98.5–99.5°. The infrared spectrum (chf) had a rather weak band at 2.8–2.9 μ.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.47; H, 8.05.

Trimethylpurpurogallin (VIII).—Purpurogallin (22 g.) was treated with a solution of 15 g. of diazomethane in 1500 ml. of ether. Nitrogen was evolved copiously. The mixture was allowed to stand overnight, and the solvent was evaporated. Recrystallization of the residue from methanol afforded 18 g. (69%) of orange crystals, m.p. 172–177°, raised to 175.5–178° by further recrystallization (reported[1a] m.p. 176°). The infrared spectrum (chf) had a doublet at 6.25–6.32 μ (shoulder at 6.14 μ) and did not show any appreciable absorption in the region of 3.0 μ.

Tetramethylpurpurogallin.—Complete methylation of purpurogallin and VIII with methyl sulfate in the presence of 20% potassium hydroxide gave in each case the tetramethyl derivative, in low yield. Recrystallization of the neutral product from ether–cyclohexane afforded material, m.p. 92–93° (reported[1a] m.p. 94°). The infrared spectrum (chf) had a doublet at 6.10–6.16 μ (shoulder at 6.05 μ).

2,3,6-Trimethoxy-4-hydroxybenzsuber-5-one (IX).—Hydrogenation of 2.3 g. of VIII in ethyl acetate at 25° in the presence of 1.0 g. of 5% (or 0.5 g. of 10%) palladium–charcoal for an hour in the usual way afforded 2.3 g. of product, m.p. 82.5–85°. Recrystallization from cyclohexane or water gave pale yellow crystals, m.p. 86–88° (lit.[1a] m.p. 86–87°). The infrared spectrum (chf) had a peak at 6.15–6.18 μ, and did not display any absorption near 3.0 μ. The compound was soluble in 5% sodium hydroxide solution and gave a deep purple ferric chloride test.

The 2,4-dinitrophenylhydrazone was recrystallized from ethanol; yellow crystals, m.p. 156–158°. The reported[1a] m.p. of this derivative is 204°. The reason for this large discrepancy is not clear at present.

Anal. Calcd. for $C_{20}H_{22}O_8N_4$: C, 53.81; H, 4.97. Found: C, 53.54; H, 4.93.

2,3,6-Trimethoxy-4,5-dihydroxybenzsuberan (X).—Hydrogenation of 1.0 g. of VIII in ethyl acetate at 80° in the presence of 2 g. of 10% palladium–charcoal[13] for 1.5 hours gave, after filtration of the catalyst and evaporation of the solvent, a mixture of glass and crystals. Trituration with ether afforded 0.4 g. of crystals, m.p. 119–123.5°. Recrystallization from cyclohexane gave colorless crystals, m.p. 129–131°. The infrared spectrum (chf) had an intense peak at 2.86 μ. The compound gave a very weak green color with ferric chloride on standing.

Anal. Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51; Found: C, 62.87; H, 7.76.

2,3-Trimethoxy-4-hydroxybenzsuberan (XI).—Hydrogenation of 2.7 g. of VIII in 100 ml. of glacial acetic acid in the presence of 1.8 g. of 10% palladium–charcoal[13] at 80° for 2 hours afforded viscous brown oil, after filtration of the catalyst and evaporation of the solvent. The crude material was dissolved in ether–ethyl acetate; the solution was washed with sodium bicarbonate solution and water, and was dried over magnesium sulfate. Evaporation of the solvents and distillation of the material *in vacuo* gave 1.4 g. of yellow, viscous oil, b.p. 150–165° (0.65 mm.), which material crystallized. Recrystallization from cyclohexane–ethyl acetate afforded 1.2 g. of very pale yellow crystals, m.p. 91–93.5° (reported[1a] m.p. 82°). The compound did not give a noticeable color with ferric chloride, but was readily soluble in 5% sodium hydroxide solution. The infrared spectrum (chf) had a strong, sharp peak at 2.85 μ. The mixed m.p. with compound VI was depressed (76–80°).

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.83; H, 7.97.

Tetraacetylpurpurogallin (XII).—Purpurogallin (4.2 g.) was refluxed with acetic anhydride (50 ml.) for 2.5 hours. Evaporation of the excess reagent and trituration of the residue with ethyl acetate gave 4.4 g. of yellow crystals, m.p. 186–188°, raised to 188–190° after recrystallization from the same solvent (reported[9] m.p. 184–186°). The infrared spectrum (chf) had a very intense peak at 5.61–5.65 μ and a strong band at 6.04–6.12 μ.

Anal. Calcd. for $C_{19}H_{16}O_9$: C, 58.76; H, 4.15; Ac, 44.3. Found: C, 58.83; H, 4.17; Ac, 44.8.

Acetylation of purpurogallin (1.7 g.) with a mixture of 30 ml. of acetic anhydride and 2 ml. of methanol (refluxed 1 hour) gave **triacetylpurpurogallin** (1.3 g.), m.p. 156–160°. Recrystallization from ethyl acetate afforded orange crystals, m.p. 160–162°. The infrared spectrum (chf) had an intense peak at 5.62–5.66 μ and a weak band at 6.08–6.11 μ.

Anal. Calcd. for $C_{17}H_{14}O_8$: C, 58.97; H, 4.08; Ac, 37.3. Found: C, 59.13; H, 4.48; Ac, 36.6.

Triacetyltetrahydropurpurogallin (XIII).—A solution of 2.2 g. of XII in 200 ml. of ethyl acetate containing 2 g. of 10% palladium–charcoal[13] was shaken under hydrogen (40 lb.) at 80° for a half-hour. Filtration of the mixture and evaporation of the solvent gave glassy material which contained acetic acid. The material crystallized in the presence of methanol. Trituration with methanol gave 0.6 g. of product, m.p. 159–165°. Recrystallization from the same solvent afforded colorless crystals, m.p. 169.5–171°. The infrared spectrum (chf) had a triplet at 5.60 (intense), 5.73 and 5.81 μ, and did not show absorption in the 3.0 or 6.0 μ regions. The compound did not give a ferric chloride test, but was soluble in 5% sodium hydroxide solution.

Anal. Calcd. for $C_{17}H_{18}O_8$: C, 58.28; H, 5.18; Ac, 36.8. Found: C, 58.19; H, 5.22; Ac, 41.0.

When the hydrogenation was allowed to proceed for longer periods at 80°, additional hydrogen was absorbed slowly, and no crystalline products were obtained.

Acetylation of tetrahydropurpurogallin (II) in refluxing acetic anhydride for an hour gave colorless crystals, m.p. 170–171°, after recrystallization from ethyl acetate. The mixed m.p. with material prepared as described above was not depressed, and the infrared spectra (chf and Nujol) were identical.

Compound XIII was recovered unchanged after treatment with bismuth oxide in warm acetic acid, and after attempted methylation with diazomethane.

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The Preparation of Some Alkyl Fumaric Acids and Maleic Anhydrides

BY WYMAN R. VAUGHAN AND KATHRYN S. ANDERSEN[1]

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Two general methods for the preparation of alkylfumaric acids and/or maleic anhydrides have been reported: one involves the conversion of paraconic esters to citraconic anhydrides by way of the itaconic acids,[2] with subsequent conversion to the mesaconic acids by prolonged heating in aqueous alkali[3] or by the action of bromine in carbon tetrachloride in the presence of sunlight.[4] Several unsuccessful attempts to prepare cyclohexylmaleic anhydride by this method[5] led to the abandonment of this route, and though the alternative route was no more successful for this compound,[5] it proved to be very convenient for most of the desired substances. The new route, which involved dibromination of 2-alkylacetoacetic esters followed by alkali induced rearrangement to the alkylfumaric acids, was first reported by Demarcay[6] in 1880, and was subsequently modified by Walden and others.[7,8] Table I lists the new 2-alkylacetoacetic esters prepared for this purpose,

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[1] Abstracted from a portion of the Ph.D. Dissertation of Kathryn G. Spackman, University of Michigan, 1954.

[2] J. Houben, "Die Methoden der Organischen Chemie," Vol. III, G. Thieme, Leipzig, 1930, p. 886.

[3] G. K. Almström, *Ber.*, **48**, 2009 (1915).

[4] R. Fittig and R. Glaser, *Ann.*, **304**, 178 (1899).

[5] K. G. Spackman, Dissertation, University of Michigan, 1954 (appendix).

[6] E. Demarcay, *Ann. chim.*, **20**, 433 (1880).

[7] P. Walden, *Ber.*, **24**, 2025 (1891).

[8] R. Anschütz, *Ann.*, **461**, 155 (1928).

TABLE I

ETHYL 2-ALKYLACETOACETATES

Alkyl group	Halide	Reflux. hr.	Distn. range °C.	Distn. range Mm.	Yield, %	B.p., °C. (25 mm.)	$n^{25}D$	Analytical data[a,b] Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Cyclopentyl	Br	17	135–140	25	63.5	139	1.4533	66.64	66.47	9.15	9.15
Cyclohexylmethyl	I	21	160–170	27–30	55.4	166	1.4588	68.99	68.74	9.80	9.89
2-Cyclohexylethyl	Br	48	168–178	20	54.5	175	1.4587	69.96	69.74[c]	10.07	10.12[c]

[a] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. [b] Boiling points uncorrected. [c] Microanalysis by Goji Kodama, University of Michigan.

TABLE II

2-ALKYLFUMARIC ACIDS

Alkyl group	Yield, %	M.p.,[a] °C.	Carbon, % Calcd.	Carbon, % Found[b]	Hydrogen, % Calcd.	Hydrogen, % Found[b]	Neut. equiv. Calcd.	Neut. equiv. Found
Cyclopentyl	36.9	230.5–231.5	58.69	58.71	6.57	6.53	92	93
Cyclohexylmethyl	28.7	204.5–206.0	62.24	62.34	7.55	7.66	106	106
2-Cyclohexylethyl	27.7	224.0–224.5	63.70	63.88	8.02	7.96	113	114
2-Phenylethyl[c]	13.7	198.5–200.0	64.44	65.22[d]	5.49	5.37[d]	110	110

[a] Melting points are uncorrected. [b] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. [c] Acetoacetic ester reported by K. von Auwers and K. Möller, *J. prakt. Chem.*, **109**, 124 (1925). [d] Microanalysis by Goji Kodama, University of Michigan.

TABLE III

2-ALKYLMALEIC ANHYDRIDES

Alkyl group	Yield, %	B.p.,[a] °C.	B.p. Mm.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found[b]	Hydrogen, % Calcd.	Hydrogen, % Found[b]
n-Butyl[c]	77.9	135	30	1.4654	62.32	62.15[e]	6.54	6.49[e]
i-Butyl[d]	45.5	134	30	1.4642	62.32	62.12[e]	6.54	6.50[e]
Cyclopentyl	84.3	95	0.7	1.5002	65.07	65.38	6.02	6.21
Cyclohexylmethyl	41.2	127	1.7	1.4980	68.02	67.96	7.26	7.22
2-Cyclohexylethyl	29.0	139	1.6	1.4647	69.20	69.28	7.75	7.58

[a] Boiling points are uncorrected. [b] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. [c] Fumaric acid reported by R. Fittig and F. Fichter, *Ann.*, **304**, 241 (1899). [d] Fumaric acid reported by Demarcay, ref. 6. [e] Microanalysis by Goji Kodama, University of Michigan.

and Table II lists the alkylfumaric acids resulting from the Demarcay–Walden reaction. All but one of the compounds listed in Table II were converted to the corresponding maleic anhydrides by distillation from phosphorus pentoxide[9]; and in addition, two previously known alkylfumaric acids were converted to the corresponding alkylmaleic anhydrides, which are reported in Table III.

Experimental

Ethyl 2-Akylacetoacetates.—These compounds were prepared according to a standard procedure[10] using freshly distilled ethyl acetoacetate (b.p. 72–79° (23 mm.)) and magnesium-dried ethanol. In each reaction, for each 1.00 mole of ester there was used 1.00 mole of sodium, 666 ml. of ethanol and 1.11 moles of alkyl halide.[11] The reaction was allowed to reflux until the mixture was neutral to moist universal indicator paper, except in the case of cyclopentyl bromide where the mixture remained alkaline. Data are summarized in Table I.

2-Alkylfumaric Acids.—A modification of the previously reported[6-8] procedure was used. For a 0.5-mole run 150 ml. of absolute ether was used. The initial reaction of the added bromine was very vigorous, but the second half-mole could be added all at once. The final mixture was then refluxed for 4.5 to 5 hr. Here an improvement in procedure involved the addition of 500 ml. of water, separation and return of the *lower* ethered layer *via* a dropping funnel to the reaction flask, now charged with 135 g. of potassium hydroxide pellets in 150 ml. of ethanol. Complete solution of the hydroxide was found unnecessary, and the mixture was vigorously stirred and cooled at 0–5° by an ice-bath. After working up essentially as described[7] the red residual slurry was triturated with hot chloroform. The crystallized acids were recrystallized from aqueous ethanol (Norit) at least three times. Additional crops for recrystallization were available by concentrating the chloroform and aqueous mother liquors. Data are summarized in Table II.

2-Alkylmaleic Anhydrides.—The procedure of Tanatar[9] was used wherein the appropriate 2-alkylfumaric acid (0.05 mole) and 0.05 mole of phosphorus pentoxide were intimately mixed in the reaction flask which was then arranged for low pressure distillation and placed in an oil-bath heated to 100°. The temperature was gradually raised until distillation commenced. It was found essential to rinse the reaction flask with glacial acetic acid, followed by acetone (before charging it), to effect very complete mixing of the reagents, to use very slow initial heating and to submerge the reaction flask completely in the oil-bath. The crude products were subsequently twice distilled from 1–2 g. of phosphorus pentoxide using a small Vigreux column and then were fractionated through a 20-plate column. Data are summarized in Table III.

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The Chemistry of Perfluoro Ethers. II. Ether Cleavage with Simultaneous Replacement of α-Fluorine by Chlorine[1a]

BY GEORGE VAN DYKE TIERS

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In Part I of this series[1b] the first known chemical reaction undergone by a perfluoro ether was re-

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[9] S. Tanatar, *Ann.*, **268**, 255 (1892).

[10] A. I. Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 465.

[11] When cyclohexylmethyl bromide was employed, a liquid, b.p. 120–122° (20 mm.), was the only product. It gave a negative ferric chloride test. Cyclohexylmethyl iodide gave satisfactory results.

(1) (a) Presented at the 126th Meeting of the American Chemical Society, New York, 1954, Abstracts, p. 27-M; (b) G. V. D. Tiers. THIS JOURNAL, **77**, 4837 (1955).