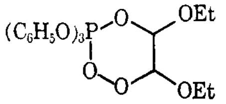
Therefore the possibility of rotation in the two successive intermediates is attractive. In addition, loss of triphenyl phosphate from **12** should leave **13** in an extended conformation with a resulting greater aptitude for rotation.

An intermediate such as **14** is probably not involved in this reaction as it would probably be no less stable than the ozonide **2** and therefore should have been observable at −78° by nmr.



14

Further work on the direct reactions of triphenyl phosphite ozonide with vinyl ethers and other olefins is in progress.

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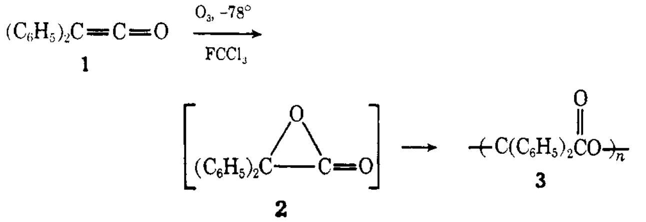
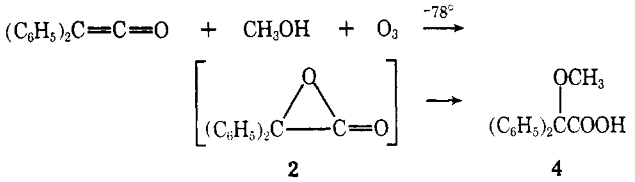
α-Lactones from Diphenylketene and Di-*tert*-butylketene

Sir:

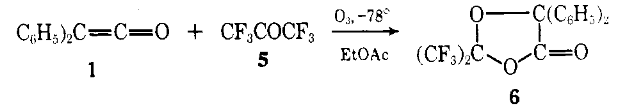
Persuasive evidence exists that α-lactones occur as intermediates in certain displacement[1,2] and free-radical[3-5] reactions. In view of past observations that ozone is an epoxidizing agent toward highly hindered alkenes,[6-8] we ozonized diphenylketene (**1**) in chlorotrifluoromethane (Freon 11) at −78°. A white, insoluble precipitate appeared at once. It was dissolved in chloroform and reprecipitated by pouring into petroleum ether; yield of purified product, 49%. Its ir spectrum, determined in chloroform solution, was identical with that of the benzilic acid polyester previously obtained from the thermal decomposition of di-*tert*-butylperoxy diphenylmalonate.[4] A determination with the vapor phase osmometer[9] gave a molecular weight of 6483, corresponding to $n = 31$ in formula **3**. Polyester **3** gave satisfactory elemental analyses. With methanol in refluxing benzene **3** yielded α-methoxydiphenylacetic acid (**4**), mp 106–107°, identified by ir.

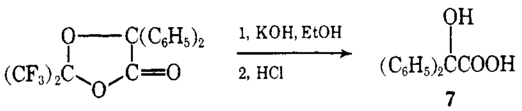


At temperatures as low as −100° the precipitate of **3** was immediate on oxonization of **1**, showing that the diphenylacetolactone (**2**) was of exceedingly short life. It could, however, be trapped in two ways. When **1** was added slowly to a solution of excess ozone in methanol at −78°, **4** resulted in a yield of 60%. Since methanol did not react with the polyester **3** under the conditions of the reaction or work-up, it is clear that the precursor of **3** had been intercepted by methanol in this experiment.

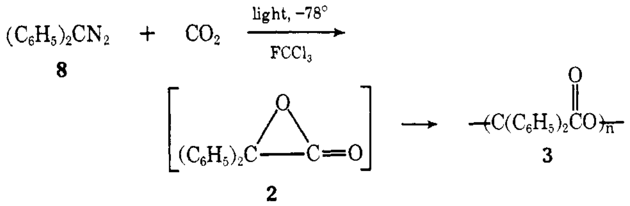


In another experiment at −78°, ozone was passed into an emulsion of **1**, ethyl acetate, and hexafluoroacetone (**5**). The product **6** could be distilled at 143° and passed unchanged through vpc at 155°, showing that it is neither a peroxylactone[10] nor an allene ozonide. The structure of **6** was confirmed by alkaline hydrolysis to benzilic acid (**7**), mp 151–152°, neut equiv 228, and by elemental analysis, ir (C=O at 1830 cm^{-1}), and mass spectrum (strong parent peak and parent $-CO_2$; base peak $C_6H_5CO^+$; prominent $(C_6H_5)_2CO^+$ peak).





A second way to produce an α-lactone is, in principle, the addition of a carbene to carbon dioxide. Diphenyldiazomethane (**8**) dissolved sufficiently in liquid carbon dioxide at room temperature in a sealed tube to yield a pink solution whose color did not fade, indicating the absence of any thermal reaction. However, when photolyzed at −78° in a slurry of Dry Ice and fluorotrichloromethane, **8** yielded **3** in 40% yield; this **3** was again converted into **4** by methanol in refluxing benzene.



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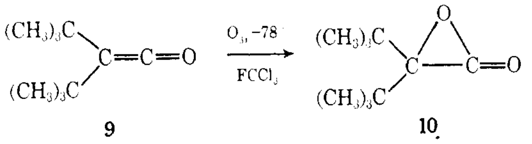
A more hindered ketene than **1**, and one whose related α-lactone seemed less likely to exist in an open, dipolar form, is di-*tert*-butylketene (**9**).[11] Ozonized in Freon 11 at −78°, **9** reacted and yielded a clear, stable solution. That this solution contained di-*tert*-butylacetolactone (**10**) was indicated by the following facts. (a) Ammonia gas gave a quantitative precipitation of di-*tert*-butylglycine (**11**), whose nmr spectrum in concentrated HCl showed the *tert*-butyl singlet at δ 2.0, and which gave a correct elemental analysis. In contrast to the nmr of **11** hydrochloride, showing a normal downfield shift due to a neighboring positive charge, the spectrum of **10** in solution at −60° showed a chemical shift of δ 1.2, identical with that of **9** and di-*tert*-butyl ketone. (b) On warming the solution of **10** to −20° a white precipitate began to form, which became a 91% yield of polyester. (c) When hexafluoroacetone (**5**) was added to the Freon 11 solution of **10** at −78° and the mixture brought to room temperature, two rearranged products were isolated after distillation, **12** in a yield of 29% and **13** in a yield of 21%. **12** shows a parent peak in its mass spectrum, exact mass 126.1403 (calcd 126.1408), a *tert*-butyl singlet in the nmr at δ 1.23, and broad peaks at 1.6 (6 H) and 1.8 (3 H). **13** has a β-lactone carbonyl absorption in the ir at 1820 cm^{-1} and shows nmr peaks for *tert*-butyl at δ 1.2 and for methyls at 1.4, 1.5, and 1.7. **13** loses carbon dioxide upon vapor phase chromatography, yielding **12**; the highest peak in its mass spectrum corresponds to $C_9H_{18}^+$.



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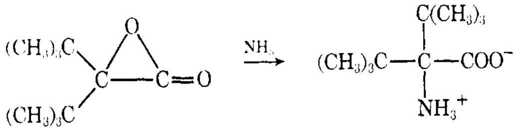
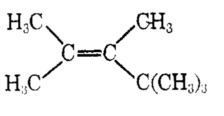


10 11



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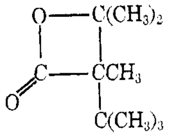
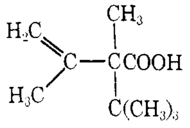


13

A similar change of solvent from Freon 11 to diethyl ether, followed by vapor chromotography, yielded **12** (27%) and, instead of **13**, a 7% yield of 2,3,4,4-tetramethyl-1-pentene-3-carboxylic acid (**14**), whose structure was shown by elemental analysis and nmr spectrum: nmr of **14**, δ 12.3 (s, 1 H), 5.04 (s, 1 H), 4.94 (s, 1 H), 1.9 (s, 3 H), 1.4 (s, 3 H), 1.2 (s, 9 H).



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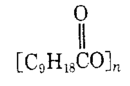
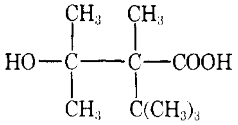


$$[C_9H_{18}\overset{O}{\overset{\|}{C}}O]_n$$

15

The polyester that precipitated on warming the α-lactone **10** was shown by elemental analysis to have a composition corresponding to di-*tert*-butylglycolic acid polyester (**15**). Its thermal decomposition began at 20° and became rapid at 80°, leading to **12** in 85% crude yield (54% yield after vpc purification) and **14** in 1.4% yield. Although this result suggests that **10** underwent total rearrangement on polymerization, two alkaline degradations of **15** are ambiguous on this point. Potassium hydroxide in ethanol at reflux brought about slow hydrolysis with isolation of 8% of the rearranged acid **14**, but sodamide in ether at room temperature afforded 23.3% of di-*tert*-butyl ketone along with 4.4% of **12**. The latter result requires that, if the units of **15** were all those of the rearranged hydroxy acid **16**, sodamide must have induced the reverse rearrangment into the original highly hindered structure **17**. Such a rearrangement seems highly improbable and we prefer to regard **15** as mainly the polyester of di-*tert*-butylglycolic acid (**17**).



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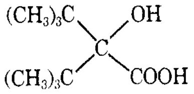
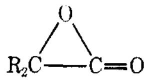
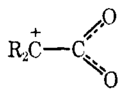


17

The behavior of the two α-lactones is consistent with the hypothesis, supported by HMO calculations,[12] that only a small energy separates the closed form of an α-lactone **18a** from its 1,3-dipolar ionic isomer **18b** as in the case of cyclopropanones.[13-15] The two phenyl groups when R = C_6H_5 so delocalize the positive charge that the compound is dipolar even at −100°, hence undergoing immediate zwitterionic polymerization. When R = $(CH_3)_3C$ the charge in **18b** is more poorly accommodated, and in Freon 11 below −30° the form **18a**, well shielded against attack, is stable. The fact that solvents more polar than Freon 11 cause a "neopentyl" rearrangement is consistent with the hypothesis that the equilibrium **18a** ⇌ **18b** is shifted to the right by even a mildly polar solvent.



18a



18b

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