94%) after crystallization from absolute ethanol melted at 206°.

Anal. Calcd. for $C_{19}H_{22}BrNO_5$: Br, 18.8. Found: Br, 18.1.

4-(α-Hydroxy-β-bromopropyl)-guaiacol Benzoate.[8]— The preferential hydrolysis of the α-bromine atom of 4-(α,β-dibromopropyl)-guaiacol benzoate was accomplished by refluxing for eighteen hours a solution of 5 g. of the dibromide in 30 ml. of 95% ethanol, 30 ml. of acetone, and 30 ml. of water with 5 g. of calcium carbonate. The filtrate on vacuum concentration yielded an oil whose ether solution was washed well with water, treated with Norit and dried over sodium sulfate. Evaporation of the ether yielded a light yellow, sweet-smelling oil (3.5 g., 83%) which resisted all attempts to induce crystallization, and which could not be distilled at 10^{-5} mm. It analyzed fairly well for the bromohydrin.

Anal. Calcd. for $C_{17}H_{17}BrO_4$: Br, 21.9. Found: Br, 23.2.

An ether solution of this material was allowed to react with pyridine over a period of two months at room temperature. There resulted only a small amount of impure solid which was not further investigated.

Summary

1. A series of four pyridinium analogs of the pressor amines which contain the guaiacol nucleus have been prepared.

2. Conditions have been found which make possible the catalytic reduction of pyridinium ketones to pyridinium alcohols.

3. Conditions have been discovered which render feasible the direct α-haloacylation of guaiacol in the presence of aluminum chloride without demethylation.

Ketene Acetals. XVI. Phenylketene Diethyl- and Dimethylacetals from the Pyrolysis of the Corresponding Orthoesters

BY S. M. McELVAIN AND CALVIN L. STEVENS[1]

Orthoesters containing certain negative substituents on the α-carbon readily pyrolyze with the loss of alcohol to the corresponding ketene acetals. The first report of such behavior was the isolation of carbethoxyketene diethylacetal in an attempt to prepare an orthoester from the iminoester hydrochloride derived from ethyl cyanoacetate.[2] Later, Staudinger and Rathsam[3] reported a similar pyrolysis of ethyl orthophenylacetate to the corresponding ketene acetal during distillation. These authors also noted that considerable amounts of ethyl phenylacetate were formed simultaneously with the ketene acetal in this pyrolysis; they stated that no diethyl ether could be detected among the pyrolysis products indicating that the normal ester did not result from the simple loss of the ether from the orthoester. Staudinger and Rathsam also reported that phenylketene diethylacetal, when heated in a bomb at 260–270°, developed pressure (presumed to be ethylene) and was converted mainly into ethyl phenylacetate; a small amount of a solid, m.p. 136–137°, which was not identified, also was obtained.

More recently Sah, Ma and Kao[4] reported a series of esters of orthophenylacetic acid, prepared by the alcoholysis of the hydrochlorides of methyl and ethyl phenyliminoacetates, but they made no mention of any facile pyrolysis of these orthoesters even when distilled at atmospheric pressure. In fact, these authors report analyses (C and H) that indicate pure orthoesters.

As phenylketene acetals were needed for other work in this Laboratory, a study of their preparation was undertaken and the present paper is a report of some of the unexpected results that were obtained, particularly in connection with the preparation of phenylketene dimethylacetal.

In general the results obtained from the pyrolysis of ethyl orthophenylacetate paralleled those of Staudinger and Rathsam.[3] This orthoester was very difficult to obtain pure and it was only possible to do so by a rapid distillation at low pressure (0.1 mm., b.p. 88–91°). When the orthoester, as obtained from the alcoholysis of the iminoester hydrochloride, was slowly distilled as in a fractional distillation, approximately 70% of the theoretical quantity of alcohol collected in the cold trap and the distillate could be separated into ethyl phenylacetate (20%) and phenylketene diethylacetal (70%), b.p. 86–88° (0.2 mm.). The residue remaining from this distillation was composed of a dimer[5] and a small amount of a white crystalline solid, m.p. 140–141°, which was identified as *meso*-diethyl α,α'-diphenylsuccinate and which undoubtedly corresponds to the material, m.p. 136–137°, isolated by Staudinger and Rathsam.[3] The formation of this compound during the pyrolysis is discussed later in connection with the pyrolysis of methyl orthophenylacetate.

Ethyl phenylacetate is formed by the loss of ethylene (identified as ethylene bromide) during the pyrolysis of the orthoester. Whether it is formed directly from the orthoester or from the

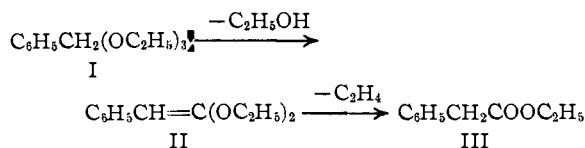(1) Wisconsin Alumni Research Foundation Research Assistant, 1944–.

(2) (a) Reitter and Weindel, *Ber.*, **40**, 3359 (1907); (b) *cf.* also Glickman and Cope, THIS JOURNAL, **67**, 1017 (1945).

(3) Staudinger and Rathsam, *Helv. Chim. Acta*, **5**, 645 (1922).

(4) Sah, Ma and Kao. *J. Chem. Soc.*, 305 (1931).

(5) This dimer could not be converted by hydrolysis into α,γ-diphenylacetoacetic ester as the dimer of ketene diethylacetal was converted to acetoacetic ester (Johnson, Barnes and McElvain, THIS JOURNAL, **62**, 964 (1940)). Instead, it invariably yielded phenylacetic acid.
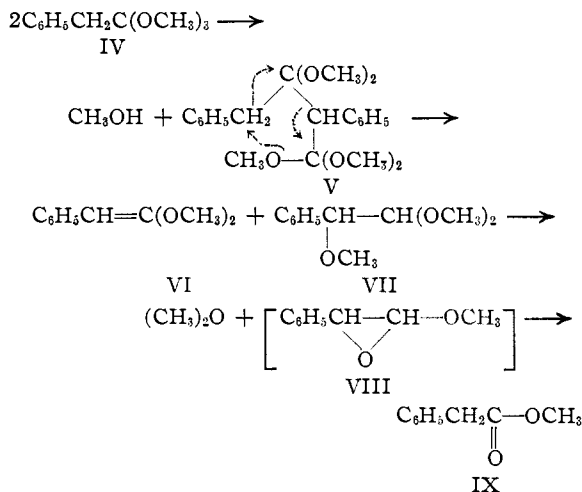
ketene acetal after the latter is formed cannot be said with certainty, since the ketene acetal also loses ethylene on heating and is pyrolyzed to a small extent to the normal ester during an ordinary distillation. It would appear, however, that the ethylene is derived from the pyrolysis of the ketene acetal, since the evolution of practically all of the alcohol precedes the evolution of ethylene when the orthoester is pyrolyzed. It seems then that, in the main, the pyrolysis of ethyl orthophenylacetate is represented by the following series of reactions.

$$C_6H_5CH_2(OC_2H_5)_3 \xrightarrow{-C_2H_5OH}$$
$$I$$

$$C_6H_5CH=C(OC_2H_5)_2 \xrightarrow{-C_2H_4} C_6H_5CH_2COOC_2H_5$$
$$II \qquad\qquad III$$

The preparation of phenylketene dimethylacetal was undertaken in the hope that methyl orthophenylacetate would pyrolyze mòre smoothly and without the formation of the normal ester. However, this orthoester showed an unexpectedly complex behavior on pyrolysis. It is much more stable than the ethyl ester, but when heated at 250–260° it gave a vigorous evolution of methyl alcohol for about fifteen minutes. This pyrolysis appears to be catalyzed by acids, the amount remaining on the glass surface after the reaction flask had been cleaned in a sulfuric acid–dichromate solution and then well washed with water, being sufficient to catalyze the pyrolysis. The most characteristic and singular feature of the pyrolysis was that invariably only 40–50% of the alcohol required for the conversion of the orthoester to the ketene acetal was evolved during the initial vigorous reaction. Thereafter eight hours of heating was required to produce an additional 30% of the expected alcohol.

This behavior would indicate that two molecules of the orthoester had interacted to produce one molecule of alcohol together with a condensation product that should boil within the range of a dimer of the ketene acetal. However, a rapid distillation under diminished pressure of the pyrolysis mixture just after the initial vigorous evolution of alcohol had subsided, gave a distillate that boiled within the range of the original orthoester and the ketene acetal derived from it. The methoxyl content (39%) of this distillate was somewhat higher than that (37.8%) of the phenylketene dimethylacetal. If this distillate were fractionally distilled through an 18-plate Fenske column a forerun of methyl phenylacetate, an intermediate fraction the boiling point of which fluctuated over a 15° range, and phenylketene dimethylacetal were obtained. Refractionation of the second fraction gave a clean separation, without any fluctuations of the boiling points, into methyl phenylacetate and phenylketene dimethylacetal; the total yields of these products amounted to 33 and 59%, respectively.

Thus it is apparent that methyl orthophenylacetate on pyrolysis gives a higher yield of the normal ester than does the ethyl orthophenylacetate. The amount of methyl alcohol evolved during the initial vigorous pyrolysis of the orthoester (IV) suggests that two molecules of the latter compound interact with the loss of alcohol to produce an intermediate (V) which then undergoes the indicated decomposition into phenylketene dimethylacetal (VI) and an isomer (VIII) of the orthoester. These latter two products account for the boiling range and the methoxyl content of the distillate obtained after the initial pyrolysis. The conversion of VII to IX, which explains the fluctuations in the boiling points during the first fractionation of this distillate, requires the loss of the elements of dimethyl ether and the rearrangement of the intermediate VIII.[6] No trace of this ether was found, but this is not surprising since it would be produced from the vapors of VII during a fractional distillation under diminished pressure.

$$2C_6H_5CH_2C(OCH_3)_3 \longrightarrow$$
$$IV$$

$$CH_3OH + C_6H_5CH_2 \overset{C(OCH_3)_2}{\underset{CH_3O-C(OCH_3)_2}{\diagdown\diagup}} CHC_6H_5 \longrightarrow$$
$$V$$

$$C_6H_5CH=C(OCH_3)_2 + C_6H_5CH-CH(OCH_3)_2 \longrightarrow$$
$$\qquad\qquad\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad\qquad\qquad OCH_3$$
$$VI \qquad\qquad\qquad VII$$

$$(CH_3)_2O + \left[C_6H_5CH-CH-OCH_3 \atop \diagdown O \diagup \right] \longrightarrow$$
$$VIII$$

$$C_6H_5CH_2C-OCH_3$$
$$\qquad\qquad || $$
$$\qquad\qquad O$$
$$IX$$

The postulation of such a complex reaction course as that shown above seems necessary in view of the behavior of mixtures of methyl orthophenylacetate and phenylketene dimethylacetal. It might seem that the low yield of alcohol from the pyrolysis of the orthoester described above is the result of reaction of the ketene acetal as it is formed with unchanged orthoester. These compounds indeed do appear to interact even at room temperature, judging by the departure from a straight line of the plotted refractive indices of mixtures of varying contents of these components. However, the pyrolysis of an equimolecular mixture of these compounds produced 90–100% of the alcohol required for the conversion of the orthoester that was present in the mixture to the
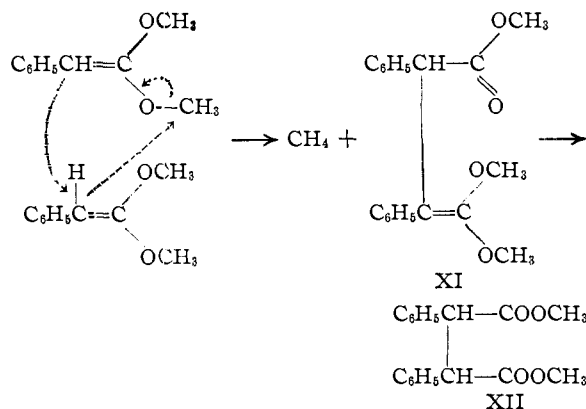
(6) Such a rearrangement is not unlike that required by the formation of α-chloroisobutyryl chloride by the action of phosphorus pentoxide and quinoline on chloretone (Price and Marshall, *J. Org. Chem.*, **8**, 532 (1943)) and the formation of trialkylacetic esters from α-bromo-s-alkyl ketones and sodium alkoxides (Aston, *et al.*, This Journal, **64**, 300 (1942)).

ketene acetal; 88% of this latter compound, but *no methyl phenylacetate*, was recovered from the pyrolysis mixture. This indicates the interaction of these compounds to form an intermediate different from V, and which can undergo pyrolysis into two molecules of the ketene acetal; X would seem to be a probable structure for this intermediate, although the isomeric structure derived from the loss of a methoxyl group from the orthoester and a hydrogen from the ketene acetal is also a possibility.

$$IV + VI \longrightarrow CH_3OH +$$
$$C_6H_5CH{=}C(OCH_3)CH(C_6H_5)C(OCH_3)_3 \longrightarrow 2VI$$
$$X$$
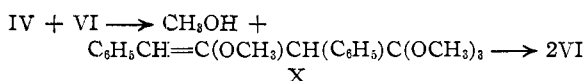
It is quite likely that some of X is formed during the pyrolysis of methyl orthophenylacetate, since the yield of the ketene acetal always exceeds that of methyl phenylacetate.
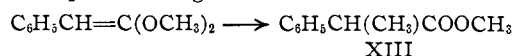
When either phenylketene dimethylacetal, or the pyrolysis product remaining after the initial vigorous evolution of methyl alcohol from methyl orthophenylacetate, was heated at 250–260° for eight hours methane was evolved and *meso*-dimethyl α,α'-diphenylsuccinate (XII) was produced in 21–29% yields. The formation of these compounds must result from the interaction of two molecules of the ketene acetal in some manner, since an equimolecular mixture of the ketene acetal and the orthoester showed the pyrolysis behavior described above, and a similar mixture of the acetal with methyl phenylacetate gave, when heated, the succinic ester (XII) in an amount corresponding to the acetal in the mixture with the normal ester remaining unchanged. The only apparent manner in which the succinic ester XII could be formed from the ketene acetal is through an elimination of a hydride ion from one acetal molecule with a methyl cation of another molecule[7] to form XI, which then is transformed to XII by further reaction and pyrolysis.

XI

$$C_6H_5CH{-}COOCH_3$$
$$|$$
$$C_6H_5CH{-}COOCH_3$$
$$XII$$

In addition to the succinic ester XII, the pyrolysis of phenylketene dimethylacetal produced a 22% yield of methyl α-phenylpropionate (XIII) by a simple rearrangement of the acetal.

$$C_6H_5CH{=}C(OCH_3)_2 \longrightarrow C_6H_5CH(CH_3)COOCH_3$$
$$XIII$$

Since the pyrolysis of methyl orthophenylacetate produced considerable of the normal ester along with the ketene acetal, an attempt was made to prepare this acetal by the action of sodium on the corresponding bromo ortho ester, a procedure which has been found very useful for the preparation of alkylketene acetals.[8] The bromo ortho ester was readily prepared and could be distilled without decomposition. Sodium was found to react with this bromo ortho ester but did not convert it to the ketene acetal. Instead, an organic sodium salt, representing approximately 75% of the original bromoester, was precipitated along with the expected sodium bromide; only the original bromo ortho ester (20%) was recovered at the point where the ketene acetal should appear.

Both phenylketene dimethyl- and diethylacetals are pale yellow liquids, which show the characteristic behavior of ketene acetals. The dimethyl-acetal is sufficiently stable to be distilled at atmospheric pressure (b.p. 240–245°) without decomposition; the diethylacetal pyrolyzes to some extent to ethyl phenylacetate and ethylene even on distillation under diminished pressure. Each of these acetals reacts exothermically at room temperature with the corresponding alcohol to form the colorless orthoester; they react similarly with water to form the normal ester. The alkylation of these ketene acetals is described in the following paper.

Experimental

Ethyl Phenyliminoacetate Hydrochloride.—A mixture of 111 g. (0.9 mole) of benzyl cyanide and 48 g. (1.1 moles) of absolute ethyl alcohol was cooled in an ice-bath and treated with dry hydrogen chloride until 38 g. had been absorbed. The resulting solution was placed in a refrigerator for twelve hours, at the end of which time the resultant viscous liquid was treated with an equal volume of ether. The salt that precipitated was filtered off, triturated with dry ether, and dried in a vacuum desiccator over phosphorus pentoxide and sodium hydroxide. The yield amounted to 136 g. (75%). If the reaction mixture was allowed to stand in the refrigerator for two weeks the yield of the salt was raised to 83%.

Following the procedure of Glickman and Cope,[2b] 72 g. of the iminoester hydrochloride was neutralized with a sodium bicarbonate solution and immediately taken up in ether. Evaporation of the ether and distillation of the free iminoester gave 52 g. (88%) of ethyl phenylimino-acetate,[9] b. p. 98–100° (2 mm.); n^{20}D 1.5126. This ester is quite stable and shows no tendency to decompose into the nitrile and alcohol.

Ethyl Orthophenylacetate and Phenylketene Diethyl-acetal.—A mixture of 126 g. (0.63 mole) of ethyl phenyl-iminoacetate hydrochloride and 200 ml. of absolute ethyl alcohol was shaken until the salt had dissolved; a marked

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(7) Such a reaction is analogous to the formation of β-phenylpro-piophenone from the interaction of α-methoxystyrene and toluene at 250°

$$C_6H_5C(OCH_3){=}CH_2 + CH_3C_6H_5 \longrightarrow CH_4 + C_6H_5COCH_2CH_2C_6H_5$$

as reported by Spielman and Mortenson, This Journal, **61**, 666 (1939).

(8) McElvain, *et al.*, This Journal, **62**, 1482 (1940); **64**, 1966 (1942).

(9) Hessler, A. *Chem. J.*, **22**, 169 (1899).

cooling accompanied solution of the salt. As the solution warmed to room temperature, ammonium chloride began to precipitate. After two days, 100 ml. of absolute ether was added to the alcohol and the precipitated ammonium chloride (30 g., 88%) filtered off. The solvent was evaporated from the filtrate at room temperature under a vacuum; as the solution became more concentrated phenylacetamide began to separate. After all the solvent was evaporated the residue was chilled and the amide (6–8%) filtered off.

The resulting ethyl orthophenylacetate could be obtained quite pure if it were distilled rapidly at 0.1 mm. pressure from a flask with a short neck. The yield was 99.5 g. (66%) of the colorless orthoester, b. p. 88–91° (0.1 mm.); n^{20}D 1.5050; d^{24}_4 1.000.

Anal. Calcd. for $C_{14}H_{22}O_3$: C_2H_5O, 56.7. Found: C_2H_5O, 56.0.

Phenylketene diethylacetal was best prepared from this orthoester by slow distillation from a 10-inch Vigreux column at 0.1 mm. pressure. During the distillation approximately 70% of the theoretical amount of ethyl alcohol collected in the cold trap. The distillate, a mixture of ethyl phenylacetate and the ketene acetal, was separated into its components by fractional distillation. From 100 g. of the orthoester 14 g. (20%) of ethyl phenylacetate, b. p. 67–69° (0.1 mm.) and 56 g. (70%) of the pale yellow phenylketene diethylacetal, b. p. 86–88° (0.2 mm.), n^{20}D 1.5385; d^{27}_4 1.005, were obtained.

Anal. Calcd. for $C_{12}H_{16}O_2$: C_2H_5O, 46.8. Found: C_2H_5O, 46.5.

A small amount of what appeared to be a dimer of the ketene acetal remained as a residue from this distillation. It boiled at 158–163° (0.2 mm.), n^{20}D 1.5635, contained 32.2% ethoxyl, and weighed 3.4 g. This dimer on hydrolysis with concentrated hydrochloric acid gave phenylacetic acid, m. p. 74–76°, and a small amount of a solid, m. p. 193–195°, which was not further investigated.

On standing for a few weeks a white solid separated from the dimer; from 4 g. of the latter 0.088 g. of crystals, m. p. 140–141°, was obtained. This product proved to be *meso*-diethyl α,α'-diphenylsuccinate,[10] sap. equiv. 164 (calcd. 163). Saponification of this ester yielded *meso*-α,α'-diphenylsuccinic acid,[10] m. p. 230–235°.

Phenylketene diethylacetal is readily converted to the orthoester by alcohol: To 2.7 g. of the pale yellow ketene acetal was added 5 ml. of absolute ethyl alcohol. The color of the acetal was discharged immediately with a noticeable evolution of heat. After removal of the excess alcohol, 2.3 g. (69%) of the colorless orthoester, n^{20}D 1.5010, was obtained by rapid distillation of the residue.

When heated to 150–160°, phenylketene diethylacetal slowly pyrolyzed into ethylene and ethyl phenylacetate; 15 g. of the acetal at this temperature for three hours gave 4.4 g. of the normal ester, b. p. 112–115° (11 mm.), 3 g. of an intermediate fraction and 7.8 g. of unchanged acetal. The evolved ethylene was identified as ethylene bromide after absorption in a solution of bromine in carbon tetrachloride.

Methyl Phenyliminoacetate Hydrochloride.—The preparation of this salt was essentially the same as that described above for the ethyl phenyliminoacetate hydrochloride; except that the salt began to precipitate while the final portion of the hydrogen chloride was being absorbed. At this point ether was added to facilitate absorption of the gas. The yields of the methyl phenyliminoacetate hydrochloride were generally better than those of the salt of the ethyl iminoester; 95% yields of the former salt were obtained consistently after cooling the reaction mixture overnight in a refrigerator.

Anal. Calcd. for $C_9H_{12}ONCl$: Cl, 19.1. Found: Cl, 18.9.

Methyl Orthophenylacetate.—A mixture of 173 g. (0.94 mole) of methyl phenyliminoacetate hydrochloride and 200 ml. of absolute methyl alcohol was shaken until the salt went into solution (about fifteen minutes). Am-

monium chloride began to precipitate as the solution came to room temperature. After two days, 100 ml. of dry ether was added to complete the precipitation of the ammonium chloride. After filtering off this salt (44 g., 88%), the solvents were removed from the filtrate at room temperature under a vacuum and the small amount of phenylacetamide (10.5 g., 8%) that precipitated at this point was filtered off. The filtrate was distilled under reduced pressure to give 120 g. (67%) methyl orthophenylacetate, b. p. 73–76° (0.4 mm.), n^{20}D 1.5065, d^{24}_4 1.0644.

Anal. Calcd. for $C_{11}H_{16}O_3$: CH_3O, 47.5. Found: CH_3O, 45.7.

The residue in the flask after distillation contained an additional 2.5 g. of phenylacetamide and a viscous liquid, which on distillation gave 7.1 g. of a dimer, b. p. 160–162° (0.1 mm.), n^{20}D 1.5965, and which contained 22.1% methoxyl.

Methyl α-Bromoorthophenylacetate.—In a round-bottom flask equipped with a stirrer and dropping funnel were placed 10 g. (0.13 mole) of pyridine, 25 g. (0.13 mole) of methyl orthophenylacetate and 50 ml. of carbon tetrachloride. This solution was cooled in an ice-bath and 20.2 g. (0.13 mole) of bromine added slowly. After the bromine was added and its color discharged, the reaction mixture was allowed to come to room temperature. The orange-colored precipitate was filtered off and the filtrate evaporated to yield pale orange crystals of the crude bromo ortho ester. Distillation of this material gave 29 g. (80%) of white crystalline methyl α-bromoorthophenylacetate, b. p. 105–107° (1 mm.); m. p. 66–68°.

Anal. Calcd. for $C_{11}H_{15}O_3Br$: Br, 29.1. Found: Br, 29.2.

Oxidation of this bromoester with alkaline potassium permanganate yielded benzoic acid.

When 50 g. (0.18 mole) of methyl α-bromoorthophenylacetate was added to a suspension of 9.2 g. (0.4 atom) of sodium sand in boiling benzene, a reaction began immediately. However, the reaction mixture developed a brown color rather than the characteristic blue color which generally accompanies the formation of a ketene acetal from a bromo orthoester.[8] After five hours of heating and stirring the reaction mixture was cooled and centrifuged. The salts obtained weighed 45 g. (calcd. 31.8 g. of the expected sodium bromide and sodium methoxide) after washing with ether and drying. Distillation of the filtrate gave 10 g. (20%) of the original bromo ortho ester. The salt precipitate, after solution in water, showed 75% of the bromine of the original bromoester as bromide ion (Volhard titration) and 83% of one-half of the sodium as titratable alkali.

Phenylketene Dimethylacetal.—In a flask with a short still-head 68 g. (0.35 mole) of methyl orthophenylacetate was heated in a metal-bath at 250–260°. During the first fifteen minutes of heating there was a vigorous evolution of methyl alcohol, 4.3 g. (40%) of which collected in the cold trap. After this time the evolution of alcohol practically ceased. At this point a rapid distillation of the pyrolysis mixture at 0.1 mm. pressure gave no indication of the presence of a dimeric substance but rather a mixture boiling within the ranges (78–88° (1.5 mm.)) of the original orthoester and the ketene acetal. The methoxyl content (39%) of this material was somewhat higher than that (37.8%) of the expected ketene acetal.

Fractionation of this pyrolysis mixture through an 18-plate Fenske column gave 12 g. of methyl phenylacetate, b. p. 57–60° (0.5 mm.); n^{20}D 1.5050, 11.4 g. of an intermediate fraction that boiled with noticeable fluctuations between 61–76° (0.5 mm.), and 28 g. of the pale yellow phenylketene dimethylacetal, b. p. 85–87° (0.5 mm.), n^{24}D 1.5390, d^{24}_4 1.0575. The intermediate fraction on refractionation was separated readily and without fluctuation into 5.5 g. of methyl phenylacetate and 5.3 g. of the ketene acetal. The total yields were 17.5 g. (33%) of methyl phenylacetate and 33.3 g. (59%) of phenylketene dimethylacetal.

Anal. Calcd. for $C_{10}H_{12}O_2$: CH_3O, 37.8. Found: CH_3O, 37.5.

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(10) Wren and Still, *J. Chem. Soc.*, **107**, 444 (1915).

The normal ester was identified by hydrolyzing 5.7 g. with aqueous alkali. This yielded 4.2 g. (82%) of phenylacetic acid, m. p. 74–76°; mixed m. p. with an authentic sample, 74–76°.

The color of this ketene acetal also is quickly discharged, with the evolution of heat, when it is treated with absolute methyl alcohol. The colorless methyl orthophenylacetate may be distilled from this reaction in 73% yield.

In contrast to the corresponding diethylacetal, phenylketene dimethylacetal may be distilled at atmospheric pressure (b. p. 240–245°) without noticeable decomposition.

Pyrolysis of Phenylketene Dimethylacetal.—In a 25-ml. flask connected in series to a cold trap and a water-filled, graduated separatory funnel inverted in a beaker of water for gas collection, 4.5 g. (0.025 mole) of the acetal was heated to 250–260° for eight hours. During this time 200 ml. of a gas collected in the separatory funnel. Carbon and hydrogen analysis of the gas indicated 4.02 atoms of hydrogen for 1.02 atoms of carbon, showing the gas to be methane; the yield of this gas amounted to 0.008 mole (32%).

On cooling the pyrolysis flask crystals appeared Petroleum ether dissolved the non-crystalline material and left a white solid, which proved to be meso-dimethyl α,α'-diphenylsuccinate,[11] m. p. 219–221°. The yield of this compound was 0.9 g. (21%). Evaporation of the solvent and distillation of the residue gave 1 g. (22%) of methyl α-phenylpropionate,[12] b. p. 98–100° (12 mm.); n^{24}D 1.5030. There remained 1.9 g. of a viscous oil which could not be distilled. Alkaline saponification of this oil gave a solid, non-crystalline acid with a neutral equivalent of 240. This acid was not further investigated.

Methyl α-phenylpropionate was characterized by its saponification equivalent (171; calcd., 164) and molecular refraction (46.6, calcd., 46.4). It also was hydrolyzed to α-phenylpropionic acid[12] in 80% yield. While phenylacetic acid is a readily crystallizable solid, α-phenylpropionic acid is an oil, b. p. 145–147° (12 mm.), n^{24}D 1.5250, $d^{24}{}_4$ 1.1035, neut. equiv. 153 (calcd. 150); MD 41.8 (calcd. 41.7).

The solid ester, meso-methyl α,α'-diphenylsuccinate, m. p. 219–221°, showed a sap. equiv. of 145 (calcd. 149) and a molecular weight (cryoscopic in benzene) of 305 (calcd. 298).

During the saponification of this meso-ester racemization occurred and the dl-α,α'-diphenylsuccinic acid[11] was isolated. It crystallized from water with one molecule of water of crystallization and in this form melted at 182–184°; but it then resolidified immediately and remelted at 218–221°; neut. equiv. was 150 (calcd. 144).

The meso-ester could be isomerized quantitatively to the dl-ester by dissolving in concentrated sulfuric acid and then reprecipitating by dilution with water. The dl-ester melted at 168–172°. The partial transformation of

the meso-ester to the dl-ester by treatment with sodium methoxide has been reported.[11] However, the transformation by means of concentrated sulfuric acid appears to be much more complete than that brought about by alkali.

Pyrolysis of methyl phenylorthoacetate under the conditions described above for the ketene acetal gave essentially the same products, except that 80% of one mole of methyl alcohol per mole of orthoester collected in the cold trap after 12–14 hours of heating at 250–260°. In this experiment at 29% yield of meso-dimethyl α,α'-diphenylsuccinate was obtained.

An equimolecular mixture of phenylketene dimethylacetal and methyl orthophenylacetate had a refractive index of 1.5175 (calcd. n^{20}D 1.5237 from a straight line joining the refractive indices of the two components), indicating some interaction of these compounds at room temperature. When this mixture was heated at 250–260°, 90–100% of the alcohol required for the conversion of the orthoester present to the ketene acetal was evolved in fifteen minutes. From a mixture of 9.6 g. of the orthoester and 8.0 g. of the ketene acetal 13.9 g. (89%) of the ketene acetal was recovered by distillation at 2 mm. pressure; no normal ester was formed in this pyrolysis.

Summary

The preparations of phenylketene diethyl- and dimethylacetals by the pyrolysis of the corresponding orthoesters, ethyl and methyl orthophenylacetates, are described. The former orthoester yields, in addition to the ketene acetal, ethyl phenylacetate (by the loss of ethylene from the acetal) and a small amount of meso-diethyl α,α'-diphenylsuccinate.

The pyrolysis of methyl orthophenylacetate also yields the normal ester, methyl phenylacetate, along with phenylketene dimethylacetal. However, in the presence of an equimolecular amount of the ketene acetal the orthoester pyrolyzes only to the acetal. An explanation for these behaviors is offered.

Phenylketene dimethylacetal undergoes pyrolysis with the evolution of methane to form meso-dimethyl α,α'-diphenylsuccinate. The manner in which this compound is formed is discussed.

Phenylketene dimethylacetal cannot be prepared by the action of sodium on methyl α-bromoorthoacetate.

Other properties of these phenylketene acetals are discussed.

(11) Wren and Still, J. Chem. Soc., 111, 1019 (1917).

(12) Tiffeneau, Ann. chim. phys., [8] 10, 352 (1908).