2-Phenylsemicarbazide (I).—1-Phenyl-1-cyanohydrazine was treated with boiling aqueous 10% potassium hydroxide.[20] On cooling the product separated in the form of coarse needles. The orange filtrate was extracted with chloroform, from which more 2-phenylsemicarbazide could be isolated to raise the total yield to 82%. The product was recrystallized from chloroform; m.p. 119.5–120.5°, lit.[20] m.p. 118–119°. The sample used for dipole moment measurements was recrystallized three times.

2-Phenylthiosemicarbazide (II).—A solution of 4.0 g. (0.03 mole) of 1-cyano-1-phenylhydrazine and 2.5 cc. of concentrated ammonium hydroxide in 28 cc. of ethyl alcohol was heated to 50°, while hydrogen sulfide was bubbled through the mixture for 2.5 hours. On cooling, 4.0 g. of white needles, representing a yield of 79.6%, separated. The sample used for dipole moment work was recrystallized three times from 50% ethanol.

2-Phenylselenosemicarbazide (III).—A solution of 3.0 g. (0.0226 mole) of 1-phenyl-1-cyanohydrazine in a mixture of 24 cc. of ethanol and 2.1 cc. of concentrated ammonium hydroxide was heated to 60°. Hydrogen selenide freshly prepared by treating aluminum selenide[31] with dilute acid was bubbled through the mixture for 3.5 hours. After cooling the coarse, gray crystals were filtered off, washed with water, dried and recrystallized from absolute ethyl alcohol. A yield of 3.5 to 4.5 g. (72 to 93%) of delicate, white needles melting at 166.0–166.5° dec. was obtained.

Anal. Calcd. for $C_7H_9N_3Se$: C, 39.26; H, 4.24; N, 19.64. Found: C, 39.48; H, 4.21; N, 19.91.

The sample used for dipole moment measurements was recrystallized three times.

Derivatives of I, II and III.—Compounds I, II or III were refluxed for 24 hours with a slight excess of aldehyde in ethanol or methanol to which a few drops of acetic acid had been added. The semicarbazones, thiosemicarbazones or selenosemicarbazones obtained on cooling were recrystallized from ethanol or methanol.

The *p*-iodobenzaldehyde derivatives (compds. 6 and 11) separated as voluminous masses of fibrous needles, which on standing in solution changed to chunky prisms, possibly indicating *cis–trans* isomerism. Compound 15 was found to form an addition complex with benzene.

Treatment of I, II and III with Cupric Sulfate.—In flasks containing 10 cc. of methanol each, were dissolved 0.0001-mole samples of I, II and III, respectively. To each of the colorless solutions was added 0.100 g. (0.0004 mole) of cupric sulfate in 10 cc. of methanol. The following colors were observed: I, unchanged; II, clear turquoise green; III, dark olive-green rapidly lightening to grass green. A greenish-yellow flocculent precipitate soon separated from the solution containing III, the other solutions remaining clear after 12 hours.

Selenourea.—The method of Verneuil[32] involving the addition of hydrogen selenide to cyanide was utilized. The product was recrystallized twice from absolute ethanol; m.p. 210.0–211.0° dec., m.p. lit.[33] 200°.

Phenylselenourea.—Hydrogen selenide was added to freshly prepared phenyl cyanamide according to the procedure of Zingaro.[33] The dipole moment sample was recrystallized three times from absolute ethanol.

Semicarbazide.—Hydrazine sulfate was permitted to react with potassium cyanate.[34] The product was recrystallized three times from absolute ethanol.

Thiosemicarbazide, Phenylurea, Phenylthiourea.—Commercial, best quality products were recrystallized three times from 50% ethanol.

Ultraviolet Spectra.—A Cary recording spectrophotometer model 11 PMS with quartz cells was utilized. Solutions were made up in volumetric flasks with absolute ethanol from weighed quantities of the compounds.

Infrared Spectra.—Measurements were made with a Perkin–Elmer model 21 infrared spectrophotometer, using perfluorokerosene mulls.

Dipole Moments.—The heterodyne-beat method was used. Solvents were purified as previously indicated.[35]

Acknowledgments.—We wish to express our thanks to Mr. M. K. Hrenoff for measuring the spectra reported, and to Mr. B. H. Tashinian of the Microanalytical Laboratory of the Chemistry Department of the University of California for performing the combustion analyses.

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[31] G. R. Waitkins and R. Shutt in W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 184.

[32] A. Verneuil, *Ann. chim.*, [6] **9**, 294 (1886).

[33] R. A. Zingaro, F. C. Bennett, Jr., and G. W. Hammer, *J. Org. Chem.*, **18**, 292 (1953).

[34] L. Bouveault and R. Locquin, *Bull. soc. chim.*, [3] **33**, 163 (1905).

[35] W. D. Kumler, THIS JOURNAL, **62**, 3292 (1940).

SAN FRANCISCO, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

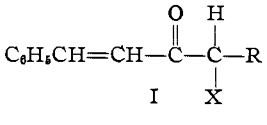
A Cleavage of Certain α,β-Unsaturated Ketones by Alkaline Hydrogen Peroxide

BY PHILIP L. SOUTHWICK, HAROLD L. DIMOND,[1] MEAD S. MOORES AND DAVID I. SAPPER[2]

RECEIVED JULY 20, 1955

The α′-substituted α,β-unsaturated ketones N-acetyl-1-*p*-chloroanilino-4-phenyl-3-butene-2-one (II) and N-acetyl-1-anilino-1,4-diphenyl-3-butene-2-one (IV) were not converted into the corresponding epoxides by alkaline hydrogen peroxide in aqueous ethanol but underwent oxidative cleavage instead. Compound II yielded *p*-chloroacetanilide and compound IV yielded benzanilide; other identified products from the reaction with IV were benzaldehyde and acetaldehyde. The hypothesis that this type of cleavage is characteristic of α,β-unsaturated ketones with functional groups in the α′-position led to the finding that cinnamoyldibenzoylmethane (VIII) is cleaved in an apparently similar manner. A partial explanation of these cleavage reactions is suggested.

Oxidation with alkaline hydrogen peroxide, as described by Weitz and Scheffer[3] in 1921, has been used successfully for preparation of the epoxides of many α,β-unsaturated ketones and aldehydes. We wish to report, however, that alkaline hydrogen peroxide oxidation can follow quite a different course in the case of α,β-unsaturated ketones of the type I, wherein certain functional groups X and one or two hydrogen atoms are present in the α′-position. In the three cases of this kind which we have thus far investigated, a cleavage of the molecule into three or more fragments has occurred,



$$\mathrm{C_6H_5CH{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}R}$$

I

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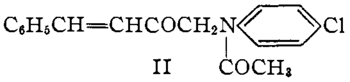
[1] Institute Fellow in Organic Chemistry, 1951–1953.

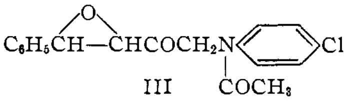
[2] Research Corporation Fellow, 1951–1952. This paper is based mainly on a portion of a thesis submitted by David I. Sapper in partial fulfillment of the requirements for the degree of Doctor of Science at the Carnegie Institute of Technology, July, 1952.

[3] E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

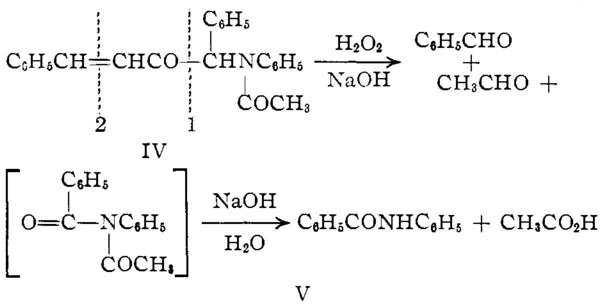
Investigation of the cleavage reaction was prompted by the observation that N-acetyl-1-*p*-chloroanilino-4-phenyl-3-butene-2-one (II), reacted rapidly with alkaline hydrogen peroxide (sodium hydroxide and hydrogen peroxide in aqueous ethanol) but produced *p*-chloroacetanilide instead of the desired epoxide III. The nature of the reaction became much more apparent when N-acetyl-1-anilino-1,4-diphenyl-3-butene-2-one (IV) in a similar oxidation gave an 88% yield of benzanilide; the benzanilide obviously resulted from oxidation at carbon atom 1 (the α'-carbon) with cleavage of that carbon atom from the rest of the chain at the point indicated by the dotted line 1 in formula IV. A search for compounds formed from the cinnamoyl group which was cleaved away from carbon 1 disclosed no products containing the intact skeleton of that group but demonstrated the presence of benzaldehyde and acetaldehyde, both of which were isolated as 2,4-dinitrophenylhydrazones. It was evident, therefore, that the molecule also had been cleaved at the olefinic double bond, as indicated by dotted line 2. A small amount of benzoic acid was obtained, and acetic acid must also have been produced, although no attempt was made to isolate it. The acetaldehyde seemingly arose from compound IV and not from oxidation of the ethanol in the solvent mixture; no acetaldehyde 2,4-dinitrophenylhydrazone was obtained from ethanol following treatment with alkaline hydrogen peroxide under the same conditions and processing of the mixture by the same procedure used in the cleavage experiment.



II

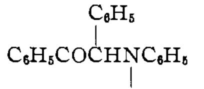


III

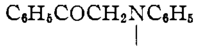


The postulation of N-benzoylacetanilide (V) as a primary cleavage product seems indicated by consideration of the necessity to account not only for the formation of benzanilide from IV but also for the formation of *p*-chloroacetanilide from II. The presumption that a diacylamine intermediate is formed in the cleavage of both compounds would accommodate these facts on the basis of a preferential hydrolysis or ethanolysis of the acetyl group from the intermediate V and a similar removal of the formyl group from the analogous intermediate, N-formyl-*p*-chloroacetanilide, expected to be formed initially from the cleavage of II.

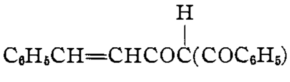
The cleavage reaction is not characteristic of the N-acetyl derivatives of α-anilino ketones in general; N-desylacetanilide (VI) and N-phenacylacetanilide (VII) are recovered unchanged after treatment with alkaline hydrogen peroxide. Like compounds II and IV, however, alkaline alcoholic solutions of these compounds show a deep-yellow color which is evidently due to the formation of enolates. These observations led to the hypothesis that α,β-unsaturation and a rather readily enolizable hydrogen on the α'-carbon are necessary and sufficient to render a ketone susceptible to the cleavage. As a test of this hypothesis the compound cinnamoyldibenzoylmethane (VIII) was synthesized and treated with alkaline hydrogen peroxide. Like II and IV it failed to yield the epoxide and was cleaved with the formation of benzaldehyde and acetaldehyde. The only other product observed was a small amount of what appeared to be impure benzoic acid. Because the procedure used with this reaction mixture was designed primarily for the separation of the aldehyde fraction, the quantity of acid obtained was too small to permit a fully satisfactory purification and identification.



$C_6H_5CO\overset{\displaystyle C_6H_5}{CH}\underset{\displaystyle COCH_3}{N}C_6H_5$ VI

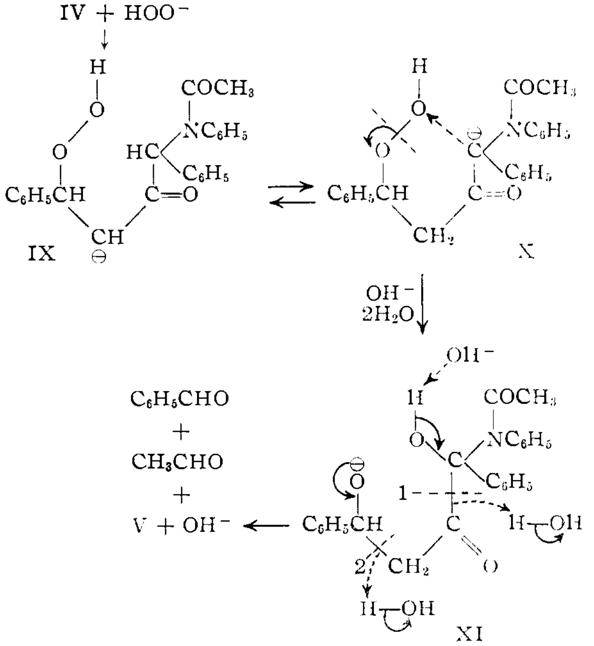


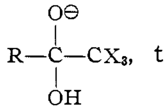
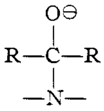
$C_6H_5COCH_2\underset{\displaystyle COCH_3}{N}C_6H_5$ VII



$C_6H_5CH{=}CHCO\overset{\displaystyle H}{C}(COC_6H_5)_2$ VIII

The failure of compounds VI and VII to be oxidized suggests that the attack upon the α'-position in compounds II and IV must be preceded by the attack which occurs on the α,β-unsaturation. Such a requirement would seem to be explained best by the assumption that the oxidation at the α'-position is accomplished by interaction with a hydroperoxide group initially introduced at the β-position. Using compound IV as the example, the following sequence may be proposed for the first stages of the cleavage



Bunton and Minkoff[4,5] have shown that in the case of other α,β-unsaturated ketones the reaction kinetics of the alkaline hydrogen peroxide oxidation (first order with respect to both the ketone and the hydroperoxide ion) is in accord with the formation of an intermediate anion such as IX. In the case of compound IV and the other compounds which undergo the cleavage reaction, a tendency for an anion such as IX to be transformed into an anion such as X would be expected because of the apparent acidity of the α′-hydrogen. Intermediate X could then undergo an internal displacement *via* a quasi six-membered ring, as indicated. The result would be a transformation into XI rather than the normal internal displacement within the first intermediate anion IX to yield an epoxide by loss of an hydroxide ion. The reverse aldol reaction represented by the cleavage of XI at dotted line 2 would follow as a normal consequence, and the only remaining aspect of the reaction which would seem to require comment is the observed cleavage of the carbon–carbon bond at dotted line 1 to yield the diacylamine V and finally benzanilide. Cleavage of the carbon–nitrogen bond at the α′-position with the formation of acetanilide might seem to be a somewhat more likely mode of decomposition for the hypothetical intermediate XI. It should be noted, however, that if the cleavage phase of the haloform reaction involves an intermediate of the form  $\mathrm{R{-}\underset{OH}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}}{-}CX_3}$, there exists an analogy not too distant from the carbon–carbon cleavage under mild conditions postulated for XI. And if reactions under more severe conditions are taken into account, the cleavage of benzophenone into benzene and a sodium derivative of benzamide by treatment with sodium amide in boiling toluene[6] would seem to constitute a precedent for the formation of an amide *via* carbon–carbon bond cleavage from an intermediate of the type  $\mathrm{R{-}\underset{{-}N{-}}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}}{-}R'}$.

Experimental[7,8]

Oxidation of N-Acetyl-1-anilino-1,4-diphenyl-3-butene-2-one (IV).—To a solution prepared from 3.7 g. (0.11 mole) of compound IV[9] and 75 ml. of ethanol was added 10 ml. of 30% hydrogen peroxide and 10 ml. of 4 *N* aqueous sodium hydroxide. The mixture was allowed to warm to 40° and was then cooled somewhat in a bath of cold water. At the end of 45 minutes the mixture was diluted with 225 ml. of water and the precipitated white crystalline product was removed by filtration and dried. This product, which melted at 160–161°, was shown to be benzanilide. A mixture of the substance with benzanilide showed an undepressed melting point. The yield was 1.8 g. (88%).

After removal of the benzanilide the filtrate was distilled. Three 100-ml. portions of distillate were collected, each of which had the odor of benzaldehyde. A sample of the first distillate fraction yielded benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 231–234°, after treatment with 2,4-dinitrophenylhydrazine in sulfuric acid and recrystallization of the product from ethanol. There was no melting point depression when the sample was mixed with an authentic sample, m.p. 235–237°.

The remainder of the first 100-ml. fraction was extracted with ether to remove the benzaldehyde, then treated with 2,4-dinitrophenylhydrazine dissolved in concentrated sulfuric acid. Crystallization of the resulting yellow precipitate from ethanol yielded two types of crystals, one melting at 144–147° after four recrystallizations from methanol and the other at 155–160° after five recrystallizations from ethanol. The fraction melting at 144–147° was not depressed in melting point by an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone (m.p. 145–147°) and analytical results also identified the substance as the acetaldehyde derivative, although the somewhat high carbon value suggested contamination with a small amount of the benzaldehyde derivative.

Anal. Calcd. for $C_8H_8N_4O_4$: C, 42.86; H, 3.59. Found: C, 43.83; H, 3.65.

A melting point of 144–149° was obtained for a mixture of the fraction of m.p. 155–160° with an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 145–147°. Acetaldehyde 2,4-dinitrophenylhydrazone is known to exist in dimorphic forms, one reported to melt at 146°,[10] and the other at temperatures somewhat above 160°.[10,11]

The residue from the original distillation was acidified and extracted with absolute ethanol. Evaporation of the ethanol yielded white crystals, m.p. 118°, after one crystallization from water. No depression of the m.p. was observed when this material was mixed with authentic benzoic acid.

Oxidation of N-Acetyl-1-*p*-chloroanilino-4-phenyl-3-butene-2-one (II).—To a solution of 2 g. (0.0064 mole) of N-acetyl-1-*p*-chloroanilino-4-phenyl-3-butene-2-one (II)[12] in 15 ml. of absolute ethanol was added 1.5 ml. of 4 *N* aqueous sodium hydroxide and 4 ml. of 30% hydrogen peroxide. The mixture was kept at 40° or below. When heat was no longer evolved, the mixture was exactly neutralized with 20% hydrochloric acid and diluted with 120 ml. of water. The oil which separated slowly from the mixture yielded 0.3 g. (27%) of *p*-chloroacetanilide, m.p. 179°, after crystallization from benzene. The melting point was not depressed when this product was mixed with an authentic sample of *p*-chloroacetanilide.

Preparation of Cinnamoyldibenzoylmethane (VIII).—To a stirred solution prepared from 25 ml. of absolute ethanol, 0.2 g. (0.009 g. atom) of sodium and 2 g. (0.009 mole) of dibenzoylmethane, 1.7 g. (0.009 mole) of cinnamoyl chloride was added slowly. The mixture was refluxed for 10 minutes after the addition was completed, then diluted with water to precipitate the product. The tan oil which separated was dissolved in warm ethanol. Cooling of the solution caused separation of the product (0.5 g., 15% yield) as lemon-yellow needles, m.p. 138°. Two recrystallizations from ethanol raised the m.p. to 140–141.5°.

Anal. Calcd. for $C_{24}H_{18}O_3$: C, 81.36; H, 5.12. Found: C, 81.37; H, 5.42.

The compound is appreciably soluble in aqueous sodium hydroxide solutions.

Oxidation of Cinnamoyldibenzoylmethane (VIII).—A solution of 0.7 g. of cinnamoyldibenzoylmethane in 25 ml. of warm ethanol was cooled to a temperature of about 40° and 2 ml. of 30% hydrogen peroxide was added, followed by 10 ml. of 4 *N* aqueous sodium hydroxide. The solution changed from yellow to brown within 30 minutes. It was allowed to stand overnight, then diluted with 150 ml. of water and distilled. The distillate had the characteristic odor of benzaldehyde. It was extracted with ether to remove benzaldehyde and then treated with 2,4-dinitrophenylhydrazine dissolved in concentrated sulfuric acid. The resulting orange precipitate melted at 143–146° after crys-

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[4] C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

[5] For a recent discussion see W. A. Waters in H. Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 1172.

[6] A. Schönberg, *Ann.*, **436**, 205 (1924).

[7] Melting points are corrected.

[8] Microanalyses by Micro Tech Laboratories, Skokie, Ill.

[9] P. L. Southwick, D. I. Sapper and L. A. Pursglove, THIS JOURNAL, **72**, 4940 (1950).

[10] C. K. Ingold, G. J. Pritchard and H. G. Smith, *J. Chem. Soc.*, 79 (1934).

[11] The m.p. of the higher-melting form is variously given as 162° (ref. 10), 167.5° (T. Malkin and T. C. Tranter, *ibid.*, 1178 (1951)) and 168.5° (W. M. D. Bryant, THIS JOURNAL, **55**, 3201 (1933)).

[12] P. L. Southwick and H. L. Dimond, *ibid.*, **76**, 5667 (1954).

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.

Acknowledgment.—The authors are greatly indebted to the Research Corporation for a Frederick Gardner Cottrell grant in support of this work.

[13] A. Bischler and P. Fireman, *Ber.*, **26**, 1336 (1893).

[14] A. F. Crowther, F. G. Mann and D. Purdie, *J. Chem. Soc.*, 58 (1943).

PITTSBURGH 13, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Vinylation and the Formation of Acylals

BY CHARLES D. HURD, ROBERT ROACH[1a] AND C. W. HUFFMAN[1b]

RECEIVED AUGUST 1, 1955

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

$$\text{RCOOH} + \text{CH}_2\text{=CHOCOR} \longrightarrow \text{CH}_3\text{CH(OCOR)}_2$$

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 RCOOCH=CH_2, when catalyzed by mercuric salts of strong acids; (2) acylal formation at higher temperatures (above 80°), yielding $\text{CH}_3\text{CH(OAc)(OCOR)}$, 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), $\text{CH}_3\text{CH(OCO(CH}_2)_n\text{COOCH}_2\text{CH=CH}_2)_2$, 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

$$\text{CH}_2\text{=CHOCOR} + \text{HOCOR} \longrightarrow \text{CH}_3\text{CH(OCOR)}_2$$

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

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[1] Pittsburgh Plate Glass Company research associates: (a) 1942, (b) 1941.

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

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

[4] R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

[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*, **51**, 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).