TABLE I

RADIATION-CATALYZED OXALYL CHLORIDE–ETHYLENE TELOMERIZATION AT 25°

Run no.[a]	$[(COCl)_2]_0$ / $[C_2H_4]_0$ (mole ratio)[b]	Telomer yield (mole % on telogen) 1:1	2:1	3:1	G (telomers)[c]	C_n[d] $n = 1$ (k_2/k_4)	$n = 2$	$n = 3$
1	0.59	0.60	4.68	0.06	500	0.21 (0.22)	~120	~6
2	0.60	..	...	...	~100	.. (0.21)[e]	...	...
3	1.1	2.9	10.2	0.08	1400	0.26 (0.26)	~110	~7
4	1.1	...	...	...	~50	..	...	...
5[f]	1.1	2.1	8.60	0.07	220	0.22 (0.22)	~110	~7
6[g]	1.1	0	0	0	0	..	...	...
7	1.9	4.2	9.55	0.02	1500	0.23 (0.23)	~180	~0.3
8	1.9	...	...	...	~50	..	...	...

[a] Dose rate in each run = 1.5 × 10^4 rep (in water); dosage = 0.63 M rep except in runs 5 (3.2 M rep) and 6 (2.4 M rep). [b] For liquid phase. [c] Based on uncorrected radiation dosages. [d] See ref. 4 for formula. [e] Only 1:1–2:1 yield ratio was determined. [f] Recovered 0.99 mole of carbon monoxide/mole of telomers. [g] Starting mixture contained 1 mole % oxygen.

b.p. 63–64° (4 mm.), lit.[12] b.p. 56–58° (2.5 mm.), neut. equiv. 77.5 (calcd. 77.5), and likewise 7-chloroheptanoyl chloride, b.p. 82° (2 mm.), neut. equiv. 91.0 (calcd. 91.5). Reaction of the acid chlorides with ethanol gave, after distillation, 99+ wt. % pure samples of ethyl 5-chloropentanoate, b.p. 83.5–84.5° (8 mm.), n^{25}_D 1.4339, lit.[13] b.p. 83.5–85° (8 mm.), n^{20}_D 1.4355, and ethyl 7-chloroheptanoate, b.p. 91.5° (2 mm.), n^{25}_D 1.4391.

---

[12] N. Clark and A. Hams, *J. Biochem.*, **55**, 839 (1953).

[13] L. Cheney and J. R. Piening, *J. Am. Chem. Soc.*, **67**, 731 (1947).

The Isolation of a Cyclic Intermediate in the Ketone–Alkoxyacetylene Reaction

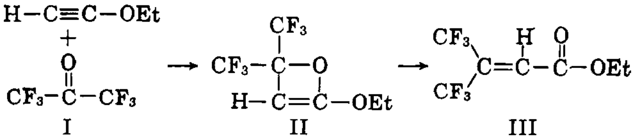
W. J. MIDDLETON

Contribution No. 1026 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received November 9, 1964

Ketones react with alkoxyacetylenes in the presence of boron trifluoride catalyst to give α,β-unsaturated esters in high yield.[1] The formation of an oxete as a cyclic intermediate has been postulated for this reaction,[1] but such an intermediate has not been isolated previously.

We have found that hexafluoroacetone (I) reacts vigorously and exothermically with ethoxyacetylene without added catalyst. When the reaction is conducted at room temperature, ethyl β,β-bis(trifluoromethyl)acrylate (III) is formed. If the reaction is carried out at lower temperatures, however, the intermediate oxete II can be isolated and characterized. This oxete II slowly isomerizes to the ester III if stored at room temperature for a few days. This rearrangement is exothermic and becomes rapid at about 70°.



I II III

Experimental[2]

2-Ethoxy-4,4-bis(trifluoromethyl)-2-oxete.—Hexafluoroacetone, 10.5 ml. measured at −78° (0.1 mole), was slowly distilled into a flask that contained 7.0 g. (0.1 mole) of freshly distilled ethoxyacetylene precooled to −78°. Strong cooling was maintained during the entire addition. The dark reaction mixture was distilled at reduced pressure to give 20.1 g. (85% yield) of 2-ethoxy-4,4-bis(trifluoromethyl)-2-oxete as a colorless oil, b.p. 29–30° (8 mm.), n^{25}_D 1.3331. The F^{19} n.m.r. spectrum showed a singlet at 10.7 p.p.m., and the proton n.m.r. spectrum showed a singlet at 4.60 p.p.m. in addition to resonance lines attributed to the ethyl group. The infrared spectra contained a band at 5.93 for C=C and at 3.14 μ for =CH.

Anal. Calcd. for $C_7H_6F_6O$: C, 35.61; H, 2.57; F, 48.28. Found: C, 35.41; H, 2.87; F, 48.22.

Ethyl β,β-Bis(trifluoromethyl)acrylate.—A sample of 2-ethoxy-4,4-bis(trifluoromethyl)-2-oxete that had been stored at room temperature for 2 weeks was found to have isomerized quantitatively to ethyl β,β-bis(trifluoromethyl)acrylate, b.p. 126–127°, n^{25}_D 1.3382.[3] The infrared spectrum of this ester contained bands at 5.96 (C=C) and 5.72 μ (C=O). The F^{19} n.m.r. spectrum showed two quartets (J = 8 c.p.s.) centered at −4.61 and −0.18 p.p.m. The proton n.m.r. spectrum contained a singlet at 7.22 p.p.m. in addition to resonance lines attributed to the ethyl group.

Anal. Calcd. for $C_7H_6F_6O_2$: C, 35.61; H, 2.57; F, 48.28. Found: C, 34.45; H, 2.73; F, 48.07.

---

[1] H. Vieregge, H. J. T. Bos, and J. F. Arens, *Rec. trav. chim.*, **78**, 664 (1959).

[2] Fluorine n.m.r. spectra were obtained with a Varian Associates high-resolution n.m.r. spectrometer operating at 56.4 Mc./sec. Spectra were calibrated in terms of higher field displacement in p.p.m. from the F^{19} resonance of 1,2-difluorotetrachloroethane used as an external reference. Proton resonance spectra were obtained with a Varian Associates A-60 spectrometer. Spectra were calibrated in terms of lower field displacement in p.p.m. from the proton resonance of tetramethylsilane used as an internal reference.

[3] I. L. Knunyants and Yu. A. Cherburkov [*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2162 (1960)] report b.p. 128° (747 mm.) and n^{20}_D 1.3414 for this compound, which was prepared by the esterification of the corresponding acid.

(+)- and (−)-(Isopropylidenaminooxy)-propionic Acid

PAUL BLOCK, JR.

Department of Chemistry, University of Toledo, Toledo 6, Ohio

Received November 16, 1964

In 1955 Newman and Lutz[1] introduced optically active α-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy)-propionic acid, subsequently abbreviated TAPA,[2] for the resolution of polycyclic aromatic hydrocarbons which do not possess a functional group capable of salt formation with an optically active acid or base. This compound consists of the complexing agent, tetranitro-

---

[1] M. S. Newman and W. B. Lutz, *J. Am. Chem. Soc.*, **78**, 2469 (1956).

[2] M. S. Newman and D. Lednicer, *ibid.*, **78**, 4765 (1956).