ACID-CATALYZED REACTIONS OF VINYL COMPOUNDS

PART I. PRELIMINARY STUDIES ON VINYL ESTERS AND BENZENE[1]

J. M. Pepper, B. P. Robinson, and G. W. Schwanbeck
The Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan

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ABSTRACT

A detailed study of the nature, and the mechanism of formation, of the products of the aluminum chloride catalyzed reaction of vinyl esters and benzene has been initiated. Using vinyl acetate the formation of the previously reported acetophenone, 1,1-diphenylethane, and 9,10-dimethylanthracene has been confirmed. By means of both column chromatography and thermal distillation, a similar carbonyl-containing fraction was obtained which, as a result of a gas chromatographic study, has been shown to be a mixture of six compounds. Of these, the two major components have been identified as acetophenone and *p*-ethylacetophenone, the latter previously unreported as a product of this reaction.

The reaction of vinyl formate and benzene has been studied for the first time. High yields of 9,10-dimethylanthracene were obtained but no carbonyl-containing compounds. A study of the effect of a variation in molar ratio of benzene to vinyl acetate indicated that a maximum yield of 9,10-dimethylanthracene was obtained using a 6:1 molar ratio.

The significance of these results is discussed.

A method has been devised for an improved synthesis of 9,10-dimethylanthracene. The generality of this procedure for the synthesis of other substituted polynuclear compounds is indicated.

Some years ago, Hopff, in a patent disclosure (1), indicated that the acid-catalyzed interaction of vinyl acetate and benzene gave rise to 2-phenylethyl acetate. The possibility thereby arose whereby this condensation followed by hydrolysis of the ester could provide a convenient method of synthesis of 2-phenylethanol, a perfume ingredient. Attempts to repeat the initial condensation were not successful, but the products that were obtained were of sufficient interest to warrant further study regarding their nature and mechanism of formation. In 1946, Korshak, Samplavskaya, and Gershanovich (2) reported the identification of acetophenone (I), 1,1-diphenylethane (II), and a compound believed to be 9,10-dimethyl-9,10-dihydroanthracene (III) in the reaction product of vinyl acetate and benzene in the presence of aluminum chloride. They proposed a mechanism involving the initial formation of I and acetaldehyde. Acetaldehyde then reacted further with benzene to produce II, two molecules of which subsequently gave rise to one molecule of III and two molecules of benzene. Some support for this theory was obtained by showing that acetaldehyde and benzene did react to yield these same compounds and also that II gave rise to III in the presence of aluminum chloride. It was also noted that the yield of III increased with increasing time of reaction. Evidence had been given much earlier for this mechanism. In 1895, Radziewanowski (3) showed that in the absence of benzene, aluminum chloride catalyzed the conversion of II to III, and in 1931, Bodendorf (4) reported that acetaldehyde, benzene, aluminum chloride, and hydrogen chloride at 0° gave rise to ethylbenzene, II, and III.

A review of the literature indicated that the acid-catalyzed interaction of vinyl compounds and benzene has been the subject of several reports since as early as 1884. The interaction with vinyl bromide was reported to yield 1-bromo-2-phenylethane and 1,4-di-(β-bromoethyl)benzene by Hanriot and Guilbert (5) in 1884; ethylbenzene, II, and III by Angeblis and Anschütz (6) in 1884. These latter workers suggested the addition of

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hydrogen bromide to vinyl bromide to give 1,1-dibromoethane, which reacted with benzene to give II and III. Later in 1886, Anschütz (7) reported the formation of some styrene, ethylbenzene, II, and III from a similar reaction.

Vinyl chloride and benzene in the presence of a catalyst made from mercuric chloride and aluminum gave rise to II and III according to Böeseken and Bastet (8) in 1913 and similar products plus ethylbenzene were reported by Davidson and Lowy (9) in 1929. The former workers first postulated the formation of styrene to which benzene added to give II. However, styrene as a reactant did not give the same products, so other mechanisms were suggested including that proposed earlier by Angeblis and Anschütz (6) and one involving the intial production of 1-chloro-1-phenylethane, which reacted with benzene to give II. However, no such intermediate was isolated. Schramm (10) had in 1893 reported that 1-chloro-1-phenylethane reacted with benzene to give ethylbenzene, II, and III. The latter investigators showed that styrene could not be an intermediate and also that the major product at 0–5° was II with only traces of III, whereas at 60–70° the yield of II decreased and that of III increased appreciably. In 1946, Korshak, Samplavskaya, and Gervanovich (2) also reported compounds II and III and showed that the yield of II decreases while that of III increases as the time of reaction is increased. These same two products along with some ethylbenzene and styrene were claimed by Malinovskii (11) in 1949 to be formed by the reaction of vinyl chloride and benzene. He claimed that III arises from 1-chloro-1-phenylethane in the presence of the aluminum chloride catalyst. The reaction of benzene with three other vinyl ethers has also been reported. Using vinyl-*n*-butyl ether, Korshak *et al.* (2) in 1946 reported small yields of *n*-butylbenzene and a polymer of the vinyl ether, whilst, in 1938, Hopff (1) claimed that vinyl ethyl ether and acrylic acid reacted with benzene in the presence of an acid catalyst to give β-phenylethyl ether and β-phenylpropionic acid respectively. The interaction of three substituted vinyl compounds with benzene in the presence of aluminum chloride has also been studied. In 1930, Gibson and Johnson (12) reacted $(CHCl{=}CH)_2AsCl$ to yield a compound $C_{16}H_{14}$ (yellow plates, m.p. 179–180°); in 1950 Kirk (13), in a patent, claimed that $C(CH_3)_2{=}CHY$ gave $C_6H_4(C(CH_3)_2CH_2Y)_2$ (Y = Ac or COOH); and in 1952, Hurd and Gershbein (14) reported that isopropenyl acetate gave rise to acetophenone (I).

The structure of the polynuclear product reported in these investigations as 9,10-dimethyl-9,10-dihydroanthracene (III) had been questioned and finally proved incorrect. As early as 1885, Friedel and Crafts (15) believed this product to be 9,10-dimethylanthracene (IV). Later in 1926, Barnett and Matthews (16) suggested that the product obtained by Anschutz (7) was really IV because it had a relatively high melting point, formed a picrate, and was identical with the product obtained by the reaction of methyl magnesium iodide and 9-methylanthrone. The relationship was finally proved when in 1941, Badger, Goulden, and Warren (17) effected a sulphur dehydrogenation of authentic 9,10-dimethyl-9,10-dihydroanthracene to produce a yellow, fully aromatic compound, m.p. 180–182°, identical with the compound III obtained as described above, and when, in 1950, Badger, Jones, and Pearce (18) performed a similar dehydrogenation with aluminum chloride. This last observation suggests the route by which 9,10-dimethylanthracene was formed in all the reactions described earlier.

It was decided, therefore, to reinvestigate the aluminum chloride catalyzed reaction of vinyl derivatives and benzenoid hydrocarbons in an attempt to establish more completely the nature of the products of the reaction and, if possible, to suggest a plausible mechanism for their formation. In a series of exploratory experiments* I, II, and III were confirmed as the major components of the product of reaction of vinyl acetate, benzene, and aluminum chloride. Compound III was identified by comparison with an authentic sample.† Other acids, including zinc chloride, zirconium tetrachloride, sulphuric acid, boron trifluoride, hydrogen fluoride, and aluminum chloride sulphate, were investigated but only zirconium tetrachloride was found to be equivalent to aluminum chloride for this reaction. Both nitromethane and carbon disulphide were studied as diluents. In the former case, product yields were decreased but with the latter solvent higher yields and less resinous material were obtained than if it had been omitted. The presence of acetophenone (I) suggested a mechanism involving attack by the acetylium ion (CH_3CO^+). It was of interest therefore to investigate the products of reaction in which vinyl formate replaced vinyl acetate. In this case no acetophenone, no benzaldehyde, nor, indeed, any carbonyl-containing fragment was detected. However, good yields of 9,10-dimethylanthracene (III) were again obtained, indicating that the formation of this compound involved the vinyl part of the ester molecule. It was further shown that in reactions involving vinyl formate, carbon monoxide was eliminated as determined by the color tests described by Fiegl (19) using phosphomolybdic acid and palladium chloride.

Conflicting reports have been noted regarding the possible intermediary role of styrene in this reaction. It may be conceived that styrene could arise as a result of the attack by the vinylium ion, $CH_2{=}CH^+$, on benzene, the product of which then may dimerize to 9,10-dimethyl-9,10-dihydroanthracene, which, as has been shown experimentally, may be dehydrogenated by aluminum chloride to give the final product 9,10-dimethylanthracene. Under the conditions used, styrene, in the presence of benzene and aluminum chloride, gave rise only to a polymeric substance, indicating the inadequacy of this mechanism. Similarly β-phenylethyl acetate was tested as a possible intermediate but in this case no anthracene derivative was detected but, instead, appreciable yields of 1,2-diphenylethane were obtained.

These preliminary observations only emphasized the need for a more thorough study of the interaction of vinyl derivatives and aromatic hydrocarbons to clarify the relationship of reaction conditions to the nature of the products and to establish a mechanism for their formation. Furthermore the ease of synthesis of 9,10-dimethylanthracene suggested that the method may be capable of development as a general one for the preparation of 9,10-dialkyl-substituted polynuclear hydrocarbons and their derivatives, depending on the choice of the unsaturated and benzenoid substances. In particular, this method of synthesis of 9,10-dimethylanthracene is an improvement over that involving the aryllithium intermediate as reported by Mikhailov and Kozminskaya (20), either of those involving a Grignard reaction as described by Sandin and Kitchen (21) and Barnett and Matthews (16), and over that in which metallic sodium is used as described by Bachmann and Chemerda (22).

Initially the emphasis has been on the yield and nature of the products of reaction of vinylacetate and benzene in the presence of aluminum chloride. The reaction procedure was essentially that described by Korshak *et al.* (2) and gave a crude reaction product in the form of a brownish yellow paste. Chromatographic separation of this crude product on alumina effected a partial separation, as shown in Table I.

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†Authentic sample of 9,10-dimethylanthracene kindly supplied by Dr. R. Sandin, University of Alberta.

TABLE I

Chromatographic separation of reaction product of vinyl acetate and benzene*

Eluent	Vol. of eluent (ml)	Nature of product	Remarks
Light petroleum	200	Colorless oil	
	100	Oil and solid	
	200	Pale yellow solid	
	100	Pale yellow solid	
	100	Yellow oil	Carbonyl-containing fraction (1.94 g) (36%)
Light petroleum: benzene (1:1)	1100	Yellow oil	
	600	Yellow solid	"Hydrocarbon fraction" (0.49 g) (9.1%)
Benzene	400	Yellow solid	
Benzene:Et_2O (1:1)	800	Viscous oil	
Methanol	2500	Dark residue	

*Crude reaction product (5.83 g); alumina (200 g).

The pale yellow crystals obtained in the light petroleum eluate were identified as 9,10-dimethylanthracene and a study of the yield of this product is reported later. The product designated as "hydrocarbon fraction" was crystallized from carbon tetrachloride, then methanol, to give white crystals, m.p. 190–210°, which have not been further investigated.

The carbonyl-containing fraction gave a negative aldehyde test but a strong haloform reaction. Attempts were made to separate further the components of this fraction by thermal distillation and rechromatography. In neither case were pure compounds obtained since subsequent gas chromatographic separation using a Beckman, 6-ft silicone column showed that all such fractions were mixtures. It was later found that an initial distillation under reduced pressure (90–140° at 12 mm) of the crude reaction product permitted of a separation of a fraction containing the same components and in the same relative abundance as the carbonyl-containing fraction obtained by column chromatography. Using gas chromatography, and by repeated injections and collections of the compound represented by its peak of the chromatogram, a sample of three of the compounds was obtained. Rechromatography, followed by distillation, gave analytically pure samples, the analytical data of which are given in Table II.

TABLE II

Gas chromatographic separation of carbonyl-containing products*

Compound	Retention time (min)	% of injected sample†	B.p. at 12 mm (°C)	Analyses C (%)	Analyses H (%)
1	6	20	88	79.44‡	7.12‡
2	9.3	2.0	85	—	—
3	13	33	120	80.86§	7.77§
4	17.6	2.5	114	82.08‖	9.29‖
5	27	2.2	—	—	—
6	29.6	5.1	—	—	—

*Six-foot silicone column, Beckman No. 17,449; temperature 220°; helium gas 0.91 cc/min; each injection 100 μl.

†Total recovery 64.8%.

‡Calc. for acetophenone: C, 79.97; H, 6.71%.

§Calc. for *p*-ethylacetophenone: C, 81.04; H, 8.16%.

‖Calc. for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

Compound 3 was readily shown to be *p*-ethylacetophenone by its oxidation to terephthalic acid, and by formation of the oxime, semicarbazone, and 2,4-dinitrophenylhydrazone derivatives. The retention time of an authentic sample of *p*-ethylacetophenone was also 13 minutes. This is the first report that this compound constitutes a major part (18.5%) of the products of the aluminum chloride catalyzed reaction of vinyl acetate and benzene. Compound 4 has an analysis corresponding to a diethyl acetophenone and its identification is under study.

At this stage it became evident that the reaction, as performed, led to a complex mixture of products. To facilitate a mechanistic study it would be desirable to modify the reaction conditions to minimize the initial number of products and later to determine the nature of any secondary reactions. To this end a study was made of the effect of variation in molar ratio of benzene to vinyl acetate under conditions of excess threefold molar ratio aluminum chloride to vinyl acetate. For comparison the following yields were determined: total product; 9,10-dimethylanthracene; a distillate, b.p. → 150° at 12 mm; a distillate, b.p. 150–175° at 0.17 mm; and the residue. It had been found that a simple washing of the crude reaction product with methanol permitted an effective separation of the slightly soluble anthracene derivative (0.1% soluble) from all other reaction products. The methanol was evaporated from the resulting solution and the residue distilled. The results of this series of experiments are given in Table III.

TABLE III

Effect of ratio of benzene:vinyl acetate in aluminum chloride catalyzed reaction*

Molar ratio benzene:vinyl acetate	Reaction product		9,10-Dimethylanthracene (%)‡	Distillate		Residue (%)‡
	(g)	(%)†		→ 150° at 12 mm (%)‡	150–175° at 0.17 mm (%)‡	
100	15.4	63.5	6	38	37	18
50	14.9	61.5	14	42	17	28
50	16.2	67.0	12	42	27	19
50	15.6	64.5	11	46	22	21
10	14.2	58.8	19	36	28	17
7.5	15.6	64.5	24	50	12	14
6	18.2	75.0	29	46	14	11
5	20.0	82.7	24	51	11	16
4.5	17.8	73.5	18	50	15	17
4	18.2	75.0	15	52	20	13
2	18.2	75.0	0	55	19	26

*Each run: vinyl acetate (8.6 g, 0.1 mole); aluminum chloride (40 g, 0.3 mole).
†Based on a calculated yield of addition of 2 moles benzene to 1 mole vinyl acetate.
‡Percentage of total product.

Some observations regarding the mechanism of this reaction may be made from these data. There is a parallel relationship to be found between the variation in yield of 9,10-dimethylanthracene and that of the higher-boiling distillate fraction, the former going through a maximum and the latter a minimum at a molar ratio of benzene to vinyl acetate of about 6:1. The relative constancy of the yield of the lower-boiling distillate, which has already been shown to be the carbonyl-containing fraction, suggests that the components of this fraction arise by a reaction involving the acetoxy part of the ester, whereas the higher-boiling fraction and the anthracene derivative are related by a reaction involving the vinyl part. The observation, too, that the yield of 9,10-dimethylanthracene decreases with dilution greater than a molar ratio of 6:1 supports the belief that this product results by a dimerization of two primary products, and not by a mechanism in which the final step involves reaction with benzene. On the other hand the increasing yield as the ratio varies from 2:1 to 6:1 is difficult to interpret at this time but may involve the availability of the aluminum chloride – vinyl acetate complex. Further identification of the reaction products will aid in the understanding of this reaction.

EXPERIMENTAL

Aluminum Chloride Catalyzed Reaction of Vinyl Formate and Benzene

Vinyl formate (7.2 g, 0.1 mole) (obtained from Monomer–Polymer Inc., Leominster, Mass.) was added slowly over a period of 1 hour to a well-stirred mixture of benzene (78 g, 1 mole) and sublimed anhydrous aluminum chloride (40 g, 0.3 mole) in a 200-ml 3-necked flask equipped with reflux condenser, dropping funnel, and mechanical stirrer. Both the condenser and dropping funnel were fitted with calcium chloride drying tubes. Throughout the addition, the flask was cooled in an ice bath and the color changed from colorless through yellow to orange. The reaction mixture was allowed to warm to room temperature, during which time the color deepened to a brown, and then refluxed for 3 hours, after which the mixture was red colored. Pouring this mixture into a mixture of concentrated hydrochloric acid (75 ml) and crushed ice (75 g) resulted in the formation of a pale yellow precipitate (4.9 g), m.p. 182–185°. A mixed melting point with an authentic sample of 9,10-dimethylanthracene showed no depression.

Aluminum Chloride Catalyzed Reaction of β-Phenylethyl Acetate and Benzene

In a manner similar to that described above, β-phenylethyl acetate (27 g, 0.16 mole) was added dropwise to a mixture of benzene (100 ml) and aluminum chloride (22 g, 0.16 mole) over a period of 0.5 hour. After hydrolysis, the benzene layer was separated and the aqueous layer extracted twice with benzene. The combined benzene extracts were evaporated to yield a pale yellow oil. When the oil was cooled, crystals separated which were removed by filtration and washed with ethanol; yield, 6 g, m.p. 45–46°. Recrystallization from ethanol gave white crystals, m.p. 50–51°. A mixed melting point with an authentic sample of dibenzyl, m.p. 50–51° (prepared by the Clemmensen reduction of benzoin (23)), showed no depression.

Aluminum Chloride Catalyzed Reaction of Vinyl Acetate and Benzene

A typical procedure involved the addition of vinyl acetate (8.6 g, 0.1 mole) to benzene (78 g, 1.0 mole) and sublimed, anhydrous aluminum chloride (40 g, 0.3 mole) followed by treatment as described above. A modification involved washing the benzene extract first with sodium hydroxide (10%), then with water, before drying it over anhydrous sodium sulphate. After removal of the solvent, a semisolid product remained (16.4 g). A portion (5.38 g) of this crude product was chromatographed through alumina (200 g) using successively, light petroleum, light petroleum – benzene (1:1), benzene, benzene – diethyl ether (1:1), and methanol, collecting 100-ml fractions.

In the series of runs involving varying ratios of benzene to vinyl acetate a similar procedure was used. In all cases except those involving the 100:1 and the 2:1 ratios the crude product solidified to a yellow-colored paste. The product was washed from the reaction flask using methanol (15 ml) and filtered. The resulting yellow solid, 9,10-dimethylanthracene, was washed again with methanol (5 ml). Two such samples of crude product melted at 176–181° and 180–184°; reported, 180–181° (21).

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