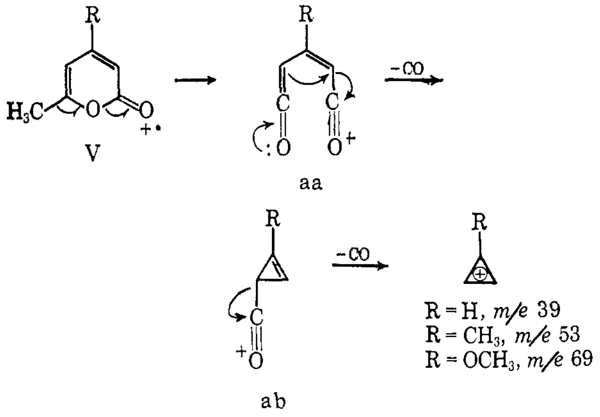
$C_3H_3^+$ is demonstrably produced by at least two processes, as shown above, the observation of gross differences in the distribution of deuterium among the fragments of these labeled 2-pyrones (III, IV) does not constitute evidence for the presence or absence of a furan intermediate (I) in the electron impact induced decarbonylation reaction.



(2)

To be more specific, Pirkle's data[3] clearly show that approximately 37% of the m/e 39 peak moves to m/e 40 in the spectrum of IV. This information permits estimation of an upper limit for the C-6 cleavage mechanism (reaction 2) of 63%, which could be lower because of other competing processes involving loss of deuterium from C-6 which may be operative. The published data[3] also show that at least 94% of m/e 39 is shifted to m/e 40 in III. This interesting fact still does not exclude a furan intermediate (I),[7] since this species could be generated in rearranged form, with C-3 (or C-4) arising from C-3 of 2-pyrone.

Registry No.—II, 504-31-4.

Acknowledgment.—The authors thank Professor Carl Djerassi for generous support and encouragement and Dr. M. Marx for helpful discussions. P. B. is grateful to the National Institutes of Health for financial support (Grant No. AM-04257). M. M. G. thanks the National Institutes of Health for a postdoctoral fellowship.

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[7] The similarity of the mass spectra of furan (I) and 2-pyrone (II) below m/e 68[8] and especially the correspondence of the metastable peak shapes[8] (determined in this laboratory on an Atlas CH-4 mass spectrometer) leaves little doubt that the major ions of mass 68 in the spectra of I and II are identical, but of as yet unknown structure.

[8] T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966).

The Synthesis of Perfluoroisobutylene from Perfluoropropylene

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A simple and excellent preparation of bis(trifluoromethyl)ketene from perfluoroisobutylene has recently been disclosed by England and Krespan.[1] The facile preparation and novel reactions of this compound make inevitable a greatly increased interest in its chemistry and prompt the publication of this Note, which describes an improved preparation of perfluoroisobutylene developed some years ago. The preparation utilizes perfluoropropylene rather than the more expensive perfluorocyclobutene or the less convenient tetrafluoroethylene, gives higher yields and conversions than other reported methods,[2-4] involves no elaborate apparatus or handling of gases boiling below −80°, and is a continuous process suitable for any quantity of materials. Although the reaction pathway may be complex, the main over-all reaction is merely the conversion of four molecules of C_3F_6 to three molecules of i-C_4F_8. The method has been used several times on an approximately 1-mole scale, with yields of 71–95% and conversions of 47–57%. The exact results obtained apparently depend to some extent on the flow rate, higher rates giving higher conversions but lower yields. No detailed study of the side products has been made but they presumably resemble those found in other pyrolytic preparations of i-C_4F_8 and also include an appreciable quantity of C_2F_6. Fractionation of the crude product through a 1-ft, low-temperature column packed with metal helices gives perfluoroisobutylene of at least 95% chromatographic purity.

Perfluoro-*t*-butyl iodide can be made in fair yield by catalyzed addition of the elements of iodine monofluoride[5] to perfluoroisobutylene, provided the reaction time is sufficiently extended; reaction for 60 hr at 130° gave $(CF_3)_3CI$ in 69% yield and 37% conversion. The iodide is a very volatile solid, mp 81° (sealed tube), and is stable indefinitely if protected from light, a sample having been stored without gross decomposition for four years at room temperature.

Experimental Section

Perfluoroisobutylene is extremely toxic and all reactions involving handling of this gas should be done in a well-ventilated area.

Perfluoroisobutylene by Pyrolysis of Perfluoropropylene.—An unpacked nickel tube (12 in. × 1 in) connected to a large trap cooled in a Dry Ice–acetone bath was continuously evacuated while being heated in a Hoskins tube furnace. The vacuum was broken with dry nitrogen and 105 g of C_3F_6 was passed through the tube over a period of 24 hr at a temperature of 750 ± 10°. The system was flushed with dry nitrogen and the crude product (103 g) fractionated to give 3 g of overhead (Dry Ice condenser), 50 g of reclaimed C_3F_6 plus side products (bp −30 to −2°), and 52 g of i-C_4F_8, boiling almost completely at 6–8°. The infrared spectrum of the product agreed with that published[6] and a gas chromatogram indicated a purity of at least 95%. The conversion, based on weight of C_3F_6 admitted, was 50% and the yield, neglecting impurities in the recovered C_3F_6, was 95%. In another run, 155 g of C_3F_6 passed through a similar tube at 750 ± 10° over 13 hr gave 30 g of recovered C_3F_6 [bp −39 to −23° (630 mm)] and 89 g of perfluoroisobutylene [bp −3 to +1° (630 mm)]; these figures represent a 71% yield and a 57% conversion.

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[1] D. C. England and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 4019 (1965); **88**, 5582 (1966).

[2] A. T. Morse, P. B. Ayscough, and L. C. Leitch, *Can. J. Chem.*, **33**, 453 (1955).

[3] M. Hauptschein, A. H. Fainberg, and M. Braid, *J. Am. Chem. Soc.*, **80**, 842 (1958).

[4] W. H. Pearlson and L. J. Hals, U. S. Patent 2,617,836 (1952).

[5] M. Hauptschein and M. Braid, *J. Am. Chem. Soc.*, **83**, 2383 (1961).

[6] D. G. Weiblen in "Fluorine Chemistry," Vol. 2, J. H. Simons Ed., Academic Press, Inc., New York, N. Y., 1954, p 477.

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

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

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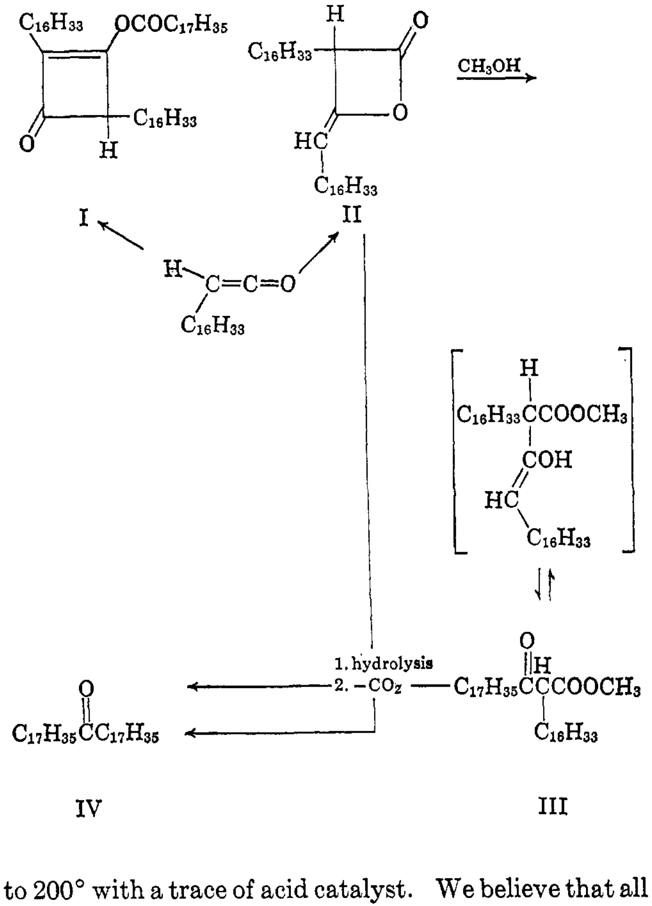
In previous publications we have described the powerful acylation activity of isopropenyl stearate such that it is capable of acylating even amides and imides, and further described the formation of stearone and 2,4-dihexadecylcyclobutane-1,3-dione (I) as enol stearate (Scheme I) by the simple heating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

Scheme I



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

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[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).