zinc and acid as above, and the products were fractionated. Ethyl (7–9)-heptafluorononanoate, b.p. 89–94° (10.0 mm.), $n^{25}\text{D}$ 1.3757, 6.0 g. (16%); an intermediate cut (3.5 g.); (7–9)-heptafluoro-5-hydroxynonanoic acid δ-lactone (**6**), b.p. 125–127° (10 mm.), $n^{25}\text{D}$ 1.3772, 30.0 g. (60%); and a residue (5.1 g.) were obtained. The lactone **6** was solid, m.p. 44–45.5°, and had a carbonyl band at 5.75 μ in its infrared spectrum, identical with ester carbonyl band position. It was a δ-lactone, therefore. N.m.r. spectra were consistent with this structure; splitting of proton and F^{19} resonances of the R_FCH_2– grouping was seen. No vinyl unsaturation or ethyl ester group resonances appeared.

Anal. Calcd. for $C_9H_9F_7O_2$: C, 38.3; H, 3.21; F, 47.1; ester number, 198. Found: C, 38.6; H, 3.7; F, 46.6; ester number, 193.

5-Iodo-(7-10)-Nonafluorodecanoic Acid.—1-Iodoperfluorobutane (19.0 g., 0.077 mole), 5-hexenoic acid (7.0 g., 0.06 mole), and AIBN (0.2 g., 0.0012 mole) were heated under nitrogen at 75° in an oil bath. Exothermic reaction carried the temperature to 90° in 4 min.; the flask was cooled to 70° and returned to the bath. After 6 hr., AIBN (0.1 g.) was added. After 11.5 hr., the reaction mixture contained very little 1-iodoperfluorobutane (g.l.c. analysis). An infrared spectrum showed no vinyl band at 6.00 μ, the carboxylic acid band at 5.80 μ, but no lactone bands at 5.60 or 5.75 μ. The liquid was light yellow in color. These results were consistent with those previously reported.[3]

(6–11)-Tridecafluoro-4-hydroxy-2,2-dimethylundecanoic Acid γ-Lactone (**2**).—1-Iodoperfluorohexane (36.0 g., 0.08 mole), 2,2-dimethyl-4-pentenoic acid (9.6 g., 0.075 mole), and AIBN (0.26 g., 0.0016 mole), while stirring under nitrogen, were heated to 85° in an oil bath. Exothermic reaction set in after a few minutes, and external heating was adjusted to keep the temperature at 80–85°. Solid precipitated and a dark color appeared. After 3 hr., a sample showed by g.l.c. analysis that reaction was incomplete, but that lactone **2** (21%) and a trace of **3** were present. 2-Heptanone peroxide (0.5 ml.) was added at 80°. The color of iodine initially faded, the temperature rose to 82°, then darkening occurred. After 7 hr., lactone **2** (25%), **3** (10%), and adduct **1** (5.4%) were present. After 10 hr., all of the 2,2-dimethyl-4-pentenoic acid was gone. Analysis showed 4% of inorganic iodine, a third of which was hydrogen iodide. The mixture was washed successively with sodium sulfite solution and water. Distillation in column A gave (1) 1-iodoperfluorohexane, b.p. 70° (160 mm.), $n^{25}\text{D}$ 1.3248, 12.4 g. (2.5 g. collected in cold trap, recovery of 42%); (2) lactone **3**, b.p. 64° (5.5 mm.) to 58° (4.5 mm.), m.p. 48–51°, 6.6 g.; and (3) lactone **2**, b.p. 90–94° (0.5 mm.), m.p. 77–79°, 6.9 g. (21%); and residue, 0.9 g. Lactone **2** was recrystallized from hexane, m.p. 82°. An infrared spectrum of **2** (Nujol mull or perfluorokerosene mull) showed a carbonyl band at 5.60 μ. An infrared spectrum of **3** (potassium bromide pellet) showed a carbonyl band at 5.65 μ and no vinyl band at 6.00 μ.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.44. Found: C, 65.1; H, 9.3.

Anal. Calcd. for $C_{13}H_{11}F_{13}O_2$: C, 35.0; H, 2.49; F, 55.35. Found: C, 35.0; H, 2.6; F, 55.4.

Ethyl (6–11)-Tridecafluoro-4-Iodo-2,2-Dimethylundecanoate (**4**).—1-Iodoperfluorohexane (25.0 g., 0.06 mole), ethyl 2,2-dimethyl-4-pentenoate (7.5 g., 0.05 mole), and AIBN (0.20 g., 0.0012 mole) were heated at 66–67° for 18 hr. A sample analyzed by g.l.c. contained (approximate weight. %) n-$C_6F_{13}I$ (15.5%), $CH_2{=}CHCH_2C(CH_3)_2COOC_2H_5$ (4.6%), lactone **3** (0.74%), lactone **2** (28.2%), and **4** (44%). The solution remained colorless. When cooled, crystalline lactone **2** separated and the yield was 2.77 g., m.p. 79–81°, and after 7 days the oil became red in color. Distillation in column A gave (1) b.p. 36–40° (48 mm.), 1.6 g. (unchanged starting materials); and (2) b.p. 80–84° (0.35 mm.), 17.4 g., low melting solid mixture of **2** and **4**. G.l.c. analysis showed lactone **2** (66%) and ester **4** (34%) in cut 2, and evidence of some decomposition of **4** (tailing of last peak). There was no residue, but a dark red liquid collected in the cold trap (3.1 g., mixture of n-$C_6F_{13}I$ and $CH_2{=}CHCH_2C(CH_3)_2$-$COOC_2H_5$). An infrared spectrum of cut 2 showed strong carbonyl absorption bands at 5.60 and 5.75 μ, and no band at 6.00 μ, confirming the composition as **2** and ester **4**. The total yield was 83%. In view of the instability of **4**, no further attempt was made to separate it from **2**.

Anal. Calcd. for $C_{16}H_{16}F_{15}IO_2$: I, 19.46. Found: I, 10.0.

Pyrolysis of Esters. XXV. Pyrolysis of Malonic Esters[1,2]

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Work in these laboratories[4–6] has shown that the pyrolysis of esters is an excellent synthetic tool, not only for the synthesis of olefins, but also for the preparation of acids, nitriles, and ketones. It was shown that the pyrolysis of ethyl esters was superior to hydrolysis in many cases for the synthesis of acids, particularly for water-soluble and sterically hindered acids.[4] It was further shown that the ketone cleavage of acetoacetic esters by pyrolysis had many advantages over the usual hydrolysis with dilute base for the preparation of ketones[5] and the pyrolysis of cyanoacetic esters gave extremely high yields of the corresponding nitriles.[6]

It appeared, therefore, that the pyrolysis of a malonic ester might be a very convenient one-step synthesis of the corresponding acetic ester. This one-step procedure presumably could replace the conventional three-step procedure of hydrolysis, acidification, and decarboxylation, followed by re-esterification of the resulting substituted acetic acid. Ethyl phenylmalonate (I) was chosen for the initial study because of its availability. In selecting the pyrolysis conditions it was obvious that quantitative conversion to the substituted acetic ester was not possible because a high temperature would result in secondary pyrolysis of the substituted acetate to the corresponding acetic acid. For these reasons, a temperature of 470° was chosen for the initial studies in this series. When the liquid ester I was dropped through the pyrolysis tube packed with glass helices, at the rate of 40 g. per hr., a 36% yield of ethyl phenylacetate (II) resulted, together with a 44% recovery of the starting malonic ester. The yield, based on unrecovered starting material was 64%.

In a similar manner, the pyrolysis of ethyl (1-methylbutyl)malonate (III) at 470° gave a 36% conversion to ethyl 3-methylcaproate (IV), plus a 57% recovery of starting material. In this case the yield, based on unrecovered starting material, was 84%. Levine and Marker[7] previously carried out the three-step hydrolysis, decarboxylation, and re-esterification to produce the ethyl 3-methylcaproate in an unreported yield.

Since the pyrolysis of the monosubstituted malonic esters appeared to be reasonably successful, an attempt was made to extend this to a series of disubstituted malonic esters. Thus, when ethyl α-ethyl-α-phenylmalonate (V) was pyrolyzed at 470°, a 25% yield of the ethyl α-phenylbutyrate (VI) was obtained. Since 33% of the starting malonate was recovered, the yield, based

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(1) Previous paper in this series, *J. Org. Chem.*, **28**, 828 (1963).

(2) Presented in part before the Division of Organic Chemistry at the 126th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1954.

(3) Office of Naval Research Fellow, 1950–1952; Union Carbide Fellow, 1952–1953; Du Pont Fellow, 1953–1954.

(4) W. J. Bailey and W. N. Turek, *J. Am. Oil Chemists' Soc.*, **33**, 317 (1956).

(5) W. J. Bailey and J. J. Daly, Jr., *J. Org. Chem.*, **22**, 1189 (1957).

(6) W. J. Bailey and J. J. Daly, Jr., *J. Am. Chem. Soc.*, **81**, 5397 (1959).

(7) P. A. Levine and R. E. Marker, *J. Biol. Chem.*, **91**, 87 (1931).

TABLE I

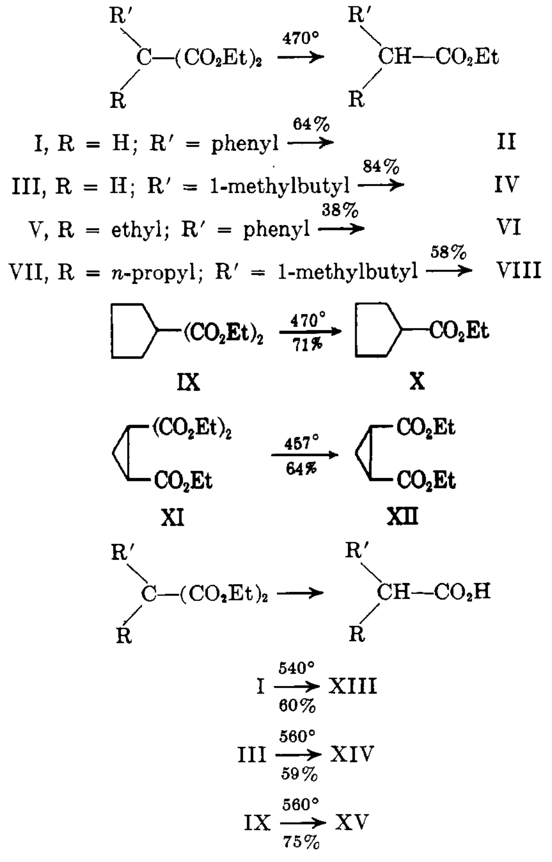
PYROLYSIS OF

Malonic ester	B.p. (mm.), °C.	n_D (°C.)	Amount, g.	Temp. of pyrolysis, °C.	Rate of addition, g./min.
Ethyl phenylmalonate (I)	158 (12)	1.4898 (25)	126	470	0.63
			50	540	0.52
Ethyl 1-methylbutylmalonate (III)	122–124 (15)	1.4262 (25)	125	470	0.50
			50	560	0.42
Ethyl α-ethyl-α-phenylmalonate (V)	168 (17)	1.4895 (26)	49	470	0.63
Ethyl α-(1-methylbutyl)-α-*n*-propylmalonate (VII)	146–149 (18)	1.4350 (25)	43	470	0.46
Ethyl cyclopentane-1,1-dicarboxylate (IX)[e]	128–131 (20)	1.4380 (26)	41.5	470	0.56
			89	560	0.49
Ethyl cyclopropane-1,1,2-tricarboxylate (XI)	139–141 (3.5)	1.4425 (26)	182.8	457	0.76

[a] See ref. 14. [b] M.p. 76–77°; R. Adams and A. M. Thal ("Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 437) report m.p. 76–76.5°. [c] See ref. 7. [d] *Anal.* Calcd. for $C_{12}H_{24}O$: C, 71.80; H, 11.97. Found: C, 71.39; H, 11.67. [e] Prepared in a 65% yield by the alkylation of malonic ester with 1,4-dichlorobutane by the method of Skinner, G. Limperos,

on unrecovered starting material, was 38%. Similarly, when ethyl α-(1-methylbutyl)-α-*n*-propylmalonate (VII) was pyrolyzed at 470°, a 32% yield of the ethyl 2-*n*-propyl-3-methylcaproate (VIII) was obtained, together with a 42% recovery of the starting material. The yield, based on unrecovered starting material, in this case was 58%. (See Scheme I.)

SCHEME I



Since the cyclopentane ring had shown marked stability during the pyrolysis of the cyanoacetic esters[6] to produce a very high yield of the 1-cyanocyclopentane, study of the pyrolysis of the malonic ester in this series was undertaken. The pyrolysis of ethyl cyclopentane-1,1-dicarboxylate (IX) at 470° resulted in a 42% conversion to ethyl cyclopentanecarboxylate (X). Since 41% of the starting malonic ester IX was recovered, the yield, based on unrecovered material, was 71%. This yield compares very favorably with the method of Whitmore, *et al.*,[8] who obtained the ethyl cyclopentanecarboxylate (X) in a 48% yield by the treatment of cyclopentylmagnesium bromide with diethyl carbonate. Whitmore and coworkers[8] stated that all methods reported in the literature for the preparation of the cyclic ester X showed little promise.

In another related problem, a quantity of ethyl cyclopropane-1,2-dicarboxylate (XII) was desired. One logical method of synthesis of this compound was from the ethyl cyclopropane-1,1,2-tricarboxylate (XI). Although it was possible to prepare ethyl cyclopropane-1,1,2-tricarboxylate (XI) in a 77% yield by the alkylation of malonic ester with ethyl dibromopropionate, it was not possible to hydrolyze and decarboxylate IX to any appreciable amount of the corresponding cyclopropane-1,2-dicarboxylic acid. Wassermann[9] reported the preparation of a 10% yield of the diacid, but we were not able even to duplicate this yield. It was possible to obtain reasonable yields of the cyclopropane-1,1,2-tricarboxylic acid, but all attempts to decarboxylate this acid failed. In contrast, the pyrolysis of the triester XI at 457° gave a 24% conversion to ethyl cyclopropane-1,2-dicarboxylate (XII) plus a 63% recovery of the starting triester. The yield of XII, based on unrecovered material, was 64%. An attempt was made to carry out this reaction on ethyl butylidenemalonate, but pyrolysis at 500° produced a complex mixture of products which had higher refractive indices than those of the expected products.

An attempt was made to extend the pyrolysis of the malonic esters to the preparation of the corresponding acetic acids. Thus, when ethyl phenylmalonate (I) was pyrolyzed at 540°, a 60% yield of phenylacetic acid (XIII) was obtained. Similarly, when ethyl 1-

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(8) F. C. Whitmore, J. N. Cosby, W. S. Sloatman, and B. G. Clarke, *J. Am. Chem. Soc.*, **64**, 1801 (1942).

(9) A. Wassermann, *Helv. Chim. Acta*, **13**, 229 (1930).

MALONIC ESTERS

Product	Found B.p. (mm.), °C.	n_D (°C.)	Reported B.p. (mm.), °C.	n_D (°C.)	Yield, g., %	Recovered malonic ester, g.	Yield, based on unrecovered starting material, %
Ethyl phenylacetate (II)	107–110 (15)	1.4951 (25)	227 (760)	1.4953 (25)[a]	31.4, 36	55.1	64
Phenylacetic acid (XIII)	151–153 (20)	*b*	176–189 (50)		17.3, 60		
Ethyl 3-methylcaproate (IV)	68–69 (15)	1.4113 (25)	60 (10)	1.4102 (30)[c]	30.7, 36	71.4	84
3-Methylcaproic acid (XIV)	110–111 (17)	1.4214 (25)	113 (17)	1.4214 (25)[c]	16.7, 59		
Ethyl α-phenylbutyrate (VI)	120–121 (17)	1.4883 (26)	238.7 (760)	1.4879 (25)[a]	9.0, 25	16.0	38
Ethyl 2-propyl-3-methylcaproate (VII)[d]	107–109 (18)	1.4258 (25)			10.1, 32	18.2	58
Ethyl cyclopentanecarboxylate (X)	73–74 (21)	1.4314 (26)	89.3 (45)	1.4360 (20)[f]	11.3, 42	17.0	71
Cyclopentanecarboxylic acid (XV)	120–123 (24)	1.4514 (26)	215–216 (760)	1.4520 (20)[g]	35.2, 75		
Ethyl cyclopropane-1,2-dicarboxylate (XII)[h,i]	115–120 (13)	1.4390 (27)			31.6, 24	115.3	64

and R. Pettebone, *J. Am. Chem. Soc.*, **72**, 1649 (1950). [f] See ref. 8. [g] W. O. Ney, *J. Am. Chem. Soc.*, **65**, 774 (1943). [h] The structure was proved by hydrolysis to *trans*-cyclopropane-1,2-dicarboxylic acid, m.p. 172–175°; C. K. Ingold, *J. Chem. Soc.*, **119**, 316 (1921). [i] *Anal.* Calcd. for $C_9H_{14}O_4$: C, 58.06; H, 7.53. Found: C, 58.16; H, 7.41.

methylbutylmalonate (III) was pyrolyzed at 560°, a 59% yield of 3-methylcaproic acid (XIV) was obtained. With these yields this process will not compete successfully with the conventional hydrolysis and decarboxylation for the preparation of these simple acids. However, the pyrolysis of the malonic ester appears to be of some synthetic use in the cyclopentane series. Thus, when the ethyl cyclopentane-1,1-dicarboxylate (IX) was pyrolyzed at 560°, a 75% yield of cyclopentanecarboxylic acid (XV) was obtained. Haworth and Perkins[10] reported the synthesis of XV by the hydrolysis and decarboxylation of the cyclic diester IX but gave no yields. Talbot and Adams[11] synthesized cyclopentanecarboxylic acid (XV) in a 56% yield by the carbonation of cyclopentylmagnesium bromide.

It can be concluded, therefore, that the pyrolysis of substituted malonic esters is a fairly good synthetic tool for the preparation of the corresponding substituted acetic esters in many cases (see Table I). However, the pyrolysis of the malonic esters directly to the substituted acetic acids is useful only in certain specialized cases. Presumably, it would be of use for the preparation of water-soluble acids or sterically hindered acids.

Experimental[12]

Ethyl Phenylacetate (II).—Through a Vycor combustion tube, packed to a depth of 12 in. with $^1/_8$-in. glass helices and externally heated at 470°, as previously described,[13] 126 g. (0.534 mole) of ethyl phenylmalonate (I), b.p. 158° (12 mm.), n^{25}_D 1.4898, was added dropwise over a period of 3.3 hr. Distillation of the pyrolysate through a 12-in., helix-packed column gave 31.4 g. (36%) of ethyl phenylacetate (II), b.p. 107–110° (15 mm.), n^{25}_D 1.4951 (lit.[14] b.p. 227°, n^{25}_D 1.4953), and 55.1 g. (44% recovery) of the starting ester I. The yield, based on unrecovered malonic ester I, was 64%.

Ethyl α-(1-Methylbutyl-α-*n*-propylmalonate (VII).—A mixture of 270 g. (1 mole) of ethyl α-allyl-α-1-methylbutylmalonate (Benzol Products Co., Newark, N.J.), b.p. 145–148° (17 mm.), n^{25}_D 1.4430, lit.[15] b.p. 95° (1 mm.); 2 g. of 5% palladium on carbon catalyst; and 300 ml. of 95% ethanol was placed in a 1-l. Pyrex bottle and shaken with hydrogen at 1-atm. After the theoretical amount of hydrogen had been absorbed, the catalyst was removed by filtration and the alcohol was removed by distillation under reduced pressure. Fractionation of the residue through a 6-in., helix-packed column gave 260 g. (96%) of ethyl α-(1-methylbutyl)-α-*n*-propylmalonate (VII), b.p. 146–149° (18 mm.), n^{25}_D 1.4350.

Anal. Calcd. for $C_{15}H_{28}O_4$: C, 66.10; H, 10.30. Found: C, 65.87; H, 10.05.

Ethyl Cyclopropane-1,1,2-tricarboxylate (XI).—By a modification of the procedure of Conrad and Gutzeit[16] 140 g. (6.1 g.-atoms) of sodium was dissolved in 1700 ml. of absolute alcohol in a 5-l., three-necked flask, fitted with a stirrer, a condenser, and a dropping funnel. After 480 g. (3.0 moles) of ethyl malonate had been added dropwise to the hot solution, the solution was stirred for an additional 10 min. and then 780 g. (3.0 moles) of ethyl α,β-dibromopropionate was added dropwise over a period of 4.5 hr. After the mixture had been stirred overnight, the excess alcohol was removed by distillation under reduced pressure. Water was added to dissolve the sodium bromide and the organic layer, after being dried over magnesium sulfate, was distilled through an 8-in., helix-packed column to give 594 g. (77%) of ethyl cyclopropane-1,1,2-tricarboxylate (XI), b.p. 139–141° (3.5 mm.), n^{26}_D 1.4425, lit.[9] b.p. 276°, 124° (2 mm.).

Cyclopropane-1,2-dicarboxylic Anhydride.—While a mixture of 50 g. (0.194 mole) of ethyl cyclopropane-1,1,2-tricarboxylate (XI) and 200 ml. of 3 *N* hydrochloric acid was heated under reflux, ethyl alcohol was slowly removed through a 12-in., helix-packed column until the temperature of the distillation head rose to 100°. The carbon dioxide evolved during the reaction was qualitatively measured by absorption into a solution of calcium hydroxide. When the evolution of carbon dioxide had ceased, the hydrochloric acid and water were removed by distillation under reduced pressure and the residue was dried by a stream of air for a period of 12 hr. An ether solution of the residue was extracted with a small amount of cold sodium bicarbonate solution and then dried over magnesium sulfate. After the ether had been removed by distillation, the residue was fractionated through a 6-in., helix-packed column to yield three fractions: (A) b.p. 70–73° (2 mm.), (B) b.p. 103–107° (1.2 mm.), and (C) 163–170° (0.7 mm.). From fraction B was isolated 0.5 g. of *cis*-1,2-cyclopropanedicarboxylic acid, m.p. 139°, lit.[9] m.p. 139–140°. Fraction C, on treatment with ether, gave 1 g. of cyclopropane-1,2-dicarboxylic anhydride, m.p. 54–56°, lit.[16] m.p. 57°.

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(10) E. Haworth and W. Perkins, *J. Chem. Soc.*, **65**, 98 (1894).

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(12) The authors are grateful to Dr. Mary H. Aldrich and Mrs. Kathryn Baylouny for the microanalyses.

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(16) M. Conrad and M. Gutzeit, *Ber.*, **17**, 1186 (1884).