the polymer thus treated was insoluble neither in benzene and other organic solvents nor in squeous alkali.
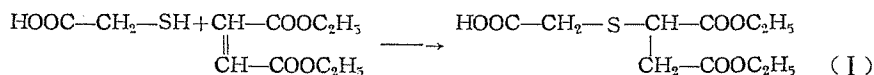
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6. Free Radical Reactions

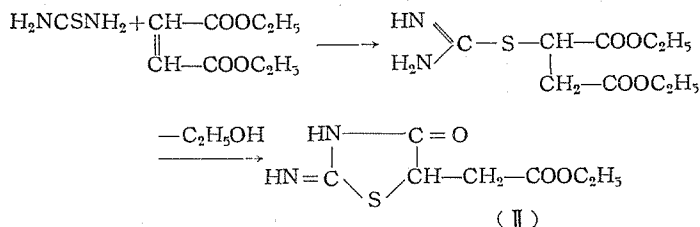Akira NAGASAKA, Shogo NUKINA and Ryohei ODA

(Oda Laboratory)

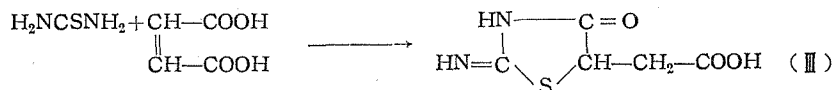1. Reactions of mercaptoacetic acid and thiourea with diethyl maleate.

Mercaptoacetic acid did not react with diethyl maleate without catalyst, while in the presence of small amount of ammonium hydroxide or benzoyl peroxide diethyl carboxymethylmercaptosuccinate (I) (b.p. 194-200°/5mm.) was obtained. The yields of (I) were 78.4% and 92.7% of calcd. value respectively. The reaction mechanism seems to be analogous to that of the reaction between mercaptoacetie acid and methyl acrylate (M. S. Kharasch, *J. Org. Chem.*, **13**, 97 (1948)).

$$HOOC-CH_2-SH + \begin{matrix} CH-COOC_2H_5 \\ \| \\ CH-COOC_2H_5 \end{matrix} \longrightarrow \begin{matrix} HOOC-CH_2-S-CH-COOC_2H_5 \\ | \\ CH_2-COOC_2H_5 \end{matrix} \quad (I)$$

Thiourea $H_2N-C(=S)-NH_2$ reacts in the form of $HN=C(SH)-NH_2$ in many cases and is regarded as a sort of mercaptan. It is expected, therefore, that thiourea adds to diethyl maleate in the same way as mercaptoacetic acid does. Thiourea reacted with diethyl maleate in alcohol, and ethyl pseudothiohydantoin acetate (II) (m. p. 164-6°) was found as the product. The effect of benzoyl peroxide as a catalyst was not profound and it increased the yield of (II) a litte.

$$H_2NCSNH_2 + \begin{matrix} CH-COOC_2H_5 \\ \| \\ CH-COOC_2H_5 \end{matrix} \longrightarrow \begin{matrix} HN \\ \hspace{1em} \diagdown \\ H_2N \diagup \end{matrix} C-S-\begin{matrix} CH-COOC_2H_5 \\ | \\ CH_2-COOC_2H_5 \end{matrix}$$

$$\xrightarrow{-C_2H_5OH} \begin{matrix} HN-\!\!\!-\!\!\!-C=O \\ | \hspace{2em} | \\ HN=C \diagdown \diagup CH-CH_2-COOC_2H_5 \\ \hspace{1.5em} S \end{matrix}$$

$$(II)$$

Thiourea and maleic acid gave the addition compound (m. p.>238°) which was considered to be a salt or condensate of some molecules of pseudothiohydantoinacetic acid (III). Any accelerating effect of benzoyl peroxide was not observed in this reaction.

$$H_2NCSNH_2 + \begin{matrix} CH-COOH \\ \| \\ CH-COOH \end{matrix} \longrightarrow \begin{matrix} HN-\!\!\!-\!\!\!-C=O \\ | \hspace{2em} | \\ HN=C \diagdown \diagup CH-CH_2-COOH \\ \hspace{1.5em} S \end{matrix} \quad (III)$$

Probably (II) and (III) are obtained, not by a radical addition, by an ionic addi-

tion between α, β-unsaturated carbonyl group and $HN=C(S\ominus H\oplus)-NH_2$.

In the reaction above mentioned, cetene-1, cinnamic acid and styrene were used instead of diethyl maleate, but no reaction was observed in every case.

2. Reaction of ethyl orthoformate with diethyl maleate.

A mixture of 1.215 moles of ethyl orthoformate, 0.395 mole of diethyl maleate and 0.050 mole of benzoyl peroxide was heated for 11 hours at 90-5° in the current of carbon dioxide, and the following products were isolated; benzene (0.006 mole), benzoic acid (0.016 mole), diethyl triethoxymethylsuccinate (IV) (0.019 mole, b. p. 100-18°/4mm.), diethyl phenylsuccinate (0.032 mole), tetraline tetracarboxylate (small mounts) and unidentified high boiling esters.

The formation of (IV) is readily accounted for as follows:

$$R\cdot + CH(OC_2H_5)_3 \longrightarrow \cdot C(OC_2H_5)_3 + RH$$

$$\cdot C(OC_2H_5)_3 + \begin{array}{c} CH-COOC_2H_5 \\ \| \\ CH-COOC_2H_5 \end{array} \longrightarrow \begin{array}{c} (C_2H_5O)_3C-CH-COOC_2H_5 \\ | \\ \cdot CH-COOC_2H_5 \end{array} \text{ (A)}$$

$$(A)+HD \longrightarrow \begin{array}{c} (C_2H_5O)_3C-CH-COOC_2H_5 \\ | \\ CH_2-COOC_2H_5 \text{ (IV)} \end{array} +D\cdot$$

$$R\cdot \longrightarrow \langle \rangle \cdot \text{ or } \langle \rangle-COO\cdot \text{ ; } HD \longrightarrow \text{Hydrogendonor}$$
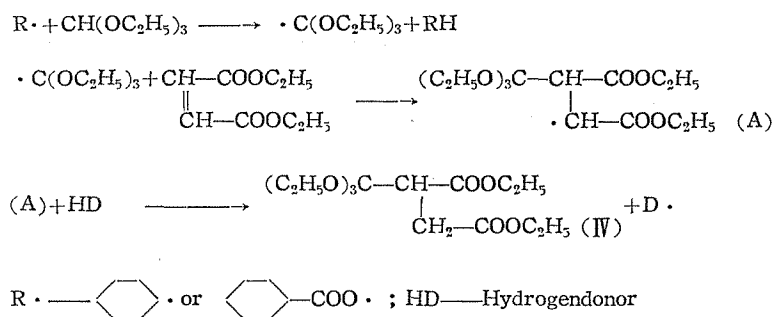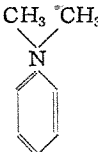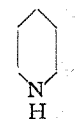
The mechanism of the formation of other products have been proposed by C. S. Warvel(*J. Am. Chem. Soc.*, **69**, 52 (1947)).

3. Reaction of benzoyl peroxide with benzothiazole.

When a mixture of 0.445 mole of benzothiazole and 0.083 mole of benzoyl peroxide was heated for 9 hours at 80-90° in the atmosphere of carbon dioxide, benzoic acid (0.086 mole), 2-phenyl-benzothiazole (V) (0.018 mole, m.p. 113°) and an unidentified basic oily matter which contained small amount of benzoate (VI) were formed. The following mechanism may be considered:
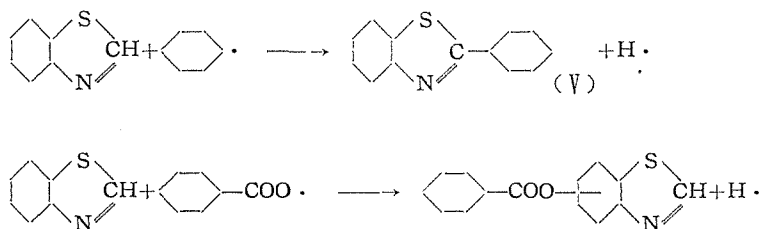
Reaction of ketene with ethylacetoacetoacetate in the presence of some orgnaic bases.

React. Temp.[1]	Catalyst / Products / K_B	None	CH₃ CH₃ N (dimethylaniline)	quinoline	pyridine	$(C_2H_5)_3N$	piperidine N–H	NH₄OH	NaOH
		—	2.4×10^{-10}	3.2×10^{-10}	1.2×10^{-9}	5.3×10^{-4}	1.6×10^{-3}	—	—
Low	O-acetyl der. [2] / C-acetyl der.	× [4]	O(rich) / C(poor)	O(rich) / C(poor)	O(rich) / C(poor)	O(rich) / C(poor)	O / C (nearly equal amount)	× [4]	C(only)
	Conv. ratio(%)	—	42	9	32	91	48	—	94
	Yield[3] (%) I.	—	40	7	26	57	37	—	49
	II.	—	95	78	81	63	77	—	52
High	O-acetyl der. / C-acetyl der.	C(only)	C(only)	C(only)	O (rich) / C(poor)	O / C (nearly equal amount)	C(only)	—	—
	Conv. ratio (%)	43	89	60	52	72	71	—	—
	Yield(%) I.	37	56	37	40	48	39	—	—
	II.	86	63	62	77	62	55	—	—

(1) Reaction Temperature : Low-cooling with ice (0-10°C); High-warming on a steam bath (70-90°C).

(2) O : O-acetyl derivative of ethylacetoacetate.
    C : C-acetyl derivative of ethylacetoacetate.

(3) Total yield of O-acetyl derivative and C-acetyl derivative :
    I. Yield based on ethylacetoacetate used.
    II. Theoretical yield.

(4) No reaction.