tion was chilled and filtered to remove a dark amorphous impurity. After removal of the solvent the acid was dissolved in ethanol, treated with Norite and crystallized by the gradual addition of water. The product (0.23 g., 48%), melted at 165–168°. Further recrystallization yielded 0.16 g. of material with a melting point of 169–170°. This product did not depress the melting point of an authentic sample of dehydroabietic acid (I).

The methyl ester, prepared with dimethyl sulfate, melted at 62–63°. A mixed melting point with an authentic sample of methyl dehydroabietate showed no depression.

Oxidation of Chloromethyldehydroabietic Acid (VIII).—A sample (4.2 g.) of crude chloromethyldehydroabietic acid, containing 8.2% of chlorine, was partially dissolved in a solution of 0.4 g. of potassium hydroxide in 100 ml. of water. A solution of 4.7 g. of potassium permanganate and 1 g. of potassium hydroxide in 100 ml. of water was slowly added with stirring over a period of five hours. Saturation of the reaction mixture with sulfur dioxide produced a precipitate which was filtered off, washed with water and dissolved in ether. The ether solution was extracted with dilute sodium bicarbonate and the aqueous extract was acidified. Upon the addition of ether to this extract the product crystallized and was filtered off. The first crop weighed 1.82 g.; an additional 0.10 g. was obtained upon concentrating the ether layer to a small volume. The neutral equivalent of the crude product was 182. It did not melt below 280°. It was purified by recrystallization from ethanol and water. *Anal.* Calcd. for $C_{21}H_{26}O_5$: C, 70.4; H, 7.3; neut. equiv., 179. Found: C, 70.6; H, 7.5; neut. equiv., 179; $[\alpha]^{25}\mathrm{D}$ +38° (1% in absolute ethanol).

The dimethyl ester (XV) prepared by treating the acid with diazomethane and recrystallizing from methanol and water, melted at 94–95°. *Anal.* Calcd. for $C_{23}H_{30}O_5$: C, 71.5; H, 7.8. Found: C, 71.7; H, 8.0.

The oxime was prepared from the above dimethyl ester by heating it under reflux with an equal weight of hydroxylamine hydrochloride in an alcohol solution containing excess pyridine. After recrystallization from dilute methanol the product melted at 192–194°. *Anal.* Calcd. for $C_{23}H_{31}O_5N$: C, 68.8; H, 7.8; N, 3.5. Found: C, 69.0; H, 7.9; N, 3.6.

Oxidation of 6-Carboxydehydroabietic Acid (III).—To a solution of 1 g. of this acid (III) in 40 ml. of water containing 0.38 g. of potassium hydroxide there was added with stirring a solution of 0.94 g. of potassium permanganate in 20 ml. of water over a period of three hours. The reaction mixture was saturated with sulfur dioxide and the precipitate was filtered off and washed with water. It was then dissolved in sodium bicarbonate solution and treated with Norite. Upon acidification there was obtained 0.75 g. of crude acid ($[\alpha]^{25}\mathrm{D}$ +31°, 1% in absolute ethanol). The product was recrystallized from ethanol and water.

Treatment of this acid with diazomethane and recrystallization from dilute methanol gave the dimethyl ester (XV) which melted at 94–95°. A mixture of this ester with the dimethyl ester obtained from oxidized chloromethyldehydroabietic acid (above) melted at the same temperatures.

Ultraviolet Absorption Spectra.—The absorption spectra were obtained from measurements made with a Beckman model DU quartz spectrophotometer. The solvent for dehydroabietic acid was ethanol and the concentration was 500 mg. per l.; that for the other compounds was methanol and the concentrations were approximately 20 mg. per l.

Acknowledgment.—The author wishes to thank Dr. Harold M. Spurlin for his helpful interest in this work.

COLLEGE PARK, MD. RECEIVED NOVEMBER 24, 1950

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. XXV. Diphenylketene Dimethylacetal

BY S. M. MCELVAIN, STANLEY B. MIRVISS[1] AND CALVIN L. STEVENS[2]

The preparation of diphenylketene dimethylacetal (IV) by the dehydrochlorination of diphenylchloroacetaldehyde dimethylacetal (III) is described. This is the principal reaction between III and potassium *t*-butoxide in dioxane, but in *t*-butyl alcohol this base causes nearly an equal amount of replacement of the halogen to form the *t*-butoxyacetal (V). Similar reactions occur between III and sodium pinacolate in pinacol solution. IV shows the expected reactions with water, methanol, benzyl bromide and bromine; it is, however, singularly unreactive toward acyl chlorides. IV undergoes a novel reaction with potassium *t*-butoxide to yield the potassium enolate of methyl diphenylacetate and methyl *t*-butyl ether. Diphenylhaloacetaldehyde acetals (II, IX and X) are found to undergo a novel thermal rearrangement into the corresponding diphenylacetic ester and alkyl halide. An attempt to prepare diphenylketene diethylacetal from IX was unsuccessful because of the interference of the halogen replacement reaction and the decomposition of the ketene acetal to the potassium enolate of ethyl diphenylacetate.

Diphenylketene dimethylacetal (IV) has been prepared by the dehydrochlorination of diphenylchloroacetaldehyde dimethylacetal (III), obtained from methyl dimethoxyacetate (I) *via* the sequence of reactions shown below. The dehydrochlorination of III with potassium *t*-butoxide in *t*-butyl alcohol, which has been used effectively for the dehydrohalogenation of a variety of haloacetals to the corresponding ketene acetals,[3] was accompanied by a concurrent replacement reaction that yielded the *t*-butoxyacetal (V). This compound and the ketene acetal (IV) were formed in 39 and 47% yields, respectively, as determined from the refractive index of a distilled mixture of these products. This mixture was partially separated by fractional distillation after a portion (*ca.* 65%) of IV, m.p. 66–68°, crystallized from the mixture on cooling. Similarly the reaction of III with sodium pinacolate in pinacol gave the ketene acetal (IV) and a compound corresponding to the pinacoloxyacetal (VI); because of the greater difference in boiling points of IV and VI, they were readily separated by fractionation in yields of 38 and 42%, respectively.

The most satisfactory procedure for the dehydrochlorination of III utilized dry potassium *t*-butoxide in refluxing dioxane. In this reaction none of the *t*-butoxyacetal (V) was formed and the pure ketene acetal (IV) was obtained readily in 50% yield. The use of the higher boiling dibutyl ether instead of dioxane gave only a 30% yield of IV, the potassium enolate of methyl diphenylacetate (see below for the formation of this product), and a considerable amount of tar.

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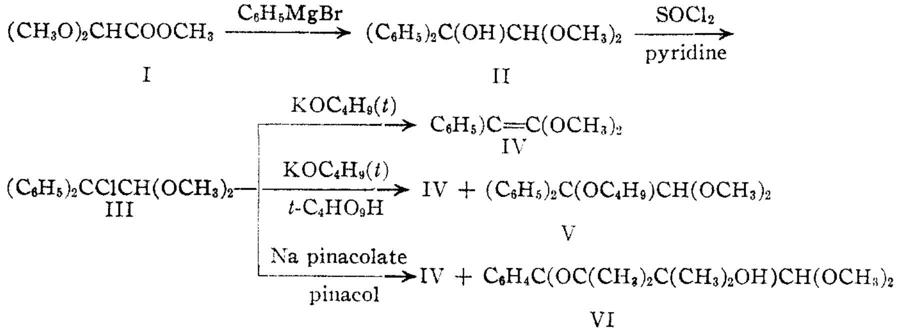
[3] S. M. McElvain, *et al.*, THIS JOURNAL, **58**, 529 (1936); **59**, 2266 (1937); **60**, 2210 (1938); **70**, 3781 (1948).



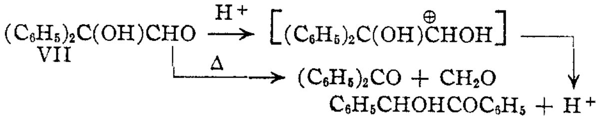
$$\underset{\text{I}}{(CH_3O)_2CHCOOCH_3} \xrightarrow{C_6H_5MgBr} \underset{\text{II}}{(C_6H_5)_2C(OH)CH(OCH_3)_2} \xrightarrow[\text{pyridine}]{SOCl_2}$$

$$\underset{\text{III}}{(C_6H_5)_2CClCH(OCH_3)_2} \xrightarrow{KOC_4H_9(t)} \underset{\text{IV}}{C_6H_5)C{=}C(OCH_3)_2}$$

$$\underset{\text{III}}{(C_6H_5)_2CClCH(OCH_3)_2} \xrightarrow[t\text{-}C_4HO_9H]{KOC_4H_9(t)} \text{IV} + \underset{\text{V}}{(C_6H_5)_2C(OC_4H_9)CH(OCH_3)_2}$$

$$\underset{\text{III}}{(C_6H_5)_2CClCH(OCH_3)_2} \xrightarrow[\text{pinacol}]{\text{Na pinacolate}} \text{IV} + \underset{\text{VI}}{C_6H_4C(OC(CH_3)_2C(CH_3)_2OH)CH(OCH_3)_2}$$

The structure of V was indicated by its analyses and chemical properties. Oxidation of V gave a quantitative yield of benzophenone and refluxing 10% hydrochloric acid converted it to benzoin in 66% yield. The latter transformation indicates the intermediate formation of diphenylhydroxyacetaldehyde (VII), which Danilow[4] has shown is converted to benzoin by heating with acid and to benzophenone and formaldehyde by distillation



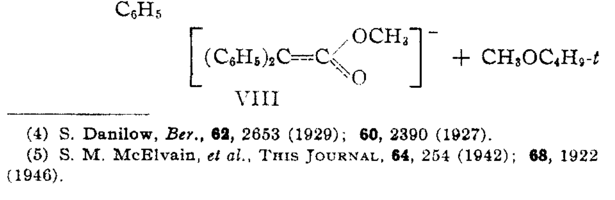
$$\underset{\text{VII}}{(C_6H_5)_2C(OH)CHO} \xrightarrow{H^+} \left[(C_6H_5)_2C(OH)\overset{\oplus}{C}HOH\right] \longrightarrow C_6H_5CHOHCOC_6H_5 + H^+$$

$$\underset{\text{VII}}{(C_6H_5)_2C(OH)CHO} \xrightarrow{\Delta} (C_6H_5)_2CO + CH_2O$$

Treatment of V with 48% hydrobromic acid yielded *t*-butyl bromide together with benzil (39%) and benzophenone (48%).

Diphenylketene dimethylacetal (IV) shows most of the expected reactions of a ketene acetal. It reacts with water in dioxane in the presence of a trace of acid to give a quantitative yield of methyl diphenylacetate; with methanol it yields methyl orthodiphenylacetate, m.p. 39–43°; and with bromine it gives a quantitative yield of methyl diphenylbromoacetate with the evolution of methyl bromide. A temperature of 200° is required to produce a reaction of IV with benzyl bromide. The products of this reaction were methyl diphenylacetate (27%), methyl α,α,β-triphenylpropionate (31%) and a viscous, high boiling, red oil. The ketene acetal IV showed an unexpected inertness to acyl halides, which have been found to react readily with other ketene acetals.[5] After extended periods of heating with acetyl chloride, benzoyl chloride or methyl chloroformate, IV and each of these acyl halides were recovered substantially unchanged.

It was noted above that the dehydrochlorination of III in dibutyl ether produces some of the potassium enolate of methyl diphenylacetate (VIII). This salt apparently is produced by the interaction of the ketene acetal (IV) and potassium *t*-butoxide, as these compounds were found to react in dioxane



$$\left[(C_6H_5)_2C{=}C\begin{matrix}OCH_3\\O\end{matrix}\right]^- + CH_3OC_4H_9\text{-}t$$

VIII

after an extended period of heating to yield VIII and methyl *t*-butyl ether. This novel reaction doubtless occurs with the ketene acetal IV because the conjugated phenyl groups enhance the electrophilic character of the methyl group to the point of reaction with the *t*-butoxy anion.

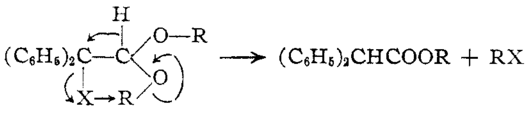
The hydroxyacetal II was obtained in 79% yield from the ester I; the corresponding diethylacetal was similarly prepared from ethyl diethoxyacetate. In each of these preparations a small amount of benzophenone was obtained, doubtless as a result of partial hydrolysis of these acetals to VII and the pyrolysis of this hydroxyaldehyde during distillation. The conversion of II to III proceeded in 88% yield. The chloroacetal III may be distilled under diminished pressure, but if heated to 180° it rapidly evolved methyl chloride and was transformed to methyl diphenylacetate.

The haloacetals IX and X were prepared from the corresponding hydroxyacetals and thionyl halides. An impure sample that showed the approximate chlorine and ethoxyl content of IX was obtained, but this compound could not be completely purified by distillation because of decomposition, which occurs at about 140°, into ethyl chloride and ethyl diphenylacetate. The preparation and distillation of IX has been reported.[6] An attempt was made to dehydrochlorinate IX to diphenylketene diethylacetal. Potassium *t*-butoxide in *t*-butyl alcohol gave an inseparable mixture, that appeared to consist mainly of the *t*-butoxyacetal corresponding to V and a smaller amount of the ketene acetal. Potassium *t*-butoxide in dioxane at 100° converted IX into the potassium enolate of ethyl diphenylacetate and a tar.

$(C_6H_5)_2CXCH(OR)_2$

IX, X is Cl, R is C_2H_5
X, X is Br, R is CH_3
XI, X is Br, R is C_2H_5

The bromoacetal X was obtained quite pure as a solid, m.p. 57–60°. At 120° it decomposed rapidly into methyl bromide and methyl diphenylacetate. After standing for a month, X had decomposed to an oil containing free bromine. From this oil methyl diphenylacetate, benzophenone and diphenylhydroxyacetaldehyde (VII) were separated. The acetal XI appeared to be too unstable to permit preparation by the procedure used for III, IX and X.



III, IX or X

The thermal decomposition of these haloacetals into an alkyl halide and an ester of diphenylacetic acid is, so far as the authors are aware, a unique reaction. It involves a shift of a hydride ion to an adjacent carbon with the simultaneous elimination

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[4] S. Danilow, *Ber.*, **62**, 2653 (1929); **60**, 2390 (1927).

[5] S. M. McElvain, *et al.*, This Journal, **64**, 254 (1942); **68**, 1922 (1946).

[6] H. Scheibler and A. Schmidt, *Ber.*, **67**, 1514 (1934).

of the alkyl halide. It would seem that this transformation involves the concerted mechanism shown below, rather than the formation of an intermediate epoxy ether, as this latter type of compound has been shown to be quite stable.[7]

Experimental

Methyl dimethoxyacetate (I) was prepared by the procedure used by Wohl and Lange,[8] and which involves the reaction of sodium dichloroacetate with sodium methoxide and esterification of the resulting dimethoxyacetic acid with methanol and hydrogen chloride. A 45% yield of I, b.p. 67° (18 mm.); $n^{25}\text{D}$ 1.4041, was obtained. The method of Cope[9] and that of Pucher[10] gave 44 and 29% yields of I, respectively.

The procedure of Wohl and Lange[8] gave a 41% yield of ethyl diethoxyacetate, b.p. 93-95° (20 mm.); $n^{25}\text{D}$ 1.4089. The method of Cope[9] gave 24% yield and that of Pucher,[10] a 20% yield of this ester.

Diphenylhydroxyacetaldehyde Dimethylacetal (II).—To a Grignard solution prepared from 30.6 g. (1.31 moles) of magnesium and 206 g. (1.31 moles) of dry bromobenzene in one liter of dry ether was added slowly 51 g. (0.38 mole) of methyl dimethoxyacetate. As the last portion of the ester was added, the gummy addition product separated and made stirring of the reaction mixture difficult. After refluxing the mixture for one hour, the addition complex was decomposed with a saturated ammonium chloride solution and the ether layer separated. The aqueous layer was extracted with ether and the combined ether extracts dried. After distillation of the ether, a small amount of biphenyl and 7 g. (10%) of benzophenone, 102 g. (79%) of II, b.p. 133-136° (0.6 mm.), $n^{25}\text{D}$ 1.5621, was obtained. On standing it solidified, m.p. 46-48°.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02; OCH_3, 24.0. Found: C, 74.20; H, 7.26; OCH_3, 23.6.

Diphenylhydroxyacetaldehyde Diethylacetal.[6]—This acetal was prepared by the above procedure, using ethyl diethoxyacetate instead of methyl dimethoxyacetate. The yield was 88% of a viscous colorless oil, b.p. 120-123° (0.2 mm.), $n^{25}\text{D}$ 1.5430, which did not crystallize either at room temperature or in the refrigerator.

Diphenylchloroacetaldehyde Dimethylacetal (III).—To a solution of 99.5 g. (0.38 mole) of diphenylhydroxyacetaldehyde dimethylacetal and 37.9 g. (0.47 mole) of dry pyridine in 200 ml. of anhydrous benzene was added dropwise 52.4 g. (0.44 mole) of thionyl chloride with stirring and cooling. The reaction mixture was then stirred while it was heated on a water-bath at 50-55° for one hour. After cooling, the benzene solution was decanted from the precipitated pyridine hydrochloride. This salt was washed with two 50-ml. portions of dry ether, the combined solution and washings were distilled under diminished pressure at room temperature and the residue then taken up in anhydrous ether. The ether solution was decanted from precipitated pyridine hydrochloride, boiled with 3 g. of Norite, and filtered. This treatment with Norite was repeated twice in order to remove completely the turbidity caused by the presence of pyridine hydrochloride. After the benzene and ether were removed under reduced pressure, III crystallized to a solid that weighed 92 g. (88%), m.p. 59-62°. Recrystallization from a mixture of petroleum ether (b.p. 40-60°) and dry ether gave material of m.p. 63-64.5°.

Anal. Calcd. for $C_{16}H_{17}ClO_2$: Cl, 12.8; OCH_3, 22.4. Found: Cl, 12.6; OCH_3, 22.5.

Distillation of 7 g. of III under reduced pressure yielded 6.5 g. of a colorless viscous liquid, b.p. 131-133° (0.5 mm.); $n^{25}\text{D}$, 1.5724 (supercooled liquid); there was no rise in pressure during the distillation. On seeding, the oil crystallized completely to a white solid, m.p. 61-63°; mixed m.p. with undistilled III, 60-64°.

Diphenylbromoacetaldehyde Dimethylacetal (X).—To a solution of 18.5 g. (0.072 mole) of II and 6.3 g. (0.08 mole) of anhydrous pyridine in 50 ml. of anhydrous benzene was added dropwise 15.6 g. (0.075 mole) of thionyl bromide[11] with cooling and stirring. After heating the mixture at 50° for one hour, the solution was cooled to 0°. The benzene solution was decanted from the precipitated pyridine hydrobromide and the precipitate washed with anhydrous benzene. The benzene solutions were combined and evaporated to leave a dark red oil, which then was dissolved in anhydrous ether. The ether solution was decanted from the precipitated pyridine hydrobromide, treated with charcoal, and filtered. This left a pale yellow solution from which all the ether was removed by distillation under reduced pressure. A yellow oil remained; after it had sat in the refrigerator overnight, crystals appeared. The oily crystals were washed with 10 ml. of cold ligroin (b.p. 40-60°). The yield of X was 7.0 g. (30%), m.p. 57-60°. Further crystallization of the remaining oil was not possible.

Anal. Calcd. for $C_{16}H_{17}BrO_2$: Br, 24.9; OCH_3, 19.3. Found: Br, 24.8; OCH_3, 17.7.

Use of different ratios of II, triethylamine or pyridine and phosphorus tribromide failed to yield the bromoacetal in a more pure condition. When an attempt was made to distil this bromoacetal under reduced pressure, there was a rise in pressure for 15 minutes, while the oil-bath was at 120°. The liquid was then distilled and gave an oil, b.p. 109-117° (0.6 mm.); $n^{25}\text{D}$ 1.5753. This oil contained 12.3% methoxyl and gave a saponification equivalent of 252 (calcd. for methyl diphenylacetate, 13.7% and 226%, respectively). Diphenylacetic acid was isolated in 71% yield after saponification of this oil.

The bromoacetal X decomposed on storage in a ground-glass stoppered brown bottle. After one month, the solid was completely liquified to an oil containing 3.3% of bromine and yielded on dilution with ether a small amount (0.05 g.) of diphenylhydroxyacetaldehyde, m.p. 158-163°. The remaining oil (6.5 g.) gave 4.0 g. of methyl diphenylacetate, m.p. 53-59°, and 1.6 g. of benzophenone on distillation under reduced pressure.

In an attempt to prepare diphenylbromoacetaldehyde diethylacetal (XI), 16.8 g. of thionyl bromide was added to a solution of 22 g. (0.077 mole) of diphenylhydroxyacetaldehyde diethylacetal and 6.7 g. (0.085 mole) of dry pyridine in 50 ml. of dry benzene. After removal of pyridine hydrobromide and benzene, a yellow-orange oil remained. This material showed an ethoxyl and bromine content 4.3 and 3.8%, respectively, lower than the calculated values for the bromoacetal (XI). On standing in a refrigerator for one week, this product failed to crystallize and had decomposed to a red-black gum.

Diphenylchloroacetaldehyde Diethylacetal (XI).—The chloro-diethylacetal was prepared from the corresponding hydroxyacetal by the procedure used in the preparation of III. The yield of this viscous, pale yellow oil, $n^{25}\text{D}$ 1.5502, was 91.5%. It failed to crystallize either in the refrigerator or from ligroin (b.p. 40-60°) in which it was partially soluble. It contained 10.75% of chlorine and 28.5% of ethoxyl (calcd. for IX: 11.65 and 29.4%).

On attempting to distil 45 g. of this chloroacetal under reduced pressure, the pressure began to rise at a bath temperature of 140°. After 2.5 hours at this temperature the pressure returned to normal and the liquid was distilled; 32.5 g. of distillate, b.p. 120-122° (0.6 mm.), was obtained. This distillate contained 16.6% ethoxyl and 3.3% chlorine. A total yield of 11 g. (30%) of ethyl diphenylacetate was obtained from the distillate by dissolving in alcohol and seeding the solution. After filtration and distillation of the alcoholic filtrate under reduced pressure at room temperature, the oily residue remaining contained 3.9% chlorine and 21.8% ethoxyl (the calculated ethoxyl content for ethyl diphenylacetate is 19.8% and for the chloroacetal (IX) is 29.4%).

When diphenylchloroacetaldehyde diethylacetal was allowed to stand for three weeks in a glass stoppered bottle, decomposition resulted; the remaining oil, $n^{25}\text{D}$ 1.5670, had lost 3.9% of its chlorine and 12.4% of its ethoxyl content. The chlorine content indicated that about 66% chlorodiethylacetal remained. Heating this material gave a 30% yield of ethyl chloride and a residue, which after distillation gave a 55% yield of pure ethyl diphenylacetate and an oil,

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[7] C. L. Stevens, *et al.*, THIS JOURNAL, **72**, 4758 (1950); W. Madelung and M. E. Oberwenger, *Ann.*, **490**, 201 (1931). In this connection, however, it should be noted that a rearrangement of 1-cyclohexyloxy-1-epoxycyclohexane has been reported (M. Mousseron and R. Jacquier, *Compt. rend.*, **229**, 374 (1949)).

[8] A. Wohl and M. Lange, *Ber.*, **41**, 3612 (1908).

[9] A. C. Cope, THIS JOURNAL, **58**, 570 (1926).

[10] G. W. Pucher, *ibid.*, **42**, 2251 (1920).

[11] J. R. Partington and H. A. Mayes, *J. Chem. Soc.*, **129**, 2594 (1926).

b.p. 121–126° (0.9 mm.); $n^{25}\text{D}$ 1.5888. This oil gave positive Fehling and Tollens tests and an orange precipitate with 2,4-dinitrophenylhydrazine reagent. Treatment with hydroxylamine hydrochloride and potassium acetate in alcohol–water solution, gave benzophenone oxime, m.p. 141–144°; with semicarbazide hydrochloride and pyridine in alcohol solution diphenylhydroxyacetaldehyde semicarbazone,[4] m.p. 243–244.5° (dec.), was obtained. When the oil, which amounted to 45% of the distillate, was dissolved in hot alcohol–water mixture, benzophenone, m.p. 45–48°, crystallized on cooling; none of the solid diphenylhydroxyacetaldehyde could be separated from the mother liquor.

The pyrolysis of IX began at an oil-bath temperature of 140°. A 9.0-g. sample of IX, after 3.5 hours at this temperature, left a residue (8.0 g.), which on distillation yielded 5.1 g. (71%) of ethyl diphenylacetate, m.p. 57–59°.

Diphenylketene Dimethylacetal (IV) (a) Reaction of III with Potassium *t*-Butoxide in Dioxane.—To a mixture of 26.8 g. (0.24 mole) of sublimed potassium *t*-butoxide[12] and 250 ml. of dry dioxane was added a solution of 55.4 g. (0.2 mole) of diphenylchloroacetaldehyde dimethylacetal (III) in 150 ml. of dry dioxane. The mixture was stirred and refluxed for 63 hours after which time the basicity of the reaction mixture was reduced to the point required for complete dehydrohalogenation. The insoluble material was separated from the reaction mixture by centrifuging and subsequent decanting of the supernatant liquid, and washed with anhydrous ether. The insoluble material was found to contain not only potassium chloride, but also the potassium enolate of methyl diphenylacetate, the presence of which was shown by its vigorous reaction with water to yield methyl diphenylacetate. The ether washings and the dioxane solution were combined and the solvents distilled. The residue was fractionally distilled under reduced pressure through a 30-cm. column packed with wire saddles. The distillate consisted solely of 23.7 g. (49%) of diphenylketene dimethylacetal (IV), b.p. 120–126° (0.5 mm.), $n^{25}\text{D}$ 1.5935 (supercooled liquid); m.p. 60–67°. After recrystallization from petroleum ether (b.p. 40–60°), it melted at 66–68°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; OCH_3, 25.8. Found: C, 79.56; H, 6.82; OCH_3, 25.5.

(b) **Reaction of III with Potassium *t*-Butoxide in *t*-Butyl Alcohol.**—To a solution of potassium *t*-butoxide, prepared by the reaction of 11.6 g. (0.0297 mole) of potassium with 250 ml. of absolute *t*-butyl alcohol, was added 82 g. (0.297 mole) of III dissolved in 250 ml. of *t*-butyl alcohol. The solution was refluxed with mechanical stirring. After 71 hours, 94% of the basicity of the solution had disappeared. The removal of both the potassium chloride formed in the reaction and the solvent was accomplished as in (a). The residual material was fractionally distilled through a fifteen plate Fenske column and twenty-three fractions taken in the boiling range of 114° (0.3 mm.) to 131° (0.7 mm.). From the first fifteen fractions, 21.6 g. (30%) of diphenylketene dimethylacetal, m.p. 59–64°, crystallized on standing. The solid was isolated from the occluded oil by collecting on a suction filter and washing with cold petroleum ether (b.p. 40–60°), in which the oil was soluble.

The other fractions (47 g.) which did not crystallize, were refractionated and fifteen fractions taken within the range of 115° (0.4 mm.) to 111° (0.15 mm.). The fractions were found to be a mixture of diphenylketene dimethylacetal and **diphenyl-*t*-butoxyacetaldehyde dimethylacetal (V).** The highest boiling material (9.5 g.), b.p. 110–111° (0.15 mm.), $n^{25}\text{D}$ 1.5337, was pure V. A plot of refractive index against composition for the intermediate fractions indicated the presence of 11.7 g. of ketene acetal (total yield 33.3 g. (47%)) and 38.0 g. (39%) of V as the products of this reaction.

Anal. Calcd. for $C_{20}H_{26}O_3$ (V): C, 76.40; H, 8.34; OR, 43.0. Found: C, 76.07; H, 8.37; OR, 34.5.[13]

When 2.0 g. of V was refluxed with 60 ml. of 10% hydrochloric acid for three hours, 1.2 g. (68%) of benzoin, m.p. 127–132°, was obtained; no diphenylacetic acid could be isolated. Oxidation of 1.0 g. of V with 6.9 g. of chromium trioxide in 15 ml. of glacial acetic acid containing a trace of sulfuric acid gave a quantitative yield of benzophenone, m.p. 44–48°.

To 10 ml. of water was added 3.3 g. of V and sufficient dioxane to give a homogeneous solution. A few drops of hydrochloric acid then was added and the solution was heated on the steam-bath for ten minutes. Removal of the dioxane and water under diminished pressure at room temperature left a yellow oil, $n^{25}\text{D}$ 1.5357, which gave a positive test with Fehling solution. Nothing crystallized from the oil but fractional distillation gave 1.2 g. (70%) of benzophenone, m.p. 43–48°.

A mixture containing 12 g. of IV and 18 g. of V was refluxed with 50 ml. of 48% hydrobromic acid for 15 minutes. The mixture was then distilled until 30 ml. of a milky distillate was collected. This distillate was saturated with sodium bromide and then extracted with ether. The ether was dried with calcium chloride and distilled through a Vigreux column. There was a small amount of residual liquid in the flask which was fractionally distilled through a 30-cm. Vigreux column to yield 0.5 g. (8%) of *t*-butyl bromide, b.p. 71–72°. This halide was converted to the Grignard reagent and treated with α-naphthyl isocyanate to form N-(α-naphthyl)-trimethylacetamide, m.p. 144–147°. The reported melting point is 147°. The residue, after distillation of the *t*-butyl bromide, was diluted with water, extracted with ether and the ether washed with sodium carbonate to remove diphenylacetic acid (19%), m.p. 142–146°. After complete removal of the ether the residue was allowed to stand in a refrigerator for a week. Washing with ether caused the separation of 3.7 g. of a white amorphous solid, which was not identified, from a dark red oil. After removal of the ether, the oil was distilled under reduced pressure. From the distillate it was possible to separate a 39% yield of benzil (based on V) and a 48% yield of methyl diphenylacetate (based on IV). The remaining material was an oil, which solidified on seeding with benzophenone; a 48% yield (based on V) of this product was obtained.

(c) **Reaction of III with Mono Sodium Pinacolate in Pinacol.**—While stirring the solution resulting from the addition of 2.8 g. (0.12 mole) of sodium to 130 ml. of anhydrous pinacol, 27.7 g. (0.10 mole) of III was added. The solution was then heated at 105° for 48 hours. The reaction mixture was cooled and worked up in the same manner as in (a). Fractional distillation under reduced pressure yielded 9.1 g. (38%) of diphenylketene dimethylacetal (IV), b.p. 117–124° (0.30 mm.), and 15.2 g. (42%). of **diphenylpinacoloxyacetaldehyde dimethylacetal** (VI), b.p. 152° (0.40 mm.) to 167° (0.60 mm.). Redistillation of this material gave 10.5 g. of pure VI, b.p. 140–141° (0.15 mm.).

Anal. Calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44; OCH_3, 17.3. Found: C, 73.88; H, 8.47; OCH_3, 17.4.[14]

(d) **Reaction of III with Potassium *t*-Butoxide in Dibutyl Ether.**—To 50 ml. of dry dibutyl ether, 13.4 g. (0.12 mole) of sublimed potassium *t*-butoxide was added. Most of the salt went into solution on refluxing. While this mixture was stirred and heated on an oil-bath at 110°, 27.7 g. (0.10 mole) of III was added. After stirring and heating at 110° for 48 hours, the color of the reaction mixture had changed from yellow to brown. The reaction mixture then was cooled and diluted with an equal volume of dry diethyl ether. The insoluble potassium chloride and potassium enolate of methyl diphenylacetate were removed by centrifuging and the supernatant liquid decanted. The solvents were distilled from the liquid. The residue from this distillation was then distilled under reduced pressure; 7.2 g. (30%) of diphenylketene dimethylacetal (IV), b.p. 114–117° (0.3 mm.), $n^{25}\text{D}$ 1.5938, was collected. There was 10 g. of a tarry resinous material left in the flask.

When the insoluble salts were treated with water, a vigorous reaction occurred and 8.8 g. of methyl diphenylacetate was separated. The aqueous solution contained 0.061 mole of titratable basicity.

Reactions of Diphenylketene Dimethylacetal (IV) (a) **With Water.**—A thermometer, previously dipped in con-

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[12] S. M. McElvain and A. N. Bolstad, This Journal, 73, 1988 (1951).

[13] The total alkoxy content (2 OCH_3 and 1 OC_4H_9) of V is 43% and the methoxyl content is 19.7%. The found value calcd. as OCH_3 amounts to 23.8%, but calcd. as 2 OCH_3 and 1 OC_4H_9 is the 34.5% value shown. This latter value was considered acceptable after it was found that only 60% of the butoxyl content of *t*-butyl alcohol was found in an analysis of this compound in the methoxyl apparatus.

[14] It was necessary to carry out the methoxyl analysis with a refluxing period of no longer than one hour in order to obtain the reported methoxyl values. Longer periods gave higher values, presumably due to interference of the pinacoloxy group.

centrated hydrochloric acid, was placed in a solution of 2.0 g. of IV in a mixture of water and dioxane. There was a slight (2°) rise in temperature. The water and dioxane were distilled under reduced pressure at room temperature. Methyl diphenylacetate (1.95 g.), m.p. 48–53°, remained as a solid residue.

When 1.5 g. of the ketene acetal IV was refluxed with a mixture of 10 ml. of concentrated hydrochloric acid and 50 ml. of water for 12 hours, 0.8 g. (62%) of diphenylacetic acid, m.p. 138–145°, was isolated. No other materials could be separated from the reaction mixture.

(b) **With Methanol. Methyl Orthodiphenylacetate.**—To a solution of 10 g. of IV in 50 ml. of absolute methyl alcohol (dried over magnesium methoxide) was added a trace of hydrochloric acid on a thermometer. There was no apparent rise in temperature. The solution was allowed to stand overnight and then made alkaline with a dry methanolic solution of sodium methoxide. After removal of the methyl alcohol under reduced pressure, a solid residue remained which was washed with 5 ml. of cold methanol, and then recrystallized from petroleum ether (b.p. 40–60°). The methyl orthodiphenylacetate, m.p. 39–43°, so obtained amounted to 8.2 g. (75%). This product showed a depression in melting point when mixed with either methyl diphenylacetate or IV.

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40; OCH_3, 34.2. Found: C, 74.97; H, 7.27; OCH_3, 33.4.

This orthoester could be distilled under reduced pressure without decomposition; b.p. 136–141° (0.8 mm.), $n^{25}D$ 1.5515.

(c) **With Bromine.**—To 10 g. of IV in a flask with a side arm connected to a Dry Ice trap, was added a 0.480 *M* solution of bromine in carbon tetrachloride through a buret until the first permanent appearance of a yellow color. There was considerable heat and gas evolved and 84.60 ml. (97%) of the bromine solution was required for the titration. The Dry Ice trap contained methyl bromide, b.p. 0–5°. The carbon tetrachloride was removed under reduced pressure. The residue of methyl diphenylbromoacetate[15] weighed 12.6 g. (100%); it contained 10.8% methoxyl (calcd. 10.2%) and 25.4% bromine (calcd. 26.2%).

(d) **With Potassium *t*-Butoxide.**—To 8 g. of IV dissolved in 60 ml. of dry dioxane was added 4.8 g. of powdered sublimed potassium *t*-butoxide. The mixture immediately turned yellow but there was no evidence of heat evolution. The mixture was refluxed and stirred for 48 hours. After the first half-hour, the potassium *t*-butoxide dissolved and there was no evidence of insoluble material. After 24 hours, a voluminous white precipitate had formed and after 48 hours, the reaction mixture was a thick, pasty mass. The mixture was cooled and centrifuged. The supernatant liquid was decanted from the precipitate and distilled through a 60-cm. Vigreux column. The first 10 ml. of distillate, b.p. 70–94°, was redistilled through a 25-cm. Fenske column and 0.15 g. of methyl *t*-butyl ether,[16] b.p. 58–60°; $n^{25}D$ 1.3798, with a characteristic camphoric odor was collected. The remainder of the dioxane was distilled and then the residue was distilled under diminished pressure. The distillate consisted entirely of 2.3 g. (29%) of IV, b.p. 135–140.5° (0.5 mm.), m.p. 63–66° after solidification.

A portion of the separated solid material was treated with water; heat was evolved and a water-insoluble oil formed. The oil was extracted with ether, which then was removed under reduced pressure at room temperature. The residue solidified when seeded with methyl diphenylacetate. The ether extracted aqueous solution was acidified and again extracted with ether. The ether was removed under reduced pressure and the solid residue was found to contain diphenylacetic acid which was contaminated with a trace of benzilic acid. The latter was indicated by its characteristic red color in concentrated sulfuric acid.

The remainder of the solid potassium enolate was stirred and refluxed for 20 hours with ethyl iodide under a nitrogen atmosphere. The reaction mixture was treated with water extracted with ether. The ether extracts were dried and the ether distilled. The residue was then distilled under reduced pressure to yield 3.5 g. (41%) of methyl α,α-diphenyl butyrate,[17] b.p. 122–131° (0.15 mm.). This ester, when saponified, yielded α,α-diphenylbutyric acid, m.p. 141–168°. Two recrystallizations from alcohol gave pure material, m.p. 172–174°.[17]

(e) **With Benzyl Bromide.**—To 10 g. (0.04 mole) of IV was added 14.2 g. (0.08 mole) of benzyl bromide. There was no evolution of gas as determined by a mercury bubbler, until the mixture was heated to the reflux temperature (approx. 200°). The solution was refluxed for two hours and then the benzyl bromide was removed by distillation. The residue was fractionally distilled under reduced pressure. The fraction b.p. 119–138° (0.05 mm.) partially solidified on standing. The solid (2.5 g. (27%)), was methyl diphenylacetate, m.p. 58–60°. The remaining liquid (0.45 g., $n^{25}D$ 1.5810) was impure ketene acetal IV. The intermediate fraction, b.p. 144–212° (0.05 mm.), when triturated with methyl alcohol solidified to yield 4.1 g. (31%) of methyl α,α,β-triphenylpropionate.[18] After two recrystallizations from methanol, the material melted at 126–128° and contained 9.3% (calcd. 9.8%) methoxyl. The highest boiling (230–270° (0.05 mm.)) fraction (3.65 g.) consisted of a red viscous oil which failed to crystallize. This material was not investigated further.

(f) **With Benzoyl Chloride.**—A solution of 10 g. (0.04 mole) of IV in 12.7 g. (0.08 mole) of benzoyl chloride was heated on an oil-bath at 150° for one-half hour. The reaction flask was connected to a Dry Ice-trap; at the end of the heating period no liquid was present in the trap. Distillation of the mixture under reduced pressure gave 11.2 g. (88%) of benzoyl chloride and 9.6 g. (96%) of IV.

A similar reaction mixture was heated at the reflux point; no methyl chloride was evolved. After removal of the benzoyl chloride by distillation, the residue was fractionally distilled under reduced pressure. The lower boiling fractions, b.p. 116–130° (0.35 mm.), consisted of 2.40 g. (45%) of methyl diphenylacetate and 1.05 g. (21%) of IV. The higher boiling fractions, b.p. 190–210° (0.35 mm.), consisted of a viscous red oil from which no crystalline material could be obtained.

(g) **With Methyl Chloroformate.**—A mixture of 4.5 g. of this halide and 10 g. of IV was heated in a sealed tube at 190° for three hours. There was no evidence of pressure when the tube was cooled and opened. Distillation of the contents yielded 3.0 g. (67%) of the methyl chloroformate and 9.15 g. (91.5%) of unchanged IV.

(h) **With Acetyl Chloride.**—Solution of 10 g. (0.04 mole) of IV in 6.5 g. (0.08 mole) of freshly distilled acetyl chloride was endothermic. The solution was refluxed for 1.5 hours. No liquid condensed in the two Dry Ice-traps connected to the apparatus. The acetyl chloride was distilled and 3.05 g. (47%) was collected in an ice-cooled receiver. The residue was distilled under reduced pressure and 9.1 g. (91%) of IV was recovered.

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[15] W. H. Carothers, THIS JOURNAL, **48**, 3192 (1926).

[16] L. Henry, *Rec. trav. chim.*, **23**, 327 (1904); A. W. Smith and C. E. Boord, THIS JOURNAL, **48**, 1512 (1926).

[17] H. Staudinger, *Helv. Chim. Acta*, **5**, 656 (1922).

[18] W. Schlenk, H. Hillemann and I. Rodloff, *Ann.*, **487**, 135 (1931).