

1.3.2.4.5-DIOXADITHIAZIN-2.2.4.4-TETRAOXIDES - NEW REAGENTS FOR [2+2] -
AND [2+4]-CYCLOADDITIONS TO OLEFINS

V.K. Belskii

L.Ya. Karpov Physico-Chemical Institute, Moscow, 107120, USSR.

I.V. Bodrikov*, A.A. Michurin, L.I. Chumakova, A.V. Zhivoderov.

Gorky Polytechnical Institute, Gorky, USSR.

Summary: The titled compounds react with olefins under mild conditions to give 1.2-thiazetid-1.1-dioxides and/or 1.4.5-oxathiazin-4.4-dioxides being formal versatile sources of 1.2- and 1.4-dipoles. Relation of these paths changes widely depending upon structural effects of alkenes and conditions of the reaction.

We found that the new heterocyclic system - 1.3.2.4.5-dioxadithiazin-2.2.4.4-tetraoxides^{1, 2} interacts with alkenes to give 1.2- and 1.4 - cycloaddition products. Thus, starting from 1a-d and 1.3.2.4.5-dioxadithiazin-2.2.4.4-tetraoxides (2), 1.2-thiazetid-1.1-dioxides (3 a-c) and/or 1.4.5-oxathiazin-4.4-dioxides (4 a-e) were obtained. The ratio observed between [2+2]- and [2+4]-cycloadducts varies widely and depends upon the structure of olefins involved and the reaction conditions (Table 1). The reaction was performed in CH₂Cl₂ solution under inert atmosphere at temperatures indicated in Table 1. The products formed were treated with water and extracted by hexane after neutralization with aqueous ammonia. Compounds 3 and 4 are easily separated owing to low solubility of the latter in hexane. According to experimental data, interconversion of the heterocycles practically does not take place under these conditions.

The structure of compounds 3 and 4 was proved by IR and PMR-spectroscopy (table 2) and X-ray analysis.

Table 2 . Characteristics of 3 and 4

R	R ¹	R ²	R ³	R ⁴	M.p., ^{a)} °C	IR, ^{b)} cm ⁻¹	PMR	δ (ppm)	C ₆ D ₆
3a	CCl ₃	H	CH ₃	CH ₃ CH ₃	110	1720	0.55-1.18 (9H,m), 3.15-3.49 (1H,m)		
3b	CCl ₃	CH ₃	CH ₃	CH ₃ CH ₃	163	1705	1.04 (6H,s), 0.87(6H,s)		
3c	ClCH ₂ CCl ₂	H	CH ₃	CH ₃ CH ₃	116	1700	0.54-1.28(9H,m), 3.09-3.51 (1H,m), 3.63-4.15(2H,m)		
4a	CCl ₃	H	CH ₃	CH ₃ CH ₃	133	1665	0.58-0.82(9H,m), 2.60-2.87(1H,m)		
4b	CCl ₃	CH ₃	CH ₃	CH ₃ CH ₃	148	1650	0.99(6H,s), 0.95(6H,s)		
4c	CCl ₃	H	H	H CH ₂ Cl	114	1665	3.90-4.32 (1H,m), 2.30-2.67 (4H,m)		
4 d	CCl ₃	H	H	CH ₃ CH ₂ Cl	87	1635	1.75(3H,s), 3.84(2H,s), 3.72(2H,d) ^{c)}		
4e	ClCH ₂ CCl ₂	H	CH ₃	CH ₃ CH ₃	110	1654	0.64-1.17(9H,m), 2.56-2.89(1H,m), 3.66(2H,s)		

a) from hexane-CH₂Cl₂; b) $\nu_{C=O}$ for 3a-c, $\nu_{C=N}$ for 4a-e; c) in CDCl₃

X-ray structure analysis was performed for 3a and 4a. Molecular geometry, bond lengths and some of bond angles are shown in Fig. 1 and 2.

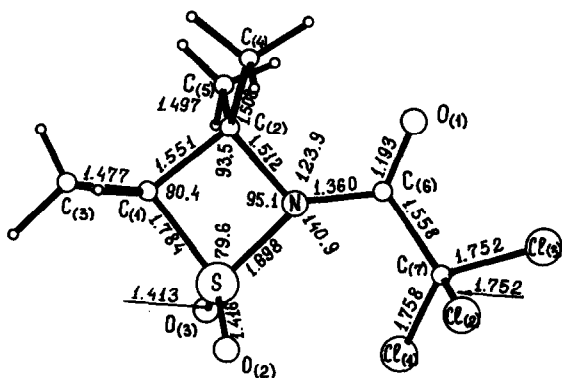


Fig. 1 Structure of 2-trichloroacetoxi-1,2-thiazethidin-1,1-dioxide

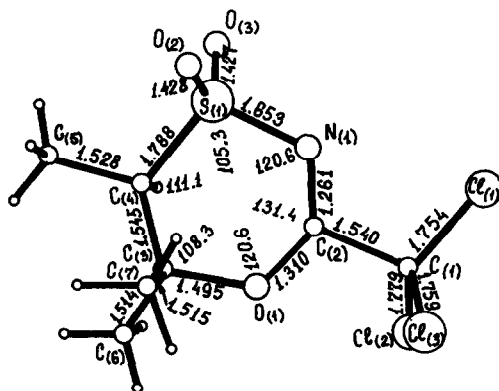


Fig. 2 Structure of 6-trichloromethyl-1,4,5-oxathiazin-4,4-dioxide

3a, $C_7H_{10}NO_3SCl_3$, triclinic, $P\bar{1}$, a 7.594(2), b 8.485(2), c 10.758(3)Å, α 109.40(2), β 95.73(2), γ 106.06(2)°, $Z = 2$, 1093 reflections with $I \geq 3\sigma(I)$, $R=0,032$.

4a, $C_7H_{10}NO_3SCl_3$, monoclinic, $P2_1/b_1$, a 9.298(2), b 11.046(3), c 11.629(3)Å, γ 95.99(2)°, $Z = 4$, 1319 reflections with $I \geq 3\sigma(I)$, $R=0,029$.

The data collection was made using an automatic Syntex $P\bar{1}$ diffractometer (λ Mo, graphite monochromator, $\theta/2\theta$ scan method). The structures were solved by direct methods, least-squares anisotropic refinement. All calculations were performed using SHELXTL (G.M. Sheldrick) programs incorporated in NICOLET R3 system on the NOVA3 computer.

In the molecule 3 a four-membered ring has a bent of 12.9° by the line C(2)...S. Six-membered ring of 4 a adopts a half-chair conformation (atoms S(I), O(I), N(I) and C(2) are coplanar to 0.01 Å, atoms C(3) and C(4) are above and below by 0.402 and 0.302 Å respectively).

The species $5 \leftrightarrow 6$ are formally formed by thermal elimination of SO_3 from the tetraoxides 2 and can function either as 1,2 or 1,4 dipolarophiles in cycloadditions to olefines.



In conclusion, detailed study of the factors governing the direction of both [2+2] - and [2+4]-cycloaddition along with mechanistic aspects of the process are now in full progress.

REFERENCES:

1. I.V. Bodrikov, A.A. Michurin, V.L. Krasnov, Zh. Org. Khim., II, 2217 (1975) and references cited therein.
2. V.K. Belskii, A.A. Michurin, A.V. Zhivoderov, I.V. Bodrikov, Doklady Akademy Nauk USSR 268, 1399 (1983).

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