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%), $\lambda_{\max} = 2394$ Å, $\epsilon_{\max}$ 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%), $\lambda_{\max} = 2448$ Å, $\epsilon_{\max} = 1540$, $W^1/_2 = 8700$ cm.$^{-1}$; and in addition 7.0 g. $(n-C_3F_7)_2S$, b.p. 88°, n_{D}^{25} 1.2872, (11%), $\lambda_{\max}$ 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 $\lambda_{\max} = 2387$ Å, $\epsilon_{\max}$ 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
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(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 $n_{\mathrm{D}}^{25} = 1.3339$.

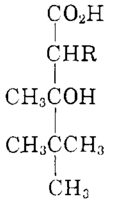
(7) "Helipak" packing from the Podbielniak Co., Chicago, Ill.

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

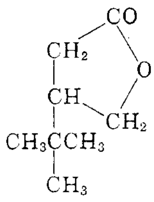
ALBERT W. BURGSTAHLER AND DAVID E. WETMORE

Received February 28, 1961

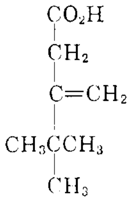
In connection with a study of structural requirements for the formation of β-lactones from β-hydroxy acids,[1] our attention was attracted to reports[2] that 3-hydroxy-3,4,4-trimethylpentanoic acid (I) undergoes dehydration by various acidic agents to yield β-*tert*-butyl-γ-butyrolactone (II).



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

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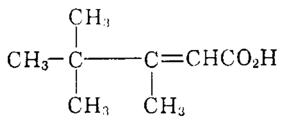
(1) For examples, *cf.* (a) N. J. Toivonen, P. Hirsjärvi, A. Melaja, A. Kainulainen, A. Halonen, and E. Pulkkinen, *Acta Chem. Scand.*, **3,** 991 (1949); (b) A. W. Burgstahler, Ph.D. thesis, Harvard University, 1952; (c) P. A. Diassi and C. M. Dylion, *J. Am. Chem. Soc.*, **80,** 3746 (1958); (d) G. 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).

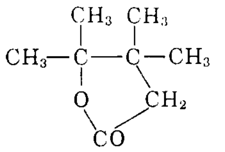
(2) A. Petschnikoff, *Chem. Zentr.*, **1901,** I, 668 [*cf. J. prakt. Chem.*, **65,** 168 (1902)]; S. Wouseng, *Ann. chim.* (*Paris*), [10], **1,** 401 (1924).

(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).

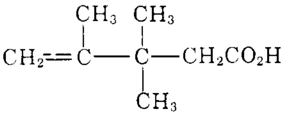
(4) M. S. Newman and R. Rosher, *J. Org. Chem.*, **9,** 221 (1944).


$CH_3C(CH_3)_2C(CH_3)=CHCO_2H$

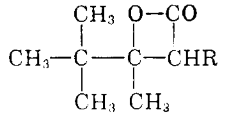
IV



V


$CH_2=C(CH_3)C(CH_3)_2CH_2CO_2H$

VI



VII. R = H

VIIa. R = CH_3

synthesized by a route involving 3,3,4-trimethyl-4-pentenoic acid (VI) or its equivalent as a final intermediate.[5] However, the possibility that V might be identical with the lactone obtained from I or IV appears to have been overlooked until now.

In the present work, before a direct comparison was made of material prepared by the two methods, some additional evidence in support of structure V for the lactone derived from I or IV was obtained. The infrared spectrum of the lactone clearly shows that it is a γ-lactone (carbonyl absorption at 5.65 μ), in agreement with structure II or V. However, the NMR spectrum (60 Mc./sec.) indicates the presence of two kinds of geminal methyl groups (singlets with an area of six protons each at 8.92 and 8.67τ in deuterochloroform, with tetramethylsilane as internal reference) and only one methylene group (two equivalent protons at 7.56τ), thus showing that structure V is correct, and not II.

By way of chemical proof, reduction of the lactone with lithium aluminum hydride afforded a distillable diol which, by oxidation with potassium permanganate and then treatment with acid, gave back the original lactone. The diol so derived from II would have been expected, on the other hand, to yield a substituted succinic acid instead of the starting lactone. Finally, as a more direct proof of structure, lactonization of the unsaturated acid VI,[5] which in our work was prepared by homologation of 2,2,3-trimethyl-3-butenoic acid[6] by the Arndt-Eistert procedure, gave the same product as that obtained from I. Likewise, the lactone from I proved to be identical with a sample of V prepared by the method of Baumgarten[5] and kindly supplied by him.

Although efforts to convert I to the corresponding β-lactone VII by means of such reagents as acetyl chloride,[1b] ethyl chloroformate,[1c] or *N,N'*-diisopropylcarbodiimide[1e] gave only mixtures of noncrystalline products, it was possible to obtain, in 60% yield, the more highly substituted β-lactone VIIa, m.p. 46–47°, by the action of the carbodiimide reagent on 3-hydroxy-2,3,4,4-tetramethylpentanoic acid (Ia). This result, taken in conjunction with structural features of other β-hydroxy acids which have been dehydrated to β-lactones,[1] suggests that steric compression[7] by α- and/or β-substituents greatly enhances the ease of β-lactone formation. However, further work will be necessary before a precise evaluation of such substituent effects can be made.

EXPERIMENTAL[8]

Reduction-oxidation sequence on the lactone V. The preparation of 3-hydroxy-3,4,4-trimethylpentanoic acid (I) and its lactonization by the action of 50% sulfuric acid were accomplished as described by Newman and Rosher.[4] For reduction, a solution containing 3.0 g. of the lactone (m.p. 99–100°) in 50 ml. of dry ether was added slowly to a well stirred solution of 1 g. of lithium aluminum hydride in 100 ml. of the same solvent. After 10 min. 5 ml. of ethyl acetate was added dropwise, and then 5 ml. of a saturated aqueous sodium sulfate solution. Anhydrous sodium sulfate (20 g.) was added, and the coagulated solids were separated by filtration and washed with additional ether. The combined filtrates and washings were dried further over anhydrous magnesium sulfate, evaporated, and the residue distilled, yielding 1.3 g. of a viscous oil, b.p. 112–114° (0.6 mm.). The infrared spectrum of this product showed strong hydroxyl absorption at 2.75–2.9 μ; the carbonyl region was transparent.

For the oxidation, 25 ml. of a 6% solution of potassium permanganate in water was added slowly at 25°, with stirring, to 25 ml. of an aqueous solution containing 0.6 g. of the foregoing product and 2 g. of sodium carbonate. After 8 hr. at 20–25° the mixture was treated with methanol to destroy the excess permanganate and filtered. After extraction with ether the filtrate was acidified with 6*N* hydrochloric acid and re-extracted with ether. Evaporation of the latter extracts afforded a viscous oil which was warmed briefly on the steam-bath and taken up in an additional 50 ml. of ether. The ether solution was washed with cold 5% aqueous sodium carbonate, dried over anhydrous magnesium sulfate, and evaporated. The residue on crystallization from benzene–petroleum ether (b.p. 60–70°) furnished 110 mg. of fine prisms, m.p. 98–100°, undepressed on admixture with the original lactone. The infrared spectrum of this product was also identical with that of the original lactone as well as with that of an authentic sample of V (see below).

Synthesis and lactonization of 3,3,4-trimethyl-4-pentenoic acid (VI). The acid chloride (3.5 g., 0.024 mole) of 2,2,3-trimethyl-3-butenoic acid, prepared by the method of Courtot,[6] was added slowly, in 15 ml. of dry ether, to 0.075 mole of diazomethane in 150 ml. of dry ether at 0°. After 24 hr. at this temperature the reaction was still incomplete (acid chloride carbonyl band at 5.6 μ still present). However, after an additional 12 hr. at 25° the reaction appeared to be essentially complete. Evaporation of the solvent under reduced pressure furnished an oily diazo ketone (IR, 4.75 and 6.15 μ), which did not show any tendency to crystallize and was therefore heated directly in ethanol with freshly precipitated silver oxide at 70° for 1 hr. and then at reflux for 4 hr. The resulting clear mixture was decanted, evaporated on the steam bath under reduced pressure, and the residue distilled at atmospheric pressure. The desired fraction, the ethyl ester of 3,3,4-trimethyl-4-pentenoic acid

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[5] H. E. Baumgarten, *J. Am. Chem. Soc.*, **75**, 979 (1953).

[6] A. Courtot, *Bull. soc. chim. France*, [4], **35**, 298 (1906).

[7] *Cf.* E. L. Eliel in *Steric Effects in Organic Chemistry*, M. S. Newman, ed., Wiley, New York, 1956, pp. 117–120.

[8] Melting points are uncorrected and were observed in capillary tubes. Infrared spectra were determined in chloroform solution on a Perkin-Elmer Model 21 double-beam recording spectrophotometer. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(VI), was collected at 200–205° (745 mm.); yield 0.85 g. (21% from the acid chloride). Hydrolysis with 10% alcoholic potassium hydroxide furnished the viscous free acid VI,[5] which was not purified but was characterized, in part, as the *amide* by the thionyl chloride–ammonia procedure. After recrystallization from benzene–petroleum ether (b.p. 40–60°), this derivative was obtained in fine plates, m.p. 140–140.5°.

Anal. Calcd. for $C_8H_{15}ON$ (141.21): C, 68.04; H, 10.71. Found: C, 67.83; H, 10.95.

A mixed m.p. of this derivative with the amide,[4] m.p. 140–141°, of the solid isomer of IV,[4] m.p. 84–85° (samples kindly supplied by Professor Melvin S. Newman), was depressed to 106–129°. The infrared spectra and the ultraviolet end-absorption of the two specimens were also characteristically different. In addition, tetranitromethane produced a light yellow color with the free acid VI but no color with the crystalline sample of IV, in accord with the conjugated structure of the latter.

Treatment of the remaining portion (*ca.* 0.3 g.) of the crude acid VI with 20 ml. of 50% sulfuric acid on the steam-bath for 1 hr., and then isolation of the neutral product by extraction with ether, furnished 145 mg. of fine prisms, m.p. 93–98°. After two recrystallizations from benzene–petroleum ether (b.p. 60–70°), these melted at 99–100° and did not depress the m.p. of the lactone obtained from I. The infrared spectra of the two preparations were also identical, and a sample of V kindly furnished by Professor Henry E. Baumgarten[5] was likewise indistinguishable from them both.

α,β,γ,γ-Tetramethyl-β-valerolactone (VIIa). Ethyl 3-hydroxy-2,3,4,4-tetramethylpentanoate, b.p. 62–64° (0.6 mm.), was obtained in 72% yield in a 0.1-mole run by the Reformatsky procedure from pinacolone and ethyl α-bromopropionate. Hydrolysis of this ester with 5% aqueous-alcoholic sodium hydroxide afforded the corresponding acid Ia, m.p. 108–110°, in 81% yield after crystallization from dilute ethanol. Two additional crystallizations from the same solvent furnished the pure acid as fine prisms, m.p. 109–110°.

Anal. Calcd. for $C_9H_{18}O_3$ (174.23): C, 62.04; H, 10.41. Found: C, 62.34; H, 10.36.

For conversion to the corresponding β-lactone, 1.0 g. of the foregoing acid was dissolved in 20 ml. of benzene and treated with 0.75 g. of freshly prepared *N,N′*-diisopropylcarbodiimide.[1e] After a reaction period of 24 hr. at 25° the precipitate of *N,N′*-diisopropylurea was collected, and the filtrate diluted with petroleum ether (b.p. 40–60°), washed rapidly with cold 5% sodium carbonate-bicarbonate solution, and dried over anhydrous magnesium sulfate. Filtration and concentration of the solution under reduced pressure afforded an oily residue which crystallized readily at −20° from petroleum ether (b.p. 40–60°), forming large prism clusters of α,β,γ,γ-tetramethyl-β-valerolactone (VIIa), m.p. 46–47°; IR, 5.52 μ; yield 0.55 g. (61%).

Anal. Calcd. for $C_9H_{16}O_2$ (156.22): C, 69.19; H, 10.32. Found: C, 69.34; H, 10.17.

When heated to 110–130° this product liberated carbon dioxide and furnished an olefin, b.p. 104–106° (735 mm.), n_D^{20}, 1.4224; IR, 12.2 μ (CS_2), which is probably largely 3,4,4-trimethyl-2-pentene [lit.[9] b.p. 109° (740 mm.), n_D^{20}, 1.4232]. Attempted lactonization of I gave only noncrystalline neutral products whose infrared spectra showed carbonyl peaks at 5.5 and 5.8 μ. Efforts to isolate a pure β-lactone from the mixture by evaporative distillation at reduced pressure[1f] were unsuccessful.

Acknowledgment. We wish to thank Professor Melvin S. Newman for helpful advice and for samples of the solid isomer of IV and its amide, and Professor Henry E. Baumgarten for an authentic specimen of V. We are also grateful to Dr. James N. Shoolery (Varian Associates, Palo Alto, Calif.) for the NMR spectrum of V and its interpretation, and the University of Kansas for a grant from the General Research Fund.

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[9] F. C. Whitmore and K. C. Laughlin, *J. Am. Chem. Soc.*, **54,** 4011 (1932).

A Convenient Synthesis of *cis*-Cyclononene

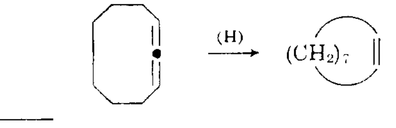
PETE D. GARDNER AND MUNISAMAPPA NARAYANA

Received February 22, 1961

Unambiguous syntheses of both *cis*- and *trans*-cyclononene have been reported.[1] However, because they are multi-stepped and include almost prohibitively low-yield steps they do not lend themselves easily to the preparation of substantial quantities of these interesting olefins. The need for such quantities prompted the search for a more efficient process, the results of which are the subject of this report.

The two-step allene synthesis reported by Doering and LaFlamme[2] was found to be nicely adaptable to the synthesis of 1,2-cyclononadiene. The required starting material, cyclooctene, was prepared by reduction of commercially available 1,5-cyclooctadiene essentially as described for cyclooctatetraene.[3] Its transformation is summarized below.

cis-Cyclononene was prepared from 1,2-cyclononadiene by either catalytic hydrogenation or sodium-ammonia reduction. The complete absence of the *trans* isomer in both of these reaction products is as expected. The *cis* isomer is the energetically more stable of the two[4] and it is probably this factor which determines the stereochemical course



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[1] A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *J. Am. Chem. Soc.*, **74,** 3643 (1952). See also A. T. Bolmquist and P. R. Taussig, *J. Am. Chem. Soc.*, **79,** 3505 (1957); A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **80,** 630 (1958); and V. Prelog, K. Schenker, and W. Kung, *Helv. Chim. Acta*, **36,** 471 (1953).

[2] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2,** 75 (1958). W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76,** 6162 (1954).

[3] W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560,** 1 (1948).

[4] R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79,** 4133 (1957).