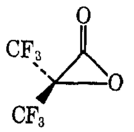
Communications

See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

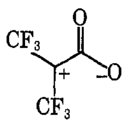
Bis(trifluoromethyl)acetolactone, a Stable α-Lactone[1]

Summary: Photolysis of bis(trifluoromethyl)malonyl peroxide (**2**) affords bis(trifluoromethyl)acetolactone (**1**), which on heating suffers decarbonylation into hexafluoroacetone (**3**) and on ethanolysis addition at the carbonyl bond leading to ethyl α-hydroxyhexafluoroisobutyrate (**6**).

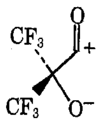
Sir: Instead of "steric stabilization" of α-lactones[2] as excercised by the *tert*-butyl group,[3] we have employed the concept of "electronic stabilization" exhibited by the trifluoromethyl group,[4] in an effort to diminish the high propensity toward self-polymerization of the elusive α-lactones. The trifluoromethyl group was expected to discourage formation of the dipolar structure since electron density should be drawn from the negative oxygen pole toward the α carbon, thereby promoting formation of the cyclic structure **1a**. Presently we are reporting the preparation and characterization of bis(trifluoromethyl)acetolactone (**1**) and its thermolysis and ethanolysis.



1a

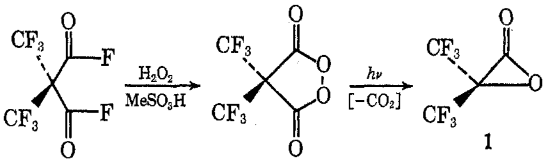


1b



1c

The precursor to α-lactone **1**, bis(trifluoromethyl)malonyl peroxide (**2**), was prepared in 20% yield by reaction of bis(trifluoromethyl)malonyl difluoride with 98% H_2O_2 in methanesulfonic acid at 0° (eq 1). This material, rectified by fractional distillation [bp 62° (760 mm), 98% pure by iodometric titration], was characterized on the basis of its ir, fmr, and mass spectra. Photolysis of a matrix of **2** at 77°K by means of a 800-W Hg high pressure arc directly in a low temperature ir cell (Air Products Co.)[5] led to immediate consumption of the C=O bands of **2** at 1870–1825 cm^{-1} and simultaneous appearance of new C=O bands at 2350 (CO_2) and 1970 cm^{-1} (α-lactone). On preparative scale, the α-lactone **1** could be more conveniently produced by photolysis of a 0.32 *M* CCl_4 solutions of **2** at −15° in a Pyrex vessel, resulting in rapid conversion of **2** (87% in 1 hr) into **1**, as evidenced by fmr monitoring. This solution which is stable toward further photolysis under the conditions employed for its formation,[6] can be stored in the freezer at −20° for many days with negligible reduction of the intensity of its 1975-cm^{-1} C=O band in the ir. At ambient conditions bis(trifluoromethyl)acetolactone (**1**) is a gas (C=O band at 1980 cm^{-1} and parent ion at *m/e* 194) persisting at 24° with a half-life of 8 hr.



2 (1)

The major product (66% yield) of the thermal decomposition of CCl_4 solutions of α-lactone **1** at 25–40° was hexafluoroacetone (**3**). Also the insoluble perfluorinated polyester **5** with C=O band at 1820 cm^{-1} settled out. The kinetics of the thermolysis of **1** in CCl_4 solution was examined directly in a thermostated ir cell and followed first-order rate law, affording $\Delta H^{\ddagger} = 18.2 \pm 0.8$ kcal/mol, $\Delta S^{\ddagger} = -12.8 \pm 2.8$ gibbs/mol, and $\Delta G^{\ddagger}$ (300°K) = 22 ± 1 kcal/mol. Significant was the observation that addition of polar solvents such as acetonitrile to the CCl_4 solution of α-lactone **1** led to a ~10-fold increase in the rate of α-lactone destruction at 300°K. Thus, efforts to isolate the pure α-lactone **1** in the condensed phase failed since **1** by itself must be sufficiently polar to promote self-annihilation.

Informative on the structural nature of α-lactone **1** is its chemical behavior toward ethanol. Addition of ethanol to a CCl_4 solution of **1** resulted in the formation of ethyl α-hydroxyperfluoroisobutyrate (**6**) and ethyl hemiacetal (**4**) in the ratio of 3:2, respectively, identified by comparison of their ir, fmr and pmr, and mass spectra with those of the authentic substances. We could not detect any α-ethoxyhexafluoroisobutyric acid, the usual alcoholysis product of α-lactones derived from the dipolar form **1b**.[2] Attempts to trap the α-lactone **1** with dipolarophiles[7] such as bis(trifluoromethyl)ketene, 1,3-cyclohexadiene, and *cis*-dimethoxyethylene have led predominantly to decarbonylation rather than 1,3-dipolar addition.

A mechanistic rationalization consistent with these facts is given in eq 2. As anticipated, the trifluoromethyl groups discourage opening of the α-carbon–ether oxygen bond into dipole **1b**, so that even at room temperature the cyclic valence isomer **1a** persists in the gaseous and condensed phases. This conclusion is supported by the fact that its C=O band lies at 1975 ± 5 cm^{-1} in the matrix, CCl_4 solution, and vapor. Consistent with the cyclic structure **1a** is the fact that on heating carbon monoxide is extruded, a reaction which is typical for the related cyclopropanones.[8]

The relatively low $\Delta H^{\ddagger}$ for decarbonylation of **1a**

---

[1] Cyclic Peroxides. XXIII. For preceding paper, see W. Adam and N. Duran, *J. Chem. Soc. Chem. Commun.*, 798 (1972).

[2] (a) W. Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971); (b) W. Adam, O. L. Chapman, O. Rodriguez, R. Rucktäschel, and P. W. Wojtkowsky, *ibid.*, **94**, 1365 (1972).

[3] Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 6057 (1970).

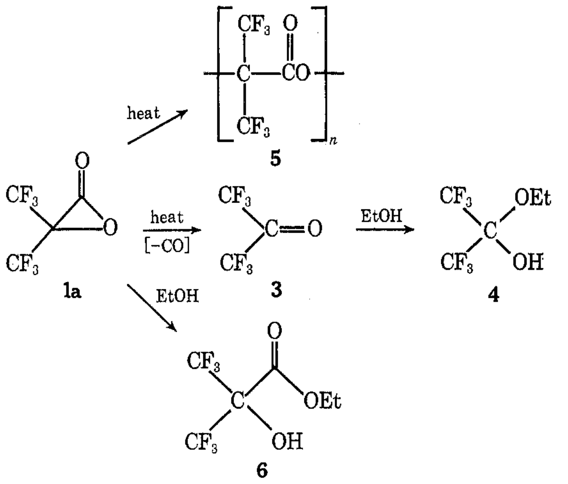
[4] D. M. Lemal and L. H. Dunlap, Jr., *J. Amer. Chem. Soc.*, **94**, 6562 (1972).

[5] We are grateful to Professor O. L. Chapman for advising us on this experimental set-up.

[6] Usually (*cf.* ref 2) α-lactones readily photodecarbonylate, but **1** is transparent above 300 nm.

[7] N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

[8] D. B. Sclove, J. F. Pazos, R. L. Camp, and F. D. Greene, *J. Amer. Chem. Soc.*, **92** 7488 (1970



(2)

hints at a considerable strain inherent with this ring system, while the rather negative $\Delta S^{\ddagger}$ suggests chelotropic decarbonylation[9] similar to the thermolysis of episulfones.[10] In polar media, *e.g.*, acetonitrile or ethanol, opening of the carbonyl carbon–ether oxygen bond in **1a** leading to dipole **1c**, first suggested as a possible α-lactone structure in the thermolysis of anhydro sulfites,[11] presumably competes with concerted decarbonylation. Thus, in the aprotic CH_3CN solvent dipole **1c**, but not **1b**, may serve as a common precursor to ketone **3** and polyester **5** owing to lowering of the activation energy for heterolysis of the carbonyl carbon–ether oxygen bond as a consequence of solvation. Even in the protic EtOH solvent the thermal decay of **1** into **3** (observed as its hemiketal **4**) competes favorably with the addition of EtOH at the carbonyl group of **1**, analogous to cyclopropanones,[7] affording the α-hydroxy ester **6**. However, the formation of dipole **1b**, the accepted reactive form of α-lactones,[2] cannot be significant since we fail to detect any α-alkoxy acids, the usual alcolysis product of α-lactones.

In conclusion, on the basis of the presented facts, particularly the thermal decarboxylation and ethanol addition at the carbonyl group, we propose that bis(trifluoromethyl)acetolactone (**1**), in contrast to previous cases,[2] acts through its cyclic structure **1a**. Although our approach of "electronic stabilization" of α-lactones has proved rewarding, we must cope with the limitation that such species can so far be preserved only in matrix form, in solutions of nonpolar solvents, or in their vapor phase since their inherent polar nature dictates their self-destruction.

Acknowledgments.—We are particularly indebted to Dr. D. C. England of E. I. du Pont de Nemours and Co. for the generous supply of bis(trifluoromethyl)malonyl difluoride, his interest, and valuable advice. Financial support by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged.

---

[9] (a) R. B. Woodward and R. Hoffmann, "Die Erhaltung der Orbital Symmetrie," Verlag Chemie, Germany, 1970; (b) A. Liberles, A. Greenberg, and A. Lesk, *J. Amer. Chem. Soc.*, **94**, 8685 (1972); (c) J. P. Snyder, R. J. Boyd, and M. A. Whitehead, *Tetrahedron Lett.*, 4347 (1972).

[10] F. G. Bordwell, J. M. Williams, E. B. Hoyt, Jr., and B. B. Jarvis, *J. Amer. Chem. Soc.*, **90**, 429 (1968).

[11] D. G. H. Ballard and P. J. Tighe, *J. Chem. Soc. B*, 702 (1967).

[12] A. P. Sloan Fellow (1968–1972).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PUERTO RICO
RIO PIEDRAS, PUERTO RICO
00931, U. S. A.

WALDEMAR ADAM*[12]
JU-CHAO LIU
OSVALDO RODRIGUEZ

RECEIVED MARCH 7, 1973