

Obviously still further condensations can take place, and more complex products make their appearance. It is difficult to deduce conditions which would favor the formation of the desired product exclusively. However, it is known that a catalyst is needed to promote any reaction at all. Acetic anhydride was first used,^{1a} but basic substances such as dilute sodium hydroxide, diethylamine and piperidine appear to be more satisfactory. A reaction medium of pH 9 has been recommended.^{1f} Various temperatures and combinations of temperatures ranging from 0° to the boiling point of acetic anhydride have been suggested as suitable for the reaction. There is no indication that the formation of methylenemalonic ester is favored by one temperature any more than another. Antipolymerization catalysts have not been used, although their presence would seem desirable. The effect of the solvent on the course of the reaction has not as yet been investigated. Alcohol has been used frequently.

THE PREPARATION OF DIETHYL METHYLENEMALONATE

In our attempts to repeat the work of the earlier investigators yields of from 0 to 20 per cent. were obtained. Occasionally, with conditions apparently the same as in successful experiments, none of the desired product was obtained. As a first variation we attempted to carry out the reaction in the vapor phase, where it was hoped the shorter times of contact with the catalyst would hinder secondary reactions leading to high-molecular-weight by-products.

In general, the reactants were passed over various catalysts packed in a glass tube mounted vertically in an electric resistance furnace. The formaldehyde and malonic ester were introduced from above (1) separately, as 40 per cent. formalin and malonic ester, (2) separately, as solid paraformaldehyde and malonic ester, or (3) as a solution of formaldehyde gas in malonic ester. The materials were introduced as nearly as possible at equimolecular rates. The temperature in the reaction chamber was measured by means of a thermocouple. The conditions employed in some of the experiments and the results obtained are summarized in Table I. It is obvious that the yields are comparable to those obtained previously.

(f) WELCH, *J. Chem. Soc.*, **1930**, 259; **1931**, 673.

(g) ZELINSKY, *Ber.*, **22**, 3295 (1889).

(h) WOJCIK AND ADKINS, *J. Am. Chem. Soc.*, **56**, 2424 (1934).

² Most authors have failed to mention yields at all, but BOTTOMLEY AND PERKIN, *J. Chem. Soc.*, **77**, 294 (1900), make the following statement: "The best yield obtained this way was 22 g. of the crude dry product (from 96 g. of diethyl malonate—a 21% yield—Authors) . . . , but for some reason the yield varies very much in different operations, although the greatest care may be taken to reproduce in each case the same conditions."

³ TANATAR, *Ann.*, **273**, 48 (1893).

Returning to a study of the preparation in the liquid phase, a large number of experiments were run in which the ratio of formaldehyde to malonic ester and the natures and amounts of both the solvent and the catalyst were varied. Eventually a procedure was developed which enabled us to obtain methylene malonic ester in yields of 40–45 per cent. consistently. Some of the more significant experiments are shown in Table II. The final procedure, which was repeated many times with satisfactory results, is given in the experimental part. It is believed that the use of an acid medium, of copper salts, of potassium salts and of two moles of formaldehyde are all important. The excess of formaldehyde

TABLE I
VAPOR PHASE REACTION OF FORMALDEHYDE AND MALONIC ESTER

MALONIC ESTER WITH:	YIELD PER 100 G. MALONIC ESTER ^b				
	Catalyst ^a	Temp., °C.	Recov. Ester, g.	Pro- duct, g.	High- Boiling, g.
40% Formalin.....	AlPO ₄	300	30	6	25
40% Formalin.....	"	420	25	17	—
Paraformaldehyde.....	"	420	52	9	—
40% Formalin + 5% piperidine.....	Glass wool	380	0	17	14
CH ₂ O gas.....	AlPO ₄	400	27	10	40
CH ₂ O dissolved.....	Soda lime	380	20	8	28
CH ₂ O dissolved.....	Al ₂ O ₃	400	16	5	23
CH ₂ O dissolved + 3% piperidine.....	Al ₂ O ₃	350	22	6	27
CH ₂ O dissolved.....	Na ₃ PO ₄	350	25	4	25
40% Formalin.....	Na ₂ HPO ₄	320	30	6	33
40% Formalin.....	Na ₂ HPO ₄	250	18	11	—
40% Formalin.....	Cu ₃ (PO ₄) ₂	300	7	15	20

^a The AlPO₄ and Al₂O₃ were supported on glass wool, the Cu₃(PO₄)₂ on copper turnings.

^b The high-boiling material was chiefly ethyl propane-1,1,3,3-tetracarboxylate. The products not otherwise accounted for consisted of undistillable residues.

serves to eliminate completely all malonic ester from the reaction mixture. This is desirable, since malonic ester combines with methylenemalonic ester to form ethyl propanetetracarboxylate.¹⁷ Sodium acetate in place of potassium acetate gives a considerably slower reaction. The yields in the absence of copper salts are irregularly lower.

THE POLYMERIZATION OF DIETHYL METHYLENEMALONATE

Diethyl methylenemalonnate may be regarded as ethylene with two negative substituents unsymmetrically placed. Compounds having the structure of ethylene with one negative substituent are known to poly-

TABLE II
LIQUID-PHASE REACTION OF FORMALDEHYDE AND MALONIC ESTER

RUN NO.	MOL RATIO CH ₂ O/MALONIC ESTER	SOLVENT, g./MOLE MALONIC ESTER	CATALYST, g./MOLE MALONIC ESTER	CO-CATALYSTS, g./MOLE MALONIC ESTER	RECOV. ESTER, g.	METHYLENE MALONIC ESTER, g.	HIGH-BOLLING FRACTION, g.	RESIDUE, g.
1	1:1	Acetic acid, 400 g.	Potassium acetate, 6 g.	None	9	10	40	30
2	2:1	Acetic acid, 400 g.	Potassium acetate, 6 g.	Hydroquinone, 1 g.	16	28	12	30
3	2:1	Acetic acid, 400 g.	Potassium acetate, 10 g.	Copper acetate, 10 g.	21	46	11	15
4	2:1	Acetic acid, 400 g.	Potassium acetate, 10 g.	Ferric acetate, 14 g.	11	23	33	30
5	2:1	Formic acid, 400 g.	Potassium acetate, 10 g.	Copper formate, 10 g.	—	9	51	30
6	2:1	Methyl alcohol, 400 g.	Potassium acetate, 10 g.	Copper chloride, 10 g.	8	25	31	30
7	2:1	Methyl alcohol, 400 g.	Piperidine, 10 g.	Copper chloride, 10 g.	9	8	22	50
8	2:1	Acetic acid, 200 g.	None	Copper chloride, 10 g.	14	41	11	30
9	1.3:1	Acetic acid, 400 g.	Potassium acetate, 10 g.	Copper chloride, 10 g.	19	31	24	20
10	2:1	Propionic acid, 400 g. { Acetic acid, 200 g. Acetic anhydride, 200 g.	Potassium acetate, 10 g.	Copper acetate, 10 g.	—	41	—	—
11	2:1	Acetic acid, 400 g.	Potassium acetate, 10 g.	Copper acetate, 10 g.	30	15	30	20
12	2:1	Acetic acid, 70 g.	Potassium acetate, 5 g.	Copper acetate, 16 g.	6	15	8	60

merize readily to form resinous products. Examples of such compounds are acrylic acid and its derivatives, vinyl chloride, vinyl acetate, styrene, etc. Compounds having the structure of ethylene with two negative substituents also polymerize, although less readily, and the polymers generally have lower molecular weights. However, certain such substances, notably maleic anhydride, co-polymerize with great ease to give products of relatively high molecular weight. It was hoped that methylenemalonic acid derivatives which are position isomers of the corresponding maleic acid derivatives would copolymerize equally easily. Since this is not the case, and since symmetrically disubstituted derivatives are less active than unsymmetrically disubstituted derivatives, it may be inferred that the structure, possibly the five-membered ring structure, of maleic anhydride is in some way uniquely suited for co-polymerizations.

Two polymeric forms of diethyl methylenemalonate are described in the literature.² The newly prepared monomer forms the so-called para-diethyl methylenemalonate, a white wax-like solid. This product melts at 154–156°, and on stronger heating decomposes to the monomer. Meta-diethyl methylenemalonate is described as a horny material of limited solubility. It melts at 225° and decomposes at 240–250°, forming the monomer.

Various samples of diethyl methylenemalonate prepared in this laboratory formed the waxy para polymer in from a few hours to several weeks. The variation in speed of polymerization is probably due to differences in the purity of the material.

Actually the first distillate of methylene diethylmalonate forms the waxy polymer very readily. Further purification by distillation yields a product which may polymerize only with considerable difficulty and be quite inert towards the usual polymerization catalysts or to ultra-violet light or heat. If, however, distillation is continued, and a fraction boiling over a narrow range, say 209–11°, is taken, it will be found that the product polymerizes readily in an hour or so on the steam bath. It is evident that impure diethyl methylenemalonate polymerizes only with difficulty. The ease with which the newly-prepared ester polymerizes is probably due to the presence in it of acrylic acid or ethyl acrylate, both of which polymerize with great ease and are capable of initiating the polymerization of diethyl methylenemalonate. These substances are probably formed in small amounts by hydrolysis and partial decarboxylation of methylenemalonic ester or its precursor, diethyl hydroxymethylmalonate (Compound I, Equation A). The potassium acetate present serves as a catalyst for this hydrolysis, while heat alone is sufficient to decarboxylate the malonic acid derivative.

⁴ DREHER, *Kunststoffe*, **8**, 220 (1937).

The polymer obtained from highly purified methylenemalonic ester is a colorless transparent glass which changes rapidly to a hard but brittle porcelain-like solid. It dissolves slowly in acetic acid, acetone and ethyl alcohol and may be precipitated from these as a white, granular powder by pouring into water or petroleum ether. It decomposes on heating to 230–240° to form the monomer and higher-boiling products. In this respect it resembles polymethacrylic esters rather than polyacrylic esters which do not depolymerize readily to the corresponding monomers.

Purified diethyl methylenemalonate will also co-polymerize with a number of substances. In the table (Table III) are shown the co-polymers studied and the results obtained. In each case the materials were heated

TABLE IV
REACTIONS OF METHYLENEMALONIC ESTER WITH CONJUGATED DIENES

DIENE	G. DIENE G. ESTER	SOLVENT, CC.	TEMP., °C.	TIME, HRS.		B.P. °C. (MM. PRESS.)	n_D^{25}	d_4^{25}	ANALYSES	
				% YIELD (ON ESTER)					Calc'd	Found
Butadiene	22/22	C ₆ H ₆ , 200	-70	24	38	117 (6)	1.452	1.020	C 63.72	63.36
	20/20	None	25	24	80				H 7.96	8.06
2-Methyl- butadiene	20/44	C ₆ H ₆ , 250	80	18	35	127 (6)	1.456	1.030	C 65.00	64.79
	20/30	None	100	3	86				H 8.33	8.11
2,3-Di- methyl- butadiene	31/65	C ₆ H ₆ , 400	80	3	73	136 (6)	1.460	1.038	C 66.14	65.89
	20/30	None	100	3	91				H 8.66	8.64
Anthracene	21/25	None	220	6	54	126–7 (m.p.)			C 75.43	75.82
									H 6.29	6.37

together on the steam bath (under a reflux condenser when necessary) until reaction ceased. The percentage yields were calculated on the basis of the amounts of material obtained when the polymerized products were dissolved in acetone, precipitated in water and dried at 60° overnight. The percentages of co-polymerizing material, when this was vinyl acetate, were determined by acetyl determinations similar to those in general use for the analysis of cellulose acetates.

Methylenemalonic ester does not resemble maleic anhydride either in the ease or completeness of its co-polymerization with other olefin derivatives. There is also no apparent tendency to form co-polymers in a definite ratio with other unsaturated substances, as is generally the case with maleic anhydride. Maleic anhydride does not, however, polymerize by itself as readily as does methylenemalonic ester.

TABLE III

CO-POLYMERIZING MATERIAL	% OF CO-POLYMERIZING MATERIAL IN REACTION MIXTURE	CATALYST	REACTION RATE	% YIELD	% OF CO-POLYMERIZING MATERIAL IN PRODUCT	NATURE OF FILM COATED FROM ACETONE
Vinyl acetate.....	33	Benzoyl peroxide	Rapid	44	21	Hard, brittle, clear
Vinyl acetate ^a	33	Benzoyl peroxide	Slow	35	30	Hard, brittle, clear
Vinyl acetate ^b	50	Benzoyl peroxide	Rapid	50	62	Hard, brittle, reticulated
Vinyl acetate ^c	66	Benzoyl peroxide	Rapid	50	76	Tacky, reticulated
Vinyl acetate.....	75	Benzoyl peroxide	Rapid	79	74	Rather brittle, reticulated
Vinyl acetate.....	80	Benzoyl peroxide	Rapid	86	84	Hard, sl. brittle, clear
Vinyl acetate.....	90	Benzoyl peroxide	Rapid	90	93	Tough and clear
Methyl methacrylate.....	35	Benzoyl peroxide	Moderate	68	—	Hard, brittle, clear
Methyl methacrylate.....	75	Benzoyl peroxide	Moderate	80	—	Hard, brittle, clear
Dimethyl itaconate.....	50	Benzoyl peroxide	Slow	40	37	Very brittle
Maleic anhydride.....	35	Benzoyl peroxide	No reaction	—	—	(Rubbery solid—not homogeneous—insoluble)
Methyl isopropenyl ketone.....	50	Benzoyl peroxide	No reaction	—	—	
Styrene.....	60	Benzoyl peroxide	Moderate	—	—	
Vinyl ethyl ether.....	29	Benzoyl peroxide	No reaction	—	—	

^a The vinyl acetate used in this polymerization was distilled from a 1% formic acid solution containing a little boron trifluoride.

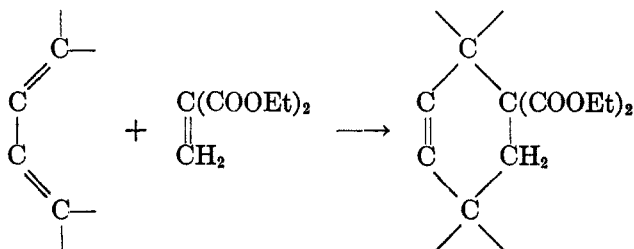
^b The diethyl methylene malonate used in this polymerization was prepared by the reaction of methylene chloride and sodium malonic ester.

^c A second portion of catalyst had to be added.

REACTIONS OF METHYLENEMALONIC ESTER WITH DIENES

In the past ten years the reactions of certain olefin derivatives with conjugated dienes⁵ has been developed into an extraordinarily useful tool for the organic chemist. Substances like acrolein, acrylic acid, vinyl ketones etc. react readily with dienes. Substances like maleic anhydride, quinones, and acetylenedicarboxylic acid esters may react violently at room temperatures with simple dienes unless sufficiently diluted with inert solvent.

Up to the present, no disubstituted olefin with two carbonyl groups unsymmetrically placed has been condensed with dienes. Diethyl methylenemalonate is a compound of this type. Diethyl methylenemalonate was found to combine readily with butadiene, isoprene, 2,3-dimethylbutadiene, and anthracene according to the following type reaction:



Reaction occurred slowly at room temperature (except with anthracene), more rapidly at elevated temperatures, and the yields in general were good. However, diethyl methylenemalonate does not seem to combine with dienes quite as readily as does maleic anhydride. In no case was a diluent essential to prevent violent reaction. With furane, polymerization rather than condensation occurred. In Table IV are shown the conditions and results of these experiments.

The 2,3-dimethylbutadiene-methylenemalonic ester adduct was readily hydrolyzed to the corresponding dicarboxylic acid by alcoholic potassium hydroxide. This compound lost carbon dioxide quantitatively at 200° and was converted into the corresponding monocarboxylic acid, 3,4-dimethylcyclohexene-3-carboxylic acid.

EXPERIMENTAL

Diethyl methylene malonate.—To 200 g. of glacial acetic acid were added 30 g. of paraformaldehyde, 80 g. of malonic ester, 5 g. of copper acetate and 5 g. of potassium acetate. The mixture was heated on the steam bath until clear (about an hour) and for an hour longer. It was then distilled under diminished pressure until the b.p. reached 130° at 35 mm. At this point the contents of the distilling flask began

⁵ DIELS AND ALDER, *Ann.*, **460**, 98 (1928).

to thicken to a paste. The receiver was changed, and the distillation continued. The blue-colored paste seemed to foam up and decompose, the product being evolved during the decomposition. When the distillation temperature reached 200° and the paste had turned dark-brown distillation was stopped. The greenish-yellow distillate solidified on standing to the waxy polymer. It was, however, impure. Redistillation yielded a fraction boiling at 205–215° which was nearly pure diethyl methylene malonate and suitable for the preparation of co-polymers or diene adducts. Yield 36.8 g. or 46% theoretical (based on malonic ester). By repeated fractionation, or by distillation through a column under diminished pressure a very pure product was obtained, although the losses at each step were considerable. The purest sample showed the following constants: b.p. 210° at 760 mm.; n_D^{25} 1.432; d_4^{25} 1.052.

Anal. Calc'd. for $C_8H_{12}O_4$: C, 55.82; H, 6.98.

Found: C, 55.88; H, 7.01.

1,1-Dicarboxy-3,4-dimethylcyclohex-3-ene.—To the solution made by adding 30 g. of sodium to 600 g. of absolute ethyl alcohol were added 94 g. of diethyl 1,1-dicarboxy-3,4-dimethylcyclohexene-3 (obtained by adding 2,3-dimethylbutadiene to diethyl methylenemalonate). The mixture was refluxed on the steam bath for 5 hours, cooled, and filtered. The sodium salt collected in this way was dissolved in 250 cc. of water, and acidified with dilute hydrochloric acid. The white precipitate was collected, dried, and recrystallized twice from 50% ethanol. Yield 59.7 g., or 86% theoretical; m.p. 186.5–188.0°, with evolution of carbon dioxide.

Anal. Calc'd. for $C_{10}H_{14}O_4$: C, 60.61; H, 7.07.

Found: C, 60.77; H, 7.27.

3,4-Dimethylcyclohex-3-ene-1-carboxylic acid.—A test-tube containing 4.0 g. of 1,1-dicarboxy-3,4-dimethylcyclohexene-3 was heated in an oil bath at 205° until the evolution of carbon dioxide had ceased. The product was recrystallized twice from a 50% methanol-water mixture. There were obtained 2.6 g. (85% theoretical) of white needles of m.p. 80–81°.

Anal. Calc'd. for $C_8H_{14}O_2$: C, 70.13; H, 9.09.

Found: C, 70.25; H, 9.38.

SUMMARY

The preparation of diethyl methylenemalonate has been studied extensively, and the yields of this product obtainable have been considerably improved. The polymerization of diethyl methylenemalonate, alone and with other polymerizable olefin derivatives, has been described. Compounds resulting from the addition of diethyl methylenemalonate to certain dienes have been isolated and characterized.