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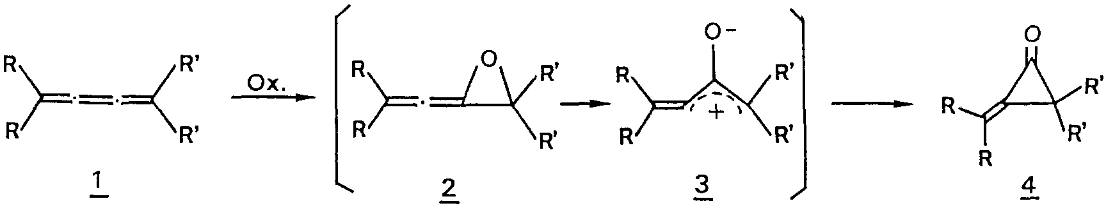
A NOVEL FORMATION OF 1,2,3-BUTATRIENE EPISULFIDES BY THIONATION OF METHYLENECYCLOPROPANONES

Wataru Ando*, Hiroshi Hayakawa, and Norihiro Tokitoh
Department of Chemistry, University of Tsukuba
Sakura-mura, Niihari-gun, Ibaraki 305, Japan

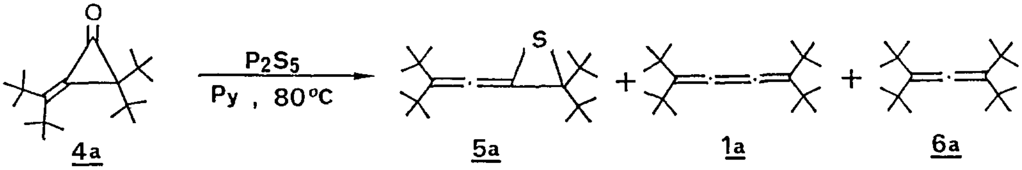
Summary; Sterically hindered methylenecyclopropanones were thionated with phosphorus pentasulfide in pyridine to afford novel 1,2,3-butatriene episulfides and thiiranoradialene derivative via methylenecyclopropanethione intermediate.

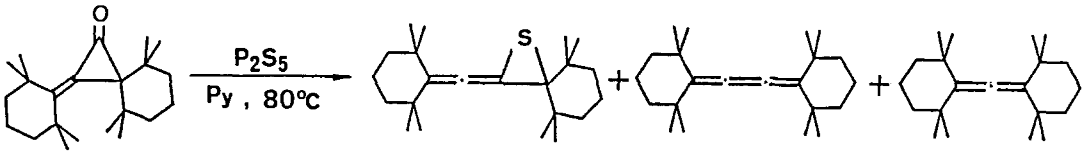
Much interest has focused on cyclopropanethione from a standpoint of tautomerism with allene episulfide via thioxyallyl intermediate,[1)] but few examples of intermediary cyclopropanethione have been reported.[1a,1b)] Recently we have described a facile formation of methylenecyclopropanones (4) by the peracid oxidation of sterically hindered 1,2,3-butatrienes (1).[2)] One might expect thionation of cyclopropanone to give cyclopropanethione.



We present here a novel formation of 1,2,3-butatriene 1-episulfides and thiiranoradialene by the thionation of the methylenecyclopropanones (4).

When methylenecyclopropanone (4a) (1 mmol, 292 mg) was treated with equimolar amount of phosphorus pentasulfide (1 mmol, 222 mg) in 4 ml of pyridine at 80°C for 10 h, butatriene episulfide (5a) was obtained as white crystals (30 mg, 10%) along with triene (1a) (66 mg, 24%) and allene (6a) (13 mg, 5%), respectively.[3)] Similarly, methylenecyclopropanone (4b) was thionated to afford the corresponding butatriene episulfide (5b) in 15% yield together with 27% of triene (1b) and 4% of allene (6b).[4)]

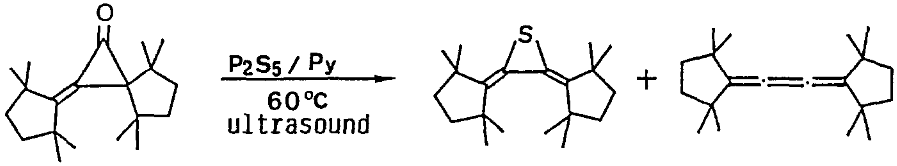




4b 5b 1b 6b

The structure of the products were confirmed by NMR, IR, and MS spectra and elemental analysis.5) Of particular note among these spectral data are the unsymmetricity and the observation of allenic carbon absorptions in the ^{1}H- and ^{13}C-NMR spectra of 5a and 5b, which convinced us of their 1,2,3-butatriene 1-episulfide skeletons. The allenic carbon-carbon stretching absorption in their IR spectra also supported the regiochemistry of the thiirane ring in 5a and 5b.

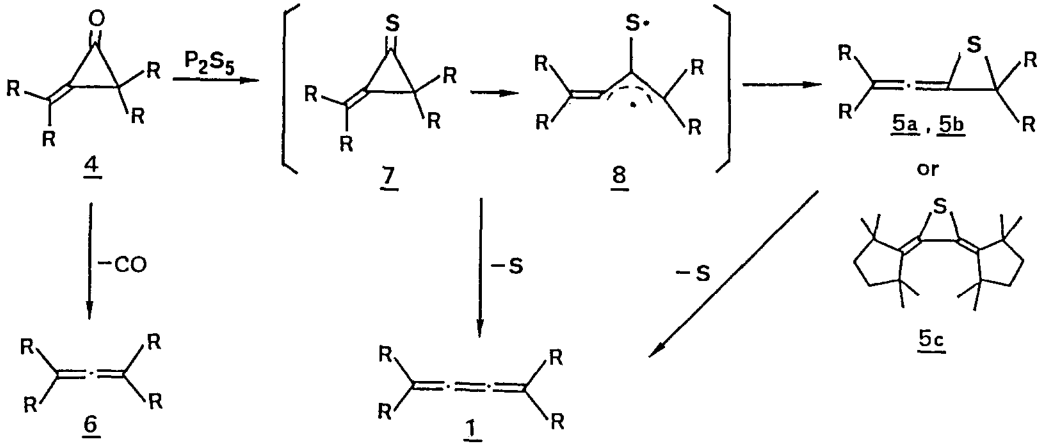
The thionation of methylenecyclopropanone (4c) with equimolar amount of phosphorus pentasulfide in pyridine at 60°C under irradiation of ultrasound afforded the thiiranoradialene (5c) as white crystals in 7% yield along with 6% of triene (1c).6) Without the irradiation of ultrasound only a complex tarry mixture was obtained.



4c 5c 1c

The structure of 5c was identified by NMR, UV, and MS spectra and elemental analysis.7) The molecular symmetricity and the absence of the allenic unit shown here were satisfactory to the thiiranoradialene structure of 5c. 8)

The 1,2,3-butatriene episulfides (5a-c) are almost certainly formed by the tautomerization of methylenecyclopropanethione (7) via the thioxyallyl-type intermediate (8) as shown below.

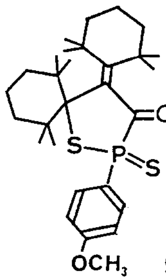


The direction of thiirane ring formation of 5a and 5b is logically attributed to the preferencial coupling of the more stable radical reaction centers. Meanwhile, the conspicuous formation of thiiranoradialene (5c) may owe to some stabilizing effect due to the coplanarity of the carbon-carbon double bond and the tetramethylpentane ring plane. The direct desulfrization via thioxyallyl-type intremediates (8) can be written for the formation of trienes (1) and such processes have postulated to occur in the thermolysis of allene episulfides.$^{10)}$ However, the thermal desulfrization of 5a-c also led to the corresponding trienes (1a-c) respectively.$^{10)}$ The formation of trienes (1) is feasible from either intermediates (8) or butatriene episulfides (5). The allenes (6) definitely seem to be the products of direct decarbonylation of the starting methylenecyclopropanones.$^{11)}$

In view of the unique and interesting structure, we believe the 1,2,3-butatriene episulfides obtained here will provide a new field for the chemistry of strained molecule.

References and Notes.

1. a) E. Block, R. E. Penn, M. D. Ennis, T. A. Owens, and Shin-Liang Yu, J. Am. Chem. Soc., 100, 7436, (1978); b) E. Jongejan, Th. S. V. Buys, H. Steinberg, and Th. J. de Boer, Recl. Trav. Chem. Pays-Bas, 97, 214, (1978); c) W. Ando, T. Furuhata, Y. Hanyu, and T. Takata, Tetrahedron Lett., 25, 4011, (1984); d) T. Furuhata and W. Ando, Tetrahedron, 42, 5301, (1986).
2. W. Ando, H. Hayakawa, and N. Tokitoh, Tetrahedron Lett., 27, 6357, (1986).
3. Preparative thin layer chromatography (silica gel/hexane) was used for the isolation and purification of the thionation products.
4. When 4b was thionated with Lawesson reagent (2,4-bis(p-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide), which is known as an effective thionation reagent for carbonyl compounds, no butatriene episulfide derivative but an unexpected addition product 9 was obtained in 40% yield.
   9; m.p.(decomp.) 173.5-4.5 °C, ^{1}H-NMR(CDCl$_3$); δ 1.07(3H, s),1.21(3H,s),1.23(3H,s),1.31(9H,bs),1.43(3H,s),1.50(3H, s),1.60-2.06(12H,m),3.83(3H,s), and 6.85-6.98 and 7.91-8.15(4H,m), ^{13}C-NMR(CDCl$_3$); δ 18.2(t), 18.4(t), 27.8(q), 32.8(q),33.1(q),36.9(s),37.1(tx2),41.5(tx2),41.8(s), 55.4(q),87.4(s),113.1(d),113.8(d),126.0(s),131.6($^{1}J_{CP}$ = 38Hz,s),132.9(d),133.5(d),135.7(s),162.7(s), and 189.0 ($^{1}J_{CP}$=13Hz,s), IR(CHCl$_3$); 2220, 1915, 1720, 1580, and 1560 cm^{-1}, Elemental anal., Found: C, 66.98; H, 8.24%. Calcd for $C_{29}H_{43}O_2PS_2$: C ,67.14; H, 8.35%.



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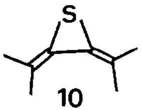
5. The spectral data of 1a, 1b, 6a, and 6b were identical with those of authentic samples; see Ref. 2.
   5a; m.p. 84-6 °C, ^{1}H-NMR(CDCl$_3$); δ 1.26(36H,s), ^{13}C-NMR(CDCl$_3$); δ 31.5(q), 32.5(q),38.0(s),39.8(s),67.7(s),102.5(s),135.3(s), and 186.3(s), IR(CCl$_4$); 1940 cm^{-1}, UV(hexane);246 nm(log ε =3.91), Elemental anal., Found: C,77.58;

H,11.87%. Calcd for $C_{20}H_{36}S$: C,77.84; H,11.76%, MS; m/z 308(M^+,2%),276(25), 251(1), and 57(100), Exact mass; m/z 308.2545 (Calcd for $C_{20}H_{36}S$,m/z 308.2538).

5b; m.p. 108-10 °C, ^{1}H-NMR($CDCl_3$); δ 1.10(6H,s),1.16(6H,s),1.20(12H,s), and 1.43-1.57(12H,m), ^{13}C-NMR($CDCl_3$); δ 18.9(tx2),28.8(q),31.0(q),31.5(q), 32.5(q), 36.4(s), 38.2(s), 40.5(t), 40.7(t), 65.5(s), 99.9(s), 132.9(s), and 184.3(s), IR(CCl_4); 1970 cm^{-1},UV(hexane); 246 nm(logε=3.92), Elemental anal., Found: C, 79.57; H, 11.01%. Calcd for $C_{22}H_{36}S$: C, 79.44; H, 10.91%, MS; m/z 332(M^+,9%),300(100), and 285(16), Exact mass; m/z 332.2549 (Calcd for $C_{22}H_{36}S$, m/z 332.2538).

6. When the thionation of 4a and 4b were carried out under irradiation of ultrasound at 60°C, the reactions underwent very slowly to afford 5a and 5b in 7 and 5% yields along with a trace amount of trienes 1a and 1b, respectively after 36 h.
7. 5c; m.p. 190-2 °C, ^{1}H-NMR($CDCl_3$);δ 1.30(12H,s),1.34(12H,s), and 1.63-1.74 (8H,m), ^{13}C-NMR($CDCl_3$); δ 26.5(q),29.0(q),40.1(t),41.0(t),45.9(s),46.9(s), 105.5(s), and 142.0(s), UV(hexane);248(log ε =4.22),257(4.35),280(4.25),303 (3.54), and 315(3.45) nm, Elemental anal.,Found: C,78.86; H,10.62%. Calcd for $C_{20}H_{32}S$: C,78.88; H,10.59%, MS; m/z 304(M^+,72%), 289(19), 272(6), and 109(100), Exact mass; m/z 304.2232 (Calcd for $C_{20}H_{32}S$, m/z 304.2225).
8. Only example (10) of thiiranoradialene we have already reported showed a similar spectral data; W. Ando, Y. Hanyu, and T. Takata, Tetrahedron Lett., 22, 4815, (1981).

   ^{13}C-NMR($CDCl_3$); 22.7(q), 23.0(q), 111.3(s), and 115.5(s).



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9. Although no triene (1) was obtained by heating of methylenecyclopropanones (4a-c) in pyridine without P_2S_5 at 80 °C in any case, butatriene episulfides (5a-c) were desulfurized at 80°C very slowly to give the corresponding trienes (1a-c). Furthermore, thermolysis of 5a-c in o-dichlorobenzene at 120 °C for several hours was found to give 1a-c quantitatively.
10. W. Ando, A. Itami, T. Furuhata, and N. Tokitoh, Tetrahedron Lett., submitted.
11. In the absence of P_2S_5, allenes 6 were obtained in a few percent yields at 80°C for 10 h, and quantitatively at 120°C for 5 h.

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