Radical Catalyzed Addition of Diethylformal and Orthoformate to Dimethyl Maleate

Akira NAGASAKA and Ryohei ODA*

(Oda Laboratory)

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A radical catalyzed reaction of diethylformal upon dimethyl maleate was investigated and α-acetylsuccinic acid ester was identified as the main product. From this fact it was made clear that the hydrogen-atom (1) and not hydrogen-atom (2), of diethylformal ($\overset{H(1)}{CH_3CH}(-O-)\overset{H(2)}{CH}(-O-C_2H_5)$) was abstracted by radical source. The authors have also undertaken the reaction of ethyl ortho-fromate upon maleate initiated by benzoylperoxide. In this case the tertiary hydrogen atom of the orthoformate was abstracted. As the reaction products, triethoxymethylsuccinic acid ester, phenylsuccinic acid ester and tetralin-tetracarboxylic acid ester were detected and the total radical chain reaction scheme was also suggested.

It is already well known that various organic radicals, produced by radicalotropy, add to α-olefins and maleates. These results were confirmed especially by M. S. Kharasch, W. H. Urry and T. M. Patrick. T. M. Patrick[1] has investigated precisely the addition of radicals, which were produced by radicalotropy of various aldehydes with radical source, to maleate.

$$R\cdot + R'-CHO \longrightarrow RH + R'-\dot{C}=O$$

$$R-\dot{C}=O + \underset{\underset{CH-COOEt}{\|}}{CH-COOEt} \longrightarrow R'-\underset{\underset{O}{\|}}{C}-\underset{\underset{\cdot CH-COOEt}{|}}{CH}-COOEt$$

$$R'-CHO \longrightarrow R'-CO-\underset{\underset{CH_2-COOEt}{|}}{CH}-COOEt + R'-\dot{C}=O$$

But in the paper of T. M. Patrick it is stated that the formaldehyde does not react at all.

The authors have investigated the above reaction with diethylformal instead of free formaldehyde, using benzoylperoxide as radical source. From the reaction products the authors could isolate α-acetylsuccinic acid ester, but detected no trace of diethylacetal of the α-formylsuccinic acid ester. The α-acetylsuccinic acid ester was identified by converting it into the following phenylhydrazone-derivative and also by converting it tnto laevulic acid by hydrolysis.

* 永阪 晃, 小田 良平

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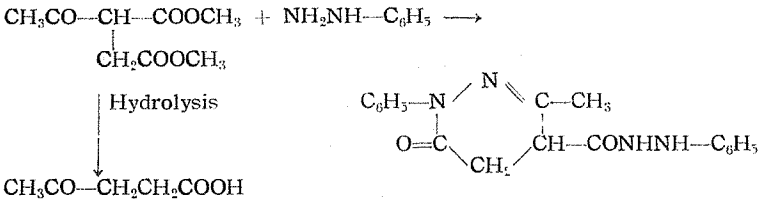
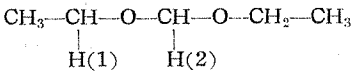
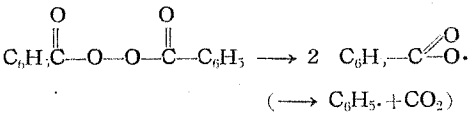
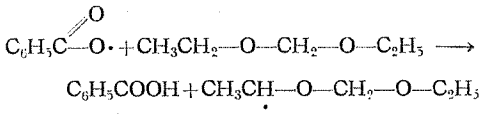


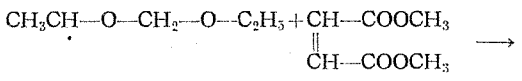
From the fact that the α-acetylsuccinic acid ester was produced, it can be concluded that the hydrogen-atom (1), and not hydrogen-atom (2), of the diethylformal was abstracted by benzoyloxy-radical, and the reaction was

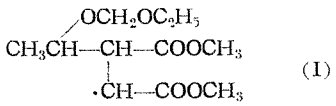


initiated in the followihg scheme :

(1) 

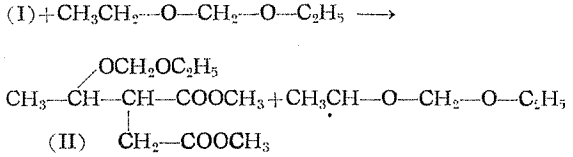
(2) 

(3) 



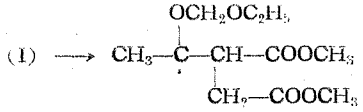
(I)

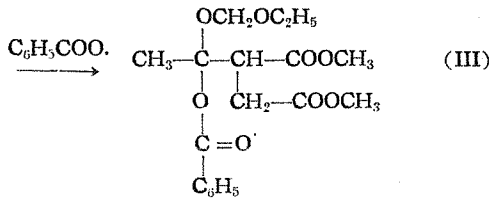
If the above intermediate radical (I) abstracts again the hydrogen-atom (1) from diethylformal, as generally normal in the radical chain propagation, then the following compound should be produced.

(4) 

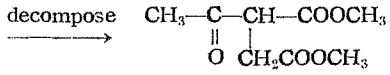
But, indeed, this is not the fact. For the production of α-acetylsuccinic acid ester the following two courses can be considered, though it is difficult to decide which is actually true.

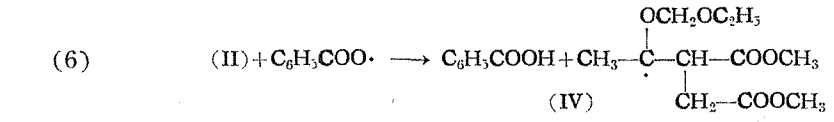
(5) Radical isomerization





(III)





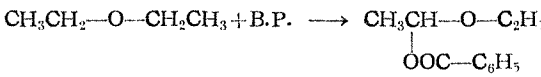
(6)

(IV)

$$(IV)+C_6H_5COO\cdot \longrightarrow (III) \longrightarrow \alpha\text{-acetylsuccinic acid ester}$$

The radical isomerization of this type (reaction 5) can be considered without doubt from the works of D. Y. Cartin[2] and M. S. Kharasch[3].

The reaction (6) can also be considered with certainty, because the compound (II) has a tertiary hydrogen-atom and this hydrogen-atom can be abstracted easily by radicals. Especially the compound (II) is a kind of ether, and it is already known that diethylether is attacked by benzoylperoxide in the following manner[4]:



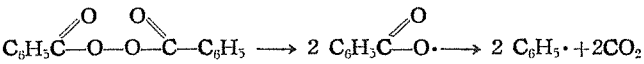
Next the authors have investigated the reaction of orthoformate with diethyl maleate, using benzoylperoxide as initiator. As the reaction products the following compounds were detected.

1. Benzene, 2. Benzoic acid, 3. Triethoxymethylsuccinic acid ester, 4. Phenylsuccinic acid ester, 5. Tetralin-tetracarboxylic acid ester and its isomer.

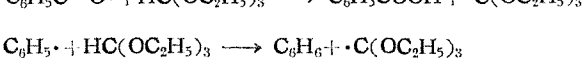
From the above results, the authors have assumed the following reaction scheme :

It is noteworthy that in this case only the tertiary hydrogen atom of the orthoformate is abstracted by radical.

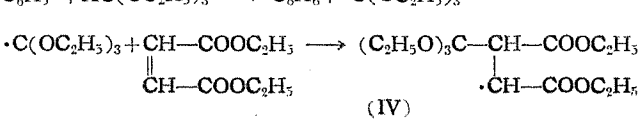
(1)



(2)



(3)



(IV)

Addition of Diethylformal and Orthoformate to Dimethyl Maleate

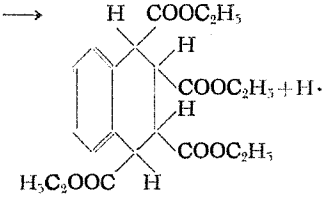
(4) $(IV) + \cdot CH(OC_2H_5)_3 \longrightarrow (C_2H_5O)_3C-\underset{\displaystyle CH_2-COOC_2H_5}{\overset{\displaystyle |}{CH}}-COOC_2H_5 + \cdot C(OC_2H_5)_3$

(5) $C_6H_5\cdot + \underset{\displaystyle CH-COOC_2H_5}{\overset{\displaystyle \|}{CH}}-COOC_2H_5 \longrightarrow C_6H_5-\underset{\displaystyle \cdot CH-COOC_2H_5}{\overset{\displaystyle |}{CH}}-COOC_2H_5$ (V)

$(V) \xrightarrow{CH(OC_2H_5)_3} C_6H_5-\underset{\displaystyle CH_2-COOC_2H_5}{\overset{\displaystyle |}{CH}}-COOC_2H_5 + \cdot C(OC_2H_5)_3$

(6) $(V) + \underset{\displaystyle CH-COOC_2H_5}{\overset{\displaystyle \|}{CH}}-COOC_2H_5 \longrightarrow C_6H_5-\underset{\displaystyle \cdot CH-COOC_2H_5}{\overset{\displaystyle |}{\underset{\displaystyle CH-COOC_2H_5}{\overset{\displaystyle |}{\underset{\displaystyle CH-COOC_2H_5}{\overset{\displaystyle |}{CH}}-COOC_2H_5}}-COOC_2H_5}}-COOC_2H_5$ (VI)

(7) (VI) $\longrightarrow$



EXPERIMENTAL

1. Reaction between diethylformal and dimethyl maleate.

A mixture of 235 g. diethylformal, 90 g. dimethyl maleate and 24 g. benzoyl-peroxide was refluxed for 12 hrs. in CO_2 stream. The reaction mixture was distilled and 191 g. of the unreacted diethylformal was recovered. The residue was made alkaline with Na_2CO_3 solution and extracted with benzene. From the aqueous alkaline solution 9 g. benzoic acid was obtained after acidification with HCl. The benzene-layer was washed with water, dried, fractionated and the following fractions were obtained. All of them were liquid.

1. 80~85°/9 mm, 8 g.
2. 100~121°/9mm, 2 g.
3. 122~135°/9mm, 25 g.
4. 135~160°/9mm, 2.5 g.
5. 185~205°/9mm, 20 g.

The main fraction 3 was redistilled into the following two fractions :

3′ 129~134°/12mm, 11 g.

3″ 135~140°/12mm, 8 g.

The fraction 3′ was converted into phenyl-hydrazone. The phenyl-hydrazone ob-

tained has the m.p. of 198~201°. The same hydrazone was obtined from α-acetyl-succinic ester, which the authors have prepared authentically by the radical reaction of acetaldehyde with dimethyl maleate, and no melting point depression was recognized. The elementary analysis of the hydrazone is as follows :

Found,	C : 67.66 %,	H : 5.92 %,	N : 17.36 %
Calc,	C : 67.08 %,	H : 5.59 %,	N : 17.39 %

The fraction 3′ (3 g.) was then hydrolyzed with 15 g. 20 % HCl, refluxing for 5 hrs. After concentration, some white precipitates were obtained. These precipitates were filtered (0.5 g.) and identified as succinic acid. From the filtrate the laevulic acid was isolated and identified as 2,4-dinitrophenylhydrazone, compared with an authentic sample.

The fraction 3″ was hydrolyzed with HCl and from the hydrolysate succinic acid was detected.

Fraction 4 was also hydrolyzed with HCl and from the hydrolysate the phenyl-succinic acid was detected and identified compaired with an authentic sample.

From fraction 5, when reacted with phenylhydrazine or hydrolyzed with HCl, no crystalline product was obtaind. It is considered that this fraction 5 consists of chiefly 2 : 1-Telomer and other complex esters.

2. Reaction between ethyl orthoformate and diethyl maleate.

A mixture of 180 g. orthoformate, 68 g. diethyl maleate and 12 g. benzoyl-peroxide was heated for 11 hrs. on water bath in CO_2 stream. The yellow reaction mixture was then diluted with benzene and extracted with Na_2CO_3 solution. From the extract 2 g. benzoic acid was obtained after acidification. In a similar experiment the reaction mixture was fractionally distilled without dilution with benzene and the following fractions were obtained.

1. 60~83°, 3.5 g. (colorless oil)
2. 137~143°, 157 g. (colorless oil)
3. 116~118°/21mm, 21 g. (colorless oil)
4. 85~129°/6mm, 18 g. (colorless oil)
5. 160~215°/10mm, 13 g. (faint yellowish, very viscous oil)
6. 210~240°/6mm, 7 g. (yellow-brownish, very viscous oil)
7. Residue, ca. 14 g. (brown-black semi-solid)

The fraction (1) was benzene, (2) was unreacted ethyl orthoformate and (3) was unreacted diethyl maleate. The fraction (4) was rectified further and the following sub-fractions were obtained.

8. 80~100°/4mm, 3 g. (colorless oil)
9. 100~118°/4mm, 6 g. (colorless oil)
10. 118~123°/4mm, 6.5 g. (colorless oil)

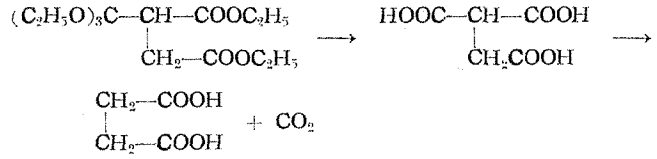
11. 153°/4mm, 2g. (colorless oil)

Fraction (5) was also rectified and the following sub-fractions were obtained.

12. 160~180°/4mm, 3.5 g. (colorless viscous oil)
13. 184~197°/4mm, 7 g. (faint yellowish, viscous oil)

The fraction (8) was hydrolyzed with HCl and from the hydrolysate fumaric acid was detected. Therefore this fraction consists chiefly of unreacted diethyl maleate.

The fracrion (9) was hydrolyzed with HCl and from the hydrolysate succinic acid was detected. The authors assume that this fraction (9) is the triethoxymethylsuccinic acid ester and this compound was converted into succinic acid by HCl hydrolization.



The fraction (10) was also hydrolyzed with HCl and from the hydrolyzate phenylsuccinic acid was isolated and identified, compared with an authentic sample. Therefore, this fraction consists of diethyl α-phenylsuccinate. The fraction (11) was also treated with HCl and also phenylsuccinic acid was detected. From fraction (12), after hydrolization with HCl, the tetralin-tetracarboxylic acid was detected and identified, compared with an authentic sample. The fractions (13) and (6) were similarly hydrolyzed, but no definite crystalline product was obtained.

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(1) T.M. Patrick, *J. Org. Chem.*, **17**, 1009 (1952).
(2) D.Y. Cartin, *J.Am. Chem. Soc.*, **74**, 5381 (1952).
(3) M.S. Kharasch, *J.Org. Chem.*, **19**, 1150 (1954).
(4) W.E. Cass, *J.Am. Chem. Soc.*, **69**, 500 (1947).