

Arbeitsvorschriften und Meßwerte • Procedures and Data

Ozonolyses of Acetylenes Revisited

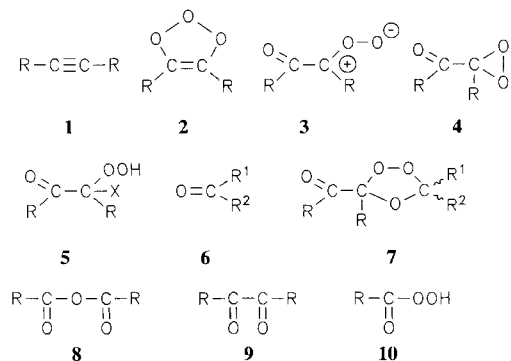
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Ozonolyses of substituted acetylenes **1** have been described to start by a Criegee-type mechanism to give sequentially intermediates of type **2** and **3** [1]. In contrast to ozonolyses of olefins, however, only anomalous products have been obtained from ozonolysis reactions of acetylene hydrocarbons **1** in non-participating solvents, *viz.* anhydrides **8**, diketones **9** and oligomeric peroxides of undetermined structures [1]. The formation of anhydrides **8** has been explained by isomerization of α -oxo carbonyl oxides **3**, possibly via α -oxo dioxiranes **4**, whereas no plausible explanation has been advanced for the formation of diketones **9**.

The intermediacy of α -oxo carbonyl oxides **3** has been convincingly demonstrated by trapping reactions with participating solvents HX (alcohols [1,2], carboxylic acids [1]) to give the corresponding hydroperoxides **5** or with carbonyl compounds **6** (aldehydes, ketones, acid derivatives) to give the corresponding α -oxo ozonides **7** [3]. The existence of α -oxo dioxiranes **4** has been inferred from the fact, that addition of cyclohexene to the crude product obtained from the ozonolysis of but-2-yne in CH_2Cl_2 gave cyclohexene epoxide [4]. But neither **4** nor peroxy acids **10**, which had been also postulated as epoxidizing agents in such crude ozonolysis products [4] could be verified. In the present study, we have readdressed the questions concerning products and their mode of formation in the ozonolysis of acetylenes in non-participating solvents.

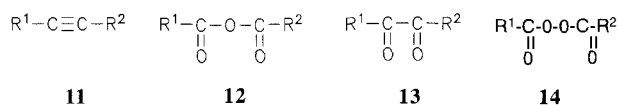


Results

The most widely used non-participating solvent for ozonolyses is pentane. However, ozonolysis of but-2-yne (**11a**) in pentane at -75°C gave a violent explosion. The ozonolysis reactions were, therefore, carried out in dichloromethane. Ozonolyses of but-2-yne (**11a**), hex-3-yne (**11b**) and 1-phenylpropyne (**11c**) at -60 to -75°C gave peroxidic reaction products, in which the corresponding compounds **12**–**14** have been identified by ^1H NMR analysis in the proportions given. To our knowledge, this is the first time that diacyl peroxides **14** have been found as ozonolysis products of acetylenes. They have been isolated in yields of 4% (**11a**), 10% (**11b**) and 7% (**11c**) and characterized by ^1H NMR spectroscopy with the help of authentic samples.

The ^1H NMR spectra of all crude reaction products showed additional, unassigned signals. In the spectrum of the ozonolysis product of but-2-yne (**11a**), these were multiplets in the range of $\delta/\text{ppm} = 1.40$ – 1.80 and 2.10 – 2.30 , which we have assumed to be due to polymeric peroxides. In order to assess their amount, we have carried out ozonolyses of **11a** in CD_2Cl_2 and in the presence of 1,1,2,2-tetrachloroethane as an internal standard. This analysis showed that the sum of the yields of **12a**–**14a** and acetic acid amounted to 92%, thus leaving room for ca. 8% of polymeric peroxides. An attempt to isolate the polymeric peroxides failed, since the product mixture deflagrated after the solvent had been evaporated. Evaporation of small samples, by contrast, was possible without any deflagration. In another experiment, the crude ozonolysis product was treated with triphenyl phosphine, whereupon the unassigned signals and that of **14a** disappeared, and compounds **12a** (52%), **13a** (13%) and acetic acid (35%) were detected as the sole products by ^1H NMR spectroscopy.

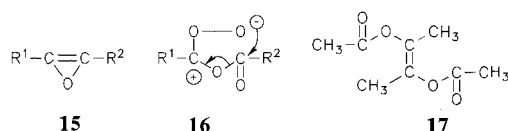
The formation of diacyl peroxides **14** may be explained by epoxidation of the acetylenes **11** to give the corresponding oxirenes **15**. The latter may be immediately ozonized to give intermediates **16**, which undergo the rearrangement indicated by the arrows to give diacyl peroxides **14**. This proposal derives support from the following facts: 1) It has been



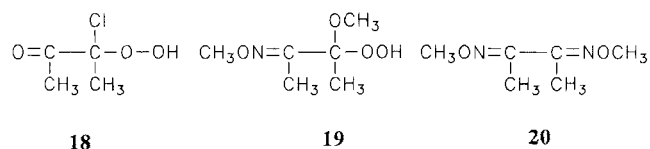
	Substrate 11		Relative proportion, %		
	R ¹	R ²	12	13	14
a	CH ₃	CH ₃	64 ^{a)}	8	7
b	CH ₃ CH ₂	CH ₃ CH ₂	52	25	23
c	C ₆ H ₅	CH ₃	54	29	17

^{a)} In addition, 21% of acetic was present

reported [4] that the crude ozonolysis product of **11a** has a high potential for the epoxidation of olefins even at -70°C . 2) Products **13** and **14** have been obtained in roughly equimolar amounts, which may indicate that α -oxo carbonyl oxides **3** or the isomeric dioxiranes **4** are the epoxidizing agents. This would also explain the origin of diketones **13**. 3) Ozonolysis of **17** in dichloromethane has been shown previously [5] to give acetic anhydride **12a** and diacetyl peroxide **14a** in a ratio of 1:1, the latter via the same intermediate **16a**, which we have postulated for the formation of **14a** from **11a**.



In some experiments, the ¹H NMR spectra of the crude ozonolysis products of **11a** showed two minute singlet signals at $\delta/\text{ppm} = 1.36$ and 2.43 . We suspected, that they may be due to the α -oxo- α -chloro hydroperoxide **18**, which could have been formed by partial oxidative decomposition of CH₂Cl₂ and addition of the formed HCl to the α -oxo carbonyl oxide derived from **11a**. Precedents for such trappings of carbonyl oxides by HCl to give α -chloro hydroperoxides are known [6]. We tested our hypothesis by ozonizing **11a** in CH₂Cl₂ which was saturated with gaseous HCl. ¹H NMR analysis showed indeed two new singlet signals, however, with different chemical shifts than the minor signals at $\delta/\text{ppm} = 1.36$ and 2.43 . These new signals at $\delta/\text{ppm} = 1.90$ and 2.40 were tentatively assigned to **18**. As expected, **18** was a rather unstable compound. It was converted into acetic acid and acetyl chloride so that it could not be isolated. Nevertheless, its existence could be proven by treatment of the reaction mixture with O-methyl hydroxylamine in methanol to give a mixture of the stable α -methoximino hydroperoxide **19** [2], and of the O-methylated dioxime of butanedione (**20**) in a molar ratio of 6:1.



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Experimental

¹H and ¹³C NMR: Bruker AC 250, CDCl₃, TMS. Chromatographic separations: Flash chromatography on silica gel; solvent: pentane/ether, 20:1.

Ozonolysis of But-2-yne (**11a**) in Pentane

When a solution of 0.62 g (11.5 mmol) of **11a** in 60 ml of pentane was exhaustively ozonized at -75°C , a colorless viscous material precipitated at the walls of the reaction flask. After termination of the ozonolysis reaction, residual ozone was flushed off with nitrogen and the cooling bath was removed to allow the mixture to warm up. After a few minutes a violent explosion occurred, which led to the complete destruction of the reaction flask.

Ozonolyses of Acetylenes **11** in Dichloromethane: Synthesis of Anhydrides **12**, Diketones **13** and Diacyl Peroxides **14** (General Procedure)

A solution of an acetylene **11** in dichloromethane was completely ozonized at low temperatures and the mixture was warmed up to room temperature. A sample of 1 ml was removed, the solvent was evaporated and the residue was submitted to ¹H NMR analysis. The bulk of the solution was admixed with an equal volume of water and the mixture was stirred overnight. The organic phase was separated, sequentially washed with a 10% aqueous solution of sodium hydroxide and with water, dried with MgSO₄ and concentrated by distilling the solvent in a rotary evaporator. From the residue the diacyl peroxide **14** was isolated by flash chromatography.

But-2-yne (11a): Ozonolysis of 0.93 g (17.2 mmol) of **11a** in 60 ml of CH₂Cl₂ at -75°C gave a crude product in which **12a** ($\delta/\text{ppm} = 2.23$, s), acetic acid ($\delta/\text{ppm} = 2.10$, s), **13a** ($\delta/\text{ppm} = 2.34$, s) and **14a** ($\delta/\text{ppm} = 2.20$, s) were detected in the ratio reported. From the residue one obtained 0.08 g (4%) of **14a**. – ¹H NMR: $\delta/\text{ppm} = 2.20$ (s). – ¹³C NMR: $\delta/\text{ppm} = 16.41$; 165.98.

Hex-3-yne (11b): Ozonolysis of 1.29 g (15.7 mmol) of **11b** in 60 ml of CH₂Cl₂ at -75°C gave a crude product, in which **12b** ($\delta/\text{ppm} = 1.19$, t), **13b** [$\delta/\text{ppm} = 1.09$ (t), 2.79 (q)], and **14b** ($\delta/\text{ppm} = 1.26$, t) were detected in the ratio reported. From the residue one obtained 0.23 g (10%) of **14b**. – ¹H NMR: $\delta/\text{ppm} = 1.26$ (t, $J = 7.6$ Hz, 6 H), 2.47 (q, $J = 7.6$ Hz, 4 H).

1-Phenylpropyne (11c): Ozonolysis of 1.71 g (14.7 mmol) of **11c** in 50 ml of CH₂Cl₂ at -60°C gave a crude product in which **12c** ($\delta/\text{ppm} = 2.38$, s), **13c** ($\delta/\text{ppm} = 2.53$, s) and **14c** ($\delta/\text{ppm} = 2.27$, s) were detected in the ratio reported. From the residue one obtained 0.27 g (10%) of **14c**. – ¹H NMR: $\delta/\text{ppm} = 2.27$ (s, 3 H), 7.40–8.20 (m, 5 H).

Ozonolysis of **11a** in CD₂Cl₂ in the Presence of 1,1,2,2-Tetrachloroethane as a Standard

A solution of 0.13 g (2.4 mmol) of **11a** and 0.35 g (2.1 mmol) of tetrachloroethane in 3 ml of CD₂Cl₂ was ozonized at -75°C and warmed up to room temp. – ¹H NMR analysis showed the signals of **12a** (54%), **13a** (21%), **14a** (8%) and acetic acid (9%), as well as a series of weak signals at $\delta/\text{ppm} =$

1.40–1.80 and 2.10–2.30, which were tentatively assigned to polymeric peroxides.

Attempted Isolation of Polymeric Peroxides

A solution of 0.47 g (8.7 mmol) of **11a** in 50 ml of CH₂Cl₂ was ozonized at –75 °C and the solvent was distilled off in a rotary evaporator at room temp. and reduced pressure. When the distillation flask was removed the residue deflagrated.

Reduction of the Crude Ozonolysis Product

Ozonolysis of 0.47 g (8.7 mmol) of **11a** in 50 mL of CH₂Cl₂ was carried out at –75 °C. A sample of 2 ml was removed and concentrated by distillation of the solvent at room temp. ¹H NMR analysis showed the presence of **12a**, acetic acid, **13a** and **14a** in a molar ratio of 61:16:13:10, along with the signals assigned to polymeric peroxides. The bulk of the crude product was admixed with an excess of triphenyl phosphine and kept at room temp. for 12 h. ¹H NMR analysis showed the presence of **12a**, acetic acid and **13a** in a molar ratio of 52:35:13, whereas the signal of **14a** and the weak signals assigned to polymeric peroxides had disappeared.

Ozonolysis of **11a** in HCl/CH₂Cl₂: Synthesis of 2-Chloro-2-hydroperoxy-3-oxo-butane (**18**)

Gaseous HCl was introduced into 60 ml of CH₂Cl₂ at room temp. until the solution was saturated. Then, 0.88 g (16.3 mmol) of **11a** was added, the solution was cooled to –75 °C and ozonized to completion. A sample of 2 ml was taken and the solvent was distilled off at room temp. and reduced pressure. ¹H NMR analysis (CDCl₃, TMS) showed the presence of **18** [δ /ppm = 1.90 (s), 2.40 (s)], acetic acid (δ /ppm = 2.11), acetyl

chloride (δ /ppm = 2.66) and butanedione **13a** (δ /ppm = 2.33) in a molar ratio of 62:27:6:5. The bulk of the cold reaction product was admixed with a solution of 2.04 g (24.4 mmol) of *O*-methyl hydroxylamine, 6 ml of pyridine and 50 ml of methanol at –20 °C and the mixture was kept at –20 °C for 5 d. Then the solvent was distilled off to give 0.75 g of a liquid residue. –¹H NMR analysis showed the presence of **19** (δ /ppm = 1.48, 1.92, 3.41, 3.90, s, each) [**2**] and of **20** [δ /ppm = 2.00 (s), 3.95 (s) [**2**]] in a ratio of 6:1, along with residual methanol and pyridine.

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