Tetrahedron Letters No. 2, pp 199 - 202, 1974. Pergamon Press. Printed in Great Britain.

REARRANGEMENT OF 4,5-BENZO-3-THIATRICYCLO[4.1.0.0^{2,7}]HEPTENE TO 3,4-BENZO-2-THIABICYCLO[3.2.0]HEPTA-3,6-DIENE

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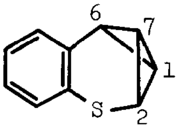
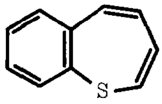
(Received in Japan 30 September 1973; received in UK for publication 3 December 1973)

We have recently reported[1,2] that 2H-1-benzothiopyran reacts with n-butyllithium and dichloromethane giving 4,5-benzo-3-thiatricyclo[4.1.0.0^{2,7}]heptene (**1**), a "valene" type valence isomer of the hitherto unknown benzo[b]thiepin (**2**).[3] In view of the extremely intriguing nature of the skeletal reorganization of a wide variety of bicyclo[1.1.0]butane derivatives,[4,5] and the potentiality of **1** as an attractive precursor of unsubstituted benzo[b]thiepin, we decided to investigate some isomerization reactions of **1**. We have now established that compound **1** undergoes an isomerization to 3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-diene (**3**) exclusively under thermal, photochemical and silver(I)-promoted reactions.



1



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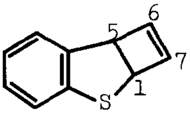
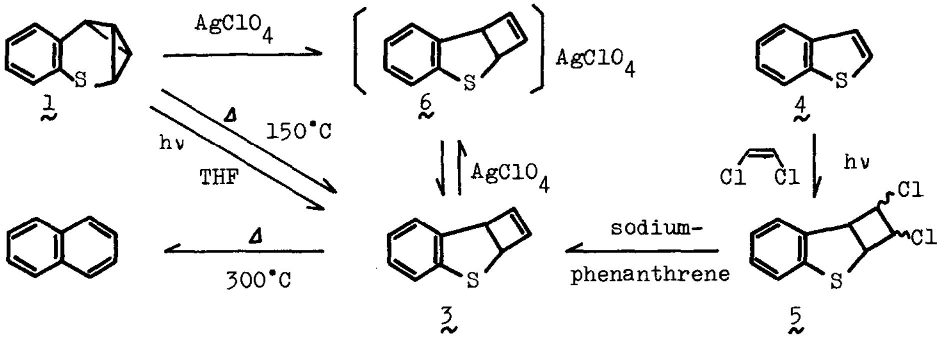


3

The thermal reaction of **1** was examined by heating a solution of 40 mg sample in carbon tetrachloride at 150°C in a sealed nmr tube. After 10 min the reaction proceeded smoothly at this temperature, as determined by nmr analysis, giving the 3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-diene (**3**) as the sole product, colorless needles, mp 51-52.5°C, Anal. Found, C, 74.94; H, 5.08; S, 20.41%, λ_{max}(cyclohexane) 215 nm (log ε 4.25), 257(3.88), 295(3.27) and 303(3.21), whose structure was proved through its mass [m/e 160 (M^+, 87%), 134 ($M^+-C_2H_2$, 100%)][6] and nmr spectra [apparent broad singlet with small satelite signals at δ 4.58 (2H, H-1 and 5), 5.93

(1H, H-7, dt, $J_{6,7}$=2.6 Hz, $J_{7,1}\simeq J_{7,5}$=0.5 Hz), 6.02 (1H, H-6, dt, $J_{6,7}$=2.6 Hz, $J_{6,5}\simeq J_{6,1}$=0.7 Hz) and 6.8-7.1 (aromatic 4H, m)]. Both the positions of the proton resonances and the small interactions between the allyl and the vinyl protons ($J_{1,7}$ and $J_{5,6}$) were consistent with the cyclobutene formulation.[7,8] Further thermolysis of 3 at 300°C for 10 min gave only naphthalene. The predominant formation of naphthalene is chemical proof of the derived structure 3.[8] Final confirmation of this structural assignment was obtained from an independent synthesis of the material. Thus irradiation (Pyrex filter, 450-w high pressure Hg lamp) of a mixture of benzo[b]thiophene (4) and cis-dichloroethylene in the presence of acetophenone as sensitizer gives an isomeric mixture of the photoadducts (5).[6] Dechlorination of 5[9] with sodium phenanthrene in tetrahydrofuran at 0°C yielded 3 (38% yield from 5) which was identical in all respects with the thermal rearrangement product.

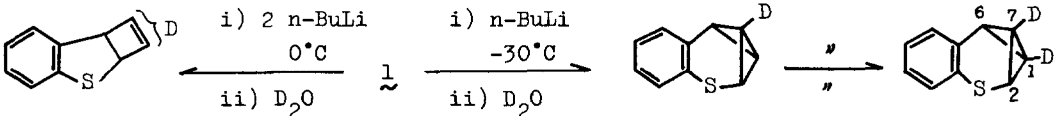


A solution of 40 mg of 1 in 1 ml of tetrahydrofuran contained in a quartz tube was irradiated with a 450-w high pressure Hg lamp at 0°C for 2.5 hr. The sole product isolated in 62% yield was identical with 3 in all respects.

In sharp contrast to the corresponding Ag(I)-bicyclobutane reaction which afforded only hexa-1,3-dienes,[10] compound 1 behaved in a dramatically different manner. When a solution of 40 mg of 1 in 0.5 ml of benzene-d_6 was treated with an equivalent of silver perchlorate in nmr tube at 25°C, an immediate reaction occurred which showed, after 10 min, nmr signals of two sets of AB-quartet with further fine structure at δ4.36, 4.69 (J=4.0 Hz) and 5.81, 5.99 (J=2.6 Hz) for allylic and vinylic protons of 6, respectively. Direct work-up of the reaction mixture by column chromatography on deactivated alumina (with 10% of water) afforded 3 in 25%

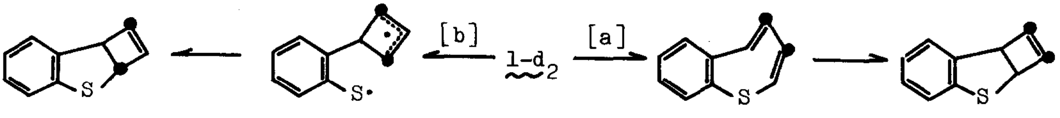
yield. An independent treatment of 3 with an equivalent of silver perchlorate regenerated the same nmr spectrum described above.

For the study of the mechanistic details of the skeletal reorganizations involved in the above mentioned reactions, compound 1 specifically labeled at the bridgehead positions of the bicyclobutane moiety was required. It was found that although 1 did give mono-vinyl deuteriated compound (7) of 3 after treatment with two mole equivalents of n-butyllithium in ether at 0°C for 40 min followed by quenching with deuterium oxide, successful preparation of the dideuterio-1 (1-d_2) was performed by two successive treatment of 1 under low temperature with an equivalent of n-butyllithium-D_2O. Thus, first treatment of 1 (in ether at -30°C for 30 min) was observed to afford monodeuterio-1 (1-d_1) [δ 1.90, bs, 1H; 3.04, dd, 1H, J=4.0, 2.8 Hz; 3.58, dd, 1H, J=4.0, 2.8 Hz] in nearly quantitative yield. After second such treatment of 1-d_1, deuterium was smoothly incorporated at 1,7-positions to give 1-d_2 [δ 3.04, d; 3.58 d, $J_{2,6}$=4.0 Hz].



7 1-d_1 1-d_2

Thermal reaction of 1-d_2 in CCl_4 at 150°C gave the labeled product (3a). The label was found exclusively in the vinyl positions by nmr, δ 4.58, bs, 2H. This finding reveals that the thermal product does not arise from the homolytic cleavage of C-S bond [path-b] which should lead to the vinyl-allyl labeled product (3b), and supports the pathway involving a symmetry allowed $_{\sigma}2_a+_{\sigma}2_s$ ring opening to (8) and a conrotatory ring closure to 3a [path-a].$^{11)}$ On the other hand, the nmr spectrum of the dideuteriated compound (3b) produced upon irradiation of 1-d_2 shows two equal-area singlets at δ4.58 and 5.93. If the photochemical conversion



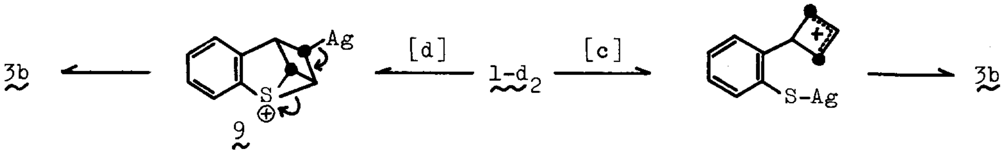
3b 8 3a

● denotes deuterium label

of 1 to 3 is completely concerted manner involving a $_{\sigma}2_a+_{\sigma}2_a$ ring opening (to 2) and a disrotatory ring closure, then the label distribution 3a is expected.

Exclusive formation of 3b strongly supports stepwise mechanism [path-b].

We have considered two mechanistic pathways as a priori possibilities for explaining the formation of 3 in the Ag(I)-promoted isomerization of 1. The first of these involves the ionic fission of the C-S bond [path-c] and the second involves the formation of the thiiranium ion12) (9) [path-d]. Unfortunately, deuterium labeling experiment does not suffice to distinguish between these alternative mechanisms since either path gives the same deuteriated product (3b). Further exploration of the utility of the compounds 1 and 3 for the synthesis of benzo-[b]thiepin is being actively pursued.



REFERENCES AND FOOTNOTES

1) I. Murata, T. Tatsuoka and Y. Sugihara, Tetrahedron Lett., 4261 (1973).

2) Originally reported yield of 1 described in ref. 1) was improved by the following procedure : To a stirred solution of 1.2 ml (18 mmol) of methylene chloride in THF-ether-n-hexane (6, 1.5 and 1.5 ml, each) there was added dropwise 22.5 ml of a 0.8 M solution of n-BuLi in n-hexane at -115°. The anion prepared from 924 mg (6.1 mmol) of 2H-1-benzothiopyran and 6.2 mmol of n-BuLi at -19° was then added at -115°. The mixture was maintained at this temperature for 30 min and quenched by water. Usual work-up gave 250 mg (25% yield) of 1.

3) Recent review for thiepin, see L. A. Paquette "Nonbenzenoid Aromatics" ed. by J. P. Snyder, Vol. 1, p. 249. Academic Press, New York, 1969.

4) Leading reference, see P. G. Gassman and J. J. Williams, J. Amer. Chem. Soc., 94, 7733 (1972) and refs. cited therein.

5) I. Murata, K. Nakasuji and H. Kume, Tetrahedron Lett., 3401, 3405 (1973).

6) D. C. Neckers, J. H. Dopper and H. Wynberg, J. Org. Chem., 35, 1582 (1970).

7) E. A. Hill and J. D. Roberts, J. Amer. Chem. Soc., 89, 2047 (1967); L. A. Paquette and W. C. Farley, J. Org. Chem., 32, 2725 (1967).

8) J. H. Dopper and D. C. Neckers, ibid., 36, 3755 (1971).

9) It has been shown that the dechlorination of 5 with zinc afforded higher molecular weight material. see ref. 6)

10) For review, see L. A. Paquette, Account Chem. Res., 4, 280 (1971).

11) Alternatively, the experimentally observed label distribution in 3a is also interpreted by a pathway involving homolytic cleavage of either peripheral bond of the bicyclobutane segment in 1-d$_2$. This mechanism seems energetically unfavorable. cf. K. B. Wiberg, "Advances in Alicyclic Chemistry" ed. by H. Hart and G. J. Karabatsos, Vol. 2, p. 197, Academic Press, New York (1968).

12) D. D. MacNicol and J. J. Mckendrick, Tetrahedron Lett., 2593 (1973); see also W. H. Mueller, Angew. Chem. Internat. Edn., 8, 482 (1969).