH 13.05; Ph 6.25, 6.69, 14.28 μ (the ketone band of I at 5.93 μ was absent).

(3) *10-Phenyl-10-undecenoic acid* (III). Three g. of II containing 0.5 g. of freshly fused and ground potassium bisulfate was heated at 160–165° (20 mm.) until all frothing and ebullition ceased (30 min.). The residue was dissolved in ether, filtered from inorganic material, and distilled. The fraction boiling at 160–161° (1 mm.) was collected; 1.2 g., (43%) n_{D}^{25} 1.5198. After two days at room temperature it crystallized, m.p. 27–29°. $\lambda_{\max}^{\text{liq}}$ COOH 5.85; C═C (conj.) 6.14, 11.18; PhCH 13.10; PhC═C 6.34; Ph 6.25, 6.69, 14.34 μ.

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.6; H, 9.3; Neut. Equiv. 260.4. Found: C, 80.0; H, 9.5; Neut. Equiv. 262.3.

(4) *10-Phenylundecanoic acid* (IV). A solution of 0.9 g. of III in 30 ml. of absolute alcohol was hydrogenated over platinum oxide (75 mg.) at atmospheric pressure. The solution absorbed 1.0 mole of hydrogen rapidly, and was filtered and distilled. The center cut consisted of 0.3 g. of colorless, fairly viscous liquid n_{D}^{25} 1.4993, $\lambda_{\max}^{\text{MeOH}}$ 260 mμ, ϵ 154. $\lambda_{\max}^{\text{liq}}$ identical to IV as prepared in (a).

Anal. Calcd. for $C_{17}H_{26}O_2$: C, 77.9; H, 10.0. Found: C, 77.8; H, 10.2.

The *amide*, prepared by warming IV with thionyl chloride and reacting with ammonium hydroxide, crystallized after three days in the cold. It was insoluble in water and soluble in hot ligroin. An analytical sample was obtained as colorless plates from ligroin, m.p. 65–65.5°. (Fourneau and Baranger[5] report m.p. 57 and 79° for the 10- and 11-phenylundecanoic acid amide, respectively.)

Anal. Calcd. for $C_{17}H_{27}ON$: N, 5.4. Found: N, 5.4.

Methyl 10-(p-acetylphenyl)undecanoic acid (V). To 55 g. (0.41 mole) of anhydrous aluminum chloride was added cautiously 39 g. (0.5 mole) of acetyl chloride. The resulting slurry was stirred until the initial reaction had subsided and then was warmed gently on the steam bath until a solid cake was formed. When cool, the complex was dispersed in 150 ml. of dry carbon tetrachloride and a solution of 55 g. (0.2 mole) of IVA in 50 ml. of dry carbon tetrachloride was added at such a rate that the temperature was maintained at 35–45°. During the addition, which took 25 min., the reaction mixture turned dark and copious fumes of hydrogen chloride were evolved. After an additional short period of stirring, the mixture was decomposed with an excess of iced dilute hydrochloric acid, the organic layer washed with water until neutral and distilled through a short, heated column. After removal of solvent and a small forerun, the product distilled at 168° (0.05 mm.); 50 g. (80%) of pale yellow liquid, n_{D}^{25} 1.5029. $\lambda_{\max}^{\text{MeOH}}$ 250 mμ, ϵ 17,000; $\lambda_{\max}^{\text{liq}}$ COOMe 5.75; (Ph)CO 5.94; conj. Ph 6.21, 6.38; p-Ph 12.01 μ.

Anal. Calcd. for $C_{20}H_{30}O_3$: C, 75.4; H, 9.5; Sapon. Equiv. 318.4. Found: C, 75.1; H, 9.3; Sapon. Equiv. 319.2.

Any substantial variation from the above procedure gave poor yields of product. For example: (a) when the order of addition of the acetyl chloride and IVA was reversed, degradation of IVA took place and acetylation of the resulting benzene led to the isolation of 20% of acetophenone,[21] (b) when the Perrier technique according to the directions of Mowry[22] was used, 85% of IVA was recovered, and (c) when the ratio of IVA to aluminum chloride was increased to 1:2.5, then there was obtained 50% of non-distillable tar.

The *2,4-dinitrophenylhydrazone* was obtained as a red oil which did not crystallize even after being chromatographed on alumina.

Anal. Calcd. for $C_{26}H_{34}O_6N_4$: C, 62.8; H, 6.9; N, 10.2. Found: C, 62.7; H, 7.3; N, 10.4.

Methyl 10-[p-(α-hydroxyethyl)phenyl]undecanoate (VI). The procedure recommended by Wilds[23] was followed. A mixture of 310 g. (0.97 mole) of V in one liter of absolute isopropyl alcohol and 200 g. (3 eq.) of aluminum isopropoxide (Matheson, pract., m.p. 135–138°) was distilled slowly until the distillate gave a negative test for acetone (3–6 hr.). The residue was decomposed with 800 ml. of 25% hydrochloric acid, the aqueous layer extracted with ether, and the combined organic layers washed and dried. After removal of the solvents the residue consisted of 309 g. (98%) of a pale yellow, somewhat viscous liquid of 97% purity. Distillation afforded 95% of water-white product, b.p. 177–178° (0.025 mm.), n_{D}^{25} 1.4893. $\lambda_{\max}^{\text{MeOH}}$ 258 mμ, ϵ 630; $\lambda_{\max}^{\text{liq}}$ OH 3.90; $COOCH_3$ 5.77; C—CH_3 7.27; p-Ph 6.62, 12.01 μ.

Anal. Calcd. for $C_{20}H_{32}O_3$: C, 75.1; H, 10.1; Sapon. Equiv. 320.5. Found: C, 75.4; H, 10.1; Sapon. Equiv. 322.5.

VI could be successfully distilled only at pressures less than 0.1 mm.; at higher pressures dehydration and polymerization of the resulting styrene took place. A crystalline derivative could not be prepared.

Methyl 10-(p-styryl)undecanoate (VII). Dehydration and simultaneous flash distillation[24] proved to be the only satisfactory method of preparation. Fifty-three g. of VI, inhibited with 0.5 g. of picric acid, was added at a rate of about 15 drops per minute to 5 g. of freshly fused and ground potassium bisulfate while maintaining a temperature of 220–225° and a pressure of at least 0.5 mm. It was necessary to replenish the catalyst at least once due to the accumulation of polymer. There was obtained 36 g. (73%) of colorless, non-viscous liquid, b.p. 170–171° (0.2 mm.), n_{D}^{25} 1.4988, per cent vinyl by bromine titration 98.5%. $\lambda_{\max}^{\text{MeOH}}$ 254 mμ, ϵ 18,000. $\lambda_{\max}^{\text{liq}}$ $COOCH_3$ 5.78; conj. CH═CH_2 6.12, 10.11, 11.07; p-Ph 6.61, 11.92 μ.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.4; H, 10.0; Sapon. Equiv., 302.4. Found: C, 79.7; H, 10.2; Sapon. Equiv. 300.1.

VII was polymerized in bulk at 60° in the presence of bisazoisobutyro-nitrile (AIBN) as initiator; after 40 hr. its infrared spectrum showed the complete absence of vinyl bands. The polymer was a soft tacky plastic which was soluble in acetone, chloroform, and ether, but not in methanol or dilute base.

10-p-Styrylundecanoic acid (VIII). Forty-nine grams (0.165 mole) of the styryl ester (VII) was refluxed for 2 hr. with 250 ml. of 5% methanolic potassium hydroxide solution. The cooled solution was diluted with water, acidified, the liberated oil taken up in peroxide-free ether, the solution washed, dried, and the solvent removed *in vacuo*. Since distillation of VIII was not practical it was necessary to remove the last traces of ether from the very viscous product by agitation under a high vacuum. The residual pale yellow oil weighed 40 g. (85%), n_{D}^{25} 1.5161, vinyl by bromine titration, 98.7%, λ (0.001N KOH) 254 mμ, ϵ 18,000. $\lambda_{\max}^{\text{liq}}$ COOH 5.86; conj. CH═CH_2 6.12, 10.12, 11.10; p-Ph 6.61, 11.96 μ.

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[21] A similar degradation is described by G. F. Hennion and S. F. McLeese, *J. Am. Chem. Soc.*, **64**, 2421 (1942).

[22] D. T. Mowry, M. Renall, and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).

[23] A. L. Wilds in *Org. Reactions*, **II**, 203 (1944).

[24] C. G. Overberger and J. H. Saunders, *Org. Syntheses*, **28**, 31 (1948).

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.1; H, 9.8; Neut. Equiv. 288.4. Found: C, 79.5; H, 9.7; Neut. Equiv., 291.3.

The styryl acid (VIII), when polymerized as described above, required 36 hr. to give a negative test with bromine. The polymer was a medium soft, flexible plastic, soluble in methanol, acetone, and aqueous caustic, but not in chloroform or ether. Polymerization was also effected in 0.2*N* aqueous potassium hydroxide solution in the presence of persulfate. After 48 hr. the polymer was precipitated by acidification, λ_{max}^{MeOH} 266 mμ, ε 600.

p-Ethyl-β-chloropropiophenone (XI). The general method of Hale and Britten[25] was followed. From 25.4 g. (0.2 mole) of β-chloropropionyl chloride [Matheson, b.p. 67–70° (50 mm.)], 100 ml. of ethylbenzene and 28 g. (0.21 mole) of anhydrous aluminum chloride there was obtained, after decomposition with acid and extraction with ether, 37 g. of a yellow oil with a pleasant, fruity odor. Crystallization from alcohol afforded 15 g. (40%) of white solid, m.p. 61–63°. An analytical sample was obtained as shiny platelets from alcohol, m.p. 65.5–66.5°. λ_{max}^{MeOH} 255 mμ, ε 15,000.

Anal. Calcd. for $C_{11}H_{13}OCl$: C, 67.3; H, 6.6; Cl, 18.0. Found: C, 67.0; H, 6.5; Cl, 18.0.

The 2,4-dinitrophenylhydrazone was obtained as short, red-orange needles from alcohol–ethyl acetate, m.p. 122–123°.

Anal. Calcd. for $C_{17}H_{17}N_4O_4Cl$: C, 54.3; H, 4.5; N, 14.8; Cl, 9.4. Found: C, 55.1; H, 4.6; N, 14.9; Cl, 9.1.

Reaction of XI with methanolic base. When 6 g. (0.03 mole) of XI, inhibited with hydroquinone, was refluxed briefly in 50 ml. of anhydrous methanol containing 2.8 g. (0.05 mole) of potassium hydroxide there was obtained 1.0 g. (50%) of potassium chloride. After dilution with water, extraction with ether, and evaporation *in vacuo*, there was isolated a mixture of viscous liquid and white solid. The solid (0.8 g., 20%) melted at 165–167° and was identified as XX by its infrared spectrum. Distillation of the liquid yielded 2.5 g. (40%) of *p-ethyl-β-methoxypropiophenone* (XVIII), b.p. 97–97.5°, n_D^{25} 1.5202.

Anal. Calcd. for $C_{18}H_{20}O_5N_4$: C, 58.2; H, 5.4; N, 15.0. Found: C, 58.4; H, 5.4; N, 14.5.

The non-distillable residue consisted of 2 g. (40%) of poly-[*p*-ethylacrylophenone], identified by its properties and infrared spectrum.

p-Ethylacrylophenone (XV). A solution of 5.0 g. (0.025 mole) of XI was refluxed for 1 hr. in 25 ml. of methanol containing 4.0 g. (0.040 mole) of anhydrous potassium acetate and a trace of picric acid. After the removal of 1.86 g. (98%) of potassium chloride the clear solution was diluted with water and extracted with chloroform. Distillation yielded 3.5 g. (85%) of colorless liquid, b.p. 72–73° (0.2 mm.), n_D^{25} 1.5480. λ_{max}^{MeOH} 269 mμ, ε 8700. λ_{max}^{liq} conj. CO 6.00; CH=CH$_2$ 6.22, 10.03, 11.70 μ.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.5; H, 7.5. Found: C, 82.4; H, 7.5.

XV was stable when kept cold but polymerized after two weeks at room temperature to a clear, hard plastic, readily soluble in chloroform and in acetone. When polymerized at 70° in the presence of AIBN it gave a negative bromine test after 15 hr.

XV was quantitatively hydrogenated to *p-ethylpropiophenone* over platinum oxide in alcohol. The oil obtained on distillation was converted to its 2,4-dinitrophenylhydrazone; red needles from alcohol–ethyl acetate, m.p. 160–170°.

Anal. Calcd. for $C_{17}H_{18}N_4O_4$: C, 59.7; H, 5.3; N, 16.4. Found: C, 59.9; H, 5.4; N, 16.1.

2-(p-Ethylbenzoyl)-6-(p-ethylphenyl)-2,3-dihydropyrane (XX). A solution of 1.0 g. of XV in 3% methanolic potassium hydroxide was left overnight at room temperature. The solid was collected and combined with an additional crop, obtained on concentrating the filtrate; 0.5 g. (50%), m.p. 159–63°. An analytical sample was obtained as a microcrystalline, white powder from ligroin, m.p. 167.5–168.5°. The structure of this compound has not been proved.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.5; H, 7.5. Found: C, 82.4; H, 7.6.

Ethyl β-chloropropiophenone-4-acetate (XII). The procedure for the preparation of XI was followed. From 21 ml. (0.2 mole) of β-chloropropionyl chloride, 16.4 g. (0.1 mole) of ethyl phenylacetate [b.p. 117.4–118.5° (18 mm.)], and 27 g. (0.2 mole) of anhydrous aluminum chloride in 100 ml. of carbon disulfide there was obtained 5 g. (20%) of white crystals. An analytical sample was obtained as white platelets from ligroin, m.p. 73.5–74.5°. λ_{max}^{MeOH} 250 mμ, ε 16,000.

Anal. Calcd. for $C_{13}H_{15}O_3Cl$: C, 61.2; H, 6.0; Cl, 13.9. Found: C, 61.0; H, 5.9; Cl, 14.1.

Methyl 10-(p-acrylylphenyl)undecanoate (XVI). Methyl 10-[*p*-(β-chloropropionyl)phenyl]undecanoate (XIII) was prepared by the preformed complex technique as described for V, substituting β-chloropropionyl chloride for acetyl chloride. The resulting dark, viscous oil could not be distilled without decomposition and was converted to XVI by treatment with potassium acetate in alcohol. The crude vinyl ketone ester (XVI) was obtained in yields of 75–85% and was purified by molecular distillation using a falling-film still (Scientific Glass, No. J-1256, slightly modified and heated with a 500-watt heating tape). When 14 g. of crude XVI was thus distilled at 10^{-5} mm. there was obtained 10 g. (72%) of pale yellow liquid, n_D^{25} 1.5127. λ_{max}^{MeOH} 269 mμ, ε 8000. λ_{max}^{liq} COOCH$_3$ 5.76; conj. CO 5.99; conj. CH=CH$_2$ 6.22, 10.01, 11.72 μ.

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.4; H, 9.1. Found: C, 76.5; H, 9.2.

Three grams of XVI was converted to *methyl 10-(p-propionylphenyl)undecanoate* by catalytic hydrogenation. Distillation yielded 2.7 g. (90%) of colorless liquid, b.p. 170–171° (0.05 mm.) n_D^{25} 1.5012. λ_{max}^{MeOH} 255 mμ, ε 15,000.

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.8; H, 9.7. Found: C, 75.4; H, 9.6.

Poly-XVI was prepared by polymerizing 3 g. of XVI in the presence of benzoyl peroxide at 60°. After 20 hr. the infrared spectrum of the soft polymer showed the complete absence of vinyl bands. The polymer was insoluble in methanol and in ethanol.

Mixture of XIV *and* XIX. The preformed complex technique was again used. The complex formed from 1 mole of β-chloropropionyl chloride and anhydrous aluminum chloride was dispersed in carbon disulfide, carbon tetrachloride, or nitromethane, and 0.5 mole of IV added dropwise. When the vigorous reaction had subsided the mixture was maintained at 50° or at reflux, depending on the solvent, and then decomposed and isolated as usual. The purity of the product, *i.e.* the absence of IV, was determined by its infrared and ultraviolet spectra; in the event that a thick film showed the presence of more than a trace of IV (bands at 13.1 and 14.5 μ), the reaction mixture was discarded since no practical method of separation was discovered. The mixture of XIV and XIX was usually obtained as a viscous, red oil in yields of 85–95%. λ_{max}^{MeOH} 255 mμ, E 37.5 g./l. λ_{max}^{liq} COOCH$_3$ 5.75; COOH 5.85; conj. CO 5.93 μ.

Anal. Calcd. for 60% $C_{20}H_{29}O_3Cl$ plus 40% $C_{41}H_{57}O_6Cl$: C, 69.7; H, 8.3; Cl, 8.2. Found: C, 69.6; H, 8.4; Cl, 8.4.

Mixture of XVII *and* XXI. Dehydrohalogenation of the above mixture was carried out with potassium acetate in alcohol as described previously. After removal of the precipitated potassium chloride and evaporation of the solvent *in vacuo* the yield of viscous, amber to red oil was 75–85%. λ_{max}^{MeOH} 264 mμ, E 24.2 g./l. Except for the carboxyl CO band at 5.83 μ, the infrared spectrum was very similar to that of XVI. Titration with base: neut. equiv. 398.2 (calcd.) 397 ± 2 (found); per cent ester (by saponification with excess base and back titration) 40% (assumed), 39 ± 2% (found).

Anal. Calcd. for $C_{20}H_{28}O_3$ plus $C_{40}H_{56}O_6$: C, 76.0; H, 8.9. Found: C, 76.2; H, 9.1.

The composition of the mixture was verified by ultraviolet spectrophotometric analysis. The band at 264 mμ

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[25] W. H. Hale and E. C. Britten, *J. Am. Chem. Soc.*, **41**, 845 (1919).

is at a shorter wave length than that typical of the pure vinyl-conjugated ketone (*cf.* XVI, λ_{max} 269 mμ) and at a longer wave length than that of the nonvinyl conjugated ketones which absorb at 255 mμ. By using a standard method of two component analysis, with XIII and XVI as standards, it was calculated that the mixture consisted of 79% of vinyl ketone equivalent to XVII, and since one half of XXI is included in this figure, this agrees very well with the postulated composition of 60% of XVII and 40% of XXI.

The mixture could be stored in the cold without change for long periods of time, but when freed from inhibitor by thorough washing, it polymerized to a soft, rubbery material after 5 hours at room temperature. A sample was also polymerized as its potassium salt in water in the presence of potassium persulfate at 50°. After 19 hours the solution no longer decolorized bromine. λ_{max}^{MeOH} 258 mμ, ϵ 15,000.

Acknowledgments. We are indebted to Miss Dorothy P. Harrington for the ultraviolet spectra and much of the analytical work, to Professor W. J. Gensler for many helpful discussions, and to the General Latex and Chemical Corp., Cambridge, Mass., for permission to publish these results.

BOSTON, MASS.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE ETHYL CORP.]

Catalytic Graphite Inclusion Compounds. I. Potassium Graphite as a Polymerization Catalyst

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Received July 8, 1957

Potassium graphite, KC_8, has been found to catalyze the polymerization of ethylene at low pressure. The effects of various reaction conditions, including concentration of catalyst, catalyst support, and additives, were studied.

Alkali metals are known to catalyze the polymerization of ethylene.[1,2] However, high temperatures and pressures are generally required, and liquid rather than solid ethylene polymers are produced. While investigating the reactivity of various alkali metal compounds with olefins, it was surprisingly found that potassium graphite, KC_8, suspended in 2,4,4-trimethylpentane (isooctane) catalyzed the polymerization of ethylene at 200° and only 1000 p.s.i.g. pressure. The products were found to consist of C_8-C_{14} *trans*-monolefins and a small quantity of low molecular weight *solid* polyethylene. Infrared analysis of the polyethylene indicated it to be essentially linear. Consequently, it was of interest to explore the catalytic activity of potassium graphite and other graphite inclusion compounds in olefin polymerizations. This paper is concerned with results obtained with ethylene.

Reaction variable study. The polymerization of ethylene in isooctane or *n*-heptane by means of catalytic amounts of potassium graphite did not occur until a temperature of 180–200° was reached. Moreover, it appeared necessary to maintain this temperature for the reaction to continue. Use of long reaction times (five days) at lower temperatures, 120–150°, resulted in no significant polymerization.

In going from isooctane to *n*-heptane the yield and degree of polymerization showed a significant increase. Use of benzene, toluene, or isopropylbenzene as solvents resulted in alkylation of these substances. They therefore were not suitable as solvents for the polymerization reaction. The alkylation reactions will be discussed in a subsequent paper.

Upon increasing the concentration of suspended KC_8 catalyst, the yield of polymerized ethylene increased in both isooctane and *n*-heptane. However, upon going to a very concentrated slurry of catalyst, no significant polymerization occurred. It therefore appears that there must be present sufficient ethylene in solution so that the initiation and chain growth reactions can favorably compete with the termination reactions.

The greater effectiveness of the potassium graphite inclusion compound over other alkali metals as an ethylene polymerization catalyst could be due to the high surface area of the potassium in the inclusion compound. To test this idea, potassium was dispersed over potassium chloride in one experiment and over sodium monoxide in another experiment. Each of these systems was tested for catalytic activity with ethylene. As was expected, K/KCl also catalyzed the polymerization of ethylene. However, no solid polymer was produced, and the yield of polymerized ethylene was only about one-third that obtained with KC_8 under comparable conditions. The K/Na_2O showed no catalytic activity toward ethylene, in the absence or presence of isopropylbenzene.[3] A plausible explanation for this apparent discrepancy is that the potassium

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(1) H. W. Walker, *J. Phys. Chem.*, **31**, 961 (1927).

(2) K. Clusius and H. Mollet, *Helv. Chim. Acta*, **39**, 363 (1956).

(3) It is interesting to note that K/Na_2O very effectively metalates such alkylbenzenes as toluene and isopropylbenzene in the α-position [C. E. Claff and A. A. Morton, *J. Org. Chem.*, **20**, 440, 981 (1955)]. Consequently, it would appear that potassium isopropylbenzene is also a relatively ineffective ethylene polymerization catalyst.