

27	$C_6H_6 \rightarrow (C_2H_5)_2O$		10	Acetone	-	-	+	+	++	+	667	20.2
28		E	30		-	-	+	+	++	+	860	19.3
29			60		-	-	+	+	++	+	663	15.0

- 1 Dried after treating with some solvents.
- 2 H : Hanging in ketene stream.  
E : Immersing in ether.
- (3) Speed of ketene gas maintained at about 0.12 mole/10 min.
- (4) Washing out ketene polymers with solvents.
- (5) Sunlight in midsummer.
- (6) (-) : colorless.  
(+) : faintly yellow.  
(++) : deep yellow.

### 13. Reaction of Ketene with Ethylacetoacetate

Toshizo ISOSHIMA

(Nodzu Laboratory)

It is well known that ketene reacts with ethylacetoacetate giving O-acetyl derivative. But there is no information about the formation of C-acetyl derivative in this reaction. As shown in the following descriptions, it was now found that C-acetylation or O-acetylation can be effected according to the conditions, under which ketene and ethylacetoacetate react.

(i) Without catalyst, ketene and ethylacetoacetate did not react near 0°C, but at about 50°C, gave C-acetyl derivative,  $CH_3-C(=O)-CH(COCH_3)-COOC_2H_5$ , and at about 80°C, in a good yield. In this reaction, no O-acetyl derivative was produced.

(ii) In the presence of conc.  $H_2SO_4$ , no reaction occurred at 0°C between the reactants, but at 80–90°C, O-acetyl derivative,  $CH_3-C(=O)-CH(COOC_2H_5)-COCH_3$ , was solely obtained in a good yield.

(iii) The sodium salt of ethylacetoacetate suspended in ether reacted with ketene at 0°C, giving C-acetyl derivative solely as the product. The conditions and the results of these reactions mentioned above are summarized in the following Table.

## Reactions of ketene with ethylacetoacetate.

Exp. No.	Ethyl-acetoacetate g. (mole)	Catalyst g. (mole)	Ketene g. (mole)	Solvent cc	React. Temp. °C	After-treatment	Products						
							Fractions (B. P.)				Yield %	M. P. of Cu-Salt	
							90-100°/20mm g. $n_D$		100-110°/20mm g. $n_D$				
1	65(0.5)	None	42(1.0)	None	2-4	None	—	—	—	—	—	—	—
2	65(0.5)	//	42(1.0)	//	45-49	//	7	1.4475 <sup>17</sup>	6 <sup>(2)</sup>	1.4680 <sup>17</sup>	15	150-151	C-Acetyl derivative
3	65(0.5)	//	42(1.0)	//	80-87	//	9	1.4590 <sup>14</sup>	23 <sup>(2)</sup>	1.4708 <sup>14</sup>	37.5	150-151	//
4	65(0.5)	conc. H <sub>2</sub> SO <sub>4</sub> 1	42(1.0)	None	0	Na <sub>2</sub> CO <sub>3</sub>	—	—	—	—	—	—	—
5	65(0.5)	1	42(1.0)	//	75-80	//	9 <sup>(1)</sup>	1.4371 <sup>11.5</sup>	34 <sup>(1')</sup>	1.4454 <sup>11.5</sup>	50	—	O-Acetyl derivative
6	65(0.5)	1	42(1.0)	//	84-94	//	13	1.4352 <sup>15.5</sup>	44.5	1.4430 <sup>15.5</sup>	67 <sup>(6)</sup>	—	//
7	65(0.5)+Na, 1(0.04)		42(1.0)	Ether 100	0	20% H <sub>2</sub> SO <sub>2</sub>	5.5	1.4454 <sup>14</sup>	15 <sup>(3)</sup>	1.4617 <sup>14</sup>	24	151-152	C-Acetyl derivative
8	65(0.5)+Na10.5 (0.45)		59(1.4)	300	0	//	15	1.4521 <sup>12</sup>	24 <sup>(4)</sup>	1.4660 <sup>12</sup>	45.5	150-151	//
9	Pure Na-Salt 17(0.112)		29(0.7)	100	0	//	0.5	—	10.5 <sup>(5)</sup>	1.4660 <sup>20</sup>	55	151-152	//

Data from Literature :

(Name)	(b. p.)	( $n_D^{20}$ )	(m. p. of Cu-Salt)
Ethylacetoacetate	80°/20 mm.	1.41937-76	[192]
C-Acetyl derivative	89°/10 mm.	1.4690	[151]
O-Acetyl derivative	94°/10 mm.	1.4420-80	—

(1) 95-105°/25 mm.  
 (1') 105-117°/25 mm.  
 (2) 100-108°/20 mm.  
 (3) 100-106°/20 mm.

(4) 100-104°/20 mm.  
 (2) 100-103°/20 mm  
 (6) 3.5g. of 100-119°/4mm.  
 ( $n_D^{15.5}$  1.4510)  
 was also obtained.