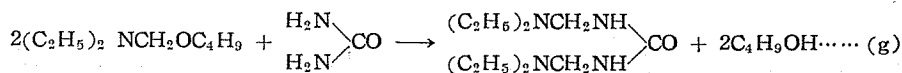


In this reaction the product was the same amine as that of experiment (A). But (II) is more reactive than (I) with Grignard reagent so that the vessel must be cooled with ice during the reaction. The yields of amine were 67.5 % (in the case of $\text{C}_6\text{H}_5\text{MgBr}$) and 89.4 % (in the case of $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$) respectively, thus much higher than that in experiment (A).

(C) Transjointing of (II) with urea

As the butoxy group of (II) was found to be very reactive we studied the trans-jointing of (II) with urea. The ether (II) (0.2 mole) was added to 0.1 mole of urea and warmed on a water bath for 20 mins. By vacuum distillation butyl alcohol was removed and NN'-bis-diethylaminomethyl urea $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{NHCONHCH}_2\text{N}(\text{C}_2\text{H}_5)_2$ remained as the residue. The yield of butyl alcohol was about 90 % of calcd. value. Thus, it is evident that reaction proceeded as follows :



12. Reaction of Ketene with Silk

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The refined silk turns gradually yellow or brown in color. The brownization is thought to be due to the presence of free amino group and especially the hydroxyl group of tyrosine in silk fibroin. A protection of these free groups by acetylation may prevent the brownization.

Some refined silk samples (yarn and cloth), therefore, were treated with gaseous ketene without any catalyst under the same conditions as free phenol and aniline were easily acetylated.

On exposure test to sunlight or ultra-violet rays, however, it was found that the ketene treatment did not improve the property of silk.

Some mechanical properties of silk seemed to be improved somewhat by an appropriate ketene-treatment. The experimental conditions and results are summarized in Tables 1. and 2.

Table 1. Action of ketene on phenol and aniline in ether and at room temperature.

Substance	Ketene* (gas)	Product
Phenol (47g)	21g	Phenylacetate 52g. (77%)
Aniline (23g)	6.854g	Acetanilide 20.488g. (93%)

* Ketene was estimated by the NaOH method.

Table 2. Brownizing and mechanical tests of ketene treated silk.

Exp. no.	Pre-treatment ⁽²⁾	Medium ⁽³⁾	Time of Reaction (min.) ⁽³⁾	After-treatment ⁽⁴⁾	Brownizing tests ⁽⁶⁾					Mechanical Tests	
					with Sunlight ⁽⁵⁾ for hours					Breaking Strength (g./cm ² .)	Elongation (%)
					0	2.5	12	22	74		
0		—	—		—	—	+	+	++	751	21.7
1			10	None	—	—	+	+	++		
2	None	H	30	None	—	—	+	+	++		
3			60		—	—	+	+	++		
4			10	Acetone	—	—	+	+	++		
5	None	H	30	Acetone	±	±	+	+	++	731	20.0
6			60		—	—	+	+	++	924	15.0
7			10		—	—	+	+	++		
8	None	E	30	Ether	±	±	+	+	++		
9			60		+	+	+	+	++		
10		—	—		—	—	+	+	++	881	20.9
11			10	None	—	—	+	+	++	924	22.7
12	H ₂ O	H	30	None	—	—	+	+	++	755	28.2
13			60		++	++	++	++	+++	942	22.8
14			10	Acetone	—	—	+	+	++	742	20.9
15	H ₂ O	H	30	Acetone	—	—	+	+	++	909	22.6
16			60		+	+	+	+	++	765	17.0
17			10		—	—	+	+	++		
18	H ₂ O → (C ₂ H ₅) ₂ O	E	30	Ether	±	±	+	+	++		
19			60		+	+	+	+	++		
20		—	—		—	—	+	+	++	668	19.3
21			10	None	—	—	+	+	++	739	24.9
22		H	30	None	—	—	+	+	++	943	22.6
23			60		—	—	+	+	++	624	19.3
24			10	Acetone	—	—	+	+	++	759	19.7
25		H	30	Acetone	—	—	+	+	++	809	20.0
26			60		—	—	+	+	++	581	19.3

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

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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 summerized in the following Table.