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# INTRAMOLECULAR PHOTOCYCLOADDITION OF 3-SUBSTITUTED DITHIOSUCCINIMIDES: FACILE SYNTHESIS AND THE CRYSTAL STRUCTURE OF HIGHLY STRAINED MULTICYCLIC FUSED THIETANE SYSTEM[1)]

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Upon irradiation, dithiosuccinimides having an olefin group at the α-position of the thiocarbonyl group undergo intramolecular cycloaddition to give highly strained thietanes 5 and 6. The structure of 6 is confirmed and discussed on the basis of its X-ray analysis.

**KEYWORDS**—dithiosuccinimide; photocycloaddition; X-ray analysis; thietane

In contrast to the extensive studies on the photochemistry of imide systems,[2)] the photochemical behavior of thioimide systems has scarcely been investigated.[3)] From our systematic studies on the photochemistry of the imides and its sulfur analogues, the thioimides, it has recently become clear that there are some distinct differences in the photochemical behavior of the imide-carbonyls and the thioimide-carbonyls.[3a,4)] For example, cyclic thioimides are inert to Norrish type I and type II reactions, representative photoreactions in the aliphatic imide system.[5)] But certain thioimides[6)] having a benzylic hydrogen at the δ- or ε-position in the N-alkyl side chain undergo the Norrish type II reaction to give cyclized products. In principle, the thiosuccinimides undergo very efficient photocycloaddition (Paterno-Büchi type reaction) to give spiro-thietanes.[3a,4)] In the imide series, the Norrish type I reaction of 3- and 4-substituted succinimides 1 causes facile ring fission leading to rearranged products such as azetidines 2,[5b,c)] and no capacities remain for the other photoreactions (Chart 1). However, this inertness of the thioimides to the type I

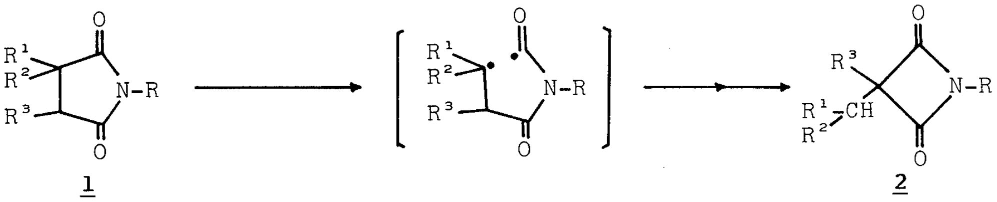

Chart 1

reaction suggests that even 3-substituted thioimides would be good substrates for some synthetic photoreactions. We now wish to report the first example of intramolecular photocycloaddition (Paterno-Büchi type reaction) of such 3-substituted dithiosuccinimides, which affords highly strained multicyclic fused ring system. An X-ray analysis of one of the photoproducts is presented.

Irradiation of 3 and 4 was carried out in benzene using a 1-kw high-pressure mercury lamp (Pyrex filter) at room temperature for 1 h to give 5 and 6 in 42 and 45% yields, along with recovery of 3 (36%) and 4 (45%), respectively. The Norrish type I reaction reported earlier[5b,c] with alicyclic imides was not observed. The structures of these products (5 and 6) were deduced from their elemental analyses and spectral data.[7]

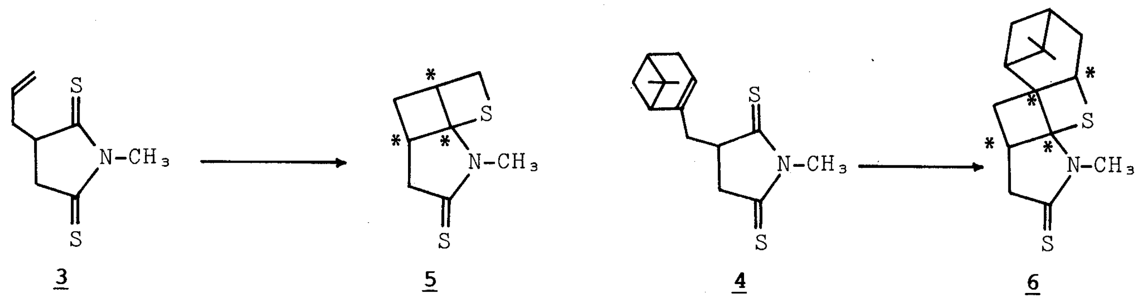

Chart 2

Further, to confirm the complex cyclic structure of 6, X-ray structure analysis[8] was performed. The structure was solved by the direct method using MULTAN and was refined by the block-diagonal least-squares procedure. The final R value was 0.124. As shown in Fig. 1 both the five-membered ring containing a nitrogen and the cyclobutane ring fused to thietane ring are almost planar. The dihedral angle between the five-membered ring and the cyclobutane planes is 126.3°. In the thietane ring, bond lengths of C2-S6 and S6-C7 are 1.83 and 1.88 Å, respectively, and the internal angle C2-S6-C7 is 76.7°. These data are analogous to those[9] of a simple thietane which has a puckered form (not flat).[10] The dihedral angle between the cyclobutane and the thietane planes is 114.0°. The bond angles and the interatomic distances of 6 are listed in Table I.

It is worth noting that the compounds (5 and 6) are both multicyclic thiolactams, consisting of a special doubly-fused cyclobutane system containing one thietane, and at least three bridged-head carbon atoms (*) are involved (Chart 2).

It is well known that [2+2] photocycloaddition of the $n,\pi^*$ state of a carbonyl compound to an unsaturated substrate proceeds generally *via* biradical intermediates.[11] Similarly thietane formation is also expected to proceed *via* biradical intermediates (7 and 8 in Chart 3).[4] In fact, the head-to-head cycloaddition product 5 was preferentially obtained in this study, whereas the head-to-tail compound 9, presumably generated *via* an intermediate 8, was not isolated. This preference may depend on the degree of substitution on the olefinic carbons in the substrates. Therefore, by introduction of substituents on an olefin moiety, the cycloaddition is expected to proceed with predictable regioselective control. Thus, the intramolecular photoreaction in this study takes predominantly the cycloaddition pathway and provides a synthetic entry to some highly strained hetero-multicycles which are otherwise inaccessible.

Table I. Interatomic Distances and Angles for 6

| Distances (Å) | | Angles (°) | | | |
|---|---|---|---|---|---|
| N1 - C2 | 1.46 | N1-C2-C3 | 104 | C12-C13-C14 | 87 |
| C2 - C3 | 1.57 | C2-C3-C4 | 106 | C8-C13-C12 | 105 |
| C3 - C4 | 1.51 | C3-C4-C5 | 105 | C11-C12-C13 | 85 |
| C4 - C5 | 1.51 | C4-C5-N1 | 111 | C12-C11-C14 | 90 |
| C5 - S18 | 1.67 | C2-N1-C5 | 114 | C10-C11-C12 | 108 |
| N1 - C5 | 1.34 | C4-C5-S18 | 125 | C11-C14-C15 | 122 |
| N1 - C17 | 1.49 | N1-C5-S18 | 124 | C13-C14-C15 | 124 |
| C2 - S6 | 1.83 | C5-N1-C17 | 123 | C10-C11-C14 | 110 |
| S6 - C7 | 1.88 | C2-N1-C17 | 124 | C11-C14-C16 | 109 |
| C7 - C8 | 1.57 | N1-C2-S6 | 120.2 | C7-C10-C11 | 110 |
| C2 - C8 | 1.51 | C2-C3-C9 | 89 | C8-C7-C10 | 119 |
| C8 - C9 | 1.57 | C3-C9-C8 | 90 | C13-C14-C16 | 107 |
| C3 - C9 | 1.54 | C2-C8-C9 | 90 | C2-C8-C13 | 134 |
| C7 - C10 | 1.52 | C3-C2-C8 | 91.0 | C7-C8-C9 | 111 |
| C10- C11 | 1.60 | C2-S6-C7 | 76.7 | C3-C2-S6 | 116.6 |
| C11- C12 | 1.54 | S6-C7-C8 | 90.0 | N1-C2-C8 | 129 |
| C12- C13 | 1.58 | C2-C8-C7 | 97 | C11-C14-C13 | 85.9 |
| C13- C14 | 1.57 | S6-C2-C8 | 93.8 | C15-C14-C16 | 107 |
| C14- C15 | 1.50 | C9-C8-C13 | 113 | | |
| C14- C16 | 1.59 | C7-C8-C13 | 109.7 | | |
| C11- C14 | 1.53 | C8-C13-C14 | 116 | | |
| C8 - C13 | 1.54 | C4-C3-C9 | 120 | | |

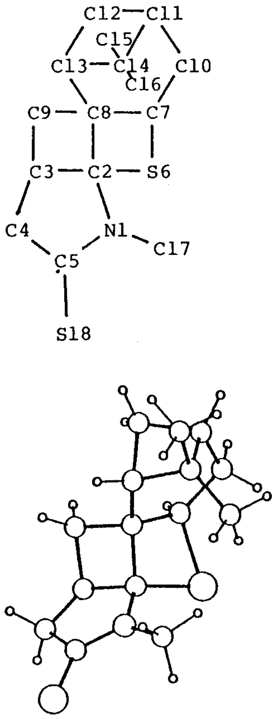

Fig. 1.

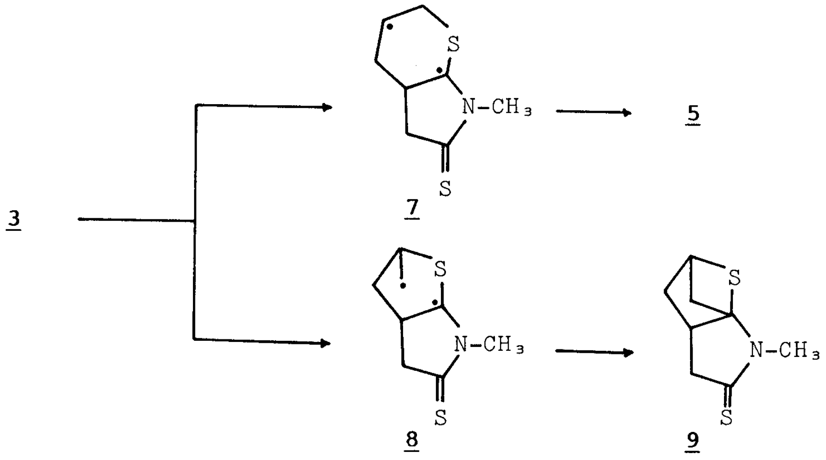

Chart 3

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7) These compounds showed reasonable analytical and spectral data (IR, Mass, $^{1}$H-NMR, and $^{13}$C-NMR). Compound **5**: pale yellow plates (from hexane), mp 124 – 125°C, MS m/z: 185 ($M^+$), 139 ($M^+ - CH_2{=}S$), $^{1}$H-NMR ($CDCl_3$) $\delta$: 2.0-3.0 (3H, m), 3.1 (1H, dd, J=3.6 Hz, 9.5 Hz), 3.35 (3H, s, N-$CH_3$), 3.4 (1H, d, J=9.5 Hz), 3.5-3.8 (3H, m), $^{13}$C-NMR ($CDCl_3$) $\delta$: 26.3 (t), 31.7 (q), 34.0 (t), 43.1 (d), 50.7 (t), 51.3 (d), 77.3 (s), 203.9 (s). Compound **6**: pale yellow plates (from benzene-hexane), MS m/z: 279 ($M^+$), $^{1}$H-NMR ($CDCl_3$) $\delta$: 0.80 (1H, d, J=10.0 Hz), 1.24 (3H, s, $CH_3$), 1.52 (1H, dd, J=6 Hz, 9 Hz), 1.60 (3H, s, $CH_3$), 2.00 (2H, dd, J=1 Hz, 6 Hz), 2.1-2.9 (5H, m), 3.36 (3H, s, N-$CH_3$), 3.4-3.5 (2H, m), 3.90 (1H, dd, J=4 Hz, 7 Hz), $^{13}$C-NMR ($CDCl_3$) $\delta$: 28.2 (q), 28.6 (t), 29.9 (q), 36.3 (t), 38.1 (d), 39.4 (d), 40.0 (s), 43.1 (d),(t),(q), 52.1 (d), 53.1 (t), 74.8 (s), 82.1 (s), 202.1 (s).

8) The crystal data are as follows: $C_{15}H_{21}NS_2$, MW=279.47, orthorhombic, space group $P2_12_12_1$, a=10.7188 (8), b=14.7885 (11), c=9.0721 (6) Å, $\underline{v}$=1400.4 (2) Å$^3$, $\underline{z}$=4, Dc=1.291 g·cm$^{-3}$. The measurements were performed on a Rigaku AFC-5 four-circle auto-diffractometer using graphite-monochromated Cu-K$\alpha$ radiation. Since the crystal was very labile, three crystals were used for the data collection.

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