Registry No.—Perfluoroisobutylene, 382-21-8; perfluoropropylene, 116-15-4; perfluoro-*t*-butyl iodide. 4459-18-1.

Acknowledgment.—The authors are grateful to the National Science Foundation for original financial support of this work.

Enol Esters. VI.[1] Hexadecylketene Lactone Dimer and Di- and Tristearoylhydroxamic Acids

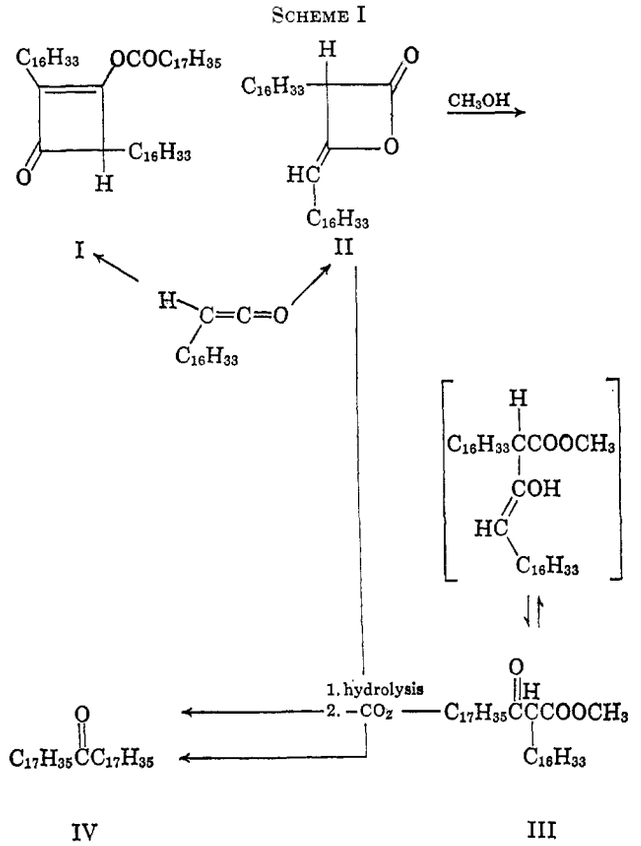
EDWARD S. ROTHMAN

Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania 19118

Received December 1, 1966

In previous publications we have described the powerful acylation activity of isopropenyl stearate such that it is capable of acylating even amides and imides, and further described the formation of stearone and 2,4-dihexadecylcyclobutane-1,3-dione (I) as enol stearate (Scheme I) by the simple heating of isopropenyl stearate

SCHEME I



IV III

to 200° with a trace of acid catalyst. We believe that all of the above reactions proceed *via* the key intermediacy of hexadecylketene and present here our reasons for such a conclusion. We have already indicated that monomeric hexadecylketene was formed in the heating of isopropenyl stearate in mineral oil medium and, in agreement with the generalization of Farnum, *et al.*,[3] have found that the trimer formed is the dialkylcyclobutanedione (I). By generating the hexadecylketene monomer by dehydrochlorination of stearoyl chloride we have been able to form, not only the expected hexadecylketene dimer, II, but also stearone, and can show that the stearone is a logical product to obtain from the proximate β-lactone product, II.

The lactonic dimer II is much less stable than the cyclobutanoid trimer I, the ring strain being so great that recrystallization from methanol is capable of effecting ring opening to form the intermediary β-keto ester III. Further hydrolysis to the free keto acid is accompanied by spontaneous decarboxylation to form stearone, IV.

The structure of the hexadecylketene dimer of mp 64° as the lactone II follows from the infrared spectrum (the bands at 1877 and 1727 cm^{-1} can be only highly strained ring carbonyl); from the lack of selective ultraviolet absorption (excludes the cyclobutanedione monoenol types and excludes the tautomer of II showing ring-conjugated carbonyl); and from the nuclear magnetic resonance (nmr) spectrum which gives evidence of the *exo*-olefin structure [triplet at δ = 4.68, 4.55, 4.44 ppm (vinyl proton); triplet at δ = 3.93, 3.81, 3.72 ppm (proton α to carbonyl)]. The strained-ring lactone structure is also indicated by the facile ring opening by attempted "recrystallization" from methanol.

The powerful acylation action of the hexadecylketene liberated from stearoyl chloride by pyridine at the reflux temperature allowed the preparation of distearoyl and tristearoylhydroxamic acids. Long-chain di- and trihydroxamic acids have not previously been described. Tristearoylhydroxamic acid (mp 66°) shows no selective ultraviolet absorption or infrared hydroxyl or NH bands, two infrared carbonyl bands at 1799 and 1722 cm^{-1}, and a strong CO band 1166 cm^{-1}. During chromatographic purification of the tristearoyl derivative some hydrolytic cleavage occurred on the Florisil column forming the distearoylhydroxamic acid, mp 108° (coinciding fortuitously with the melting point of the monostearoylhydroxamic acid; a mixture melting point determination shows sharp depression, however). The distearoyl derivative crystallizes in very regular forms (hexagonal plates) unusual in fatty acid compounds. The elementary analysis distinguishes the two compounds plainly, but the infrared spectra run as crystal films due to compound insolubility, while different, are very similar. Both show NH bands near 3180–3220 cm^{-1}, but only the monosubstituted derivative shows the hydroxyl band near 3300 cm^{-1}.

Experimental Section

Hexadecylketene Lactone Dimer. (3-Hexadecyl-4-heptadec-1-enyloxetane-2-one) (II).—To a refluxing electromagnetically stirred solution of 6 ml (0.02 mole) of stearoyl chloride in 100 ml of absolute ether was added dropwise 5 ml (0.036 mole) of triethylamine in 100 ml of absolute ether. A precipitate of triethylammonium chloride formed immediately, but refluxing was continued for 4 hr. The salt was filtered off through a pad of powdered sodium sulfate in a column (dry atmosphere) and

(1) For the previous paper in this series, see E. S. Rothman, submitted for publication.

(2) One of the laboratories of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Am. Chem. Soc.*, **87**, 5191 (1965).

the filtrate was taken to dryness. The infrared spectrum at this stage showed two carbonyl bands of moderate strength at 1877 and 1727 cm^{-1} [4] indicating that the residue was essentially hexadecylketene lactone dimer formed in very high yield.

On cautious crystallization from methanol the lactone was freed of traces of other carbonyl components to give purified lactone: mp 64°; ultraviolet transparent, $\tilde{\nu}_{max}^{CS_2}$ 1877, 1727, 839 cm^{-1}; yield 91%.

Anal. Calcd for $C_{36}H_{68}O_2$: C, 81.13; H, 12.85. Found: C, 81.08; H, 12.90.

Methyl 2-Hexadecyl-3-oxoarachidate (17-Carbomethoxy Stearone) (III).—A sample of hexadecylketene lactone dimer was recrystallized from methanol one time without change but a repetition of the operation from boiling methanol gave complete conversion to the methanolytic ring-opened product: mp 63°; $\tilde{\nu}_{max}^{CS_2}$ 1748 (COOMe), 1718 (CO), 1165, 1198, 1262 cm^{-1}; nmr δ 3.55 (OCH_3), 0.86, 1.21, 2.09, 2.20. A trace of alkali catalyses the methanolysis markedly.

Anal. Calcd for $C_{37}H_{72}O_3$: C, 78.66; H, 12.85. Found: C, 78.74; H, 12.85.

Direct Conversion of Hexadecylketene Lactone Dimer to Stearone. A.—The lactone (60 mg) was refluxed in pure methanol for 1 hr without undergoing change but when a trace of potassium hydroxide was added the methanolysis product was obtained after an additional 1 hr of reflux. The solution was then made acid with diluted hydrochloric acid. The product, [stearone (45 mg) isolated by ether extraction] was identical in every respect to an authentic specimen.

B.—Chromatography of hexadecylketene lactone dimer on Florisil "dried" at 180° for 72 hr gave "hydrolysis" to stearone. The first two cuts eluted with pentane showed traces of unreacted lactone followed by a trace of contaminant methyl stearate. The stearone eluted with methylene chloride.

Distearoylhydroxamic Acid and Tristearoylhydroxamic Acid.—Stearoyl chloride (3 molar equiv), 1 equiv of hydroxylamine hydrochloride, and 100 ml of dry (over Linde Molecular Sieve 4A) pyridine were refluxed for 7 hr. Much of the excess pyridine was removed under reduced pressure, and the residue was taken up in chloroform and rapidly washed with ice water and dried by quick filtration through a column of sodium sulfate. The solvent was removed under reduced pressure, and the residue dissolved in pentane, was rapidly filtered through a short inefficient column of Florisil in order to decolorize. The residue, 790 g, mp 65.5–66.0 with refractile material persisting up to 92°, was essentially tristearoylhydroxylamine with a small distearoylhydroxylamine contamination. Fractional crystallization from pentane (discarding the least soluble small first crop) gave 748 g of pure tristearoyl hydroxamic acid: mp 66°, $\tilde{\nu}_{max}^{CS_2}$ 1799, 1722, 1166 cm^{-1}.

Anal. Calcd for $C_{54}H_{105}NO_4$: C, 77.91; H, 12.72; N, 1.68; mol wt, 832. Found: C, 78.18; H, 12.78; N, 1.61; mol wt, 753–889 thermistor method, 829 *vs.* benzil standard in chloroform.

The remaining material, whose infrared spectrum showed that the material was essentially the tristearoyl derivative, was dissolved in methylene chloride and chromatographed on dried Florisil. Methylene chloride elution gave 20% of the original weight of recovered tristearoyl hydroxamic acid. Elution with 1:1 absolute ethyl ether–methylene chloride gave distearoylhydroxamic acid, mp 107–108°, melting point unchanged by recrystallization. The distearoylhydroxamic acid is a very insoluble material.

Anal. Calcd for $C_{36}H_{71}NO_3$: C, 76.40; H, 12.65; N, 2.48. Found: C, 76.57; H, 12.46; N, 2.44.

Registry No.—II, 10126-68-8; III, 10126-69-9; distearoylhydroxamic acid, 10126-70-2; tristearoylhydroxamic acid, 10126-71-3.

Acknowledgment.—The author wishes to express his appreciation to C. T. Leander for infrared and ultraviolet spectra, R. J. Szamborski for nmr spectra, Miss C. Tylenda for technical assistance, and L. Scroggins and K. Davis for microanalyses.

(4) The authors of ref 3 report 1852 and 1706 cm^{-1} for a phenyl ketene lactone dimer.

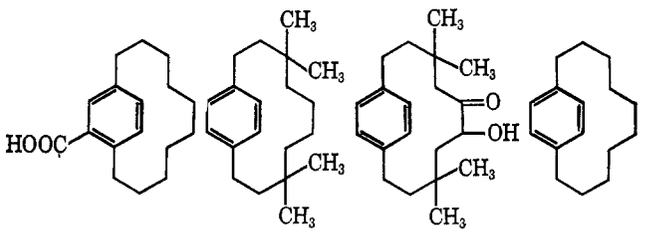
Many-Membered Carbon Rings. XXV. Derivatives of 3,3,8,8-Tetramethyl[10]paracyclophane[1,2]

A. T. BLOMQUIST AND BRANDES H. SMITH[3]

Baker Laboratory of Chemistry, Cornell University, Ithaca, New York

Received September 1, 1966

In the course of studies[4] leading to the resolution of [10]paracyclophane-12-carboxylic acid (I), we had occasion to examine the related system, 3,3,8,8-tetramethyl[10]paracyclophane (II), whose acyloin precursor, 3,3,8,8-tetramethyl-6-hydroxy[10]paracyclophan-5-one (III), has been reported .[5] Work with this tetramethyl system was deemed desirable at the time



I II III IV

since the phenomenon of bridge migration in the parent [10]paracyclophane (IV) had not been fully elucidated.[4] Once success had been achieved with the simpler system I, further study of the tetramethyl compound became needless. We do, however, wish to report these partial studies as they further illustrate certain elements of behavior which are characteristic of many of these bridged systems. Additional and extensive background may be found elsewhere.[4,5]

When problems arose in the substitution and resolution studies on the hydrocarbon IV, it was decided to replace hydrogen by methyl at four positions as in II. This was done so as to create bulk in the bridge with attendant restriction of rotation about its carbon–carbon single bonds. This course of action presented several challenging syntheses, not the least of which was the intramolecular acyloin cyclization of the diester, dimethyl *p*-phenylenebis(β,β-dimethyl-δ-valerate). Only by continued refinement of technique was a 38% yield obtained. Clemmensen-type reductions of acyloin functions are well known[6] to produce hydrocarbon and ketone, conditions in general dictating which. However, subjection of the acyloin III to strenuous Clemmensen conditions repeatedly resulted only in incomplete reduction to the ketone, 3,3,8,8-tetramethyl-

(1) Abstracted from part of the dissertation presented by B. H. Smith in June, 1960, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The nomenclature used throughout is discussed more fully by B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, pp 8–22.

(3) Proctor and Gamble Fellow, Cornell University, 1958–1959. Esso Research and Engineering Co., Linden, N. J.

(4) A. T. Blomquist, R. E. Stahl, Y. C. Meinwald, and B. H. Smith, *J. Org. Chem.*, **26**, 1687 (1961).

(5) A. T. Blomquist and F. Jaffe, *J. Am. Chem. Soc.*, **80**, 3405 (1958).

(6) V. Prelog, L. Frankiel, M. Kobelt, and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947); D. J. Cram and H. U. Daeniker, *J. Am. Chem. Soc.*, **76**, 2743 (1954); *Org. Syn.*, **36**, 14; K. L. Wiesner, D. M. MacDonald, E. B. Ingraham, and R. B. Kelly, *Can. J. Res.*, **28B**, 561 (1950).