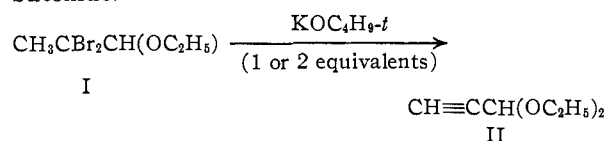


[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

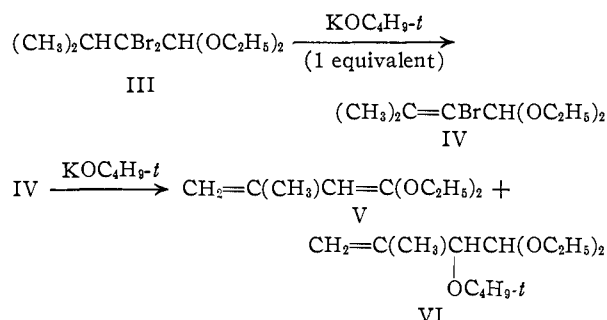
Ketene Acetals. XXVIII. The Dehalogenation of  $\alpha,\alpha$ -Dibromoacetals. Isopropenylketene DiethylacetalBY S. M. McELVAIN AND LEO R. MORRIS<sup>1</sup>

The dehydrobromination of certain  $\alpha,\alpha$ -dibromoacetals was studied in an attempt to prepare allenes of the type,  $R_2C=C=C(OC_2H_5)_2$ . Reaction of the dibromopropionaldehyde acetal (I) yielded only propionaldehyde acetal (II). The dibromoisovaleraldehyde acetal (III) was readily dehydrohalogenated to the  $\alpha$ -bromosenecialdehyde acetal (IV), but the dehydrobromination of this compound with either potassium *t*-butoxide or sodium ethoxide was quite slow and produced a mixture of the isopropenylketene acetal (V) and the corresponding  $\alpha$ -alkoxyacetal (VI or VIII). The attempted dehydrobromination of  $\alpha$ -bromo- $\beta$ -phenylcinnamaldehyde acetal (XI) gave low (25%) yields of the debrominated product,  $\beta$ -phenylcinnamaldehyde acetal (X) as the only volatile product. In the preparation of XI by the reaction of pyridine perbromide with X, an interesting side reaction involving the brominolysis of X to 1,1-diphenyl-2-bromoethylene was encountered and found to be reduced by the presence of an excess of pyridine. Isopropenylketene diethylacetal was characterized by reactions with water, ethanol and maleic anhydride; its ultraviolet absorption spectra also indicated absence of the allene structure  $(CH_3)_2C=C=C(OC_2H_5)_2$ . The alkoxyacetals (VI and VIII) show distinctly different behaviors with 2,4-dinitrophenylhydrazine; VI yields a bis-hydrazone (osazone) of  $\alpha$ -ketoisovaleraldehyde while VIII forms the hydrazone of the  $\alpha$ -ethoxy unsaturated aldehyde.

It was previously shown<sup>2</sup> that dibromomalon-aldehyde tetraethylacetal underwent replacement of one of the halogens by hydrogen and subsequent dehydrohalogenation to diethoxymethylketene diethylacetal when treated with potassium *t*-butoxide. In a continuation of this study of dibromoacetals, the dehydrobrominations of  $\alpha,\alpha$ -dibromopropionaldehyde diethylacetal (I) and of  $\alpha,\alpha$ -dibromoisovaleraldehyde diethylacetal (III) have been effected. Dibromoacetal I gave propionaldehyde diethylacetal (II) as the only product, when treated with either one or two equivalents of potassium *t*-butoxide.

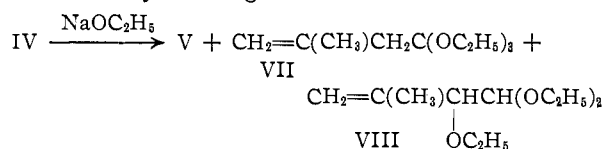


The dibromoacetal III, however, could be dehydrobrominated with one equivalent of base to give  $\alpha$ -bromosenecialdehyde diethylacetal (IV) in good yield. When IV was further treated with another equivalent of potassium *t*-butoxide, isopropenylketene diethylacetal (V) was isolated, along with some higher boiling material, part of which appeared to be the *t*-butoxyacetal (VI).



When the unsaturated bromoacetal IV was treated with sodium ethoxide, the ketene acetal V, the orthoester VII and a compound believed to be the ethoxyacetal VIII were obtained. The production of orthoester VII was not surprising, since the ketene acetal V would be expected to add ethanol

to some extent under the reaction conditions used for the dehydrohalogenation.



It has been previously found<sup>3</sup> that monobromoacetals of the general structure  $R_2CHCHBrCH(OR')_2$  undergo dehydrohalogenation to give the  $\alpha,\beta$ -unsaturated acetals, indicating that the hydrogen on the aldehyde carbon is more difficult to remove than the  $\beta$ -hydrogen. The reaction of  $\alpha,\alpha$ -dibromopropionaldehyde diethylacetal (I) would seem to substantiate this observation, since only  $\beta$ -hydrogens were eliminated. However, an alternative mechanism might involve the formation of an allene structure,  $CH_2=C=C(OC_2H_5)_2$ , which could then rearrange to give II. Although there is no direct evidence against such an acetylene rearrangement it would seem unlikely in view of the demonstrated stability of other ketene acetals under such reaction conditions.<sup>3</sup>

It is of interest to note that none of the expected intermediate  $\alpha$ -bromoacrolein diethylacetal was isolated, even from the reaction of I with a single equivalent of base. This indicates that the  $\alpha$ -bromoacrolein acetal, if it is formed as an intermediate, is more readily dehydrobrominated than the dibromoacetal (I).

In the case of  $\alpha,\alpha$ -dibromoisovaleraldehyde diethylacetal (III) only one  $\beta$ -hydrogen is available so that removal of two equivalents of hydrogen bromide must necessarily involve the hydrogen on the carbon holding the alkoxy groups. That the second dehydrobromination step is indeed more difficult is shown by the much slower rate of bromine removal from IV than from III to produce IV, about 23 hours were required for the transformation IV  $\rightarrow$  V + VI as compared with four hours for the dehydrobromination of III to IV.

The intermediate monobromoacetal IV was found to be rather unstable at room temperature but stable at refrigerator temperature. The structure was indicated by the slow reaction with silver

(1) Standard Oil Company of Indiana Fellow, 1950-1951.

(2) S. M. McElvain and L. R. Morris, *THIS JOURNAL*, **73**, 206 (1951).(3) S. M. McElvain, R. L. Clarke and G. D. Jones, *ibid.*, **64**, 1966 (1942).

nitrate (suggesting the absence of an allylic bromide structure) and by the production of acetone by oxidation with alkaline permanganate. The acetal IV readily decolorized the latter reagent but reacted quite slowly with bromine.

Initial attempts to dehydrohalogenate IV with potassium *t*-butoxide were complicated by the high reactivity of the isopropenylketene diethylacetal (V). Strictly anhydrous conditions and absence of air were found to be necessary at all times to prevent its decomposition. It seems likely that a rearrangement of the double bond of IV occurred prior to the elimination of hydrogen bromide<sup>4</sup>; the resulting allylic bromide would then undergo the concurrent reactions: (a) Replacement of the halogen by alkoxy to produce VI (or VIII) and (b), dehydrobromination to the ketene acetal V. Alkoxy determinations on V and VII generally gave values considerably higher than the theoretical (usually analyses for these groups are low with ketene acetals and orthoesters) and could not be depended upon for identification purposes. These high alkoxy values doubtless were due to the conversion of senecioic acid ( $\beta$ -methylcrotonic acid) to *t*-butyl iodide *via* decarboxylation to isobutylene, as an alkoxy determination on this acid showed that about 0.8 mole of an alkyl iodide was formed per mole of acid.

In order to study the dehydrohalogenation of a compound in which there was no possibility for such a shift of the double bond that appeared to occur in IV,  $\alpha$ -bromo- $\beta$ -phenylcinnamaldehyde diethylacetal (XI) was treated with potassium *t*-butoxide under a variety of conditions. When the reaction was carried out in solvents such as *t*-butanol or dioxane, the only volatile product obtained was a 25% yield of  $\beta$ -phenylcinnamaldehyde diethylacetal (X). Only intractable tars were found in the distillation residues from these reactions. However, at a higher temperature with dry, sublimed<sup>5</sup> potassium *t*-butoxide, a 60% yield of  $\beta$ , $\beta$ -diphenylpropionic acid was isolated from the residue remaining from the distillation of volatile material. In another experiment a mixture of sublimed *t*-butoxide and XI was heated under vacuum in order to distil any volatile products as they were formed from the reaction. In this manner the theoretical amount of *t*-butanol and a 26% yield of X was collected. The residue was a tar similar to those obtained from the reaction using solvents; from this residue small amounts of  $\beta$ -phenylcinnamic acid and an orange powder, m.p. 268–269°, were obtained. Analyses indicated the latter compound to have the formula  $C_{30}H_{24}O_3$  and to contain one ethoxyl group; no further identification of this product was undertaken.

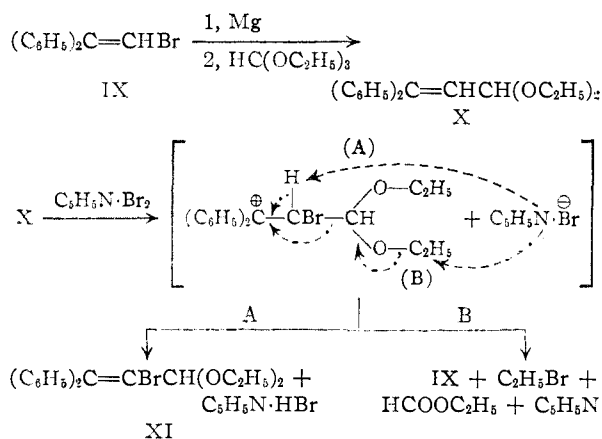
The debromination of XI to X with potassium *t*-butoxide is similar to that previously observed with dibromomalonaldehyde tetraethylacetal. Pre-

sumably the two phenyl substituents exert sufficient electron attraction to promote the separation of positive halogen.

The mode of formation of the  $\beta$ , $\beta$ -diphenylpropionic acid in the experiment at high temperature with no solvent is not clear. At first it was thought that this acid was  $\beta$ -phenylcinnamic acid, which has similar properties and whose formation would be more understandable. However, a careful check definitely showed that the reaction product was the saturated acid. Besides a debromination of XI, the production of the propionic acid requires a cleavage of the ethoxyl groups with an oxidation of the acetal carbon and a simultaneous reduction of the double bond.

There was no evidence to indicate that dehydrohalogenation of XI had occurred to give any of the allene,  $(C_6H_5)_2C=C=C(OC_2H_5)_2$ , except perhaps that the tar formation was indicative of an easily polymerizable product; from certain runs a small amount of  $\beta$ -phenylcinnamic acid was isolated from this tar.

The preparation of I and III was best achieved by direct, low-temperature bromination of the appropriate aldehyde, followed by conversion of the dibromoaldehyde to the acetal. III was also prepared by the reaction of pyridine perbromide with  $\alpha$ -bromoisovaleraldehyde diethylacetal, but in lower yield. The preparation of XI was effected from  $\beta$ -phenylcinnamaldehyde diethylacetal (X), which was obtained in 48% yield by the reaction of ethyl orthoformate with the Grignard reagent prepared from 1,1-diphenyl-2-bromoethylene (IX). X is quite unreactive to bromine, but when heated with one equivalent of pyridine perbromide, it gave a 26% yield of XI, a 42% yield of IX, together with some ethyl bromide and ethyl formate. The manner in which these reaction products are formed is illustrated in the reactions



(4) A similar rearrangement has been noted in the reaction of  $\alpha$ -bromo  $\alpha$ - $\beta$  unsaturated acids with alcoholic alkali to give  $\alpha$ -alkoxy unsaturated acids. (L. N. Owens and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3088 (1949).) Evidence was presented to indicate that rearrangement of these  $\alpha$ - $\beta$  unsaturated acids to  $\beta$ - $\gamma$  unsaturated acids occurred before replacement of the halogen by an alkoxy group, and was prerequisite for the replacement reaction.

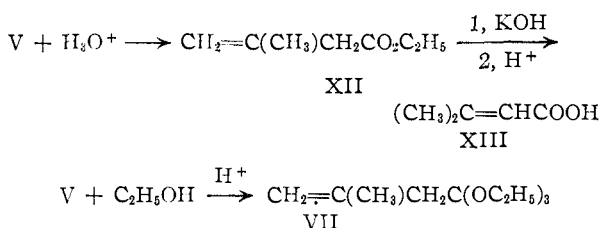
(5) S. M. McElvain and A. N. Bolstad, *ibid.*, **73**, 1988 (1951).

The intermediate carbonium ion may be stabilized either by elimination of the  $\alpha$ -proton to the anion (*via* (A)) or by an attack of this anion on an ethyl group of the acetal (*via* (B)). This latter reaction course, which is simply a brominolysis of X, is similar to the brominolysis of tribenzoylmethane reported by Bartlett and Cohen.<sup>6</sup> Support for the above postulated reaction path was found when the bromination of X was carried out in the presence of

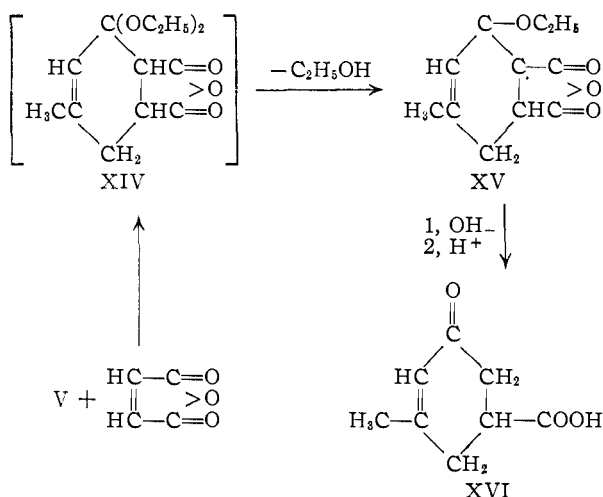
(6) P. D. Bartlett and S. G. Cohen, *J. Org. Chem.*, **4**, 88 (1939).

excess pyridine. In this more basic environment, which should facilitate removal of the proton *via* (A), the yield of XI was increased to 41% and that of IX decreased to 16%.

Isopropenylketene diethylacetal (V) was characterized by reactions with water, ethanol and maleic anhydride and by ultraviolet absorption data. Water containing a trace of acid reacted with V to give the unsaturated ester XII, the double bond of which is placed in the  $\beta,\gamma$ -position since oxidation failed to give any detectable acetone. Hydrolysis of XII gave the known seneciolic acid ( $\beta$ -methylcrotonic acid (XIII)), which, in contrast to XII, yields acetone on oxidation. The reaction of V with ethanol gave an orthoester with properties identical to those of the orthoester VII, obtained in the sodium ethoxide dehydrohalogenation of IV.



Maleic anhydride reacted readily with isopropenylketene diethylacetal to give an 85% yield of 3-ethoxy-5-methyl-1,6-dihydrophthalic anhydride (XV), a yellow-orange product, m.p. 141–144°. The ketal XIV was probably an intermediate,<sup>7</sup> since evidence of a spontaneous loss of alcohol at about 10° was noticed during the isolation of XV. The addition product, XV, was further characterized by hydrolysis to a ketoacid, XVI, and by conversion to the 2,4-dinitrophenylhydrazone of XVI.



Further evidence for the conjugated structure of V was afforded by the ultraviolet absorption curve which showed a maximum at 246  $\mu$  ( $\log \epsilon$  4.12). Allenes have been shown<sup>8</sup> to exhibit little or no absorption in this region, so the alternative structure,  $(\text{CH}_3)_2\text{C}=\text{C}=\text{C}(\text{OC}_2\text{H}_5)_2$ , appears quite unlikely.

(7) Cf. S. M. McElvain and H. Cohen, *THIS JOURNAL*, **64**, 260 (1942).

(8) F. B. Ingorge and F. Acree, *J. Org. Chem.*, **7**, 416 (1942).

Compounds VI and VIII have been tentatively assigned the structures of alkoxyacetals, based chiefly on their reactions with carbonyl reagents. Compound VI formed a bis-2,4-dinitrophenylhydrazone, but only a monophenylhydrazone. Analysis of the former derivative indicated that the acidic reagent had converted VI into the saturated keto-aldehyde,  $(\text{CH}_3)_2\text{CHCOCHO}$ , which then yielded the dihydrazone. The position of the double bond in both VI and VIII was assigned on the basis that no acetone was obtained upon oxidation. Compound VIII, in contrast to VI, formed a mono-dinitrophenylhydrazone that still contained an ethoxyl group. Apparently the acidic reagent is capable of effecting only the hydrolysis of the acetal group of VIII.

### Experimental

$\alpha,\alpha$ -Dibromopropionaldehyde Diethylacetal (I).—The procedure of Dworzak and Piffierling<sup>9</sup> was followed, except that monomeric propionaldehyde was used as the starting material. The dibromoacetal was prepared in 56% yield as a colorless liquid, b.p. 103–105° (18 mm.),  $n_D^{25}$  1.4768,  $d_4^{25}$  1.537, with a bromine content of 55.1% (calcd. 55.1).

**Reaction of I with Potassium *t*-Butoxide.**—To a slurry of potassium *t*-butoxide prepared by dissolving 17.0 g. (0.43 atom) of potassium in 250 of dry *t*-butanol, 125.0 g. (0.43 mole) of  $\alpha,\alpha$ -dibromopropionaldehyde diethylacetal (I) was added and the reaction mixture stirred under nitrogen for three hours at 100–105°. After cooling the mixture and adding 200 ml. of absolute ether, the cloudy solution was centrifuged, decanted and the residue washed with ether. Combined decantate and ether wash was concentrated at reduced pressure and then fractionated through a 20 cm. Vigreux column to give 16.0 g. (54% on unrecovered I) of propionaldehyde diethylacetal (II), b.p. 45–47° (18 mm.),  $n_D^{25}$  1.4100, and 60.0 g. (48%) of I, with no significant intermediate fraction. Analysis of II showed 68.2% ethoxyl (calcd. 70.3).

By using essentially the above procedure with excess base (2.5 mole of base per mole of I) an 81% conversion to II was effected, based on unrecovered I.

In each case the propionaldehyde acetal was characterized by the formation of the silver, mercuric and cupric salts, the latter being a yellow powder, m.p. 152–153° dec. (reported<sup>10</sup> m.p. 160° dec.). A 2,4-dinitrophenylhydrazone, prepared from II by the usual procedure, after recrystallization from 95% ethanol, melted at 120–121°.

*Anal.* Calcd. for  $\text{C}_9\text{H}_{16}\text{O}_4$ : N, 23.9. Found: N, 23.4.

$\alpha,\alpha$ -Dibromoisovaleraldehyde Diethylacetal (III).—Two procedures were used for this preparation; (b) was found to be the most efficient and convenient.

(a) By the method of Fischer<sup>11</sup>  $\alpha$ -bromoisovaleraldehyde diethylacetal was prepared from isovaleraldehyde in 53% yield, b.p. 79–81° (7 mm.),  $n_D^{25}$  1.4445. Pyridine perbromide was prepared by mixing equimolecular amounts of bromine and pyridine in carbon tetrachloride, followed by washing of the red precipitate by decantation, and complete removal of the solvent at reduced pressure. To 50.0 g. (0.21 mole) of the dry yellow perbromide in a flask equipped with stirrer and reflux condenser, 48.0 g. (0.21 mole) of  $\alpha$ -bromoisovaleraldehyde diethylacetal was added under an atmosphere of nitrogen. Upon warming to 50° the reaction became exothermic, but was maintained at 80° for three hours during which the dark red mixture became very viscous. After cooling and decanting, ether washes of the residue were combined with the decantate and distilled through a 20-cm. Vigreux column to give 21.5 g. (32%) of III, b.p. 105–113° (6 mm.),  $n_D^{25}$  1.4850.

(b) Essentially the same procedure as that of Dworzak and Enenkel<sup>12</sup> was followed. In a two-liter flask 95.0 g. (1.1 moles) of freshly distilled isovaleraldehyde was mixed with 80 ml. of chloroform and cooled by an ice-salt-bath.

(9) R. Dworzak and P. Piffierling, *Monatsh.*, **48**, 253 (1927).

(10) M. Grard, *Ann. chim.*, [10] **13**, 336 (1930).

(11) F. G. Fischer, *et al.*, *Ber.*, **64**, 30 (1931).

(12) R. Dworzak and A. Enenkel, *Monatsh.*, **50**, 456 (1928).

To this stirred solution 354 g. (2.2 moles) of bromine in 100 ml. of chloroform was added dropwise over two hours. The temperature was maintained at  $-5^{\circ}$  during the addition and then allowed to warm to  $20^{\circ}$  over another two hours. To this reddish solution 440 ml. of absolute ethanol and 80 ml. of ethyl orthoformate were carefully added; this addition caused the temperature to rise to about  $70^{\circ}$ . After standing overnight the solution was poured into two liters of water and ice. The organic layer was separated, extracted five times with sodium bicarbonate solution, and finally washed with sodium carbonate solution until colorless. After drying with calcium chloride and finally with anhydrous potassium carbonate, distillation yielded 178.0 g. (51%) of III, b.p.  $78-83^{\circ}$  (0.3 mm.),  $n_D^{25}$  1.4832, which contained 48.4% bromine and 28.8% ethoxyl (calcd.: Br, 50.2;  $C_2H_5O$ , 28.3).

**$\alpha$ -Bromosenecialdehyde Diethylacetal (IV).**—In a one-liter flask 31.5 g. (0.81 atom) of potassium was dissolved in 500 ml. of dry *t*-butanol. After removal of most of the excess alcohol to give a heavy slurry, 248.0 g. (0.78 mole) of  $\alpha,\alpha$ -dibromoisovaleraldehyde diethylacetal (III) was added under a nitrogen atmosphere. By slow heating the reaction was controlled and the temperature finally maintained at  $110^{\circ}$  for about four hours. After cooling the mixture, 700 ml. of anhydrous ether was added and the mixture centrifuged. Distillation of the decantate and ether washes of the residue gave 130.0 g. (70%) of  $\alpha$ -bromosenecialdehyde diethylacetal (IV), b.p.  $92-94^{\circ}$  (12 mm.),  $n_D^{25}$  1.4610,  $d_4^{25}$  1.190.

*Anal.* Calcd. for  $C_9H_{17}O_2Br$ : Br, 33.7;  $C_2H_5O$ , 38.0. Found: Br, 33.4;  $C_2H_5O$ , 38.0.

This acetal showed very slow absorption of bromine, but readily decolorized permanganate solution. Silver nitrate slowly gave a precipitate at room temperature. While this acetal was stable for several months at refrigerator temperature, it became dark red on standing for several days at room temperature.

A 2,4-dinitrophenylhydrazone prepared from IV was recrystallized from benzene to give bright red needles, m.p.  $214^{\circ}$  when placed in a melting point block preheated to  $210^{\circ}$ .

*Anal.* Calcd. for  $C_{11}H_{11}O_4N_4Br$ : N, 16.3. Found: N, 16.6.

Oxidation of IV by heating with excess alkaline permanganate gave acetone (10%) identified in the distillate by the formation of iodoform and dibenzalacetone, m.p.  $111-112^{\circ}$ .

**Reaction of IV with Bases (a) Potassium *t*-Butoxide.**—After dissolving 23.0 g. (0.59 atom) of potassium in 400 ml. of dry *t*-butanol, excess alcohol was removed to give a thick paste. To this cooled residue 88.5 g. (0.37 mole) of IV was added, followed by stirring and heating of the mixture under a nitrogen atmosphere for about 18 hours at  $90-100^{\circ}$ . A stillhead was then attached and alcohol slowly removed over a five-hour period until about 250 ml. of solution remained. Then 100 ml. of anhydrous ether was added, the solution centrifuged and the decantate, together with an ether extract of the residue, concentrated under reduced pressure. Distillation through a 50-cm. Stedman column gave 12.7 g. (21.6%) of isopropenylketene diethylacetal (V), b.p.  $65-69^{\circ}$  (7 mm.),  $n_D^{25}$  1.4630,  $d_4^{25}$  0.898. The ultraviolet absorption of this compound, as determined in purified petroleum ether (b.p.  $60-80^{\circ}$ ), showed a smooth curve with  $\lambda_{max}$  at  $246 m\mu$  ( $\log \epsilon$  4.12).

*Anal.* Calcd. for  $C_9H_{16}O_2$ : C, 69.20; H, 10.32;  $C_2H_5O$ , 57.7. Found: C, 68.60, 69.07; H, 10.20, 10.53;  $C_2H_5O$ , 63.5, 68.2, 71.1.<sup>13</sup>

Continued distillation of the residue from above gave about 21 g. of an intermediate cut, b.p.  $69-95^{\circ}$  (7 mm.), which could not be fractionated to yield any definite product. The highest boiling fraction, 9.4 g., b.p.  $46-52^{\circ}$  (0.1 mm.),  $n_D^{25}$  1.4310, was a 2-*t*-butoxy-3-methyl-3-butenal diethylacetal (VI).

*Anal.* Calcd. for  $C_{13}H_{26}O_3$ : C, 67.78; H, 11.38. Found: C, 67.86; H, 11.08.

**(b) Sodium Ethoxide.**—A mixture of 0.30 mole of sodium ethoxide in 25 ml. of ethanol and 59.3 g. (0.25 mole) of IV was treated as in (a). Distillation yielded three principal fractions: (1) 6.9 g. (0.044 mole), of V, b.p.  $63-66^{\circ}$  (7 mm.),  $n_D^{25}$  1.4501, which probably contained some orthoester

(VII); (2) 10.5 g. (0.051 mole), b.p.  $67-70^{\circ}$  (7 mm.),  $n_D^{25}$  1.4252, of ethyl ortho-3-methyl-3-butenate (VII).

*Anal.* Calcd. for  $C_{11}H_{22}O_3$ : C, 65.31; H, 10.96;  $C_2H_5O$ , 66.9. Found: C, 65.46; H, 10.68;  $C_2H_5O$ , 65.7.

The final fraction (3) was 6.7 g. (0.032 mole) of 2-ethoxy-3-methyl-3-butenal diethylacetal (VIII), b.p.  $86-89^{\circ}$  (7 mm.),  $n_D^{25}$  1.4303.

*Anal.* Calcd. for  $C_{11}H_{22}O_3$ :  $C_2H_5O$ , 66.9. Found:  $C_2H_5O$ , 61.9.

**Reactions of Isopropenylketene Diethylacetal (V) (a) With Water.**—When 1.6 g. of V was mixed with 0.5 g. of water containing a trace of acetic acid, an immediate warming occurred. After standing overnight the mixture was extracted with ether, dried over calcium chloride, and distilled to give 0.8 g. of the crude ethyl 3-methyl-3-butenate (XII), a fragrant liquid, b.p.  $140-155^{\circ}$ ,  $n_D^{25}$  1.4197. Upon oxidation of a portion of this ester with alkaline permanganate solution, no acetone was detected in the distillate.

*Anal.* Calcd. for  $C_7H_{12}O_2$ : C, 65.59; H, 9.44;  $C_2H_5O$ , 35.2. Found: C, 65.25; H, 9.51;  $C_2H_5O$ , 42.8.<sup>13</sup>

This ester was saponified by boiling with 10% potassium hydroxide for about four hours; acidification with dilute sulfuric acid gave an oil which was extracted with ether. After drying this extract and removal of solvent under reduced pressure, the crude, crystalline senecioic acid (XIII) was recrystallized from water, m.p.  $66-68^{\circ}$  (reported<sup>14</sup> m.p.  $68.5-69^{\circ}$ ); neut. equiv., 100.7 (calcd. 100.1). Oxidation of this acid with alkaline permanganate gave acetone in the distillate, which was isolated as the 2,4-dinitrophenylhydrazone, m.p.  $122.5-124.5^{\circ}$ .

**(b) With Ethanol.**—A mixture of 3.0 g. of V and 10.5 ml. of absolute ethanol gave no evidence of reaction. Upon adding a trace of glacial acetic acid an immediate warming occurred, after which the reaction mixture was allowed to stand at room temperature for five hours. The solution then was neutralized with sodium ethoxide and distilled to give as the main fraction 2.8 g. (0.014 mole) of ethyl ortho-3-methyl-3-butenate (VII), b.p.  $66-69^{\circ}$  (7 mm.),  $n_D^{25}$  1.4250. No acetone was detected following a permanganate oxidation of VII. This product appeared to be identical with the sample of VII, obtained as fraction (2) from the action of sodium ethoxide on IV.

**(c) With Maleic Anhydride.**—To 15 ml. of anhydrous ether containing 1.96 g. (0.02 mole) of maleic anhydride, a solution of 3.11 g. (0.02 mole) of V in 5 ml. of ether was added while cooling the solutions to about  $0^{\circ}$ . A yellow precipitate appeared immediately, from which the ether was removed under diminished pressure. Upon warming the residue to about  $10^{\circ}$  evidence of alcohol evolution occurred, leaving a viscous red oil which was recrystallized from toluene-ligroin to give 1.4 g. of red-orange crystals, m.p.  $135-140^{\circ}$ . Further recrystallizations gave an orange product, m.p.  $141-144^{\circ}$ , which was shown to be 3-ethoxy-5-methyl-1,6-dihydrophthalic anhydride (XV). Another 2.1 g. (total yield 0.017 mole) of XV was obtained from the mother liquors.

*Anal.* Calcd. for  $C_{11}H_{12}O_4$ : C, 63.45; H, 5.81;  $C_2H_5O$ , 21.6. Found: C, 63.22; H, 5.97;  $C_2H_5O$ , 20.9.

XV was hydrolyzed by first heating with alkali and then with dilute acid to give a white keto acid, presumably 3-carboxy-5-methyl-5-cyclohexenone (XVI), m.p.  $83-85^{\circ}$ ; neut. equiv., 154 (calcd. 151).

*Anal.* Calcd. for  $C_8H_{10}O_3$ : C, 62.32; H, 6.54. Found: C, 61.53; H, 6.60.

A 2,4-dinitrophenylhydrazone of XVI was prepared from XV by heating with methanolic 2,4-dinitrophenylhydrazine sulfate (Brady reagent<sup>15</sup>) and allowing to stand overnight. Upon scratching the flask, a yellow-orange precipitate was formed, which after recrystallization from toluene-ligroin melted at  $168-170^{\circ}$ .

*Anal.* Calcd. for  $C_{14}H_{14}O_6N_4$ : C, 50.30; H, 4.22. Found: C, 51.04; H, 4.48.

**Reactions of the Alkoxyacetals, VI and VIII.**—Upon heating VI with Brady reagent<sup>15</sup> and allowing to cool, a red-brown product formed which upon recrystallization from dioxane-ethanol gave a red-orange bis-dinitrophenylhydra-

(14) A. W. Crossley and H. R. LeSueur, *J. Chem. Soc.*, **75**, 165 (1899).

(15) G. T. Newbold, *ibid.*, 2959 (1950).

(13) See discussion section for explanation of high ethoxyl values.

zone, m.p. 206–208°, dec. 210°. Protection from moisture and air was necessary to prevent decomposition of this derivative.

*Anal.* Calcd. for  $C_{17}H_{16}O_8N_8$ : C, 44.35; H, 3.50. Found: C, 44.56; H, 3.42.

Treatment of VI according to the usual procedure with phenylhydrazine gave a yellow monophenylhydrazone, m.p. 173–174° dec., in small yield. Further heating of the reaction mixture gave no other isolable product.

*Anal.* Calcd. for  $C_{18}H_{22}ON_2$ : N, 11.4. Found: N, 10.5.

A hydrolysis of VI with dilute sulfuric acid was effected at room temperature in about one day. Ether extraction and distillation of the products gave a colorless oil of sharp odor, b.p. 55–62° (7 mm.),  $n_D^{25}$  1.4268, which gave the same bis-2,4-dinitrophenylhydrazone as obtained directly from the acetal VI.

From an oxidation of VI with alkaline permanganate, no acetone was isolated.

Compound VIII when heated with Brady reagent<sup>15</sup> gave a bright red-orange dinitrophenylhydrazone, which after recrystallization from 95% ethanol melted at 170–172°. Analysis showed one ethoxyl group present in the molecule, indicating that only the acetal grouping had been hydrolyzed by the reagent.

*Anal.* Calcd. for  $C_{13}H_{16}O_5N_4$ : C, 50.65; H, 5.23;  $C_2H_5O$ , 14.6. Found: C, 50.99; H, 5.30;  $C_2H_5O$ , 14.3.

**$\beta$ -Phenylcinnamaldehyde Diethylacetal (X).**—The preparation of 1,1-diphenyl-2-bromoethylene (IX) followed the procedure of Lipp<sup>16</sup> using 1,1-diphenylethylene.<sup>17</sup> For the synthesis of X the method of Kohler and Larsen<sup>18</sup> was modified so as to give the acetal instead of the aldehyde. In a 500-ml. three-neck flask fitted with stirrer, reflux condenser, and dropping funnel, 7.2 g. (0.3 atom) of magnesium turnings was placed and the system swept out with dry nitrogen. To the magnesium was added 15 ml. of anhydrous ether containing a small crystal of iodine and about five drops of ethyl iodide. A solution of 77.7 g. (0.3 mole) of IX in 150 ml. of anhydrous ether was placed in the funnel and about 10 ml. run into the flask. After the reaction was started by heating on the steam-bath, the remainder of the solution was added dropwise over a 1-hr. period. At the end of the addition, refluxing was continued for another hour, and then 44.5 g. (0.3 mole) of ethyl orthoformate in 50 ml. of dry ether was added over a 3-min. interval. Following a further 5-hr. period of refluxing, a stillhead was substituted for the dropping funnel and ether carefully removed. When the volume of the residue reached about 150 ml., an exothermic reaction, which was controlled by an ice-bath, began. When the bubbling had subsided and before the mixture was completely cooled, the viscous brown liquid was poured with stirring into 500 ml. of cracked ice and water and immediately extracted with ether. The aqueous layer, still containing a heavy suspension, was covered with ether and thoroughly mixed with 13.7 ml. (0.24 mole) of acetic acid in 150 ml. of water. Further ether extractions were made and combined with the original extract, which then was washed with 10% sodium carbonate solution and dried overnight with anhydrous potassium carbonate. After filtering the solution to remove the desiccant and a yellow precipitate of 1,1,4,4-tetraphenyl-1,3-butadiene, the filtrate was concentrated and distilled through a 20-cm. Vigreux column to give a forerun containing 12.0 g. (27%) of unreacted ethyl orthoformate and 7.0 g. (13%) of 1,1-diphenylethylene, followed by the main fraction of 40.6 g. (48%) of X, a viscous, pale yellow liquid, b.p. 140–145° (0.1 mm.),  $n_D^{25}$  1.5544,  $d_4^{25}$  1.025.

*Anal.* Calcd. for  $C_{19}H_{22}O_2$ :  $C_2H_5O$ , 31.9. Found:  $C_2H_5O$ , 30.4.

Although 0.7 mole runs were successfully carried out by the above procedure, the exothermic reaction, which occurs during the removal of the ether, is not easily controlled with such quantities.

X absorbed bromine quite slowly in carbon tetrachloride, but readily decolorized alkaline aqueous permanganate. Hydrolysis of X with dilute sulfuric acid gave very pale yellow crystals of  $\beta$ -phenylcinnamaldehyde, m.p. 41–42°

(reported,<sup>18</sup> 44°). A 2,4-dinitrophenylhydrazone, prepared directly from X, recrystallized from ethanol-ethyl acetate as red needles, m.p. 203–204° (reported,<sup>19</sup> 195–196°); the semicarbazone, also prepared from X, melted at 218.5–219.5° when placed in a melting point block preheated to 215°; a longer heating period gave a m.p. of 213° (reported,<sup>20</sup> 217–219°).

**$\alpha$ -Bromo- $\beta$ -phenylcinnamaldehyde Diethylacetal (XI) (a).**—In a three-neck, 100-ml. flask equipped with stirrer, reflux condenser with outlet to Dry Ice-acetone trap, and inlet for dry nitrogen, 22.6 g. (0.08 mole) of X was mixed with 19.1 g. (0.08 mole) of dry pyridine perbromide. A mildly exothermic reaction began; it was held at 40° for one hour, after which the temperature was gradually raised over another three hours until 95° was reached. A slow stream of nitrogen was passed through the system during this heating. The resulting brown mixture was cooled, diluted with 50 ml. of dry ether and, after decantation, the residue was triturated several times with ether. After concentrating the combined ether extracts, distillation was carried out to give the following fractions: (1) 8.7 g. (42%) of IX, b.p. 130–139° (0.1 mm.),  $n_D^{25}$  1.6200. After recrystallization from ethanol, the melting point of this fraction was 48–50°, and remained undepressed when mixed with known IX; analysis showed a bromine content of 29.8% (calcd. 30.8); (2) 5.3 g., b.p. 139–147° (0.1 mm.); (3) 7.5 g. (26%) of XI, b.p. 147–160° (0.1 mm.),  $n_D^{25}$  1.5741, which solidified on standing. After several recrystallizations from absolute ethanol, XI was obtained as white crystals, m.p. 78–79°.

*Anal.* Calcd. for  $C_{19}H_{21}O_2Br$ : C, 63.16; H, 5.93; Br, 22.1;  $C_2H_5O$ , 24.9. Found: C, 63.19; H, 5.97; Br, 21.8;  $C_2H_5O$ , 23.2.

XI was inert toward alcoholic silver nitrate and bromine in carbon tetrachloride but readily decolorized alkaline permanganate solution. Hydrolysis with dilute sulfuric acid at room temperature, or even by prolonged standing in water converted XI to  $\alpha$ -bromo- $\beta$ -phenylcinnamaldehyde, a pale yellow solid, m.p. 128–130°.

*Anal.* Calcd. for  $C_{18}H_{19}OBr$ : Br, 27.8. Found: Br, 27.4.

A 2,4-dinitrophenylhydrazone prepared either from this aldehyde or XI was recrystallized twice from ethanol-ethyl acetate to give yellow-orange crystals, m.p. 224–245°.

*Anal.* Calcd. for  $C_{21}H_{15}O_4N_4Br$ : C, 53.97; H, 3.24. Found: C, 54.51; H, 3.45.

In the cold trap from the above bromination was collected 2.8 g. of liquid, which upon fractionation gave 1.1 g. (14%) of ethyl bromide, b.p. 37–49°,  $n_D^{25}$  1.3939, and 1.2 g. (20%) of ethyl formate, b.p. 52–55°,  $n_D^{25}$  1.3602.

(b).—Essentially the same procedure as (a) was followed except that 12.8 g. (0.08 mole) of bromine was slowly added to 16.0 g. (0.20 mole) of pyridine and 22.6 g. (0.08 mole) of X. After the addition, the homogeneous red solution was stirred at 65° for 9.5 hours and then worked up as in (a) to give 3.3 g. (16%) of IX and 11.8 g. (41%) of XI.

**Reaction of XI with Potassium *t*-Butoxide (a) in *t*-Butanol.**—To a solution of potassium *t*-butoxide prepared from 0.47 g. (0.012 atom) of potassium and 10 ml. of dry *t*-butanol, 3.61 g. (0.01 mole) of XI was added and the resulting dark solution gently refluxed under nitrogen for 24 hours. A brown precipitate had appeared after this time, but the solution was concentrated without removing the solids and distilled to give 0.8 g., b.p. 140–145° (0.1 mm.),  $n_D^{25}$  1.5591 as the only volatile material, which was shown to be X by the formation of the 2,4-dinitrophenylhydrazone and comparison with a known sample.

The residue from the distillation was extracted with a water-ether mixture and the layers separated. Titration of the aqueous solution showed 0.0081 equivalent of bromide ion and 0.0015 equivalent of base to be present. After removing all solvent from the ether extract, 2.9 g. of an intractable tar remained.

(b) In Dioxane.—From a solution obtained from the reaction of 0.7 g. (0.018 atom) of potassium with 23 ml. of absolute *t*-butanol, the excess alcohol was removed by distillation under reduced pressure. To the residue was added 25 ml. of dioxane, followed by a solution of 5.4 g. (0.015 mole) of XI in 5 ml. of dioxane. The resulting dark brown solution was stirred and heated at 100° for 15 hours after

(16) P. Lipp, *Ber.*, **56**, 570 (1923).

(17) C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.

(18) E. P. Kohler and R. G. Larsen, *This Journal*, **57**, 1451 (1935).

(19) H. Lorenz and R. Wizinger, *Helv. Chim. Acta*, **28**, 600 (1946).

(20) G. Wittig and R. Kethur, *Ber.*, **69**, 2085 (1936).

which it was centrifuged. The decantate was concentrated and distilled to give 1.16 g. (27%) of X. The residue from the distillation gave mainly tar from which the only isolable solid was 0.05 g. of an orange powder, m.p. 268–269°, which was relatively insoluble in all solvents except an ethyl acetate–chloroform mixture. *Anal.* Found: C, 83.45; H, 5.69;  $C_8H_8O$ , 10.9 (calcd. for  $C_{10}H_{12}O_2$ : C, 83.31; H, 5.59;  $C_8H_8O$ , 10.4). No further study of this material was made.

(c).—In a 100-ml. flask, 0.95 g. (0.025 atom) of potassium was dissolved in *t*-butanol; the excess alcohol then was removed and the residue heated to 180° under the vacuum of an oil-pump. To the cooled white residue, 6.5 g. (0.018 mole) of XI was added and the thick mixture heated at 100–110° for one hour, then at 160° for 2.5 hours. Distillation then gave 1.8 g. (0.024 mole) of *t*-butanol,  $n_D^{25}$  1.3848, and as the only other volatile fraction 1.05 g., b.p. 170° (20 mm.) – 130° (0.1 mm.),  $n_D^{25}$  1.5705. No pure component could be separated from this material.

When the residue from the distillation was dissolved in an ether–water mixture and the aqueous layer acidified, 2.4 g. (60%) of tan-colored  $\beta$ ,  $\beta$ -diphenylpropionic acid was obtained. Two recrystallizations from dilute alcohol gave a white product, m.p. 153–155°; neut. equiv., 229 (calcd. 224). A known sample of this acid was prepared by reduction of  $\beta$ -phenylcinnamic acid<sup>21</sup> (m.p. 158–160.5°) with sodium in ethanol. The acid thus prepared had a m.p. of 153–155.5°, which was not depressed upon mixing with the acid isolated above. Both samples of this acid yielded identical anilides, m.p. 178–179° (lit.<sup>22</sup> m.p. 177–178°).

The following modification of (c) was made: A 50-ml. dis-

tilling flask with attached still-head was connected through a Dry Ice–acetone trap to a vacuum pump. A 3.4 g. (0.03 mole) sample of sublimed<sup>6</sup> potassium *t*-butoxide was intimately mixed with 10.8 g. (0.03 mole) of XI and the system then evacuated to 0.1 mm. pressure. Upon heating the mixture a vigorous evolution of *t*-butyl alcohol started and necessitated removal of the heating-bath for several minutes. As soon as possible the oil-bath (at 165°) was replaced and the distillation continued. A temperature of 200° was finally used to give two fractions, both of which were mixtures of X and XI: (a) 2.5 g., b.p. 142–149° (0.1 mm.),  $n_D^{25}$  1.5613 and (b) 1.2 g., b.p. 150–165° (0.1 mm.),  $n_D^{25}$  1.5680, which solidified on standing. Bromide analyses ((a), 5.8%; (b), 15.9%) and refractive indices showed that 2.2 g. (26% yield) of X was present in the combined fractions. Fraction (a) was redistilled to give 1.1 g. of nearly pure X, b.p. 138–140° (0.1 mm.),  $n_D^{25}$  1.5607, with a bromide content of 1.1%. From 22.4 mg. of this fraction, 21.0 mg. of a 2,4-dinitrophenylhydrazone was obtained. Upon recrystallization from ethanol–ethyl acetate, the more soluble portion yielded a product, m.p. 201–202°, which was not depressed when mixed with the authentic derivative of X.

In the cold trap from the above reaction, 2.25 g. (100%) of *t*-butanol,  $n_D^{25}$  1.3841, b.p. 81°, was isolated. An ether–water extract of the residue from the above distillation gave 3 g. of ether-soluble tar, and a small amount of precipitated tar upon acidification of the water extract. Attempted recrystallization of these tars gave only amorphous material, except for about 0.1 g. of an orange solid, m.p. 267.5–268.5°, identical to that isolated in (b). By repeated extraction of these tars with hot water, a small amount (0.1 g.) of  $\beta$ -phenylcinnamic acid was isolated, which had a m.p. of 155–158°, alone or mixed with a known sample.<sup>21</sup>

(21) H. Rupe, *Ann.*, **395**, 141 (1913); T. Posner, *J. prakt. Chem.*, [2] **82**, 439 (1910).

(22) J. F. Eijkman, *Chem. Weekblad*, **5**, 655 (1908).

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RECEIVED NOVEMBER 2, 1951

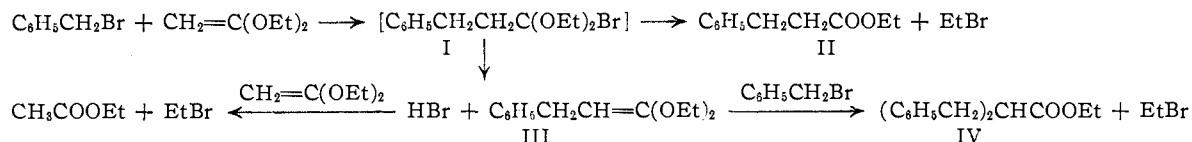
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## Ketene Acetals. XXIX. The Mechanism of the Reaction of Ketene Acetal with Various Halides

By S. M. McELVAIN AND HERBERT F. McSHANE, JR.<sup>1</sup>

The reaction of benzyl bromide with excess ketene diethylacetal is found to yield benzylketene acetal as one of the reaction products. However, determinations of the relative reactivities of these ketene acetals show that the substituted ketene acetal is not the intermediate in the formation of the large amount of ethyl dibenzylacetate, which is produced when ketene acetal reacts with benzyl bromide. A reaction mechanism to account for the formation of this dibenzylated product is suggested. The formation of only monoalkylation products from the reaction of benzyl bromide with methylketene diethylacetal and from the reactions of ethyl iodide and trityl chloride with ketene diethylacetal are offered in support of this mechanism. Acetylketene diethylacetal may be directly prepared from the reaction of acetyl chloride with an excess of ketene acetal.

In the seventh paper<sup>2</sup> of this series the allylation and benzylation of ketene diethylacetal by reaction with the respective bromides was reported. A remarkable feature of these reactions was the high ratio of the disubstituted to the monosubstituted acetic esters that was produced in each case. At that time it was suggested that the disubstituted ester (IV) was formed *via* a monosubstituted ketene acetal (III), which resulted from a loss of hydrogen bromide from the intermediate I.



Such a reaction course would require that the rate

of formation of IV from III should be at least as great as that at which II is formed from the unsubstituted ketene acetal. Later work,<sup>3</sup> however, indicated that certain alkyl- and phenyl-substituted ketene acetals reacted considerably slower with benzyl bromide, as judged by the higher temperature required to evolve the alkyl bromide, than did the unsubstituted ketene acetal. High yields of the monobenzylated esters were obtained, but there was no indication that any of the di-

(1) Wisconsin Alumni Research Foundation Research Assistant 1948–1950; Shell Oil Company Fellow 1950–1951.

(2) S. M. McElvain and D. Kundiger, *THIS JOURNAL*, **64**, 254 (1942).

benzylated ester (a trisubstituted acetic ester), was formed. The only monosubstituted ketene acetal that has been found to undergo dibenzyla-

(3) S. M. McElvain, R. E. Kent and C. L. Stevens, *ibid.*, **68**, 1922 (1946).