The kinetic runs were carried out essentially as described by Hine and Haworth.[5] As noted in Table I, runs were made in sets using three different hydroxides in each run to ensure comparability of results. Each hydroxide was run in duplicate samples, and two aliquots were withdrawn from each sample for titration at each time. The value obtained for k_2 at any time was thus an average of four determinations. The data for a typical run follows.

Into a nitrogen-purged, 250-ml. polyethylene bottle were placed 1.9399 g. of benzil and 100 ml. of dioxane. The solution was equilibrated in the constant temperature bath, 50 ml. of $0.1476M$ lithium hydroxide at the same temperature was added and the bottle vigorously shaken. Two 10-ml. aliquots were withdrawn as quickly as possible into 10 ml. of cold acetone and titrated to the phenolphthalein end-point. The time of withdrawal of samples was noted as zero time, and the base concentration given by the titration as "initial base concentration." The difference between the base concentration obtained by an analogous procedure with the omission of benzil, and the "initial base concentration" as above, was subtracted from the original benzil concentration (assuming that the partial molal volume of benzil was ideal) to correct for the reaction of benzil before zero time (maximum correction in any run, 3.3%). The result was taken as the "initial benzil concentration." Samples were then withdrawn at various times during the runs and titrated analogously to give the results shown in Table II.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF BENZIL WITH LITHIUM HYDROXIDE IN 67% DIOXANE–33% WATER AT 49.5°

$[\text{Benzil}]_0 = 0.06167M$; $[\text{LiOH}]_0 = 0.04756M$

Time, sec.	[LiOH]	$10^5\ k_2$, l./mole^{-1}/sec.$^{-1}$
68,400	0.01887	30.94
86,400	0.01629	29.87
169,200	0.00881	29.17
237,600	0.00558	29.88
		29.96 ± 0.49

Larger scale run with benzil and lithium hydroxide. In a 500 ml. Erlenmeyer was placed a solution of 10.2 g. (0.0485 moles) of benzil in 260 ml. of dioxane, to which was added 0.05 mole of lithium hydroxide monohydrate dissolved in 130 ml. of water. The solution was shaken and maintained in a thermostated bath at 49.5° for 72 hr. (time required for approximately 90% reaction), after which it was transferred to a separatory funnel and extracted with several portions of ether. The solvent was removed from the dried ether solution to yield only 0.3 g. of semisolid yellow residue whose infrared spectra showed it to consist mainly of benzil. The aqueous portion from the above extraction was evaporated to a small volume under reduced pressure and then acidified to yield 9.03 g. (82%) of solid acid with a neutralization equivalent of 242 (benzilic acid = 228). Recrystallization from water yielded benzilic acid, m.p. 149.3–151° (reported[12] m.p. 150°), neutralization equivalent 231. Evaporation of the filtrates from the acidification and from the recrystallization steps gave only 0.75 g. of solid acid, neutralization equivalent 233. No other products were found.

Acknowledgment. The authors are indebted to the National Science Foundation for a grant (NSF-G11318) which supported this research.

DEPARTMENT OF CHEMISTRY
THIEL COLLEGE
GREENVILLE, PA.

Fluorocarbon Sulfides. I. Synthesis of Bis(perfluoropropyl) Sulfide and Bis(perfluoroheptyl) Disulfide

GEORGE VAN DYKE TIERS

Received November 28, 1960

From the reaction of perfluoropropyl iodide with sulfur at 250° Hauptschein and Grosse[1] recovered bis(perfluoropropyl) disulfide and trisulfide, but at most only a trace of monosulfide, insufficient to permit isolation. They attributed this to a rapid attack by sulfur upon the (supposedly) first-formed monosulfide.[1] However, the author has now found that by carrying out the reaction at a higher temperature, 300°, an appreciable yield (11%) of the monosulfide is obtained. The mechanism suggested does not satisfactorily explain this observation, and it appears more likely that the first-formed disulfide (or perfluoropropylthiyl radical) subsequently reacts with free perfluoropropyl radicals to produce the (stable) monosulfide.

Several years after Hauptschein and Grosse's report, Haszeldine and Kidd[2] claimed that little or no reaction occurred between 1-iodo perfluoropropane and sulfur in a stainless steel autoclave at temperatures up to 350° (fourteen hours), that partial reaction occurred at 400°, and that 450° was required to convert all 1-iodoperfluoropropane to (principally) disulfide, lesser amounts of mono- and trisulfide being present in the reaction product also. It is surprising that Haszeldine and Kidd failed to recognize their error, (their reaction temperature may have been read from a Fahrenheit thermometer or themocouple chart), as Hauptschein and Grosse had reported exactly the same reaction at a much lower temperature; the latter work[1] is of course fully confirmed by the present study. The ultraviolet spectroscopic data reported by Haszeldine and Kidd for $(C_3F_7)_2S_2$ are incorrect; apparently much $(C_3F_7)_2S_3$ was in their "pure" sample.

The synthesis (by the same general method), purification, and physical properties of bis(perfluoroheptyl) disulfide are also reported. It is of interest that attempted oxidation of this disulfide by fuming nitric acid resulted in preferential elimination of higher sulfides. Such purification was apparently not achieved by simple recrystallization, for despite a good melting range, the sulfur analysis was high; formation of a solid solution is suggested.

---

(1) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.* 73, 5461 (1951).

(2) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).

EXPERIMENTAL

Bis(perfluoropropyl) sulfide. Perfluoropropyl iodide,[3] 105 g., (0.36 mole) was treated with 11.5 g., (0.36 g.-atom) of sulfur in a 180 ml. stainless steel rocking autoclave[4] for 10 hr. at 300°. By fractional distillation of the reaction product there was recovered 37.4 g. of $(n\text{-}C_3F_7)_2S_2$[1], b.p. 123°, n_D^{25} 1.3231, (53%), λ_{max} = 2394 Å, ϵ_{max} 327, $W^1/_2$ = 7150 cm.$^{-1}$; and 11.0 g. $(n-C_3F_7)_2S_3$,[1] b.p. 155.5°, n_D^{25} 1.3594, (14.5%), λ_{max} = 2448 Å, ϵ_{max} = 1540, $W^1/_2$ = 8700 cm.$^{-1}$; and in addition 7.0 g. $(n-C_3F_7)_2S$, b.p. 88°, n_D^{25} 1.2872, (11%), λ_{max} below 2100 Å, and ϵ (2100 A) = 70, ϵ (2400 A) = 14.

Anal.[5] Calcd. for $C_6F_{14}S$: C, 19.47%;F , 71.87%. Found: C, 19.5%; F, 72.1%.

The infrared spectrum of the liquid monosulfide very closely resembles those of the disulfide and trisulfide, (the band at 12.59 μ reported for the trisulfide[1] was spurious, as it is completely absent in my preparation),[1] but may be distinguished from them by the presence of medium-strength bands at 8.75 μ and 14.90 μ, and the virtual absence of those at 9.24 μ and 14.70 μ.

Bis(perfluoroheptyl) disulfide. Perfluoroheptyl iodide,[6] 61.6 g. (0.124 mole) and sulfur, 3.96 g. (0.124 g.-atom) were divided equally between two 30 ml. heavy-walled borosilicate glass ampoules, which were sealed and heated for 17 hr. at 255° ± 5°. The ampoules were chilled in liquid air and opened cautiously, then warmed to melt the crystalline product; after filtration to remove iodine crystals liquid had n_D^{25} 1.3305 (supercooled), and weighed 45.8 g. (about 95% yield, crude). A small amount, recrystallized from carbon tetrachloride and from benzene-heptane had m.p. 37.5°–39.5°, but the sulfur analysis was high: calcd. for $C_{14}F_{30}S_2$, S, 8.00%; found, S, 8.65%. It appeared that higher sulfides were present. The remaining material, 44.0 g., was refluxed for 65 hr. with 25 ml. of red fuming nitric acid. There was recovered 41.5 g. of colorless product having n_D^{25} 1.3242 (supercooled), from which 25.2 g. was distilled through a 10-cm. packed[7] fractionating column. Crystalline bis(perfluoroheptyl) disulfide, 20.1 g., having b.p. 246.5° and m.p. 38.5°–39.5° (recrystallized from carbon tetrachloride) was thus produced in 60% yield.

Anal. Calcd. for $C_{14}F_{30}S_2$; C, 20.96%; F, 71.04%; S, 8.00%. Found: C, 21.0%; F, 71.3%; S, 7.99%.

Its ultraviolet spectrum (2.00 mg./ml. in isooctane) had λ_{max} = 2387 Å, ϵ_{max} 389, width at half-height, $W^1/_2$ = 7340 cm.$^{-1}$

Acknowledgment. I am greatly indebted to B. W. Nippoldt and P. B. Olson for development of the modified analytical technique required for such sulfur-bearing samples.[5] The infrared spectra were interpreted by Dr. J. J. McBrady and Dr. W. E. Keiser.

CONTRIBUTION NO. 184
CENTRAL RESEARCH DEPT.
MINNESOTA MINING AND MANUFACTURING CO.
ST. PAUL 19, MINN.

---

(3) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73,** 2461 (1951).

(4) Aminco Instrument Co., Silver Spring, Md.

(5) H. E. Freier, B. W. Nippoldt, P. B. Olson, and D. G. Weiblen, *Anal. Chem.*, **27,** 146 (1955).

(6) G. V. D. Tiers, *J. Am. Chem. Soc.*, **82,** 5513 (1960); an erroneous refractive index was reported for $n\text{-}C_7F_{15}I$, the correct value being n_D^{25} = 1.3339.

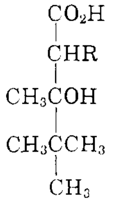
(7) "Helipak" packing from the Podbielniak Co., Chicago, Ill.

Lactonization of 3-Hydroxy-3,4,4-trimethylpentanoic Acid

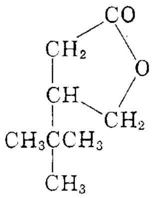
ALBERT W. BURGSTAHLER AND DAVID E. WETMORE

Received February 28, 1961

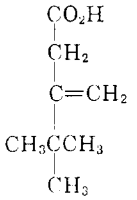
In connection with a study of structural requirements for the formation of β-lactones from β-hydroxy acids,[1] our attention was attracted to reports[2] that 3-hydroxy-3,4,4-trimethylpentanoic acid (I) undergoes dehydration by various acidic agents to yield β-*tert*-butyl-γ-butyrolactone (II).



I. R = H
Ia. R = CH_3



II



III

Curiously, this formulation of the lactonic product appears to have been widely accepted,[3] despite the fact that the generation of such a structure from I, presumably by way of 3-*tert*-butyl-3-butenoic acid (III), would be contrary to the Markownikoff rule. On the other hand, even though a neopentyl type alcohol system is present in I, the two isomeric unsaturated acids which can be prepared from I or its esters by dehydration under milder conditions, and which are also convertible to the lactone, have been shown to possess the unrearranged structure IV (or III).[4] However, all attempts to establish the constitution of the lactone by methods based on hydrolysis, oxidation, or reduction were reported to be unsuccessful.[4]

As I, and also III and IV, by treatment with acid under sufficiently vigorous conditions might be expected to undergo rearrangement leading to β,β,γ-trimethyl-γ-valerolactone (V), it was of interest to note that the melting point recorded for "II" (99–100°) is the same as that reported for V as

---

(1) For examples, *cf.* (a) N. J. Toivonen, P. Hirsjärvi, A. Melaja, A. Kainulainen, A. Halonen, and E. Pulkkinen, *Acta Chem. Scand.*, **3,** 991 (1949); (b) A. W. Burgstahler, Ph.D. thesis, Harvard University, 1952; (c) P. A. Diassi and C. M. Dylion, *J. Am. Chem. Soc.*, **80,** 3746 (1958); (d) G. A. Boswell, W. G. Dauben, G. Ourisson, and T. Rull, *Bull. soc. chim. France*, 1598 (1958); (e) J. C. Sheehan, K. Hasspacher, and Y. Lieh Yeh, *J. Am. Chem. Soc.*, **81,** 6086 (1959); (f) E. Testa, L. Fontanella, and L. Mariana, *J. Org. Chem.*, **25,** 1812 (1960).

(2) A. Petschnikoff. *Chem. Zentr.*, **1901,** I, 668 [*cf. J. prakt. Chem.*, **65,** 168 (1902)]; S. Wouseng, *Ann. chim. (Paris)*, [10], **1,** 401 (1924).

(3) J. E. Dubois and Y. Maroni-Barnaud, *Bull. soc. chim. France*, 949 (1953); R. Heilmann and R. Glenat, *Bull. soc. chim. France*, 1586 (1955); M. F. Ansell, J. W. Hancock, and W. J. Hickinbottom, *J. Chem. Soc.*, 911 (1956).

(4) M. S. Newman and R. Rosher, *J. Org. Chem.*, **9,** 221 (1944).