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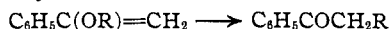
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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

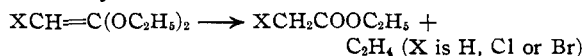
Ketene Acetals. XI. The Pyrolysis of Ketene Acetals and Orthoesters

BY S. M. McELVAIN, HARRISON I. ANTHES AND SYDNEY H. SHAPIRO

The C-alkylation of α -methoxystyrene¹ and ketene acetal^{1a} by means of certain reactive organic halides shows the similarity in behavior and the high reactivity of the heterooid systems that are present in these two structures. It seemed of interest, therefore, to undertake a study of the effect of heat on the ketene acetals to ascertain if they would undergo the same type of thermal rearrangement as the α -alkoxystyrenes which have long been known² to rearrange into phenyl alkyl ketones



It previously has been reported³ that ketene diethylacetal may be heated at 190–240° in *new* Pyrex tubes without any perceptible polymerization. In the work which is now reported, the effect of heat on ketene diethylacetal and its chloro and bromo derivatives has been studied. These ketene acetals have been heated under three different sets of conditions, *viz.*, (a) in glass tubes at 200° for six hours, (b) in a steel bomb at 150–200° for six to seventy-two hours, and (c) during rapid passage over a variety of surfaces in a furnace at 300–400°. Under all of these conditions the ketene acetals that were studied showed only one type of behavior, *viz.*, pyrolysis into ethylene and the acetic ester



There was no indication in any experiment that

(1) Mortenson and Spielman, *THIS JOURNAL*, **62**, 1609 (1940).

(1a) McElvain and Kundiger, *ibid.*, **64**, 254 (1942).

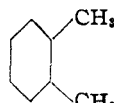
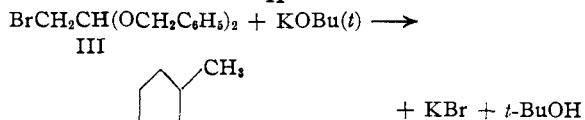
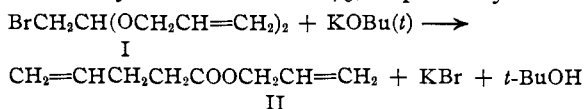
(2) Claisen, *Ber.*, **29**, 2931 (1896); Claisen and Haase, *ibid.*, **33**, 3778 (1900).

(3) Johnson, Barnes and McElvain, *THIS JOURNAL*, **62**, 964 (1940).

an ethyl group had rearranged from an oxygen to a carbon as it does in ethoxystyrene.³

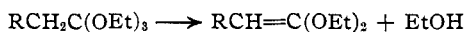
Under the conditions (six hours at 200°) that caused complete pyrolysis of ketene diethylacetal in glass tubes, ketene dimethylacetal remained unaffected. Indeed, 95% of this dimethylacetal was recovered after twenty-four hours of heating at 200°.

The failure of ketene, chloroketene and bromoketene diethylacetals to undergo thermal rearrangement as do the alkoxystyrenes led to a study of the thermal behavior of ketene diallyl- and dibenzylacetals. These compounds contain the necessary structure, $\text{>C}=\text{C}-\text{O}-\text{CH}_2-\text{C}=\text{C}$, for the well-known Claisen or allylic rearrangement and would be expected to rearrange quite readily. As a matter of fact, neither of these ketene acetals could be isolated from the products of the reaction of potassium *t*-butoxide in *t*-butyl alcohol with either diallylbromoacetal (I) or dibenzylbromoacetal (III); the only products that could be separated were allyl allylacetate (II) and benzyl *o*-tolylacetate (IV) which were obtained in yields of 43 and 46%, respectively.



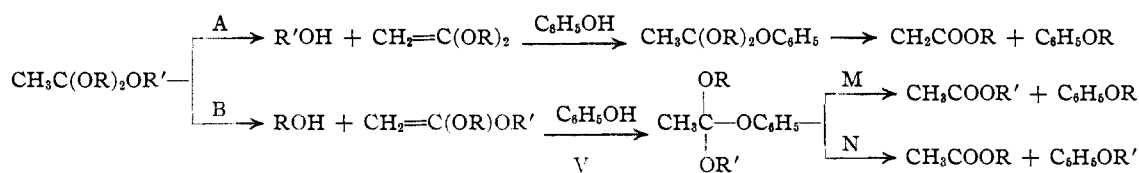
Undoubtedly the ketene acetal was the intermediate in each of these reactions, but it was so susceptible to rearrangement that it passed into the substituted acetic ester (II or IV) as rapidly as it was formed. It is interesting to note that these allylic rearrangements occur at or below the refluxing temperature (*ca.* 80°) of *t*-butyl alcohol which is an unusually low temperature for a rearrangement of this type. Also it should be noted that in the more widely studied rearrangements of the phenol ethers the allyl phenyl ethers generally rearrange with inversion of the allyl radical, while benzyl phenyl ether, in contrast to the allyl ethers and to the above benzylacetal, rearranges to the *o*- and *p*-benzyl phenols,⁴ without any inversion of the benzyl radical.

Two reports of the pyrolysis of an orthoester into a ketene acetal and alcohol



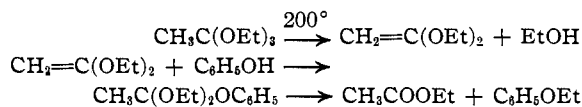
have appeared in the literature. Reitter and Weindel⁵ reported this pyrolysis for the compound in which R is carbethoxy and Staudinger and Rathsam⁶ reported a similar behavior for the compound in which R is phenyl. These latter authors also reported that ethyl orthoacetate underwent a different type of pyrolysis, *viz.*, into ethyl acetate and ether, when passed over nickel on pumice at 250–260°.

Since, in some cases, orthoesters appear to py-



rolyze into ketene acetals it seemed of interest to undertake a study of the pyrolysis of a variety of orthoesters and to determine, if possible, if there is any general tendency for them to pyrolyze into ketene acetals. In some preliminary experiments with ethyl orthoacetate it was found that this orthoester, when heated at 200° for twenty hours in a steel bomb with a glass liner, yielded alcohol, ethyl acetate and ethylene. These products could be the result of the pyrolysis of the orthoester into alcohol and ketene acetal followed by the pyrolysis of the acetal into ethylene and ethyl acetate. That this was actually the course which

the pyrolysis took was shown by the products obtained when the orthoester was heated with an equivalent of phenol. It has been found in earlier work that the mixed orthoester obtained by the addition of phenol to ketene acetal decomposed on distillation into ethyl acetate and phenetole.⁷ When ethyl orthoacetate was heated with phenol no ethylene was formed and practically quantitative yields of ethyl acetate and phenetole were obtained. The following sequence of reactions illustrates these transformations



The ability of phenol to divert the ketene acetal into phenetole as rapidly as it is formed and before it is pyrolyzed into ethylene and ethyl acetate made possible the study of the decomposition of a mixed orthoester of the type $\text{CH}_3\text{C}(\text{OR})_2\text{OR}'$. Such an ester, on pyrolysis, could follow two reaction courses, A and B, and the extent of each reaction would be measured by the amount of each of the alcohols, ROH and R'OH, among the reaction products. An additional measure of the extent of reaction B would be given by the sum of the products, $\text{C}_6\text{H}_5\text{OR}'$ and $\text{CH}_3\text{COOR}'$, which result from the decomposition of the mixed orthoester (V) by reactions M and N.

Table I is a summary of the results obtained from the pyrolysis of a number of orthoesters. In general, the esters of the unsubstituted acetic acid (runs 1–9) were heated at 200° for twenty hours in order to insure complete pyrolysis. The esters of the substituted acetic acids were heated at the same temperature and, in some cases, for shorter periods of time in order to show roughly their relative tendency to pyrolysis. In the cases of the mixed orthoesters (runs 3–9) the total percentage of reaction (100% in all runs) is subdivided into the per cent. of each of the reactions A, B, M and N and the ratios of the pyrolysis products ROH to R'OH and $\text{CH}_3\text{COOR}'$ to $\text{C}_6\text{H}_5\text{OR}'$, *i. e.*, B/A and M/N is indicated. The

(4) Behaghel and Freiuensehner, *Ber.*, **67**, 1368 (1934); Short, *J. Chem. Soc.*, 528 (1928); Hickenbottom, *Nature*, **142**, 930 (1938); **143**, 520 (1939).

(5) Reitter and Weindel, *Ber.*, **40**, 3358 (1907).

(6) Staudinger and Rathsam, *Helv. Chim. Acta*, **5**, 646 (1922).

(7) Barnes, Kundiger and McElvain, *This Journal*, **62**, 1281 (1940).

TABLE I
 PYROLYSIS OF ORTHOESTERS, XCH₂C(OR)OR' AT 200°

Run	XCH ₂ is	R is	R' is	Reaction time, hr.	React. A, %	React. B, %	B/A	Total reaction, %		M/N
								React. M, %	React. N, %	
1	CH ₃	C ₂ H ₅	C ₂ H ₅	10	80					
2	CH ₃	C ₂ H ₅	C ₂ H ₅	20	100					
3	CH ₃	C ₂ H ₅	<i>n</i> -C ₄ H ₉	20	33	67	2.0	49	51	1.0
4	CH ₃	C ₂ H ₅	<i>i</i> -C ₄ H ₉	20	33	67	2.0	60	40	.7
5	CH ₃	C ₂ H ₅	<i>s</i> -C ₄ H ₉	20	22	78	3.5	14	86	6.1
6	CH ₃	C ₂ H ₅	<i>i</i> -C ₅ H ₁₁	20	34	66	1.9	52	48	.92
7	CH ₃	C ₂ H ₅	(CH ₃) ₃ CCH ₂	20	44	56	1.3	100	0	0
8	CH ₃	C ₂ H ₅	C ₆ H ₅ CH ₂	20	16	84	5.4	11	89	8.1
9	CH ₃	<i>n</i> -C ₄ H ₉	C ₂ H ₅	20	39	61	1.6	51	49	.96
10	EtOCH ₂	C ₂ H ₅	C ₂ H ₅	2.5	84					
11	EtOCH ₂	C ₂ H ₅	C ₂ H ₅	5.0	100 ^a					
12	ClCH ₂	C ₂ H ₅	C ₂ H ₅	10	74					
13	ClCH ₂	C ₂ H ₅	C ₂ H ₅	20	100					
14	BrCH ₂	C ₂ H ₅	C ₂ H ₅	13	21 ^b					
15	BrCH ₂	C ₂ H ₅	C ₂ H ₅	32	37 ^c					
16	Br ₂ CH	C ₂ H ₅	C ₂ H ₅	32	15 ^d					

^a In another run of this orthoester in which phenol was used, the total yield (97%) of the acetic ester in this run was composed of ethyl ethoxyacetate (47%) and phenyl ethoxyacetate (53%). ^b In this run 43% of the bromo-orthoester was recovered unchanged. ^c In this run no orthoester was recovered; in addition to the bromoacetic ester indicated above, 0.5 g. of acetaldehyde (identified as the 2,4-dinitrophenylhydrazone), 4 g. of ethyl bromide, 4.3 g. of ethyl acetate and a small amount of water (copper sulfate test) were obtained from a 30 g. run of the orthoester. ^d In this run 0.6 g. acetaldehyde, 11 g. of ethyl bromide, 2.9 g. of ethyl acetate, 10.8 g. of ethyl monobromoacetate and some water and alcohol were isolated from a 50 g. run of the orthoester.

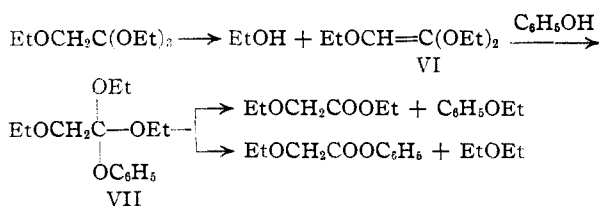
simple orthoesters (R = R' = C₂H₅) in runs 10–16 were pyrolyzed without phenol and the total percentage of reaction is given in the sixth (reaction A) column of the table. These values were obtained from the amounts of acetic ester and unchanged orthoester that were present in the bomb after the heating period shown.

Runs 1 and 2 of Table I show that the time necessary for complete pyrolysis of ethyl orthoacetate at 200° is between ten to twenty hours. The behavior of the mixed orthoesters in runs, 3, 4, 6 and 9 show that the primary alkyl groups of either the normal or iso structure have practically the same tendency to be eliminated in the form of R'OH (reaction A). In each of these runs approximately one-third of the orthoester decomposes with the loss of the single alkyl group (R') and two-thirds by the course in which one of the two like alkyl groups (R, reaction B) is lost. The neopentyl group (run 7) shows a noticeably greater tendency to be eliminated than do the other primary alkyl groups. The *s*-butyl group (run 5) and the benzyl group (run 8) are decidedly more resistant to elimination than are the ethyl and the other primary alkyl groups. Since the pyrolysis of an orthoester to a ketene acetal (reactions A and B) involves a rupture of the bond that holds the alkoxy group in the orthoester, the

behavior of the various alkyl groups in the mixed orthoesters is in line with the well-known fact that the oxygen–hydrogen bond is more reactive and the alkyl–oxygen bond less reactive in primary alcohols than in secondary (or benzyl) alcohols. In the decomposition of the mixed orthoester V it seems safe to assume that the phenyl ether is eliminated as C₆H₅O— and R (or R') since in phenol the phenyl–oxygen bond is very stable as compared to the oxygen–hydrogen bond and also because of the high yields of the *s*-butylphenyl ether and benzylphenyl ether (reaction N, runs 5 and 8). It is interesting to note that reactions M and N take place to practically the same extent when R' is *n*-butyl, isobutyl, isoamyl and ethyl (runs 3, 4, 6 and 9). This shows that these primary alkyl–oxygen bonds are, as are the bonds that hold the RO— and R'O groups in the orthoester, of the same order of strength. The failure of the mixed orthoester V, when R' is neopentyl (run 7, Table I), to follow reaction N to any extent in its decomposition, together with the relatively high amount of reaction A in the run, shows the marked difference in the strength of a bond attached to a neopentyl group and one attached to a neopentoxy group.

In the group of ethyl esters of the substituted orthoacetic acids a number of interesting results

appear. Of all of the orthoesters that were studied the ethyl orthoethoxyacetate was pyrolyzed (runs 10 and 11) most readily. In one run (see footnote (a), Table I) in which the orthoester was pyrolyzed in the presence of phenol the resulting acetic ester was composed of about equal amounts of the phenyl and the ethyl esters. These products indicate that the mixed orthoester (VII), resulting from the addition of phenol to ethoxyketene acetal (VI), breaks down in two different ways, thus

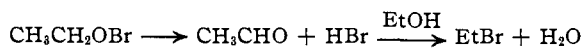
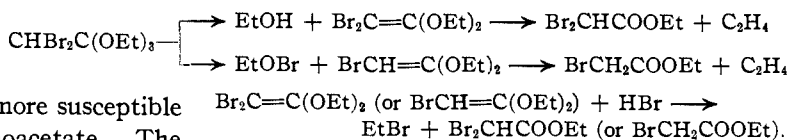


The ethyl orthochloroacetate (runs 12 and 13) behaved as did the other orthoesters and, in contrast to the ethoxyacetate, is no more susceptible to pyrolysis than is ethyl orthoacetate. The bromo-substituted orthoesters, however, show a marked variation from the other orthoesters in the pyrolysis behavior. The yields of the corresponding bromo-acetic esters that were obtained from the pyrolyses that went to completion (runs 15 and 16) are quite low. Numerous other unexpected products (see footnotes *c* and *d*, Table I) were isolated from these pyrolyses. These products can best be explained upon the assumption that two competing modes of decomposition are followed by these esters. The one of these that occurs to the lesser extent, is the route (reactions A and B) that is followed by the other orthoesters.

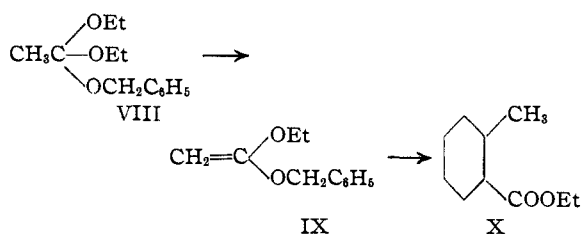
The other, and main, reaction route appears to be connected with the positive character of the bromine of the mono and dibromo derivatives of ethyl orthoacetate⁸ and to involve the loss of the elements of ethyl hypobromite from the orthoester. A ketene acetal with one less bromine than the original orthoester would be the result of this decomposition.⁹ This ketene acetal would then pyrolyze into the corresponding acetic ester and ethylene or add hydrogen bromide (see below) to form the same acetic ester and ethyl bromide. Ethyl hypobromite does not

appear to have been described in the literature, but if it were momentarily formed it would be expected to decompose into acetaldehyde and hydrogen bromide in a manner similar to that reported for ethyl hypochlorite.¹⁰ The interaction of hydrogen bromide and alcohol to produce water explains the last of the various and unexpected products that were isolated from the pyrolyses of the orthobromoesters. The formation of these products from the pyrolysis of ethyl orthodibromoacetate is illustrated below.

The isolation of benzyl *o*-tolylacetate (IV) instead of the ketene acetal from the dehydrobromination of dibenzylbromoacetal (III) suggested the pyrolysis of benzyldiethyl orthoacetate (VIII) in the absence of phenol. This orthoester appears from run 8 of Table I to decompose to the extent of 84% into the mixed ketene acetal (IX) which,

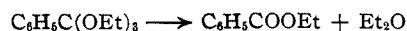


if not immediately diverted through reactions M and N by phenol, should rearrange into ethyl *o*-tolylacetate (X), thus



When the orthoester VIII was heated alone at 200° for twenty-four hours there was considerable non-distillable tar produced, but from the volatile liquid portion of the pyrolysis mixture it was possible to isolate about 14% of the theoretical amount of X.

Finally an orthoester that has no α -hydrogen, and consequently cannot be converted into a ketene acetal, was pyrolyzed. Ethyl orthobenzoate, when refluxed gently under atmospheric pressure (b. p. 220–225°), slowly decomposed into the normal ester and diethyl ether.



After six hours this decomposition amounted to 60%.

(10) Sandmeyer, *Ber.*, **18**, 1768 (1885).

(8) McElvain and Walters, *THIS JOURNAL*, **64**, 1963 (1942).
(9) The general method of preparation of ketene acetals involves the removal of the elements of ethyl hypochlorite from α -halogenated orthoesters by means of sodium [Walters and McElvain, *ibid.*, **62**, 1482 (1940); McElvain, Clarke and Jones, *ibid.*, **64**, 1966 (1942)].

Experimental

The ketene diethylacetals that were used in the pyrolysis experiments and for the preparation of mixed orthoesters were prepared by procedures previously described.^{3,11} In the pyrolysis experiments ketene, chloroketene and bromoketene diethylacetals were used.

Methyl Orthobromoacetate and Ketene Dimethylacetal.—This acetal could not be prepared from the bromodimethylacetal by the action of potassium *t*-butoxide in *t*-butyl alcohol because the ketene acetal boiled (89–91°) too near to the alcohol to allow them to be separated. Consequently, it had to be prepared from methyl orthobromoacetate by the action of metallic sodium.¹² This bromoester was obtained by the bromination of methyl orthoacetate, prepared by the method of McElvain and Nelson¹³ from acetonitrile, according to the procedure described for the preparation of ethyl ortho- α -bromoisovalerate.¹⁴ **Methyl orthobromoacetate**, b. p. 74–75° (17 mm.); d_{25}^{25} 1.4771; n_D^{25} 1.4501, was obtained in yields of 70% of the theoretical.

Anal. Calcd. for $C_5H_{11}O_2Br$: Br, 40.15. Found: Br, 40.33.

Ketene dimethylacetal, b. p. 89–91° (740 mm.); d_{25}^{25} 0.9274; n_D^{25} 1.3962, was obtained from the bromoester¹² in 65% yields.

Anal. Calcd. for $C_4H_8O_2$: C, 54.53; H, 8.93. Found: C, 54.31; H, 9.15.

The Pyrolysis of Ketene Diethylacetals

(a) **In Glass Tubes.**—Pyrex bomb tubes of 80-ml. capacity were washed with alcohol and ether and then filled with concentrated aqueous sodium hydroxide and allowed to stand for four hours. Then they were washed with distilled water, alcohol and ether. When rigorous anhydrous conditions were used the tubes were heated in a bunsen flame, stoppered with a calcium chloride tube, and allowed to cool. Approximately 5 g. of the ketene acetal was placed in the tube; when extreme precautions against moisture were used the acetal was distilled directly into the dried bomb tube. After sealing, the tube was heated in a bomb furnace at 200° for six hours, after which time it was cooled in an acetone-dry-ice mixture and opened. All tubes contained a high pressure of an inflammable gas (ethylene). The acetic ester remaining in the tube was distilled and weighed. When new, rigorously dried tubes were used the pyrolysis never amounted to more than 20% of the ketene acetal; in used tubes, similarly dried, the amount of pyrolysis rose to 50%; in air-dried, used tubes the pyrolysis was complete in six hours at 200°.

(b) **In a Steel Bomb.**—A solution of 20–30 g. of the ketene acetal in 40–60 ml. of cyclohexane (if a solvent is not used the reaction product is invariably a tar) was placed in a 500-ml. steel hydrogenation bomb that was fitted with a valve for the release of gas pressure and heated at 200° for six hours. Under these conditions the pyrolysis of the ketene acetals was complete. However, when a temperature of 150° was used there was no appreciable decomposi-

tion of the ketene acetal even after twenty-four hours. After cooling the ethylene was slowly released from the valve in the bomb, through two dry-ice traps, into an aspirator from which the ethylene determination was made. The yields of ethylene in these runs generally were 5–10% lower than those of the esters. The amounts of esters were determined in the case of ethyl acetate from the refractive index of the cyclohexane solution and, in the cases of the ethyl halogenoacetates, by fractional distillation.

(c) **In Furnace.**—A 50-cm. Pyrex tube, loosely packed for a length of 17 cm. with either glass chips, manganese dioxide, aluminum oxide, zinc oxide or chromic oxide was heated in a short (35 cm.) electric furnace. The temperature was read from a pyrometer placed in the interior of the tube. The ketene acetal in 10–20 g. samples, was added dropwise into one end of the furnace from a dropping funnel protected with a calcium chloride tube and the gases from the furnace were conducted into a 50-ml. receiving flask that carried an efficient reflux condenser. The vapors that passed from the top of the reflux condenser were led through a cold trap surrounded by a dry-ice-acetone mixture and into a pair of 25-cm. test-tubes in series, each containing 50 g. of bromine. The last bromine tube was connected to an aspirator of about 8-liters capacity.

The acetic ester formed in the pyrolyses was determined by distillation of the material in the first receiving flask and the cold trap. The only contaminant of this ester was a small amount of unchanged ketene acetal. The amount of ethylene bromide in the two bromine tubes gave a measure of the ethylene (generally 10–25% below the yields of the esters) that was formed in the reaction. The yields of ester from all of the ketene acetals used, either through an unpacked tube or one packed with glass chips, were 80% or more at 400° and practically zero at 300°. With manganous oxide and aluminum oxide, however, ester yields of 80% and 60%, respectively, were obtained at 300°. Zinc and chromium oxides gave very little improvement in ester yield at this lower temperature over that obtained from an unpacked tube.

A 20-g. sample of ketene dimethylacetal was heated in a sealed glass tube at 200° for twenty-four hours as in procedure (a). When the tube was cooled, opened and the contents distilled, 95% of unchanged ketene dimethylacetal was recovered.

Diallylbromoacetal.—To 86.1 g. (1 mol) of freshly distilled vinyl acetate was added with stirring 60 g. (1 mol) of bromine over a period of two hours. The temperature was not allowed to go above 5°. The resulting mixture was added with stirring to 290 g. (5 ml.) of anhydrous allyl alcohol over a period of three hours. The reaction mixture then was allowed to come to room temperature slowly and stirred overnight. After this time 100 ml. of water was added to the vigorously stirred mixture, followed by small portions of potassium carbonate, until the solution was no longer acidic. The aqueous layer was removed and the remaining product dried over anhydrous potassium carbonate. On distillation the fraction boiling at 101–102° (20 mm.); n_D^{25} 1.4712¹⁵ was collected. The yield amounted to 100 g. (45%); % Br, 35.9 (calcd. 36.0).

Allyl Allylacetate from Diallylbromoacetal.—To a solution of 39 g. (1 atom) of potassium in 550 g. of *t*-butyl

(11) McElvain, *et al.*, *THIS JOURNAL*, **60**, 2210 (1938); **64**, 1059 (1942).

(12) Walters and McElvain, *ibid.*, **62**, 1482 (1940).

(13) McElvain and Nelson, *ibid.*, **64**, 1825 (1942).

(14) McElvain, Clarke and Jones, *ibid.*, **64**, 1966 (1942).

(15) *Cf.* Hurd and Pollack, *THIS JOURNAL*, **60**, 1905 (1938).

TABLE II
 PROPERTIES AND ANALYSES OF ORTHOESTERS, $\text{CH}_3\text{C}(\text{OR})_2\text{OR}'$

R is	R' is	Formula	B. p.,		n_D^{25}	d_4^{25}	Calcd. C	Analyses, %		
			°C.	mm.				H	C	H
C_2H_5	$n\text{-C}_4\text{H}_9$	$\text{C}_{10}\text{H}_{22}\text{O}_3$	70-72	15	1.4057	0.8682	63.12	11.66	62.99	11.55
C_2H_5	$i\text{-C}_4\text{H}_9$	$\text{C}_{10}\text{H}_{22}\text{O}_3$	64-66	14	1.4017	.8616	63.12	11.66	63.09	11.70
C_2H_5	$s\text{-C}_4\text{H}_9$	$\text{C}_{10}\text{H}_{22}\text{O}_3$	63-65	15	1.4016	.8648	63.12	11.66	63.21	11.73
C_2H_5	$i\text{-C}_5\text{H}_{11}$	$\text{C}_{11}\text{H}_{24}\text{O}_3$	80-82	15	1.4077	.8626	64.66	11.84	64.56	11.83
C_2H_5	$(\text{CH}_3)_3\text{CCH}_2$	$\text{C}_{11}\text{H}_{24}\text{O}_3$	87-88	28	1.4037	.8481	64.66	11.84	64.88	11.77
C_2H_5	$\text{C}_6\text{H}_5\text{CH}_2$	$\text{C}_{13}\text{H}_{20}\text{O}_3$	121-122	8	1.4778	.9839	69.61	8.99	69.51	8.87
$n\text{-C}_4\text{H}_9$	C_2H_5	$\text{C}_{12}\text{H}_{18}\text{O}_3$	98-100	13	1.4119	.8623	66.01	12.01	65.92	12.00

alcohol was added 220 g. (1 mol) of diallylbromoacetal. After refluxing for five hours the mixture was cooled to room temperature and the precipitated potassium bromide removed by centrifuging. It weighed 108 g. (90%). After removal of the *t*-butyl alcohol the reaction product was fractionated carefully through a 15-cm. Widmer column. After 7 fractionations 60 g. (43%) of allyl allylacetate was obtained; b. p. 48-50° (8 mm.) or 160-162° (740 mm.); n_D^{25} 1.4198; d_4^{25} 0.8808; sap. equiv., 141 (calcd. 140).

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}_2$: C, 68.55; H, 8.63. Found: C, 68.71, 68.53; H, 8.97, 8.67.

Saponification of this ester yielded allyl alcohol, 3,5-dinitrobenzoate,¹⁶ m. p., 47-48°, and allylacetic acid, the anilide of which melted at 92°.¹⁷

Dibenzylbromoacetal.—This compound was prepared in the same manner as the allyl acetal described above, except that benzyl alcohol instead of allyl alcohol was used. The yield of product when 1 mole each of vinyl acetate and bromine and 5 moles of benzyl alcohol were used amounted to 475 g. (75%); b. p. 190-195° (2 mm.); n_D^{25} 1.5620; d_4^{25} 1.2181.

Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{Br}$: Br, 28.8. Found: Br, 28.7.

Benzyl *o*-Tolylacetate from Dibenzylbromoacetal.—The dehydrobromination of this bromoacetal was carried out in the same manner as described above for the diallylbromoacetal. From 321 g. (1 mol) of the bromoacetal was obtained 146 g. of a distillate which after three fractionations gave 110 g. (46%) of benzyl *o*-tolylacetate; b. p. 158-162° (1.5 mm.); n_D^{25} 1.4575; d_4^{25} 1.0773.

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 79.97; H, 6.71. Found: C, 80.01, 79.90; H, 6.81, 6.90.

This ester showed a saponification equivalent of 242 (calcd., 240) and from its saponification was isolated benzyl alcohol, the α -naphthylurethan of which¹⁸ melted at 133-134°, and *o*-tolylacetic acid,¹⁹ m. p. 89-90°.

Preparation of Orthoesters.—The mixed orthoesters were prepared by the addition of the alcohol, R'OH, to the ketene acetal, $\text{CH}_2=\text{C}(\text{OR})_2$. Triethyl orthoethoxyacetate and triethyl orthochloroacetate were prepared from the corresponding nitriles.^{8,13} The mono- and dibromo-orthoacetates were prepared by the bromination of ethyl orthoacetate.^{8,20} Ethyl orthobenzoate was prepared in the following manner. To a cold (5°) solution of 69 g.

(3 atoms) of sodium in 1200 ml. of absolute alcohol in a 2-liter, 3-neck flask, fitted with a reflux condenser, a stirrer and a dropping funnel, was added dropwise 195 g. (1 mol) of benzotrichloride, b. p. 85-87° (10 mm.). After the chloride had been added the ice-bath was removed and the solution stirred for five hours while it came to room temperature. The reaction mixture then was refluxed for eleven hours, after which time it was cooled and the salt filtered off. This salt was washed with ether and the ether washings added to the alcoholic filtrate. The yield of salt was 100 g. (58%). After distillation of the ether and alcohol the remaining orthoester was fractionated through a modified Widmer column. The yield of ester, b. p. 108-112 (13 mm.)²¹ amounted to 50 g. (22%).

The properties and analyses of those orthoesters that have not been described previously are listed in Table II.

Pyrolysis of the Orthoesters.—A 0.1-mole sample of the ester and one equivalent of phenol (in runs 3-9) were placed in the glass liner (40-ml. capacity) of a steel bomb and the bomb electrically heated for the time indicated in Table I. After this time the bomb was cooled and opened and its contents fractionated through a 15-cm. modified Widmer column. In the cases of the mixed orthoesters (runs 3-9, Table I) the ROH and CH_3COOR were taken off as one fraction and R'OH and $\text{CH}_3\text{COOR}'$ as another fraction under atmospheric pressure. The ester was determined in each of these fractions by saponification values and the remainder of the fractions calculated as the alcohol. The ethers, $\text{C}_6\text{H}_5\text{OR}$ and $\text{C}_6\text{H}_5\text{OR}'$, were removed from the remainder of the reaction mixture by fractionation under diminished pressure.

The properties of *n*-butyl-, isobutyl-, isoamyl- and benzyl phenyl ethers correspond to those previously reported in the literature.^{22,23,24,25}

s-Butylphenyl ether appears not to have been previously described in the literature. The product isolated from run 5, Table I boiled at 184-185°; d_4^{25} 0.9210; n_D^{25} 1.4828.

Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}$: C, 80.0; H, 9.4. Found: C, 79.9; H, 9.3.

In runs 10-16, Table I, the substituted acetic esters, $\text{XCH}_2\text{COOC}_2\text{H}_5$ and other pyrolysis products were separated by fractional distillation. In these runs no phenol was used. However, one run with ethyl orthoethoxyacetate was carried out in the presence of one equivalent of phenol and both the ethyl ethoxyacetate and the

(16) Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

(17) Wohlgenuth, *Ann. chim.*, **3**, 329 (1914).

(18) Bickel and French, *THIS JOURNAL*, **48**, 747 (1926).

(19) Radiszewski, *Ber.*, **18**, 1281 (1885).

(20) Beyerstedt and McElvain, *THIS JOURNAL*, **59**, 1274 (1937).

(21) Limpricht, *Ann.*, **135**, 87 (1865); Tschitschibabin, *Ber.*, **38**, 563 (1905).

(22) Pinette, *Ann.*, **243**, 32 (1887).

(23) Reiss, *Ber.*, **3**, 779 (1870).

(24) Orndorff and Hopkins, *THIS JOURNAL*, **15**, 519 (1893).

(25) Stadel, *Ann.*, **217**, 40 (1883).

phenyl ethoxyacetate²⁶ along with diethyl ether and phenetole were isolated (*cf.* footnote *a* Table I).

The pyrolyses of the halogen containing orthoesters were carried out in sealed glass tubes as these esters at the temperature of the reaction attacked the inside of the iron bomb. When the glass tube was opened after the pyrolysis there was a considerable release of pressure (ethylene). The remaining liquid material was fractionated. From the ethyl orthobromoacetate pyrolysis (run 15, Table I) the following fractions were collected (a) 0.5 g., b. p. about 20°; (b) 10 g., b. p. 37–38°; (c) 6.6 g., b. p. 61–73°; (d) 11.2 g., b. p. 55–60° (11 mm.). Fraction (a) was acetaldehyde, m. p. of 2,4-dinitrophenylhydrazone, 146–147°; fraction (b) after washing with concentrated sulfuric acid weighed 4 g., and had the density and index of refraction of ethyl bromide; fraction (c) was composed of ethyl alcohol, ethyl acetate and water and saponification indicated the presence of 4.3 g. of the ester; fraction (d) possessed the lachrymatory characteristics of ethyl bromoacetate and its bromine content indicated that it contained 7.7 g. of this ester.

The fractionation of the liquid portion of run 16, Table I, yielded the products listed in footnote (d) of the table, together with 5.8 g. (15%) of ethyl dibromoacetate, b. p. 38–45° (2 mm.).

Pyrolysis of Benzyl-diethyl Orthoacetate in the Absence of Phenol.—A 34-g. (0.15 mole) sample of this orthoester was heated at 200° for twenty-four hours, after which time the bomb was opened and the products fractionated. There was the usual pressure of ethylene produced by the pyrolysis. In the first fractionation the following fractions were collected (a) 6.7 g., b. p. 73–78° (740 mm.); (b) 4 g., b. p. 190–210° (740 mm.); (c) 5.6 g., b. p. 104–120° (10 mm.); (d) 1.5 g., b. p. 120–160° (10 mm.). A considerable amount of tar remained after this distillation. Fraction (c) was refractionated and collected as the following fractions (c-1) 0.3 g., b. p. 60–71° (3 mm.); (c-2) 0.4 g., b. p. 72–74° (3 mm.); (c-3) 0.6 g., b. p. 74–75° (3 mm.); (c-4) 0.8 g., b. p. 76–77° (3 mm.); (c-5) 2.3 g., b. p. 78–83° (3 mm.). A 1-g. residue remained after this second fractionation. Fraction c-4 showed the correct carbon and hydrogen content for ethyl *o*-tolylacetate²⁷ and had n_D^{25} 1.4990; d_4^{25} , 0.9988.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.1; H, 7.8.

Fraction c-5 was saponified and the *o*-tolylacetic acid obtained was identified as its amide.¹⁹ If fractions c-3, c-4 and c-5 are considered to be ethyl *o*-tolylacetate, the

(26) Sommelet, *Bull. soc. chim.*, [4] 1, 368 (1907).

(27) The use of ethyl *o*-tolylacetate has been mentioned in two instances in the literature [Ruzicka and Hosking, *Helv. Chim. Acta*, 13, 1411 (1930); V. Braun and Zobel, *Ber.*, 56, 2147 (1923)] but no reference to a description of its properties or to its analysis could be found.

yield of this rearrangement product amounts to approximately 14% of the theoretical.

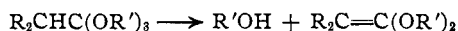
Pyrolysis of Ethyl Orthobenzoate.—A 10-g. sample of this orthoester was gently refluxed (b. p. 220–225°) for six hours under a 40-cm. air condenser, the top of which was connected to a cold trap. After this time 1.6 g. of ether, b. p. 35°, had collected in the cold trap. The ester in the flask was fractionated and separated into 4 g. (60%) of ethyl benzoate and 4 g. of unchanged ethyl orthobenzoate.

Summary

Ketene diethylacetal and its halogenated derivatives have been found to undergo pyrolysis at 200° with the formation of ethylene and the corresponding ethyl acetate. Ketene dimethylacetal, however, is quite stable at this temperature.

Attempts to prepare ketene diallyl- and dibenzylacetal have resulted in the isolation of the respective rearrangement products, allyl allylacetate and benzyl *o*-tolylacetate.

Ketene acetals have been shown to be the intermediates in the pyrolysis of a variety of orthoesters that have a structure that permits the decomposition to take the course



The pyrolysis of mixed orthoesters of the type $CH_3C(OR)_2OR'$ has been studied and the relative tendencies of these esters to eliminate the OR and OR' groups determined. Diethylbenzyl orthoacetate on pyrolysis yields some ethyl *o*-tolylacetate as the result of the rearrangement of the intermediate ketene ethylbenzylacetal.

While ethyl orthochloroacetate follows the course of the other orthoesters on pyrolysis, the ethyl orthobromo- and orthodibromoacetates give only a small amount of this type of decomposition. The main products that result from the pyrolysis of these bromoesters appear to be the result of an initial loss of the elements of ethyl hypobromite (instead of ethyl alcohol) from the bromoester with the formation of a ketene acetal that contains one less bromine than the original orthoester.

Ethyl orthobenzoate, which has no α -hydrogen, yields the normal ester and diethyl ether on pyrolysis.