be just as probable as the association of ethylene with alkyl radicals to generate a higher alkyl radical. It is not at all unlikely that the reaction of allyl radical with an olefin to produce the higher allyl radical results in little or no loss of resonance.

Summary

It has been found that the polymerization reactions of ethylene and of acetylene and the hydrogenation reaction of ethylene are inhibited by small initial additions of nitric oxide. The results have been interpreted as indicating a chain mechanism for the above reactions, and that the nitric oxide acts by combining with the free radicals or atoms and effectively prevents their further participation in the chain reaction.

The polymerization and hydrogenation reactions of propylene were found not to be inhibited by small additions of nitric oxide. On the contrary, a slight acceleration of these reactions is caused by the addition of nitric oxide. Although no explanation for this is offered, it is pointed out that this is only one of the instances in which the reactions of ethylene differ in wide respects from the corresponding reactions of its next higher homolog, propylene. The catalytic effect of nitric oxide neither favors nor denies the possibility of a chain mechanism in the propylene reactions studied.

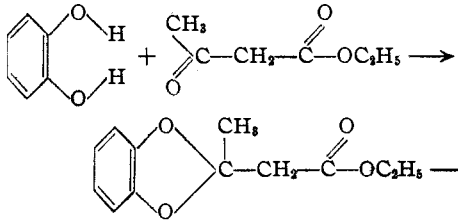
PRINCETON, N. J. RECEIVED FEBRUARY 2, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

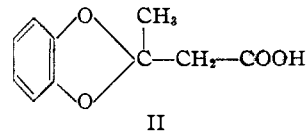
The Base-catalyzed Cleavage of Methylenedioxy Rings

BY RICHARD T. ARNOLD, NEWMAN BORTNICK AND ENOS MCMULLEN

Catechol reacts with acetoacetic ester in the presence of phosphorus pentoxide to form 2-methyl-2-carbethoxymethyl-1,3-benzodioxole (I).[1] This ester is reported to undergo hydrolysis leading to an acid (II) which melts at 61° although no directions were given in the original paper.



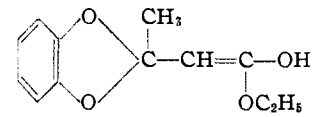
I



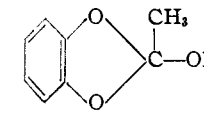
II

In another connection, a relatively large quantity of the acid (II) was required, and it was proposed to prepare it by the hydrolysis of I. Basic saponification of I followed by careful acidification of the reaction mixture gave the acid described by Slooff, but the yields were poor and the acid was accompanied by considerable quantities of catechol. It has been demonstrated repeatedly that simple methylenedioxy compounds, in agreement with their acetal (or ketal) structure, are stable toward bases. Thus Späth and Quietensky[2] have shown that dihydrosafrole is scarcely attacked by sodium ethoxide at 175° or by sodium hydroxide at 200°, and there are numerous other examples of this sort to be found in the literature. The surprisingly easy cleavage of the methylenedioxy ring system when I is hydrolyzed is an exception to the general behavior of these compounds, and it seemed likely that this is due to the relative position of the ester grouping to the ketal carbon atom.

A consideration of the formula III of the enol of I shows that this enol is a first vinylog[3] of a partially hydrolyzed ortho ester IV



III



IV

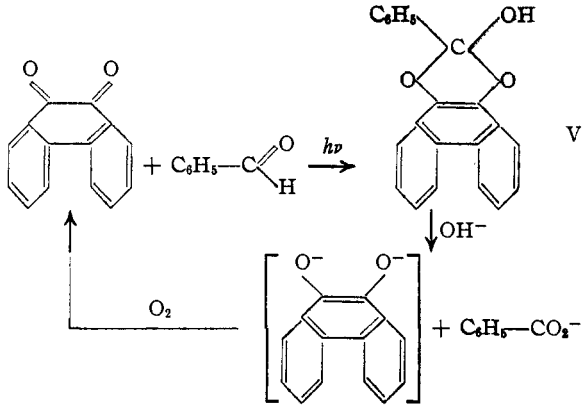
One substance of the type IV is known; it (V) is formed when an equimolecular mixture of benzaldehyde and phenanthraquinone is subjected to the action of ultraviolet light.[4] When V is hydrolyzed, there is formed an alkali soluble material which yields phenanthraquinone on mild oxidation. These transformations are shown below.

(1) Slooff, *Rec. trav. chim.*, **54**, 995 (1935).

(2) Späth and Quietensky, *Ber.*, **60**, 1882 (1927).

(3) Fuson, *Chem. Rev.*, **16**, 1 (1935).

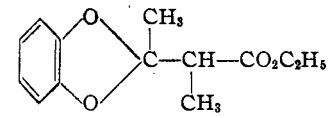
(4) Schönberg and Moubacher, *J. Chem. Soc.*, 1430 (1939).



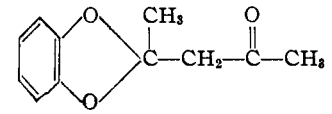
V

The instability of the ketal ring in I toward alkali becomes easy to understand, by analogy with the properties of V, provided that the methylenedioxy compound (I) is capable of enolization; for only in this way is it possible for a substance such as I to assume the structure of a vinylog of IV. It would be predicted then that those methylenedioxy compounds which when enolized give vinylogs of IV would be cleaved by alkali at the heterocyclic ring while those substances incapable of enolization to give vinylogs of IV would be stable in basic solutions. The results described below substantiate this line of reasoning.

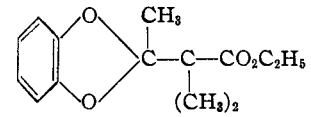
Using the previously mentioned procedure,[1] catechol and 4-methylcatechol have been condensed with a series of ketones including methylacetoacetic ester, acetylacetone, dimethylacetoacetic ester and ethyl levulinate to give products of the type VI, VII, VIII and IX.



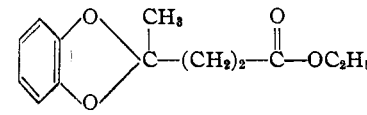
VI



VII



VIII

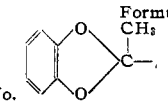
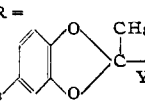


IX

The complete list of compounds prepared during the course of this investigation and a semi-quantitative determination of the rate of catechol formation when these substances were treated with alkali are given in Table I. The amount of catechol present in the basic hydrolyzates was

TABLE I

THE PREPARATION AND BASIC CLEAVAGE OF METHYLENEDIOXY COMPOUNDS, $T \simeq 80°$

No.	Formula: R =  R′ = 	Yield, %	B. p., °C.	Mm.	M. p., °C.	Calculated, % C	Calculated, % H	Observed, % C	Observed, % H	t, (hrs.)	Cleavage,[a] %
I	R—CH_2—$COOC_2H_5$	50	146–148	17		...	...	...	...	13.5	20.0
II	R—CH_2—COOH	small			61.5–62	...	...	...	...	14.5	5.1[b]
VI	R—$CH(CH_3)$—$COOC_2H_5$	42	146–148	17		66.10	6.78	66.02	7.00	13.5	71.0
VII	R—CH_2—CO—CH_3	16	136–138	20		68.75	6.67	68.87	6.40	20	99.0
VIII	R—$C(CH_3)_2$—$COOC_2H_5$	32	111–113	5		67.20	7.20	67.35	7.35	5.5	0
IX	R—$(CH_2)_2$—$COOC_2H_5$	50	157–160	17		66.10	6.78	65.83	6.87	4.0	0
X	R—$CH(CH_3)$—COOH	small			89.5–90	63.43	5.87	63.78	6.03	14.5	31.0[b]
XI	R—$C(CH_3)_2$—COOH	90			90 –90.5	64.86	6.31	64.68	6.57		
XII	R—$(CH_2)_2$—COOH	90			73 –73.5	63.46	5.77	63.29	5.76		
XIII	R′—CH_2—$COOC_2H_5$	41	157–159	19		66.10	6.78	65.84	7.10	24	7.2
XIV	R′—$CH(CH_3)$—$COOC_2H_5$	37	162–164	21		67.20	7.20	66.72	7.49	24	53.4
XV	R′—$C(CH_3)_2$—$COOC_2H_5$	40	164–166	21		68.18	7.64	66.90	7.74	21	(4.5)[c]
XVI	R′—$(CH_2)_2$—$COOC_2H_5$	50	172–174	19		67.20	7.20	67.20	7.40	21	0
XVII	R′—$CH(CH_3)$—COOH	small			91.5–92.5	64.84	6.35	64.97	6.50		
XVIII	R′—$C(CH_3)_2$—COOH				89 –89.5	66.10	6.78	66.33	6.78		
XIX	R′—$(CH_2)_2$COOH				56 –57	64.86	6.36	65.20	6.63		

[a] Unless specified, all hydrolyses were carried out with 1 g. of sample, 5 g. of potassium hydroxide, and 25 cc. of ethanol (95%). [b] No cleavage was observed in aqueous alkali. [c] This compound in quantity was not obtained pure. A small sample (300 mg.) of the ester prepared from the silver salt of the acid XVIII and ethyl iodide gave no 4-methylcatechol on hydrolysis with alkali.

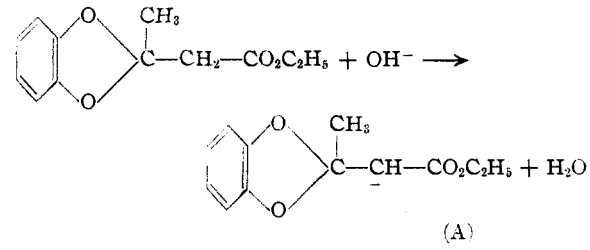
determined with the specific nitrite–molybdate reagent described by Arnow.[5]

Inspection of Table I will show that the products VI, VII, VIII and IX, respectively, are sharply differentiated into two classes depending on their behavior toward alkali. Compounds VI and VII gave considerable quantities of catechol on basic hydrolysis. In contrast to these, compound VIII cannot enolize and compound IX even if it did enolize would not give a vinylog of IV. These esters with alkali undergo normal saponification to carboxylic acids and yield no trace of catechol. Not even the usual color tests for phenols could be obtained when applied to the neutralized hydrolyzates of VIII and IX. It is noteworthy that where cleavage of the heterocyclic ring occurred the rate of reaction decreased in the order ketones > esters > acids (as carboxylate). This order is in excellent agreement with the generally recognized view of the ease with which enolization (*i. e.*, ionization at the α-carbon atom) can take place in these homologous series.

Also evident is the fact that compound I yields less catechol than does VI which has a methyl group on the α-carbon atom. This difference must be due to the fact that ester I is hydrolyzed more readily than VI to the corresponding carboxylate ion which then cleaves very slowly to catechol.

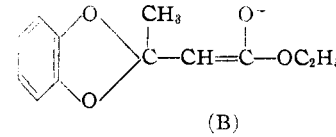
Some very interesting effects were observed when the methylenedioxy acids II and X were treated with aqueous and alcoholic alkali. No cleavage to catechol occurred in water but appreciable amounts of catechol were formed in alcohol solutions. We have attributed this difference to the partial formation of esters which easily cleave to give catechol.

The application of modern electronics to this problem makes it appear most probable that the initial step in the cleavage reaction involves the ionization of the ester by a base. This removal of a proton from the α-carbon atom is facilitated by the combined polar effects of the groups attached to the β-carbon atom.

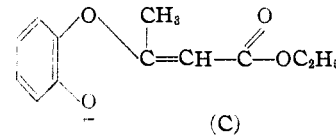


(A)

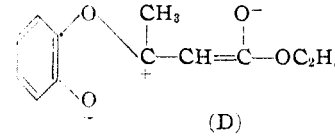
The anion (A) first formed is in resonance with three other structures represented by (B), (C) and (D).



(B)

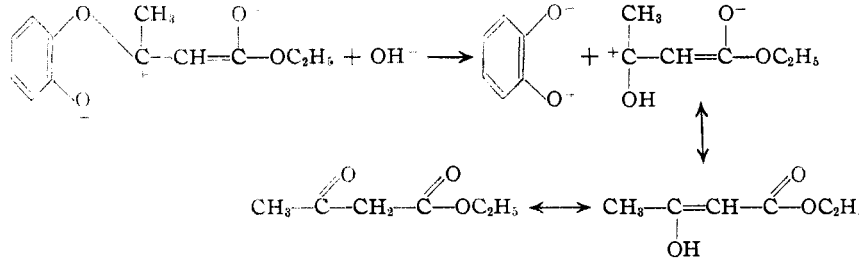


(C)

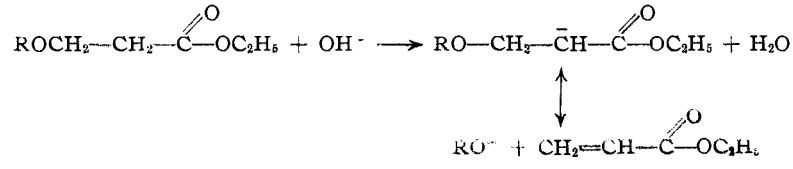


(D)

Since no hetero ring is present in the contributing structures (C) and (D), it is apparent that the opening of the methylenedioxy ring is concurrent with the initial ionization. The final step is presumably a direct attack by a hydroxide ion on the carbonium ion; this results in the simultaneous formation of catecholate ion and acetoacetic ester.



The analogy between the reactions discussed in this paper and the reversible formation of α,β-unsaturated esters from β-alkoxy esters is very striking. It is probable that the latter transformation is best described by the equation



(5) Arnow, *J. Biol. Chem.*, **118**, 531 (1937).

Summary

1. It has been shown that certain methylenedioxy compounds are cleaved by base in spite of the fact that they are ketals.

2. A detailed mechanism has been offered for this unusual reaction.

MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 2, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Mechanism of the Haloform Reaction
The Preparation of Mixed Haloforms

BY J. G. ASTON, J. D. NEWKIRK, JULIAN DORSKY AND D. M. JENKINS

The present paper records a detailed investigation of the preparation of chloroform, dichlorobromomethane, chlorodibromomethane and bromoform from the dihaloacetophenone derivative by the haloform reaction with particular attention to the cleavage reaction of the corresponding trihaloacetophenone.

When dichloroacetophenone is treated with sodium hypobromite in the presence of excess alkali in the cold, dichlorobromomethane is produced practically instantaneously. When chlorobromoacetophenone is similarly treated, chlorodibromomethane is likewise instantaneously produced. In the same way dibromoacetophenone yields bromoform. In these last two cases mandelic acid is produced in 12% yield due to rearrangement of the dihaloacetophenone by alkali. Alkaline hypochlorite reacts similarly on dichloroacetophenone, chlorobromoacetophenone and dibromoacetophenone.

For a reason which will appear presently it was not convenient to prepare the intermediate mixed trihaloacetophenones which would yield, respectively, the mixed haloforms on cleavage. It is a simple matter, however, to prepare trichloroacetophenone and tribromoacetophenone and to study their cleavage to chloroform and bromoform, respectively.

In the preparation of these two compounds it was merely necessary to add sodium acetate to obtain smooth replacement of the last alpha hydrogen by halogen. Without the sodium acetate the equilibrium favors the reverse reaction, a fact which seems to have been overlooked and is possibly the reason why tribromoacetophenone has never been prepared until now.

We were considerably surprised to find that tribromoacetophenone can be recovered unchanged from 5 *N* alkali at zero degrees. In addition warming to 80° with one normal alkali did not effect rapid cleavage. The cleavage was not noticeably increased in the presence of alkaline hypobromite.

Fuson and co-workers[1] found that acetophenones with both alpha positions occupied do not yield the corresponding substituted benzoic acids on treatment with sodium hypobromite solution. Instead the corresponding α,α,α-tribromo derivative could be recovered from the solution. In some cases the α-bromo and the α,α-dibromo acetophenones were isolated. The substituted α,α,α-trihaloacetophenones could then be cleaved under conditions primarily involving solubility. Fuson concluded that, in the haloform reaction alpha substitution of halogen occurs until the trihaloacetyl group is formed, which then immediately cleaves in the presence of alkali yielding the sodium salt of the carboxylic acid and the haloform, providing the cleavage is not sterically hindered.

To explain the results the possibility was considered that during the action of sodium hypobromite on the dihaloacetophenone, the trihaloacetophenone was formed in highly supersaturated solution and then cleaved due to its high concentration. Accordingly the action of sodium hypobromite at zero degrees on dibromoacetophenone was investigated in the presence of crystalline tribromoacetophenone which would presumably tend to remove any supersaturation. No additional tribromoacetophenone was produced; in fact that originally added disappeared.

However, it was found that the cleavage of tribromoacetophenone proceeds practically instantaneously by the action of one mole of sodium hydroxide per mole of tribromoacetophenone in aqueous dioxane (1 volume of water to 2 volumes of dioxane) when the solution is 0.13 volume formal with respect to each. This indicates that

(1) Fuson and Bull, *Chem. Rev.*, **15**, 275 (1934).