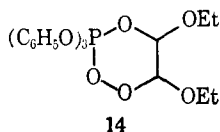


Therefore the possibility of rotation in the two successive intermediates is attractive. In addition, loss of triphenyl phosphite from **12** should leave **13** in an extended conformation with a resulting greater aptitude for rotation.

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  $-78^\circ$  by nmr.



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

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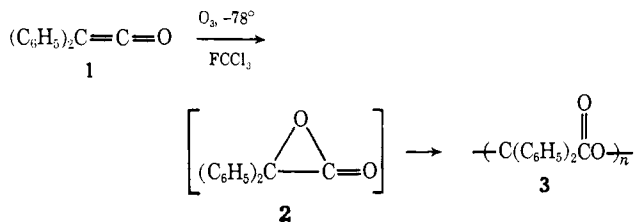
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 Received July 18, 1970

### $\alpha$ -Lactones from Diphenylketene and Di-*tert*-butylketene

Sir:

Persuasive evidence exists that  $\alpha$ -lactones occur as intermediates in certain displacement<sup>1,2</sup> and free-radical<sup>3-5</sup> reactions. In view of past observations that ozone is an epoxidizing agent toward highly hindered alkenes,<sup>6-8</sup> we ozonized diphenylketene (**1**) in chlorotrifluoromethane (Freon 11) at  $-78^\circ$ . 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.<sup>4</sup> A determination with



(1) W. A. Cowdrey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1208 (1937).

(2) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 841 (1948).

(3) C. Walling and E. S. Savas, *ibid.*, **82**, 1738 (1960).

(4) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963).

(5) J. E. Leffler and R. G. Zepp, *ibid.*, **92**, 3713 (1970).

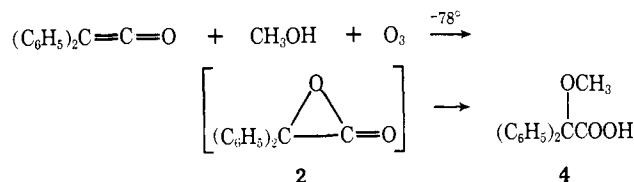
(6) P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2806 (1955).

(7) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(8) P. S. Bailey and A. G. Lane, *J. Amer. Chem. Soc.*, **89**, 4473 (1967).

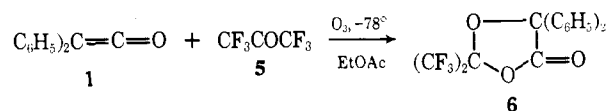
the vapor phase osmometer<sup>9</sup> gave a molecular weight of 6483, corresponding to  $n = 31$  in formula **3**. Polyester **3** gave satisfactory elemental analyses. With methanol in refluxing benzene **3** yielded  $\alpha$ -methoxydiphenylacetic acid (**4**), mp  $106\text{--}107^\circ$ , identified by ir.

At temperatures as low as  $-100^\circ$  the precipitate of **3** was immediate on ozonization 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  $-78^\circ$ , **4** resulted in a yield of 60%. Since

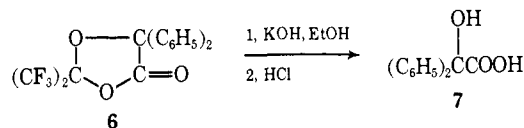


methanol did not react with the polyester **3** under the conditions of the reaction or work-up, it is clear that the precursor of **3** had been intercepted by methanol in this experiment.

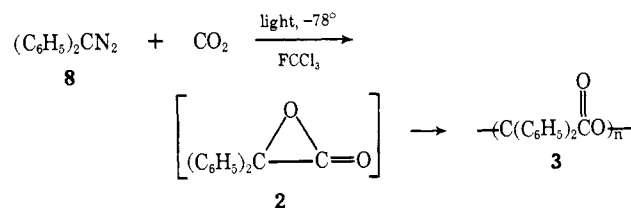
In another experiment at  $-78^\circ$ , ozone was passed into an emulsion of **1**, ethyl acetate, and hexafluoroacetone (**5**). The product **6** could be distilled at  $143^\circ$



and passed unchanged through vpc at  $155^\circ$ , showing that it is neither a peroxy lactone<sup>10</sup> nor an allene ozonide. The structure of **6** was confirmed by alkaline hydrolysis to benzilic acid (**7**), mp  $151\text{--}152^\circ$ , neut equiv 228, and by elemental analysis, ir ( $\text{C}=\text{O}$  at  $1830\text{ cm}^{-1}$ ), and mass spectrum (strong parent peak and parent  $-\text{CO}_2$ ; base peak  $\text{C}_6\text{H}_5\text{CO}^+$ ; prominent  $(\text{C}_6\text{H}_5)_2\text{CO}^+$  peak).



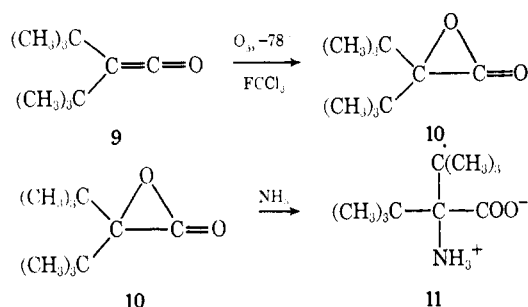
A second way to produce an  $\alpha$ -lactone is, in principle, the addition of a carbene to carbon dioxide. Diphenyldiazomethane (**8**) dissolved sufficiently in liquid carbon dioxide at room temperature in a sealed tube to yield a pink solution whose color did not fade, indicating the absence of any thermal reaction. However, when photolyzed at  $-78^\circ$  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.



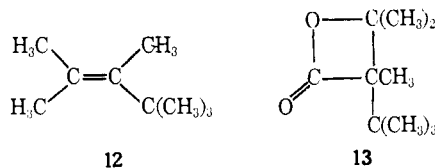
(9) By Galbraith Laboratories, Knoxville, Tenn.

(10) W. Adam and Y. M. Cheng, *J. Amer. Chem. Soc.*, **91**, 2109 (1969).

A more hindered ketene than **1**, and one whose related  $\alpha$ -lactone seemed less likely to exist in an open, dipolar form, is di-*tert*-butylketene (**9**).<sup>11</sup> Ozonized in Freon 11 at  $-78^\circ$ , **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  $\delta$  2.0, and which gave a correct elemental analysis. In contrast to the nmr of **11** hydrochloride, showing a normal

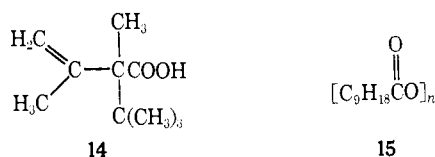


downfield shift due to a neighboring positive charge, the spectrum of **10** in solution at  $-60^\circ$  showed a chemical shift of  $\delta$  1.2, identical with that of **9** and di-*tert*-butyl ketene. (b) On warming the solution of **10** to  $-20^\circ$  a white precipitate began to form, which became a 91% yield of polyester. (c) When hexafluoroacetone (**5**) was added to the Freon 11 solution of **10** at  $-78^\circ$  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



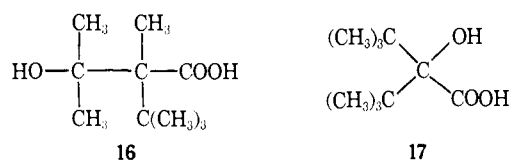
parent peak in its mass spectrum, exact mass 126.1403 (calcd 126.1408), a *tert*-butyl singlet in the nmr at  $\delta$  1.23, and broad peaks at 1.6 (6 H) and 1.8 (3 H). **13** has a  $\beta$ -lactone carbonyl absorption in the ir at  $1820\text{ cm}^{-1}$  and shows nmr peaks for *tert*-butyl at  $\delta$  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  $\text{C}_9\text{H}_{18}^+$ .

A similar change of solvent from Freon 11 to diethyl ether, followed by vapor chromatography, 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**,  $\delta$  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).

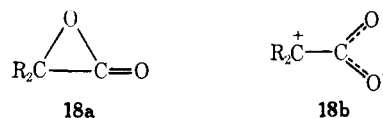


(11) M. S. Newman, A. Arkell, and T. Fukunaga, *J. Amer. Chem. Soc.*, **82**, 2498 (1960).

The polyester that precipitated on warming the  $\alpha$ -lactone **10** was shown by elemental analysis to have a composition corresponding to di-*tert*-butylglycolic acid polyester (**15**). Its thermal decomposition began at  $20^\circ$  and became rapid at  $80^\circ$ , 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 rearrangement 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**).



The behavior of the two  $\alpha$ -lactones is consistent with the hypothesis, supported by HMO calculations,<sup>12</sup> that only a small energy separates the closed form of an  $\alpha$ -lactone **18a** from its 1,3-dipolar ionic isomer **18b** as in the case of cyclopropanones.<sup>13-15</sup> The two phenyl



groups when  $\text{R} = \text{C}_6\text{H}_5$  so delocalize the positive charge that the compound is dipolar even at  $-100^\circ$ , hence undergoing immediate zwitterionic polymerization. When  $\text{R} = (\text{CH}_3)_3\text{C}$  the charge in **18b** is more poorly accommodated, and in Freon 11 below  $-30^\circ$  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  $\text{18a} \rightleftharpoons \text{18b}$  is shifted to the right by even a mildly polar solvent.

**Acknowledgment.** This work was supported by the National Science Foundation and the National Institutes of Health. R. Wheland thanks the National Science Foundation for a Graduate Fellowship from 1966 to the present.

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(13) J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

(14) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(15) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968), but see N. Bodor, M. T. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

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