Experimental

All analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected. Infrared spectra were measured on a Perkin-Elmer Infracord.

2,2,4,4-Tetraphenyl-3-hydroxy-3-butenoic Lactone (II).—Freshly distilled diphenylketene[9] (5.0 g.) was added to 0.43 g. of *N*-methylimidazole.[10] The mixture became hot and was stored at room temperature under nitrogen for a day. (The yield of II varied and the details of processing depend on this yield.) Benzene (15 ml.) was added to the reaction mixture and it was heated gently until all the solid dissolved. The solution was cooled and any solid that formed was filtered off. (This solid is the diphenylketene dimer, tetraphenyl-1,3-cyclobutandione.[11]) Petroleum hexane (20 ml.) was added to the benzene solution. (The solid that forms at this point is mostly the adduct I; however, it may contain appreciable amounts of II.) The solid was collected on a filter, and the filtrate was evaporated to dryness. The residue was primarily II. Since I is more soluble in ethanol than II, II was purified readily by recrystallization from ethanol. The yield of II, m.p. 146–148°, lit.[2] m.p. 148°, varied from 0.3 to 1.5 g. (The identity of the dimer can be established by a strong absorption at 5.4 μ in the infrared.) The observed infrared spectrum checks with that in the literature.[2]

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.6; H, 5.2. Found: C, 86.4; H, 5.1.

Reaction of II with Ammonia.—A mixture of 50 ml. of absolute ethanol containing 2.58 mmoles of ammonia and 1.00 g. (2.58 mmoles) of II was kept stoppered at 25° for a week. The solvent was evaporated and the solid residue was recrystallized from ethanol. The yield of V was 0.79 g. (82%), m.p. 174–175°; infrared spectrum ($CHCl_3$): 2.78, 2.88, 3.23, 5.90, 5.94, 6.68, 6.89, 7.45, 9.27, and 9.98 μ.

Anal. Calcd. for $C_{28}H_{23}NO_2$: C, 82.9; H, 5.7; N, 3.4. Found: C, 82.8; H, 5.5; N, 3.3.

Reaction of II with Excess Ammonia.—A mixture of 50 ml. of absolute ethanol saturated with anhydrous ammonia at 0° and 0.50 g. of II was kept stoppered at 25° for 3 days. The volatile material was evaporated and the residue was boiled with 10 ml. of water. The aqueous solution was decanted and the water was evaporated. The yield of urea was 0.05 g. (67%), m.p. 124–131°, m.m.p. 126–133°. When heated in an oil bath at 150–180°, this substance formed biuret and gave off ammonia, identified by its odor and its effect on moist red litmus. The biuret was identified by the characteristic purple color it gave with a solution of cupric ions which was made basic.[12] The residue from which the water was decanted was recrystallized from ethanol to yield 0.35 g. (75%) of *sym*-tetraphenylacetone, m.p. 133–135°, lit.[8] m.p. 133–134°.

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.5; H, 6.1. Found: C, 89.6; H, 6.4.

Reaction of V with Excess Ammonia.—The above procedure with 0.50 g. of V gave essentially identical results.

Reaction of II with Piperidine.—A solution of 0.50 g. of II in 5 ml. of piperidine was kept at 25° for 2 days. The white solid precipitate was filtered and washed with 2 ml. of ethanol. This ethanol and 8 ml. more were added to the filtrate and more crystals formed; the total yield of X was 0.45 g. (75%), m.p. 193–195°. After recrystallization from ethanol the melting point was 195–196°; infrared spectrum ($CHCl_3$): 5.79, 6.16, 6.69, 6.93, 8.01, 8.76, 9.41, and 9.78 μ.

Anal. Calcd. for $C_{33}H_{31}NO_2$: C, 83.7; H, 6.6; N, 3.0. Found: C, 83.5; H, 6.6; N, 2.9.

Reaction of X with Excess Ammonia.—A mixture of 20 ml. of absolute ethanol, saturated with anhydrous ammonia at 0°, and 50 mg. of X[8] was kept stoppered at 25° for 3 days. The volatile material was evaporated and the solid residue was triturated with 2 ml. of ethanol to yield 40 mg. (77%) of diphenylacetamide, m.p. 164–167°, lit.[13] m.p. 168°, m.m.p. 165–167°.

For comparison purposes, *N*-(**diphenylacetyl**)**piperidine** was made from diphenylacetyl chloride[14] and excess piperidine; the yield, recrystallized from aqueous ethanol, was 1.0 g. (83%), m.p. 117–118°; infrared spectrum ($CHCl_3$): 6.12, 6.71, 6.95, 7.89, 8.83, 9.30, 9.88, 10.51, and 11.73 μ.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.7; H, 7.5; N, 5.0. Found: C, 81.3; H, 7.4; N, 5.0.

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[9] L. I. Smith and H. H. Hoehn, *Org. Syn.*, **20**, 47 (1940).

[10] M. Hoering, *Helv. Chim. Acta*, **42**, 1845 (1959).

[11] H. Staudinger, *Ber.*, **44**, 530 (1911).

[12] L. Gattermann, H. Wieland, and T. Wieland, "Die Praxis des organischen Chemikers," Walter DeGruyter and Co., Berlin, 1959, p. 122.

[13] F. Klingemann, *Ann.*, **275**, 85 (1893).

[14] H. Staudinger, *Ber.*, **44**, 1619 (1911).

Lactone Formation in the Free-Radical Addition of Iodoperfluoroalkanes to Alkenoic Acids and Esters

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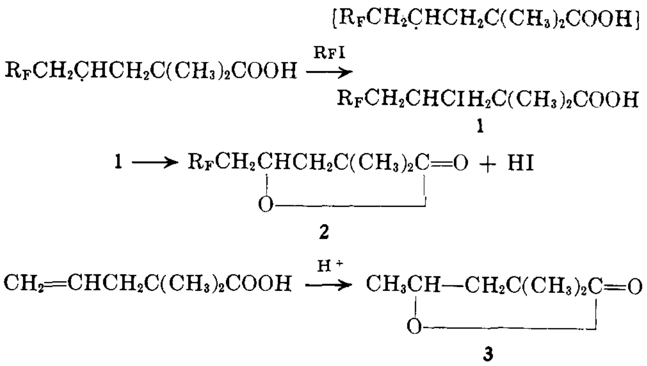
Received November 15, 1963

The tendency for acids with unsaturation in the γ- or δ-position to cyclize to lactones is well-known.[1,2] The primary adduct, $R_FCH_2CHI(CH_2)_3COOH$, was obtained[3] by free-radical-induced reaction of iodoperfluoroalkanes (R_FI) with 5-hexenoic acid or esters, using azonitrile initiator at 75°. By contrast, the products from thermally induced reaction of 5-hexenoic acid and R_FI at 175 or 200° included both the primary adduct and the derived δ-lactone. This has precedent in the thermal conversion at 150 to 180° of $CH_3CHBr(CH_2)_2COOC_2H_5$ to ethyl bromide and 4-hydroxypentanoic acid γ-lactone.[4] The formation of γ-*lactone* from $R_FCH{=}CH(CH_2)_3COOH$ (the expected dehydrohalogenation product)[3] or from the primary adduct would have required shifting of the double bond in our case.

In reaction of R_FI with 2,2-dimethyl-4-pentenoic acid, lactone formation was unusually facile, occurring even at 75° with the cleavage of hydrogen iodide. Soon after initiator was added to the 2,2-dimethyl-4-pentenoic acid–R_FI mixture, a reddish color of hydrogen iodide–iodine appeared; samples analyzed by gas–liquid chromatography (g.l.c.) showed both γ-lactones **3** and **2** were present. That γ-lactone rather than δ-



$$R_FI + CH_2{=}CHCH_2C(CH_3)_2COOH \xrightarrow{R\cdot} [R_FCH_2\dot{C}HCH_2C(CH_3)_2COOH]$$

$$R_FCH_2\dot{C}HCH_2C(CH_3)_2COOH \xrightarrow{R_FI} R_FCH_2CHIH_2C(CH_3)_2COOH$$

1

$$\mathbf{1} \longrightarrow R_FCH_2CHCH_2C(CH_3)_2C{=}O + HI$$

2

$$CH_2{=}CHCH_2C(CH_3)_2COOH \xrightarrow{H^+} CH_3CH{-}CH_2C(CH_3)_2C{=}O$$

3

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[1] See, for example, L. F. Fieser and Mary Fieser, "Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1956, p. 324.

[2] M. F. Ansell and M. H. Palmer, *J. Chem. Soc.*, 2640 (1963).

[3] N. O. Brace, *J. Org. Chem.*, **27**, 4491 (1962).

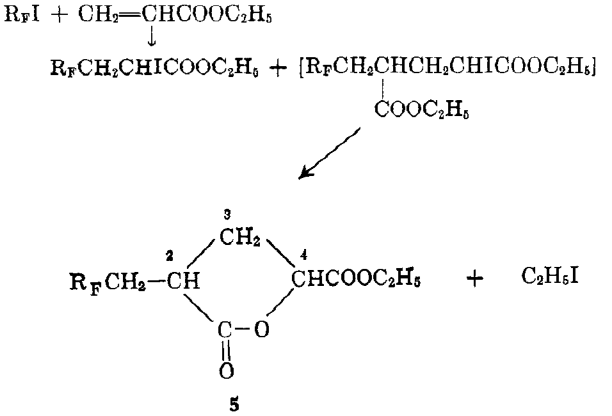
[4] M. S. Kharasch, P. S. Skell, and P. Fisher, *J. Am. Chem. Soc.*, **70**, 1055 (1948).

lactone was obtained was to be expected from the results of Ansell and Palmer.[2]

Lactone **2** also was formed from reaction of ethyl 2,2-dimethyl-4-pentenoate and R_FI at 70°, with ethyl iodide being cleaved in this instance. An 83% yield of a mixture of $R_FCH_2CHICH_2C(CH_3)_2COOC_2H_5$ (**4**) (34%) and **2** (66%) was isolated by distillation; none of lactone **3** was isolated and g.l.c. showed only a very small amount of **3** was present in the reaction mixture.

This extraordinary cleavage of ethyl iodide was convincing evidence that ring closure is greatly facilitated by *gem*-dimethyl substitution. Brown and van Gulick[5] have suggested that geminate alkyl substitution affects the distribution of molecular conformations, favoring those coiled structures which have minimum nonbonded interactions. A reduction in the activation entropy for the process leading to ring-closed product results. These authors presented some calculations to show that, in spite of an unfavorable equilibrium, the entropy effect may suffice to give a measurable conversion to cyclic product.

A third instance of lactone formation in the free-radical addition of R_FI to unsaturated esters was discovered. 1-Iodoperfluoroheptane and ethyl acrylate at 200° in ethyl acetate solution gave primary adduct and a lactone **5** derived from the 2:1 telomer.[3,6]



5

The infrared spectrum of **5** (and the reaction product mixture) had carbonyl bands at 5.60 and 5.75 μ. The band at 5.60 is characteristic for γ-lactones and the band at 5.75 μ is typical for carboxylic esters (or δ-lactones).[7] An n.m.r. spectrum of **5** showed both the ethyl ester group and a -CH resonance of C-4 split into a doublet and shifted downfield, consistent with the structure anticipated.

Experimental

Source of Starting Materials.—The 1-iodoperfluoroalkanes, azobisisobutyronitrile (AIBN), 5-hexenoic acid, and ethyl acrylate used were those previously described.[3] 2-Heptanone peroxide ("Cadox MAK") was a product of Cadet Chemical Corporation, Burt, New York. 2,2-Dimethyl-4-pentenoic acid from Eastman Chemical Products, Inc., was redistilled, b.p. 82° (4.2 mm.), $n^{25}D$ 1.4318. Infrared spectrum was consistent with structure. Reaction[8] with thionyl chloride gave 2,2-dimethyl-4-pentenoyl chloride, b.p. 69° (50 mm.), $n^{25}D$ 1.3995. The infrared spectrum was consistent. Acid chloride (19.5 g., 0.13 mole) and pyridine (11.9 g., 0.15 mole) were added simultaneously from two dropping funnels to ethanol (9.2 g., 0.2 mole) at 26–40° (ice-bath cooling) while stirring during a 20-min. period. The funnels were rinsed with 10 ml. of diethyl ether, and the white slurry was extracted by shaking with 100 ml. of water. After drying with magnesium sulfate, **ethyl 2,2-dimethyl-4-pentenoate** was distilled in a 12-in. platinum spinning band column (column A), b.p. 78° (39 mm.), $n^{25}D$ 1.4272. An infrared spectrum showed $CH_2=CH$ bands at 3.22, 6.10, and 10.05 μ, and a carbonyl stretching band at 5.75 μ.

Anal. Calcd. for $C_9H_{16}O$: C, 69.19; H, 10.3. Found: C, 69.0; H, 10.3.

Gas chromatography (g.l.c. analysis) was performed using a Perkin-Elmer vapor fractometer at 172°, with 15 p.s.i. of helium applied pressure. A 2-m. column packed with firebrick on which was absorbed 20% of a telomer oil of tetrafluoroethylene and propylene was used. Infrared spectra were obtained with a Perkin-Elmer Model 221 spectrophotometer with the assistance of Dr. R. K. Miller. N.m.r. spectra were taken, using a Varian Associates high-resolution spectrometer, by T. E. Beukelman.

2-[(2–8)-Pentadecafluorooctyl]-4-hydroxy-4-ethoxycarbonylpentanoic Acid γ-Lactone (5).—Ethyl acrylate (20.0 g., 0.2 mole), 1-iodoperfluoroheptane (100 g., 0.2 mole), and ethyl acetate (100 ml.) were heated at 200° for 6 hr. while shaking in a 400-ml. Hastelloy C lined steel shaker tube. Distillation in a 30-in. platinum spinning band column (column B) gave (1) a foreshot of ethyl iodide and ethyl acetate, $n^{25}D$ 1.4039, 2.1 g.; (2) ethyl acetate, b.p. 75°, $n^{25}D$ 1.3732, 100 g.; and (3) residual oil (106.2 g.). An infrared spectrum of cut 3 showed an intense C=O stretching band at 5.56 μ (γ-lactone[7]) and an ester band at 5.72 μ. Cut 3 also contained 1-iodoperfluoroheptane. The oil (106 g.), ethanol (100 ml.), and zinc (20–40 mesh, 10.0 g., 0.15 g.-atom) were stirred while hydrogen chloride was bubbled in. Exothermic reaction carried the temperature to reflux; after 4 hr. heating at 80°, solid perfluorotetradecane (23.8 g., 32%) had sublimed into the reflux condenser. The solid was recrystallized from 2-propanol, m.p. 99–101°, and from 1,1,2-trichloro-1,1,2-trifluoroethane, m.p. 102.5–104°.

Anal. Calcd. for $C_{14}F_{30}$: C, 22.78; F, 77.2. Found: C, C, 21.2; F, 75.6; H, <0.1.

After quenching in water, extraction into benzene, and drying, fractionation of the product in column B gave ethyl (4–10)-pentadecafluorodecanoate,[3] b.p. 98–99° (10 mm.), $n^{25}D$ 1.3291, 16.0 g. (17%); and lactone **5**, b.p. 126° (0.5 mm.), 24 g. (22%); leaving a residue (6.2 g.). An infrared spectrum of **5** showed two carbonyl bands at 5.57 and 5.72 μ of equal intensity in carbon tetrachloride or methanol solution. The γ-lactone was recrystallized from cyclohexane and from ethanol, m.p. 83–84.5°. An oil (10%) remained.

Anal. Calcd. for $C_{15}H_{10}F_{15}O_4$: C, 33.35; H, 2.04; F, 52.8; ester number, 208.5. Found: C, 33.4; H, 2.0; F, 52.5; ester number, 201.

An n.m.r. spectrum of **5** at 56.4 Mc. in deuteriochloroform solution gave resonances (tetramethylsilane, internal reference): at −1.30 p.p.m., a triplet (CH_3 of C_2H_5); at −4.25 p.p.m., a 4-line pattern (CH_2 of C_2H_5); at −4.84 and −5.01 p.p.m., a doublet of one-proton area; and broad undefined resonances of 5 protons from −1.70 to −2.75 p.p.m. The doublet may be ascribed to a proton on C-4.

(7–9)-Heptafluoro-5-hydroxynonanoic Acid δ-Lactone (6).—5-Hexenoic acid (50.0 g., 0.44 mole), 1-iodoperfluoropropane (100 g., 0.33 mole), di-*t*-butyl peroxide (1.0 g., 0.03 mole), and ethyl acetate (20 ml.) were heated at 140° for 5 hr. and at 175° for 5 hr., and the shaker tube was rinsed with 15 g. of ethyl acetate. Fractionation (column B) gave 1-iodoperfluoropropane (40 g., 40% recovery); ethyl iodide, b.p. 68–71°, $n^{25}D$ 1.448; ethyl acetate, b.p. 54–58° (100 mm.), $n^{25}D$ 1.3702, 47.0 g. (total); 4- and 5-hexenoic acid, b.p. 90–99° (10 mm.), $n^{25}D$ 1.4355–1.4332, 29.0 g. (52% recovery); and residual oil, 48.5 g. An infrared spectrum showed in the hexenoic acid cuts both $CH_2=CH$ and $CH_3CH=C$–. The residual oil was reduced by

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[5] R. F. Brown and N. M. van Gulick, *J. Org. Chem.*, **21**, 1046 (1956).

[6] R. N. Haszeldine, *J. Chem. Soc.*, 1199 (1953).

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 178.

[8] R. F. Brown and N. M. van Gulick, *J. Am. Chem. Soc.*, **77**, 1092 (1955).

zinc and acid as above, and the products were fractionated. Ethyl (7–9)-heptafluorononanoate, b.p. 89–94° (10.0 mm.), n^{25}_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}_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}_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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Received September 24, 1962

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).