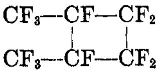
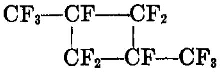


III



IV

or head-tail dimer (IV). In general, unsymmetrical fluoroolefins tend to form head-head dimers and therefore (III) would be the expected form.

EXPERIMENTAL

Tetramer of perfluorobutyne-2. Perfluorobutyne-2 (30 g.) was placed in a previously evacuated 300-ml. stainless steel reaction vessel and heated at 320° for 31 hr. After cooling to room temperature, the reaction vessel was opened to the vacuum system and 23.8 g. of unreacted perfluorobutyne-2 recovered by transfer to a liquid-air cooled trap. The total solid material was removed by washing the reaction vessel with acetone. Subsequent removal of the acetone left a solid that was sublimed three times at atmospheric pressure, then recrystallized twice from benzene to produce 2.3 g. of white crystals, m.p. (sealed tube) 208–209°.

Anal.[7] Calcd. for $C_{16}F_{24}$: mol. wt. 648; C, 29.7; F, 70.3. Found: mol. wt. (ebullioscopic in benzene) 650; C, 29.9; F, 69.7.

Dimer of perfluoropropene. Perfluoropropene (150 g.) was condensed in a previously evacuated 300-ml. stainless steel reaction vessel and heated at 400° for 18 hr. Pressure in the vessel rose to a maximum of 2140 psi. and gradually decreased to 1100 psi. at the termination of the heating period. The vessel was cooled to room temperature, 73 g. of unreacted perfluoropropene recovered by transfer in the vacuum system, and the remaining higher boiling liquid fractionated in a column packed with nickel helices to give 72 g. of perfluorodimethylcyclobutane, b.p. 44.7–45.1°, d^{25} 1.667, n_D^{25} 1.2618.

Anal. Calcd. for C_6F_{12}: mol. wt., 300. Found: mol. wt. (Dumas), 300.

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[7] Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

2-Pyrones. XXVII.
4-Methyl-6-alkyl-2-pyrones

RICHARD H. WILEY AND J. G. ESTERLE

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It has been demonstrated previously[1] that the acylation and subsequent decarboxylation of β-methylglutaconic anhydride (I) offers a unique procedure for the preparation of 4-methyl-6-alkyl-2-pyrones (III). The utility of this procedure is, however, limited by the fact that conditions required for successful isolation of the intermediate 5-acyl-β-methylglutaconic anhydride (II) where the acyl group has more than four carbons have never been devised. Because of the interest in certain of the structures available by this synthesis as intermediates in the biosynthesis of cholesterol[2] we have reinvestigated the possibility of preparing 4-methyl-6-alkyl-2-pyrones with 6-alkyl groups of four or more carbons by this route.

The results of these studies have established that the intermediate acyl-β-methylglutaconic anhydrides need not be isolated and purified. The crude acylated anhydrides can be decarboxylated and rearranged to the 4-methyl-6-alkyl-2-pyrones in overall yields of 12–45% from the anhydride. Using this technique we have prepared and characterized the seven 4-methyl-6-alkyl-2-pyrones described in Table I. These illustrate preparations with 5 to 10 carbon acyl halides and establish a correspondingly broader utility for the reaction. Infrared absorption data, summarized in Table IV, establish the presence of characteristic absorption maxima in the 1730–1736 cm.$^{-1}$; 1634–1647 cm.$^{-1}$; 1560–1567 cm.$^{-1}$; 1140–1220 cm.$^{-1}$; and 840 cm.$^{-1}$ regions. The first of these is a carbonyl stretching frequency characteristic of the 2-pyrone carbonyl. The 1640 cm.$^{-1}$ and 1560 cm.$^{-1}$ maxima are carbon-carbon double bond stretching frequencies and again serve to characterize the 2-pyrone structure. In the 2'-methylpropenyl derivative, in which there is a double bond conjugated with the ring unsaturation, the 1560 cm.$^{-1}$ maximum is shifted to 1536 cm.$^{-1}$ Three maxima occur in the 1140–1220 cm.$^{-1}$ region where absorption characteristic of the C—O stretching frequency in esters is observed. It has been noted previously[3] that unsaturated esters have two absorption maxima in this region. In the 2-pyrones there are three bands which occur at about 1200 cm.$^{-1}$, 1140 cm.$^{-1}$, and 1120 cm.$^{-1}$ in this region. One of these is presumably the adsorption maximum associated with the C—O stretching frequency. The maxima in 840 cm.$^{-1}$ region are the most prominent in the spectra. This is assigned to the C—H out of plane deformation of one of the ring C—H groups. It occurs in approximately the same place as the maximum observed for the C—H deformation in 1,3,5-substituted benzenes (835 cm.$^{-1}$)[4]. The ring hydrogens are situated between two substituents in each case. The 3-bromo derivatives, listed in Table II, were observed to have infrared absorption characteristics, summarized in Table IV, similar to those of the unsubstituted pyrones. The carbonyl stretching frequency is shifted to slightly longer wave lengths (1712–1730 cm.$^{-1}$). The intensities of the maxima associated with the carbon-carbon double bond stretching frequencies are reversed. The 1640 cm.$^{-1}$ maxima is the more intense of the two in the bromo compounds. In the bromo compounds the 1560 cm.$^{-1}$ maxima is shifted to 1529–1536 cm.$^{-1}$ There is generally only

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[1] Richard H. Wiley and N. R. Smith, *J. Am. Chem. Soc.*, **74**, 3893 (1952).

[2] Richard H. Wiley and J. G. Esterle, *J. Org. Chem.*, **21**, 1335 (1956).

[3] L. J. Bellamy, *Infra-Red Spectra of Complex Molecules*, John Wiley and Sons, N. Y., 1954, p. 163.

[4] L. J. Bellamy, *op. cit.*, p. 68.

TABLE I

4-METHYL-6-ALKYL-2-PYRONES

Alkyl	B.P. (°C./mm.)	n_D^{25}	Yield, %	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-Butyl	108/1	1.5040	23.8	72.26	72.21	8.49	8.48
Isobutyl	101/1	1.4999	45.0	72.26	72.12	8.49	8.33
2′-Methyl-1′-propenyl	[a]		12.0	73.14	73.08	7.37	7.37
n-Amyl	103/1	1.5035	27.8	73.29	73.43	8.95	9.04
Isoamyl	128/3	1.5004	17.4	73.29	73.07	8.95	9.16
n-Hexyl	109/1	1.5003	19.0	74.19	74.21	9.33	9.24
2′,6′-Dimethylheptyl	92/1	1.4936	17.0	76.22	76.05	10.24	10.20

[a] M.p. 46–47°.

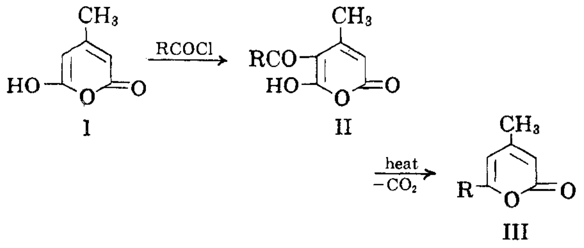
TABLE II

3-BROMO-4-METHYL-6-ALKYL-2-PYRONES

Alkyl	M.P. (°C.)	Yield, %	Analyses: Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-Butyl	35–36	50	49.00	49.08	5.35	5.49
n-Hexyl	49–49.5	45	52.76	52.55	6.27	6.36
1,2-Dibromo-2-methylpropyl	121–122	55	29.80	30.21	2.73	3.02

one absorption maximum, and this at about 1160 cm.$^{-1}$, in the C—O stretching region. The 840 cm.$^{-1}$ absorption maximum is modified or shifted in the 3-bromo compounds.

Several new tetrahydro 2-pyrones were prepared in 26–50% yields by catalytic reduction of the 2-pyrones. The infrared absorption of these compounds is characteristic of that of a saturated lactone structure. The carbon-carbon double bond absorption in the 1640 cm.$^{-1}$ and 1560 cm.$^{-1}$ region is lacking; the ester carbonyl absorption maximum is at 1733–1739 cm.$^{-1}$, the normal ester (δ-lactone) positions; and the C—O stretching frequency maximum is observed in the 1220–1240 cm.$^{-1}$ region. The last is much more intense than it is in the unsaturated 2-pyrones. Contamination of the tetrahydro compound with traces of the unsaturated derivative, insufficient to modify the refractive index, is readily detected by the appearance of absorption maxima at 1560 or 1640 cm.$^{-1}$



EXPERIMENTAL[5]

All of the 4-methyl-6-alkyl-2-pyrones were prepared in a similar manner. Details are given for a typical preparation. The yields, physical properties, and analytical data for the others are given in Table I.

4-Methyl-6-hexyl-2-pyrone. A slurry prepared from 30 ml. of dry ether and a solution of 5.0 g. (0.04 mole) of β-methylglutaconic anhydride in 10 ml. of dry pyridine was cooled to −5°. The stirrer was started, and a solution of 4.98 g. (0.04 mole) of heptoyl chloride in 20 ml. of dry ether was added with stirring to this slurry. After 0.5 hr. additional stirring 15 ml. of concentrated hydrochloric acid and 30 g. of ice were added. The mixture was stirred until all the solid material had dissolved. The ether layer was separated. The aqueous solution was extracted with two 100-ml. portions of ether. The ether extractions were combined and dried over sodium sulfate.

The ether solutions from three such runs were combined and the ether removed. The remaining 30 g. of red, viscous oil was flash-distilled at a temperature of 350°. The distillate was distilled from a Claisen flask (b.p. 100°/1 mm.) and fractionated through a spinning-band column to give 4.40 g. (19%) of the product, b.p. 109°/1 mm., n_D^{25} 1.5003.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.33. Found: C 74.21; H, 9.24.

The 3-bromo-4-methyl-6-alkyl-2-pyrones were prepared by dissolving the pyrone in carbon tetrachloride and adding an equivalent amount of bromine. After completion of the reaction, the solvent was evaporated and the residue crystallized from ligroin. The 3-bromo derivatives of 4-methyl-6-amyl, 4-methyl-6-isoamyl and 4-methyl-6-(2′,6′-dimethylheptyl)-2-pyrones were liquids at room temperature and were not characterized. Yields, physical properties, and analytical data for the solids are given in Table II.

The tetrahydro-4-methyl-6-alkyl-2-pyrones were prepared by catalytic hydrogenation. The 4-methyl-6-alkyl-2-pyrones were dissolved in ether and hydrogenated in a Parr hydrogenation apparatus over 5% palladium-on-carbon catalyst with an initial pressure of 50 lb./sq. in. The product were fractionated in a spinning-band column. The yields, physical properties, and analytical data are given in Table III.

The infrared absorption measurements were made with a Baird double beam recording spectrometer with sodium chloride optics. The pyrones and their tetrahydro derivatives were examined as carbon tetrachloride solutions. The bromo derivatives, except the *n*-butyl compound which was examined in carbon tetrachloride, were examined as potassium bromide pellets. All measurements are corrected against the 3.419 μ absorption maxima of polystyrene.

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[5] Analyses by Micro Tech Laboratories, Skokie, Ill.

TABLE III

4-METHYL-6-ALKYLTETRAHYDRO-2-PYRONES

				Analyses			
				Carbon		Hydrogen	
Alkyl	B.P. (°C./mm.)	n_D	Yield, %	Calcd.	Found	Calcd.	Found
n-Butyl[a]	114/4	1.4517					
Isobutyl	110/5	1.4484	40	70.55	70.22	10.67	10.73
Isoamyl	89/1	1.4509	26	71.69	71.66	10.94	10.76
n-Hexyl	89/1	1.4545	50	72.68	72.90	11.18	11.05

[a] See R. H. Wiley and H. G. Ellert, *J. Am. Chem. Soc.*, **79**, 2266 (1957).

TABLE IV

INFRARED ABSORPTION MAXIMA OF 4-METHYL-6-ALKYL-2-PYRONES AND THEIR 3-BROMO AND TETRAHYDRO DERIVATIVES[a]

6-Alkyl Group	C=O Stretching	C=C Stretching		C—O Stretching Region			C—H Out of Plane Deformation
2-Pyrones:							
Methyl	1736s	1645m	1565s	1227w	1147w	1130w	846m
n-Butyl	1730s	1637m	1567s	1222w	1142w	1125w	846m
Isobutyl	1736s	1639m	1562s	1225w	1145w		842m
2′-Methylpropenyl	1730s	1642m	1536s	1228w	1179w	1159w	840m
Amyl	1730s	1634m	1567s	1218w	1140w	1124w	845w
Isoamyl	1730s	1634m	1560s	1219w	1143w	1126w	846w
Hexyl	1736s	1647m	1567s	1222w	1147w	1130w	847m
2′,6′-Dimethylheptyl	1736s	1745m	1567s	1225w	1149w	1126w	844m
3-Bromo-2-pyrones:							
Methyl	1712s	1645m	1536w	—	1185m	—	846m
n-Butyl	1730s	1639m	1531w	—	1168w	—	—
1′,2′-Dibromo-2′-methyl	1724s	1631m	1531w	—	1186w	—	836w
n-Hexyl	1718s	1637m	1529w	—	1165w	—	—
Tetrahydro-2-pyrones:							
Methyl	1733s	—	—	1235s	1181m	1138w	—
n-Butyl	1736s	—	—	1236m	1170w		
Isobutyl	1739s	—	—	1235s	1168w	1147w	—
Isoamyl	1736s	—	—	1233s	1161w	—	—
n-Hexyl	1739s	—	—	1240s	1161w	—	—

[a] In cm.$^{-1}$ s, strong; m, medium; w, weak.

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Cleavage of Trialkylamines by Chloroformates

J. ALLAN CAMPBELL

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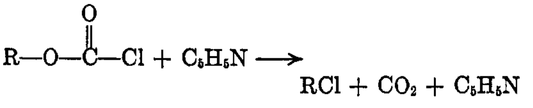
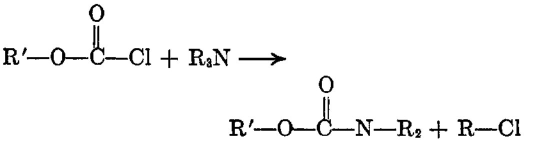
Girrard and Schild[1] have reported that chloroformates react with pyridine and quinoline to give an alkyl chloride, carbon dioxide, and the free base (Equation 1). It has been found in this laboratory that chloroformates will cleave trialkyl amines in boiling benzene to give the alkyl chloride and a carbamate (Equation 2). Both reactions take place with ethyl chloroformate and triethyl amine since carbon dioxide, ethyl chloride, and ethyl diethylcarbamate were produced. However, stigmasteryl chloroformate and triethyl amine react as in Equation 2 exclusively.



$$R\text{—O—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—Cl} + C_6H_5N \longrightarrow RCl + CO_2 + C_5H_5N \quad (1)$$



$$R'\text{—O—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—Cl} + R_3N \longrightarrow R'\text{—O—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—N—}R_2 + R\text{—Cl} \quad (2)$$

Stigmasteryl chloroformate cleaved both *N*-ethyl and *N*-methyl piperidine to give stigmasteryl *N*-piperidinylformate. These reactions are in

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[1] W. Girrard and F. Schild, *Chemistry & Industry*, 1232 (1954).