tallization from ethanol, and no depression of the m.p. was noted upon admixture with authentic acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 145–147°.

Evaporation of the ether extract of the distillate left a residue which was treated with 2,4-dinitrophenylhydrazine dissolved in ethanolic sulfuric acid. The resulting precipitate melted at 215–230° and evidently consisted chiefly of the benzaldehyde derivative, but the amount obtained by this procedure was too small to permit further purification.

The residual solution from the distillation was acidified with 10% hydrochloric acid. A small amount of white crystalline material separated. White leaflets, m.p. 112–114°, were obtained after one crystallization. Lack of sufficient material prevented further purification and positive identification of this substance, which resembled benzoic acid in solubility and appearance. From another similar run the acid fraction was obtained as white leaflets, m.p. 117–120.5°, and the m.p. was not depressed by admixture with benzoic acid.

No substance with properties which might have corresponded to those of the epoxide of cinnamoyldibenzoylmethane was found. The molecule of compound VIII was apparently degraded completely.

Attempted Oxidation of N-Desylacetanilide (VI) and N-Phenacylacetanilide (VII).—A 1-g. sample of N-desylacetanilide (VI)[13] or N-phenylacylacetanilide (VII)[14] was dissolved in 25 ml. of warm ethanol and 4 ml. of 4 *N* aqueous sodium hydroxide or alcoholic potassium hydroxide was added. The solution turned deep yellow when the alkali was added. Similar color changes had been noticed previously in the experiments with compounds II and IV. However, after 4 ml. of 30% hydrogen peroxide had been added to the alkaline solution of VI or VII and the solution had been allowed to stand for 1 hour, dilution of the mixture with water precipitated unchanged starting material. The same result was obtained with compound VI when the oxidation mixture was allowed to stand overnight.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Vinylation and the Formation of Acylals

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The reaction of the allyl acid esters of several dicarboxylic acids with acetylene gives rise not only to allyl vinyl esters but also to acylals such as ethylidene bis-(allyl succinate) and ethylidene bis-(allyl adipate). Ethyl hydrogen fumarate undergoes acid-catalyzed addition to ethyl vinyl fumarate, yielding ethylidene bis (ethyl fumarate). Two more acylals, 1-acetoxyethyl vinyl adipate and sebacate, were prepared by reactions of vinyl acetate with adipic and sebacic acids, respectively. Isopropenyl acetate and adipic acid yielded, instead, adipic anhydride.

A considerable literature deals with the formation of vinyl esters by reaction of an acid with either acetylene or vinyl acetate. Not only monocarboxylic acids but also some dicarboxylic acids as well as their half esters have been studied.[2–7] In such conversions, continuing reaction of the acid with the vinyl esters may lead to acylals

$$\mathrm{RCOOH + CH_2{=}CHOCOR \longrightarrow CH_3CH(OCOR)_2}$$

Although this is well known as regards vinyl acetate and ethylidene acetate it has received but little notice in more complex systems. The problem has been discussed by Adelman[4] who calls attention to the three modes of reaction which are encountered when a carboxylic acid reacts with vinyl acetate: (1) ester formation at low temperatures (20–30°), yielding $\mathrm{RCOOCH{=}CH_2}$, when catalyzed by mercuric salts of strong acids; (2) acylal formation at higher temperatures (above 80°), yielding $\mathrm{CH_3CH(OAc)(OCOR)}$, in the presence of acid catalysts; (3) acid anhydride formation, by operating in the vapor phase in the presence of acid catalysts.

In the present investigation, our work was concerned with vinylation of acid esters of dicarboxylic acids using both acetylene and vinyl acetate as reagents. Starting with acetylene and the appropriate allyl hydrogen ester we prepared the allyl vinyl esters of succinic, adipic, sebacic and fumaric acids; and from ethyl hydrogen fumarate we obtained ethyl vinyl fumarate. The catalyst used was the mercuric salt of the acid taken, together with boron fluoride and hydrofluoric acid.

The esters were purified by giving them an alkaline wash, then vacuum distillation. A higher boiling residue was always present which contained acylals. This is noteworthy since these experiments were conducted at room temperature, rather than above 80° which was the temperature mentioned by Adelman[4] for the acid-catalyzed addition of acids to vinyl acetate, and the difference may have been caused by the type of catalyst used in the former system. The acylals were separated in some of the runs but not all, namely, with the derivatives of succinic and adipic acids. These acylals were ethylidene bis-(allyl succinate) and ethylidene bis-(allyl adipate), $\mathrm{CH_3CH(OCO(CH_2)_{\mathit{n}}COOCH_2CH{=}CH_2)_2}$, wherein $n = 2$ or 4.

To explain the formation of these acylals from acetylene it is reasonable to assume that the acid, after first adding acetylene to yield the vinyl ester, added to the vinyl ester in the manner of this equation

$$\mathrm{CH_2{=}CHOCOR + HOCOR \longrightarrow CH_3CH(OCOR)_2}$$

Indeed, it was established that ethyl hydrogen fumarate added readily to ethyl vinyl fumarate

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[2] T. Asahara and M. Tomita, *Yushi Kagaku Kyôhaishi*, 1, 76 (1952); *C. A.*, **47**, 3232 (1953).

[3] C. Walling, THIS JOURNAL, **67**, 441 (1945).

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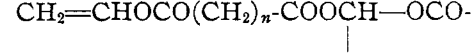
[5] *N. V. de Bataafsche Petroleum Maatschappij*, Dutch patent 70,514; *C. A.*, **47**, 3040 (1953).

[6] J. Furukawa, A. Onishi and Y. Hashiguchi, *J. Chem. Soc. Japan*, **61**, 42 (1946); *C. A.*, **44**, 9185 (1950).

[7] O. Nicodemus, H. Lange and O. Horn, German patent 638,003; *C. A.*, **31**, 3939 (1937); U. S. Patent 2,153,987, *C. A.*, **33**, 5412 (1939).

at 100° (but not at 65°) in the presence of *p*-toluenesulfonic acid to yield ethylidene bis-(ethyl fumarate), $CH_3CH(OCOCH{=}CHCOOC_2H_5)_2$.

In the vinylation of adipic and sebacic acids with vinyl acetate (catalysts: mercuric acetate, *p*-toluenesulfonic acid) at reflux temperature vinyl adipate and vinyl sebacate were formed as expected but acylals were produced also, appearing in the higher boiling products. These acylals were 1-acetoxyethyl vinyl adipate and 1-acetoxyethyl vinyl sebacate,  $CH_2{=}CHOCO(CH_2)_n\text{-}COOCH(CH_3)\text{—}OCO\text{-}CH_3$, wherein $n = 4$ or 8. It would seem, therefore, that the diacid gave rise not only to divinyl esters by vinyl interchange but also to some vinyl acid ester, $CH_2{=}CHOCO(CH_2)_nCOOH$, which added in part to the vinyl acetate under conditions of the reaction. Another acylal, ethylidene acetate, was formed also, its formation being caused by addition of vinyl acetate to the acetic acid which was formed in the first step.

A reaction of adipic acid and isopropenyl acetate was carried out to see whether isopropenylation could be accomplished, analogous to vinylation with vinyl acetate. Instead of ester formation, however, the product isolated was adipic anhydride. Similar treatment of benzoic acid and isopropenyl acetate gave excellent yields of benzoic anhydride.

Experimental

Diallyl esters of succinic, adipic, sebacic and fumaric acids were prepared. Their boiling points, respectively, were 125–126° at 10 mm., 149° at 9 mm., 198° at 13 mm., 116–120° at 8 mm. In part, these esters were intentionally prepared but in part they appeared as concurrent reaction products during the preparation of the half esters (as allyl hydrogen succinate). Accordingly, in most of the preparations of the half esters, the diester was diluted with about an equal volume of butyl ether and mixed with about a 5-fold excess of the corresponding diacid. Concentrated hydrochloric acid was added as catalyst and the mixture was refluxed for 3 to 6 hours. Then allyl alcohol was added and the refluxing was continued for 5 hours more. At the end of this period, the monoester and unused diacid were dissolved in sodium bicarbonate solution and the unreacted diester (which was always present) was extracted with ether. After acidification of the aqueous solution the allyl hydrogen succinate was removed by repeated extraction with chloroform or ether. Allyl hydrogen adipate and sebacate were extracted with ether. The acid esters were purified further by distillation: allyl hydrogen succinate at 148° at 8 mm. (m.p. about 5°), allyl hydrogen adipate at 168–170° at 9.5 mm. (m.p. about 6°), allyl hydrogen fumarate at 145–149° at 9 mm. (m.p. 66–68°). Ethyl hydrogen fumarate, b.p. 146–149° at 18 mm. (m.p. 67°) was prepared also. Yields were about 80%.

Allyl Hydrogen Sebacate.—This acid ester was prepared similarly. These details of its separation from sebacic acid are of interest. After removal of allyl sebacate from the sodium salts, the alkaline solution was partly neutralized. The end-point of addition of hydrochloric acid was reached when the stirred solution became very turbid with oil droplets but before separation of solid sebacic acid. The oily acid ester floated to the surface, was separated, and the aqueous layer was extracted with ether. Then, on addition of more hydrochloric acid to the water layer, a white flocculent sebacic acid separated.

The ether layer of acid ester was washed with water, dried (Na_2SO_4), and distilled; b.p. 210–216° (15 min.). On redistillation, a sample was collected at 205–208° (9 mm.) for analysis. It solidified in white flakes of m.p. 34–35°, which were pressed on a porous plate prior to analysis.

Anal. Calcd. for $C_{13}H_{22}O_4$: neut. equiv., 242.3. Found: neut. equiv., 241.3.

Vinylation Using Acetylene.—This general procedure was used for allyl (or ethyl) hydrogen succinate, adipate, sebacate and fumarate. The weight of acid ester taken ranged from 50 to 160 g. One gram of mercuric oxide was taken for each 50 g. of acid ester, and this mixture was warmed at 90–100° until the oxide had dissolved. Then a little boron fluoride (1 g.) was dissolved in a small amount (5 g.) of the pure acid ester.

The acid ester containing the mercuric oxide was diluted with 50–100 ml. of dioxane, which seemed to augment the yield of vinyl ester and to lessen the production of the higher boiling acylals. Then, 0.2–0.5 g. of hydroquinone or pyrogallol was added and the apparatus containing it was flushed out with acetylene. Next, about one-third of the BF_3-catalyst was added together with 8–10 drops of 47% hydrofluoric acid to start the absorption of acetylene. An attached bubble counting device was used to measure the rate of absorption. When it slackened more of the fluorides were added. In the several runs, a total of 20 to 50 drops of hydrofluoric acid was used. The color change was from yellow-orange at the start to brown at the finish. The duration was 22–36 hours, during which times a little more than the calculated volume of acetylene was absorbed. Undissolved brown solid, seemingly polymeric material, was always formed and was separated. This weighed 1–4 g. per 50 g. except that from the fumaric derivative which weighed 10 g. The filtrate was diluted with ether, and unused acid ester was removed by extraction with a little sodium hydroxide solution, then with an excess of sodium bicarbonate solution. Recovery of the acid ester (after acidification of the alkaline solution) from 50 g. each of the sebacate and fumarate was 18–22 g., whereas 13 g. was recovered from the succinate.

The allyl vinyl esters and the acylals were next separated by vacuum distillation. The yield of allyl vinyl esters on this first distillation was 45–53%, based on unrecovered acid ester, except for allyl vinyl sebacate which was 70%. These esters were purified further by redissolving in ether, extracting again with sodium bicarbonate solution, washing with water, drying and distilling in a 2° range. A mid-fraction was used for determination of constants and analyses. Analyses were all performed by Dr. T. S. Ma. The results are collected in Table I. The density of allyl vinyl fumarate was 1.0799 at 25°; $n^{25}D$ 1.4725. The density of ethyl vinyl fumarate was 1.0703 at 25°; $n^{25}D$ 1.4592.

TABLE I

ESTERS OF DICARBOXYLIC ACIDS

Allyl vinyl ester	B.p. °C.	Mm.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Succinate	110	10	58.7	59.2	6.57	6.57
Adipate	135–136.5	9	62.2	62.7	7.60	7.60
Sebacate	143–144	2	67.1	67.4	9.02	9.18
Fumarate	100–101	9	59.3	58.9	5.53	5.43
Ethyl vinyl fumarate	95	13	56.4	56.4	5.92	6.17

Acylals.—The higher boiling residues from the succinate and the adipate were processed for the acylal content. In an experiment starting with 95 g. of allyl hydrogen succinate of which 23 g. was recovered, there was collected 23.2 g. of a fraction boiling at 140–200° (8 mm.), chiefly at 190°. Since this fraction contained not only ethylidene bis-(allyl succinate) but also a little allyl hydrogen succinate it was washed in ether solution with sodium bicarbonate solution and water, then dried and redistilled. Twelve grams was collected at 186–187° (3 mm.). A central cut was analyzed. The % H was acceptable for the acylal (6.72, 6.67, 6.78) but the % C was high (57.4, 57.3, 57.8); calculated values for $C_{16}H_{22}O_8$ are C, 56.1; H, 6.48.

In the adipic experiment, 158 g. of allyl hydrogen adipate was taken, of which 25 g. was recovered. In the high boiling portion of the products, 28 g. was collected at 150–205° (5 mm.). This fraction contained not only the acylal [ethylidene bis-(allyl adipate)] but also considerable allyl hydrogen adipate which escaped the bicarbonate treatment. The fraction was dissolved in ether and washed repeatedly with sodium bicarbonate solution and water. Eight grams of unextracted material of b.p. 163–215° (1 mm.) was obtained which, on redistillation, yielded a 4-g. fraction of ethylidene bis-(allyl adipate), b.p. 206° (1 mm.).

Anal. Calcd. for $C_{20}H_{30}O_8$: C, 60.3; H, 7.59. Found: C, 60.8; H, 7.67.

Vinylation Using Vinyl Acetate. Adipic Acid (2-hr. heating).—A mixture of 109.5 g. of adipic acid, 344 g. of vinyl acetate, 4 g. of mercuric acetate, 1 g. of pyrogallol and 1 g. of *p*-toluenesulfonic acid monohydrate was refluxed for 2 hours. Five grams of adipic acid separated on cooling and was removed. The mixture was then washed with sodium bicarbonate solution to remove vinyl hydrogen adipate. The remaining vinyl adipate was collected at 115–140° (15 mm.); yield 49.4 g. (33.3%). Most of this fraction was collected at 133°.

The vinyl hydrogen adipate was released by acidification. After extraction with ether and distillation, 28.4 g. (22%) was collected between 166–175° (15 mm.). On redistillation, it boiled at 170.5° (15 mm.). Its melting point was 38.5–40°. The neutral equivalent was 171 (theory, 172).

Adipic Acid (36 hours).—This run differed from the preceding only in that 73 g. of adipic acid and 322 g. of vinyl acetate were used and that the heating period was 36 hours. The sodium bicarbonate extraction gave rise to no vinyl hydrogen adipate. A fraction, b.p. 125–140° (15 mm.), was reëxtracted with sodium bicarbonate to remove any possible adipic acid, then was redistilled: yield 40.0 g. of vinyl adipate, b.p. 126–133° (15 mm.); $n^{25}\text{D}$ 1.4510, d^{25} 1.0460.

A higher boiling fraction was collected from this run. On redistillation 11.4 g. of it was collected at 167–177° (15 mm.). This cut was washed with sodium bicarbonate solution and with water. It then distilled at 128° (3 mm.); $n^{25}\text{D}$ 1.4435. The carbon analysis indicates the presence of some impurity (possibly vinyl hydrogen adipate, which is of comparable b.p.) but essentially it was the ester acylal, 1-acetoxyethyl vinyl adipate. A test portion of this was converted into acetaldehyde (identified as the 2,4-dinitrophenylhydrazone, m.p. 164–166°) by heating in water containing a little *p*-toluenesulfonic acid and mercuric acetate.

Anal. Calcd. for $C_{12}H_{18}O_6$: C, 55.8; H, 7.02. Found: C, 56.8; H, 7.15.

Sebacic Acid.—A mixture of 50.5 g. of sebacic acid, 172 g. of vinyl acetate, 2 g. of mercuric acetate, 0.5 g. of *p*-toluenesulfonic acid and 0.5 g. of pyrogallol was heated for 40 hours on a steam-bath. The solution was cooled, filtered from a gram of solid polymer, washed twice with 5% sodium hydroxide solution then with sodium bicarbonate solution. From these aqueous extracts 2.4 g. of sebacic acid separated on acidification.

After drying and distilling the organic layer, these fractions were collected: unused vinyl acetate and ethylidene acetate, 36.5 g. of a vinyl sebacate fraction at 165–200° (14 mm.), and 19.7 g. of residue. The vinyl sebacate fraction, dissolved in ether, was washed with sodium bicarbonate solution and water, then was dried and redistilled: 1.6 g. of ethylidene acetate (which distilled chiefly at 167° (750 mm.), 21.3 g. of vinyl sebacate at 173–183° (14 mm.), 9.1 g. at 183–215° (14 mm.).

Vinyl Sebacate.—Redistillation of this fraction gave an intermediate cut with these physical properties, which was analyzed: b.p. 172° at 12 mm., *d* 0.9929 (25°), $n^{25}\text{D}$ 1.4544.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.48; H, 8.84.

Vinyl 1-Acetoxyethyl Sebacate.—The fractions boiling higher than vinyl sebacate were combined and distilled at 12 mm. (°C., g., $n^{25}\text{D}$): 180–197°, 3.0, 1.450; 197–205°, 4.2, 1.448; 205–209°, 5.4, 1.446. The density of the last fraction at 25° was 1.022.

Anal. Calcd. for $C_{16}H_{26}O_6$: C, 61.1; H, 8.33. Found: C, 61.8; H, 8.25.

Ethyl Hydrogen Fumarate and Ethyl Vinyl Fumarate.—A mixture containing 0.144 mole each of these two reactants, 0.6 g. of *p*-toluenesulfonic acid and 0.2 g. of pyrogallol was heated on a steam-bath for 17 hours, it having been found that no reaction occurred in 5 hours at 65°. The products were separated by the customary method with sodium bicarbonate into alkali soluble ethyl hydrogen fumarate (18 g. at 142–146° (15 mm.)) and an alkali-insoluble portion. The latter contained 6 g. of ethyl vinyl fumarate (b.p. 98–120° (15 mm.)) and 10 g. of a 120–215° fraction which was taken up in ether, washed with sodium bicarbonate solution, dried and distilled. There was collected 7.1 g. at 161–165° (1 mm.). Another distillation gave the b.p. as 162° (1 mm.); $n^{25}\text{D}$ 1.4638. This material was ethylidene bis-(ethyl fumarate), $CH_3CH(OCOCH{=}CHCOOC_2H_5)_2$. It showed no tendency to polymerize on standing and very little tendency to do so on distillation.

Reactions of Isopropenyl Acetate. Adipic Acid.—A mixture of 100 g. of isopropenyl acetate, 36.5 g. of adipic acid, 2 g. of mercuric acetate, 0.5 g. of pyrogallol and 0.5 g. of *p*-toluenesulfonic acid hydrate was heated on a steam-bath for 9 hours. After cooling and filtration to remove about 2 g. of mercuric acetate, the filtrate was heated to take off the acetone and unreacted isopropenyl acetate. From the residue, 26.2 g. of solid, m.p. 60–65°, was obtained after crystallization from acetone. The solid distilled at 135–190° (8 mm.), the temperature depending on the rate of distillation. The oil distillate gradually solidified; m.p. 60–64°. It underwent slow hydrolysis in sodium bicarbonate solution. These properties are characteristic of adipic anhydride.[8]

Benzoic Acid.—The above experiment was repeated, substituting 50 g. of benzoic acid for the 36.5 g. of adipic acid. The heating period was 12 hours. After removal of the mercuric salt the filtrate was distilled: b.p. 55–63° (acetone), 16 g.; 63–90°, 22 g.; 90–103° (isopropenyl acetate) 40 g.; 137–139° (acetic anhydride), 9.5 g. Practically all of the residue distilled at 192–193° (8 mm.); yield 42 g. (90%). It solidified on cooling; m.p. 41.5–42.5°. This was benzoic anhydride.

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[8] J. W. Hill, THIS JOURNAL, **52**, 4110 (1930); W. Carothers, *ibid.*, **52**, 3471 (1930).