fractions can be isolated; however, the formation of the cyclic trimer was not observed. With an increase in the initial ratio of catalyst to monomer, the amount of macromolecular products decreases, and increasing amounts of cyclohexanetrione are formed. Finally, by the technique described by Erickson, if the reaction is started with catalytic amounts of sodium alcoholate and if after about half an hour a subsequent addition of catalyst is made, two steps of the process can be clearly distinguished; the first consists of the formation of linear macromolecules with a polyester structure, the second of degradation to form hexamethylcyclohexanetrione. The basic character of the catalyst seems to have a marked influence on the behavior of the reaction; for example, in the presence of sodium hydride or of sodium amide, dimethylketene at 110° polymerizes to a polyester and, even after several hours, the yield of hexamethyl-1,3,5-cyclohexanetrione is low. These results will be discussed in more detail in a subsequent paper.

In addition the dimethylketene dimer, 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (VI) is rapidly transformed at 110° into the cyclic trimer (I) by alkaline catalysts. If the reaction is stopped after a few minutes, it is possible to separate polyester IV in high yields, but high yields of hexamethylcyclohexanetrione are formed (Table II) in the presence of a sufficient amount of alcoholate or metallic sodium.

We have also observed that dimethylketene polymers having a polyacetalic (V) or polyketonic (II) structure can be transformed into the cyclic trimer rather slowly by sodium alcoholate. In the case of II, the conversion is low when molten polymer or a toluene suspension of polymer react directly; on the other hand, as was previously described,[4] the low solubility in nonpolar solvents and, perhaps, the chemical structure of polyketone make the chemical attack difficult in some cases. However, if the polymer is pyrolyzed at 300° and the viscous liquid thus formed reacts with sodium alcoholate, hexamethyl-1,3,5-cyclohexanetrione is isolated in high yield (80%).

The degradation of the dimethylketene polymers to cyclic trimer is only formally similar to that observed by Shashoua and co-workers for polyisocyanates.[3] While the trisubstituted cyanuric acid is formed by heating the linear polymer (together with the monomer), the conversion of dimethylketene polymers to cyclohexanetrione occurs only in the presence of a catalyst. In fact, the thermal degradation of polyketone II gives oily products which are apparently linear oligomers of dimethylketene, polyester IV is converted into β-lactone dimer[5] and polyacetal V partly cross-links and partly decomposes into the original monomer. In these three cases, the presence of the cyclic trimer was not observed. The mechanism of the reactions described will be discussed in a subsequent paper.

Experimental

Hexamethyl-1,3,5-cyclohexanetrione (I) from Dimethylketene.—Anhydrous toluene (50 ml.) and 0.5 g. of sodium methoxide were introduced under a nitrogen atmosphere into a flask immersed in an oil bath at 110°. The flask was equipped with a stirrer, a reflux condenser, and a jacketed dropping funnel cooled to −78°. During a period of 10 min., 22 ml. of dimethylketene was added to the stirred suspension. After the addition, the mixture was quickly cooled to room temperature, treated with an excess of ether, and then filtered. Distillation of the solution removed the ether and toluene leaving 10 g. of a white solid which, after crystallization from petroleum ether (b.p. 40–70°), melted at 80°. A mixed melting point with a sample of hexamethyl-1,3,5-cyclohexanetrione was undepressed.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.83; H, 8.83; mol. wt., 210.3. Found: C, 68.54; H, 8.83; mol. wt. (by cryoscopy in benzene), 207.

The precipitate which resulted by treating the reaction mixture with excess ether was washed with ether and dried *in vacuo* to give 8 g. of a solid. This product was soluble in boiling ether to the extent of 16.2% and on the basis of its infrared spectrum was polydimethylketene with a regular polyester structure (IV).

Polymerization of Dimethylketene without Formation of I.—Toluene (30 ml.) and 0.1 g. of sodium methoxide were introduced under a nitrogen atmosphere into a flask immersed in an oil bath at 110°. The flask was equipped with a stirrer, a reflux condenser, and a jacketed dropping funnel cooled to −78°. During a period of 2 min., 10 ml. of dimethylketene was added; after the addition, the contents of the flask were quickly cooled to room temperature and a large quantity of ethyl ether was added. The polymer formed was separated by filtration, and the ethereal filtrate was dried over anhydrous sodium sulfate. Evaporation left a few drops of oily residue. The polymer, washed with methanol and dried *in vacuo,* weighed 7.3 g. and was soluble in boiling ethyl ether to the extent of 5%. On the basis of its infrared spectrum it had a regular polyester structure.

Hexamethyl-1,3,5-cyclohexanetrione from 3-Hydroxy-2,2,4-trimethyl-3-pentenoic Acid β-Lactone (VI).—Sodium methoxide (0.5 g.) was added to 10 g. of VI in 30 ml. of toluene and the reaction flask was immersed in an oil bath at 150° for 2 hr. with frequent shaking. Toluene and unconverted β-lactone were distilled under slightly reduced pressure. Ether was added to the residue and the catalyst removed by filtration. The solvent then was evaporated to leave 8.0 g. of cyclohexanetrione residue (m.p. 78–80°, crystallized from petroleum ether).

Hexamethyl-1,3,5-cyclohexanetrione (I) from Polydimethylketene with a Polyketonic (II) Structure.—Eight grams of polydimethylketene with a polyketonic structure was introduced into a glass flask equipped with a distillation head. The flask was immersed in a bath of Wood's metal at 300°, and when the polymer was completely molten, 0.5 g. of sodium methoxide was rapidly introduced. Soon afterwards a yellow oily liquid began to distil. Six grams of liquid was collected in 1 hr., and about 0.1 g. of hexamethyl-1,3,5-cyclohexanetrione crystallized in the distillation head and in the condenser. Two grams of the pyrolysis product, dissolved in 10 ml. of toluene, was refluxed for 15 min., in the presence of 0.1 g. of sodium methoxide, and finally 1.6 g. of cyclic trimer of dimethylketene was isolated.

Hexamethylcyclohexanetrione from Polydimethylketene with a Polyacetalic Structure (V).—Four grams of polydimethylketene having a polyacetalic structure, 30 ml. of anhydrous toluene, and 0.5 g. of sodium methoxide were introduced in a flask equipped with a reflux condenser. The flask was immersed in an oil bath heated to 150° and the mixture was refluxed for 20 hr. A distillation head was then connected to the flask and toluene and any volatile products were removed by distillation (initially at atmospheric pressure and then under reduced pressure). The distillation residue was extracted by petroleum ether (b.p. 40–70°) and after filtration and subsequent evaporation the ether solution yielded 3.1 g. of a crystalline product (m.p. 78–80°). No depression was observed in a mixed melting point determination with hexamethylhexanetrione.

Reaction of 1-Ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene with Alkoxide Ion; Evidence for the S_N2' Mechanism

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Previous work in this laboratory[1] showed that 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (I) reacts

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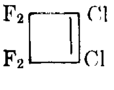
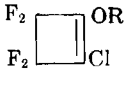
(1) J. D. Park, C. M. Snow, and J. R. Lacher, *J. Am. Chem. Soc.* **72**, 2342 (1951).

with either methoxide or ethoxide ion to form the monoether, IIa or IIb. Further reaction with alkoxide ion gives a triether, IIIa or IIIb, whose structure had been demonstrated.[2]

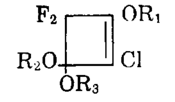


I



II

a. R = Me
b. R = Et

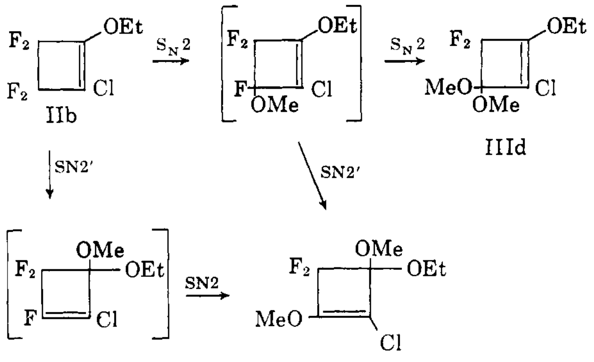


III

a. $R_1 = R_2 = R_3 =$ Me
b. $R_1 = R_2 = R_3 =$ Et
c. $R_1 = R_2 =$ Me
$R_3 =$ Et
d. $R_1 =$ Et
$R_2 = R_3 =$ Me

Until now it was not known whether the reaction of the monoether with alkoxide ion proceeded *via* two S$_N$2 processes, or a combination of one S$_N$2 and one S$_N$2′ step,[3] as either path would give the same product if the same alkoxide were used throughout.

We have now shown that this reaction involves one S$_N$2′ step, by reaction of the monoether with an alkoxide ion different from that used to form the monoether. Thus, reaction of IIb with methoxide ion should give IIIc if an S$_N$2′ step is involved, but IIId if only S$_N$2 steps are involved. We have found that IIIc is the only product obtained, as shown by gas chromatography and n.m.r. analysis.[4]



That the correct structure of this triether is IIIc rather than IIId was determined from its n.m.r. spectrogram.[5] Clearly, with IIId both groups of methyl protons would be equivalent, whereas with IIIc the methyl groups would not be equivalent. Furthermore, in the spectrum of IIIb there are two distinct resonance positions of the methylene and methyl protons with relative intensities of 1 to 2. The high intensity methylene quartet is centered at 6.23 τ and is obviously the resonance of the ketal ethyl group. The presence of *two* methyl peaks at 6.00 τ and 6.53 τ and a methylene quartet centered at 6.23 τ in the spectrogram of this product thus conclusively demonstrates the correctness of structure IIIc.

Experimental

1-Ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene.—To a stirred solution of 24.0 g. (0.123 mole) of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene in 55 ml. of 95% ethanol was added dropwise a solution of 6.9 g. (0.12 mole) of potassium hydroxide in 120 ml. of ethanol, over a period of 1 hr. The reaction mixture was poured into cold water, extracted with methylene chloride, and the methylene chloride extract washed five times with water. The methylene chloride solution was dried twice over sodium sulfate, followed by magnesium sulfate, and rectified through a 20-in. Fenske column. There was obtained 12.4 g. (0.061 mole) of the monoether, b.p. 73.5–75.5°(100 mm.), n^{25}_{D} 1.3813, (lit.,[2] b.p. 129°, n^{25}_{D} 1.3818)

1,3-Dimethoxy-3-ethoxy-2-chloro-4,4-difluorocyclobutene.—To a stirred solution of 11.4 g. (0.056 mole) of the monoether in 50 ml. of anhydrous methanol was added a solution of 6.3 g. (0.11 mole) of potassium hydroxide in 75 ml. of methanol. After refluxing for 2 hr., the solution was only slightly alkaline. The reaction mixture was poured into cold water, extracted with methylene chloride, and the methylene chloride extract washed five times with water. The solution was dried twice over sodium sulfate, followed by magnesium sulfate, and the solvent stripped on a Rotovac under vacuum. Vacuum distillation of the residue yielded 8.2 g. (0.038 mole) of triether, IIIc, b.p. 107–108° (22 mm.), n^{25}_{D} 1.4272, d^{25}_{4} 1.277. Molar refraction: calcd. 46.62; obsd. 46.00.

Anal. Calcd. for $C_8H_{11}F_2ClO_3$: C, 42.15; H, 4.86; F, 16.63; Cl, 15.48. Found: C, 42.24; H, 4.85; F, 16.80; Cl, 15.42.

Analysis by gas–liquid chromatography showed this material to be greater than 99.5% pure, with less than 0.5% of the monoether present.

Acknowledgment.—The authors wish to express their appreciation to Professor Melvin Hanna of this Chemistry Department for assistance in the interpretation of the n.m.r. spectra.

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(2) J. D. Park, S. Cohen, and J. R. Lacher, *ibid.*, **84**, 2919 (1962).

(3) For evidence supporting the S$_N$2′ mechanism for the reaction of nucleophiles with fluoroolefins, see: (a) W. T. Miller, Jr., J. H. Fried, and N. Goldwhite, *ibid.*, **82**, 3091 (1960); (b) John H. Fried and William T. Miller, Jr., **81**, 2078 (1959).

(4) It seems more likely to us that the first step in the mechanism is S$_N$2, followed by an S$_N$2 displacement of the vinyl fluoride, but as we have been unable so far to isolate either of the compounds shown in brackets, we cannot say with certainty that this assumption is correct. Further work on these reactions is continuing in this laboratory, and will be reported in the near future.

(5) N.m.r. spectra were taken using a Varian A-60 analytical spectrometer. Pure liquid samples were used with tetramethylsilane as an internal reference

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A Novel Preparation of Tetraethylpyrophosphite

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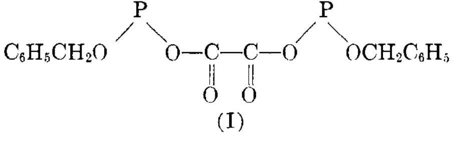
Mason and Todd[1] have described a preparation of tetrabenzyl pyrophosphate based on the reaction of oxalyl chloride and dibenzyl phosphate to give the comparatively stable intermediate (I)



(I)

which subsequently rearranges losing carbon dioxide and carbon monoxide. We wish to report the preparation of tetraethyl pyrophosphite (III) by a closely related method, from diethyl phosphorochloridite and silver carbonate in an inert solvent.

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(1) H. S. Mason and A. R. Todd, *J. Chem. Soc.*, 2267 (1951).