22. Synthesis of 1, 1-Diphenylcyclopropane Derivatives

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Several compounds having cyclopropane ring were synthesized in order to test their insecticidal activities. When benzophenone was added to the ethereal solution of methylmagnesium iodide, diphenylmethylcarbinol was obtained. This carbinol was changed to 1.1-diphenylethylene by the dehydroxylation. When ethyldiazoacetate was added to the diphenylethylene in the presence of copper catalyst, ethyl ester of 2,2-diphenylcyclopropanecarboxylic acid was obtained. By the hydrolysis of this ester the free acid was obtained. On the other hand, ethereal solution of diazomethane was added to the 1.1-diphenylethylene and the resulting solution was stored for two weeks and then the crystals of 5,5-diphenylpyrazoline were separated by the removal of ether. This compound was decomposed to 1.1-diphenylcyclopropane by heat. The respective compounds of 1,1-bis (p-chlorophelnyl)- and 1,1-bis (p-bromphenyl)-cyclopropane series were also synthesized by the same way.

Melting and boiling points of these synthesized compounds were as follows:

	(no substitution)	p,p-dichloro derivatives	p,p-dibromo derivatives
1,1-diphenylmethylcarbinol	mp.78—80°	mp. 68—9°	mp. 85°
1,1-diphenylethylene	bp. 135°/mm	mp. 86—8°	mp. 85—6°
ethyl 2,2-diphenylcyclopropanecarboxylate	bp. 183—5°/5mm	bp. 205—8°/5mm	—
2,2-diphenylclopropanecarboxylic acid	mp. 169—70°	mp. 170.5—71°	mp. 195—5.5°
5,5-diphenylpyrazoline	mp. 64.5—5.5°	mp. 90.5—1.5°	mp. ca. 100° (decomp.)
1,1-diphenylcyclopropane	bp. 122—3°/5mm	bp. 165-68°/4.5mm mp. 103.5—4°	mp. 132.5—3°

The results of insecticidal tests of these compounds will be reported, another day.

23. Distillation of Rice Oil Fatty Acid

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In the distillation of rice oil fatty acid, at about 1 mm. Hg pressure and 200–230°C temperature, we can increase the yield of distilled fatty acid by diminishing the polymerization degree of unsaturated fatty acid, being heated at higher temperature for a long time. In order to explain this matter, we compared distillation processes by two kinds of apparatuses at the same pressure; one was common flask type apparatus and the other was E. H. Farmer's cylindrical molecular distillation type apparatus. We used liquid component of rice oil fatty acid (at about 10°C) as samples, which had the properties recorded in Table 1.

Table 1.

	A.V.	I.V.	Unsaturated component		
			%	A.V.	I.V.
rice oil fatty acid (A)	168	114	84	177	126
〃 (B)	184	119	83	201	127

The yied of distilled fatty acid by cylindrical type apparatus was about 5% larger than that by flask type apparatus.

When rice oil fatty acid was intentionally polymerized by heating with a catalyser, such as PbO, MgO or Al_2O_3 ect., and distillated, large portion of distillate was palmitic acid and oleic acid, and residue was almost linolic acid. The results are given in Table 2.

Table 2.

Sample	Polymerization	Distillate		Unsaturated fatty acid in distillate	
		Yield (%)	I.V.	%	I.V.
(A)	none	72	126	85	118
〃	Pb0,2%; 270-280°C, 4h	63	113	83	110
〃	Pb0,2%; 300-310°C, 5h	46	83	55	92
(B)	none	84	114	89	113
〃	Pb0,2%; 300-310°C, 5h	43	80	58	90

In the polymerization-distillation process, I. V. of unsaturated fatty acid separated from distillate was nearly equal to that of oleic acid, 90.

24. On the Semi-Commercial Scale Purification of Rice Oil by an Emulsive Washing Method

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In the previous paper, it was reported that the difficulty in the purification of rice oil was removed by the application of an emulsive washing method. (This