CYANO SUBSTITUTED OZONIDES: PREPARATION, PROPERTIES AND UNUSUAL BEHAVIOR TOWARDS REDUCING AGENTS

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Abstract: Ozonolyses of 2-cyanopropene (la) and of 2,4-dicyano-1-butene (lb) gave the corresponding ozonides 3-cyano-3-methyl-(2a) and 3-cyano-3-(2-cyanoethyl)-1,2,4-trioxolane (2b) as the first examples of their kind. Reduction with DMS yielded the expected fragments acetyl cyanide (4a) and B-cyanopropionyl cyanide (4b), along with formaldehyde. Reduction with triphenylphosphine, however, gave cyanomethyl acetate (<u>6a</u>) and cyanomethyl-B-cyanopropionate (<u>6b</u>), respectively.

In connection with our interest in ozonides which bear substituents exerting a negative inductive effect (e.g. Cl^1 , OAc^2 or OR^3), we have tried to prepare examples of the hitherto unknown class of cyano substituted ozonides by ozonolysis of the substituted acrylonitriles <u>la</u> and <u>lb</u>. Ozonolysis of <u>la</u> (0.80 g) on polyethylene⁴ at -78°C and subsequent evacuation of the mixture at room temperature and 0.015 Torr afforded the liquid ozonide <u>2a</u> [0.46 g; 34%; ¹H NMR (CDCl₃) δ 1.90 (s, 3 H), 5.04 (s, 1 H), 5.56 (s, 1 H); ¹³C NMR (CDCl₃) δ 20.50, 95.53, 97.78, ll6.18; Anal. calcd for C₄H₅NO₃: C, 41.74; H, 4.38; N, 12.17. Found: C, 41.72; H, 4.33; N, 12.03] which was collected in a trap at -30°C. Ozonolysis of <u>lb</u> (1.0 g) in dichloromethane at -78°C, followed by evaporation of the solvent (0°C; 0.01 Torr) and flash chromatography⁵ of the residue on Florisil gave the liquid ozonide <u>2b</u> [0.40 g; 28%; ¹H NMR (CDCl₃) δ 2.52 - 2.78 (m, 4 H), 5.12 (s, 1 H), 5.64 (s, 1 H); ¹³C NMR (CDCl₃) δ 11.40, 29.99, 96.09, 98.32, 114.50, 117.05].

Ozonide <u>2a</u> is stable, whereas <u>2b</u> undergoes slow decomposition at room temperature (hence, no elemental analysis was performed). Both <u>2a</u> and <u>2b</u> are very reactive towards reducing agents. Thus, neat <u>2a</u> and <u>2b</u> reacted explosively with DMS at room temperature, and a dry filter paper which had been impregnated with ammonium iodide caught fire when neat <u>2a</u> was added. Yet, controlled reductions of <u>2a</u> and <u>2b</u> with DMS in CHCl₃-solutions at -20°C gave the expected products DMSO, formaldehyde (<u>3</u>) and the corresponding acyl cyanides <u>4a</u> [¹H NMR (CDCl₃) δ 2.56 (s); ¹³C NMR δ 32.20, 113.70, 173.80] and <u>4b</u> [¹H NMR (CDCl₃ δ 2.73 (t, <u>J</u> = 6.8 Hz, 2 H), 3.23 (t, <u>J</u> = 6.8 Hz, 2 H); ¹³C NMR δ 12.77, 29.90, 112.63, 116.90, 173.53] in molar ratios of ca. 1:1:1. By contrast, and in deviation from all previously known examples, controlled reductions of <u>2a</u> and <u>2b</u> with triphenylphosphine at temperatures below 0°C gave the corresponding esters <u>6a</u> [¹H NMR (CDCl₃) δ 2.14 (s, 3 H), 4.71 (s, 2 H); ¹³C NMR (CDCl₃) δ 20.04, 48.23, 113.85, 169.12] and <u>6b</u> [¹H NMR (CDCl₃): AA'XX' system with δ_A 2.84, δ_A . 2.82, δ_X 2.71, $\delta_{X'}$ 2.69 (J_{AA} = 3.8, J_{XX'} = 4.4, J_{AX} = 8.0, J_{AX'} = 6.5, J_{A'X} = 6.6, J_{A'X'} = 6.9 Hz), δ 4.81 (s, 2 H); ¹³C NMR (CDCl₃) δ 12.76, 29.42, 49.01, 113.84, 117.77, 168.83] as the single major products. This can be rationalized by the intermediate formation of the substituted 2,4,6-trioxaphosphoranes <u>5</u>⁶, probably caused by the enhanced reactivity of the

peroxide bonds in $\underline{2a}$ and $\underline{2b}$, due to the neighboring cyano groups. Ring-opening of $\underline{5}$ in the sense indicated by the arrows, with the formation of a P=O-bond as driving force and with migration of the cyano group as a consequence, leads to triphenylphosphine oxide and to the unusual reduction products $\underline{6}$. It appears, that the ring-opening of $\underline{5}$ is a concerted reaction. For, attempts at trapping the expected intermediate $\underline{7}$ of a step-wise ring-opening of $\underline{5a}$ by reduction of $\underline{2a}$ in the presence of methanol did not provide $\underline{8}$ in detectable amounts, although added $\underline{8^7}$ was shown to be stable under the reaction conditions applied.



Preliminary experiments showed, that the scope of existence of cyano substituted ozonides can be extended to higher substituted acrylonitriles and to cyclic olefins bearing cyano groups in vinylic positions. Application of the new mode of reduction to such ozonides may open interesting synthetic perspectives.

References

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