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DI-t-BUTYLTHIOKETENE S-BIS(ALKOXYCARBONYL)METHYLIDE: FORMATION, REACTIONS, AND ITS EQUILIBRIUM WITH 2-ALKYLIDENE-1,3-OXATHIOLE ISOMER

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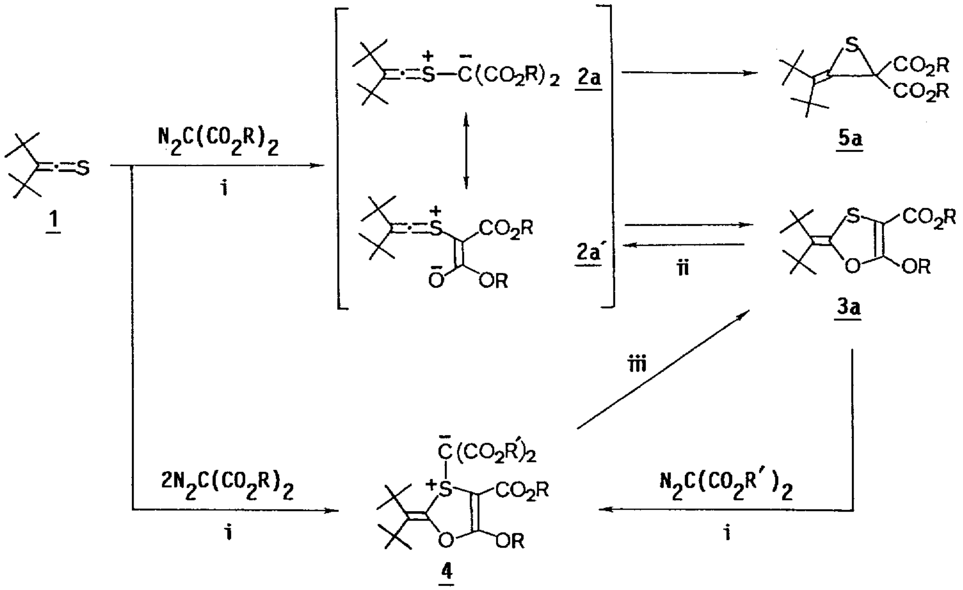
Summary: Generation and reactions of the title compound including its novel intramolecular cyclization and intermolecular cycloaddition reaction with a 1,3-dipolarophile are described.

Although thiocarbonyl ylides,[1] as well as the related carbonyl ylides[2] and azomethine ylides,[3] have been of great interest from both structural and synthetic viewpoints, simple thiocarbonyl ylides lacking ylide stabilizing substituents are so far known as transient species[1e,4] and there have been reported only a few examples which are stabilized by charge delocalization.[5] Meanwhile, thioketene S-ylides, the methylene homologue of thiocarbonyl ylides, have also been postulated as an intermediate in carbene addition reaction with thioketene.[6] However, the nature of them has not been fully investigated because of their high reactivity leading to a ready formation of stable allene episulfides.

In relation to our recent studies on the synthesis and reactions of substituted allene episulfides,[7] we present here (i) a novel intramolecular cyclization of the thioketene S-methylide(**2**), derived from the reaction of di-t-butylthioketene(**1**) with bis(alkoxycarbonyl)carbene, resulting in a facile formation of 2-alkylidene-1,3-oxathiole(**3**),[8] (ii) the existence of an equilibrium between S-methylide(**2**) and **3**, and (iii) 1,3-dipolaroaddition and intramolecular thermal cyclization of **3**.

When a benzene solution(4 ml) of **1** (340 mg, 2.0 mmol) and dimethyl diazomalonate (330 mg, 2.1 mmol) was heated at 50 °C for 12 h in the presence of catalytic amount of rohdium(II) acetate ($[(CH_3CO_2)_2Rh]_2$), stable white crystalline product(**3a**; R=Me, mp 94-6 °C) with a molecular composition of $C_{15}H_{24}O_4S$ was obtained in 66% yield (395 mg). Treatment of **1** with excess amount of dialkyl diazomalonates under similar reaction conditions afforded stable 1:2 adducts, i. e. sulfonium ylides(**4a**;R=R'=Me) and (**4b**;R=R'=Et), in moderate to good yields (82 and 33%). The sulfonium ylides **4a** and **4c**(R=Me, R'=Et) were also produced from the reaction of once isolated **3a** with newly added corresponding diazomalonates. **3a** was fairly labile to undergo a ready and quantitative intramolecular recyclization into allene episulfide(**5a**) by heating in carbon tetrachloride at 70 °C for 3 h.

Scheme 1

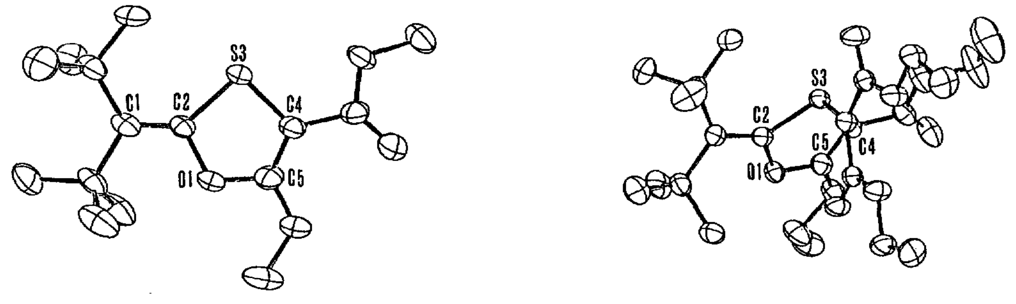


a:R=R′=Me 82 %
b:R=R′=Et 33 %
c:R=Me, R′=Et 38 %

i) cat. [Rh(OAc)$_2$]$_2$/50°C/benzene
ii) 70°C/CCl$_4$
iii) 150°C/o-dichlorobenzene

The spectral data of **3a** were consistent with the intramolecularly cyclized 2-alkylidene-1,3-oxathiole structure,[9] which was finally determined by the X-ray structure analysis as well as the sulfonium ylide structure of **4b** as shown in Fig.1.[10]

On the other hand, some reactions of **3a** suggested a possible existence of equilibrated ring-opened thioketene S-methylide(**2a**) which should resonate with the charge delocalized betaine form(**2a'**). When **3a** was treated with execess amount of 4-phenyl-1,2,4-triazoline-3,5-dione(PTAD), highly reactive 1,3-dipolarophile, in dichloromethane at 0 °C for 1 h afforded the corresponding 1:2 adduct(**6**) in 64% yield as yellow crystals along with the 1,2,3,4-tetrazolidine(**7**, 12%) and the regenerated thioketene(**1**, 15%).[11] No cycloaddition products were obtained from the reactions of **3a** with the other dipolarophiles such as N-phenylmaleimide, dimethyl acetylenedicarboxylate, dimethyl azodicarboxylate, and thiobenzophenone, but only the intramolecular cyclization into **5a** proceeded by slight heating in any case. The formation of **6**, **7** and **1** in the reaction of **3a** is interpreted in terms of the intermediacy of the thioketene S-methylide(**2a**) as illustrated in Scheme 2.[12] The interconversion of **3a** into **2a**

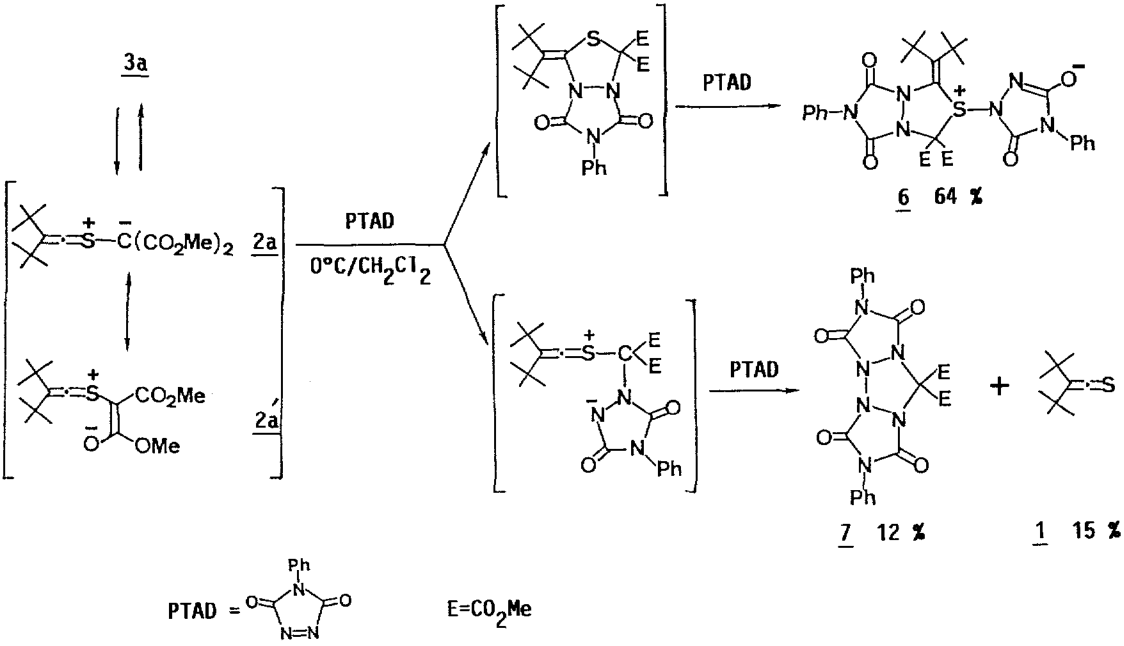


3a 4b

Fig.1. ORTEP drawings of 3a and 4b

also took place in the thermolysis of the sulfonium ylides(**4a**) and (**4c**) in o-dichlorobenzene at 150 °C resulting in the formation of an identical allene episulfide(**5a**) with exclusive extrusion of the secondarily introduced carbene unit.

Scheme 2



In summary, we have found a new type of reaction mode in the carbene addition to thioketene leading to the formation of 2-alkylidene-1,3-oxathiole and elucidated the characteristic intramolecular cyclization mechanism of the intermediary thioketene S-methylide, though it was limited to the case of bis(alkoxycarbonyl)carbene. In view of the high reactivity and instability, the cycloaddition reaction of **2a** with PTAD is of particular note as the first example of the intermolecular trapping of thioketene S-ylide.

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8. Similar molecular interconversion of 1,3-oxathioles via thiocarbonyl ylides has already been reported; K. Oka, A. Dobashi, and S. Hara, J. Am. Chem. Soc., **103**, 2757 (1981) and references cited therein.
9. **3a**: ^{1}H-NMR($CDCl_3$) δ1.35(s,18H), 3.69(s,3H), 4.00(s,3H); ^{13}C-NMR($CDCl_3$) δ 32.2(q), 32.4(q), 36.4(s), 39.0(s), 51.5(q), 59.0(q), 78.6(s), 126.6(s), 139.8(s), 158.1(s), 161.6(s); IR(KBr) 1620, 1715 cm^{-1}; UV(CH_2Cl_2) λ_{max} 256(log ε = 3.83), 297(3.58), 330(3.69) nm; MS(m/z, %) 300(M$^+$, 14%), 57(100); Elemental Analysis, found: C, 60.10; H, 8.15 %, calcd for $C_{15}H_{24}O_4S$: C, 59.97; H, 8.05 %. All the other products described in this paper also gave satisfactory spectral and analytical data unless otherwise noted.
10. Crystal data of **3a**: $C_{15}H_{24}O_4S$, MW 300, monoclinic, space group C2/C, a=37.048(8), b=6.056(1), c=15.334(3) Å, β=107.22(3)°, V=3286(1) Å^3, D_c=1.21 g cm^{-3}, μ(Mo-Kα)=2.1 cm^{-1}, z=8, R=0.131; **4b**: $C_{24}H_{34}O_8S$, MW 486, triclinic, space group P1, a=8.501(3), b=12.584(4), c=13.726(4) Å, α=105.69(3), β=88.90(6), γ=110.42(2)°, V=1320.2(5) Å^3, D_c=1.22 g cm^{-3}, μ(Mo-Kα)=1.74 cm^{-1}, z=2, R=0.074. Details of the X-ray crystallographical analysis of these interesting sulfur compounds will be reported elsewhere.
11. The use of equimolar amount of PTAD did not give the expected 1:1 adduct but only resulted in the formation of **6** with the recovery of **3a**. The structures of **6** and **7** were ascertained by the following spectral data: **6**, mp 154-155 °C; ^{1}H-NMR($CDCl_3$) δ1.45(s,9H), 1.46(s,9H), 3.84(s,3H), 3.88(s,3H), 7.13-7.43(m,10H); ^{13}C-NMR(CD_2Cl_2) δ32.8(q), 33.0(q), 37.0(s), 40.1(s), 55.0(q), 55.1(q), 79.8(s), 114.3(s), 119.7(s), 126.1(d), 127.2(d), 129.7(d), 129.8(d), 130.0(s), 130.1(d), 130.2(d), 130.7(s), 133.5(s), 138.6(s), 149.7(s), 150.9(s), 156.7(s), 164.9(s); IR(CCl_4) 1730, 1740, 1800 cm^{-1}; Elemental Analysis, found: C, 57.17; H, 5.55; N, 12.47 %, calcd for $C_{31}H_{34}O_8N_6S$: C, 57.22; H, 5.27; N, 12.92 %; **7**, mp 234-235 °C; ^{1}H-NMR($CDCl_3$) δ3.94(s, 6H) and 7.39(s, 10H); ^{13}C-NMR(CD_2Cl_2) δ55.5(q), 81.0(s), 126.7(d), 129.6(d), 129.8(d), 130.7(s), 153.6(s), 154.7(s), 162.6(s); IR(KBr) 1720, 1750 cm^{-1}; MS, m/z 465(M$^+$-Me); Elemental analysis was prevented by the sublimation of the sample.
12. Furthermore, another supporting evidence for the existence of the equilibrium of **3a** with **2a** was the fact that the variable-temperature ^{13}C-NMR spectra of **3a** indicated slight but regular changes in chemical shifts for C_1, C_2, and C_3 which are thought to be most susceptible to temperature changes.

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