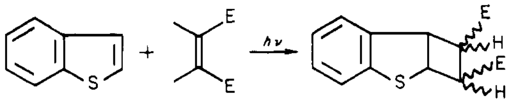
J. Org. Chem. 1981, 46, 3939-3940 3939

Synthesis of 3,4-Benzo-2-thiabicyclo[3.2.0]hepta-1,3-diene

Summary: The first synthesis of the title compound (I) is reported.

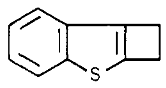
Sir: The $[{}_{\pi}2_{S} + {}_{\pi}2_{S}]$ photocycloaddition of olefins and benzo[*b*]thiophene provides a route to strained 3,4-benzo-2-thiabicycloheptenes. First reported by Dopper and Neckers,[1] these additions derive from triplet benzo[*b*]thiophene and electron-poor olefins to produce high yields of cycloadducts[2] (eq 1).



(1)

E = electron attracting group

We have now used this process in the first synthesis of the parent benzo[*b*]thiophene in the series, 3,4-benzo-2-thiabicyclo[3.2.0]hepta-1,3-diene (I) a highly strained bridgehead double bond system made stable, in part, because it is a fused derivative of benzo[*b*]thiophene.

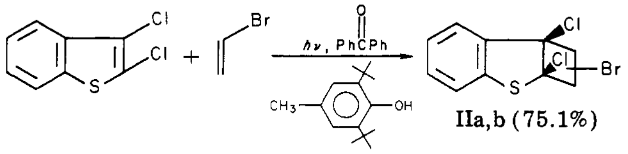


I

There are few reports of the synthesis of cyclobutanes which require readily polymerized olefins as addends in a photochemical reaction. Yields are good only if exciplexes, or ground-state charge-transfer complexes, intervene and vinyl polymerization is precluded.

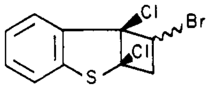
We report that by the simple expedient of adding a classical hydrogen-atom-donor free-radical inhibitor, photopolymerization of the olefin can be prohibited to a large extent and $[{}_{\pi}2_{S} + {}_{\pi}2_{S}]$ photocycloaddition observed as the major process even in a slower cycloaddition reaction.

2,3-Dichlorobenzo[*b*]thiophene[3] was added in a benzophenone-sensitized[4] reaction to vinyl bromide. The most

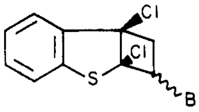


IIa,b (75.1%)

successful recipe included 2,6-di-*tert*-butyl-*p*-cresol as a free radical inhibitor. 2,3-Dichlorobenzo[*b*]thiophene (20.0 g, 0.099 M), vinyl bromide (280 mL), 2,6-di-*tert*-butylcresol (4.0 g), and benzophenone (2.0 g) were irradiated for 26 h with a Hanovia 450-W lamp through Pyrex, filtered through Norite, and irradiated again for 68 h to produce a mixture of isomeric adducts (0.0474 M, 75.1%). Two isomers, IIa and IIb, formed in roughly equal amounts and could be separated on silica gel (hexanes eluant). Isomer IIa [*m*/*e* 308 (M$^+$, 6), − CH$_2$=CHBr (100), − Cl, Br (50%)] had typical dihydrobenzo[*b*]thiophene UV absorption [λ_{max} 305 (1520), 264 (1420), 242 (11 600)] and crystallized from hexane (mp 83–84 °C). Its NMR spectrum [(ABX system: AB centered at δ 3.05 (2 H), H$_A$ − 3.35 (J_{AX} = 9.0 Hz, J_{AB} = 13 Hz), H$_B$ ~ 2.73 (J_{BX} = 10.0 Hz, J_{AB} = 13 Hz), H$_X$ centered at δ 5.02 (1 H, J_{AX} = 9 J_{BX} = 10 Hz), 7.0–7.6 (4 H), aromatic (CDCl$_3$)] was consistent with that of a $[{}_{\pi}2_{S} + {}_{\pi}2_{S}]$ cyclobutane adduct.[1] Isomer IIb (mp 74–77 °C) [*m*/*e* 308 (M$^+$, 3.6), − CH$_2$=CHBr (100), − Br, Cl (17.6)] showed a similar dihydrobenzo[*b*]thiophene UV absorption [λ_{max} 303 (1330), 238 (10 800)]. The NMR spectrum was also consistent with that of a $[{}_{\pi}2_{S} + {}_{\pi}2_{S}]$ cyclobutane adduct [ABX systems: AB centered at δ 3.33 (2 H), H$_A$ ~ 3.45 (J_{AX} = 7.0 Hz, J_{AB} = 12.5, Hz, H$_B$ ~ 3.13 (J_{BX} = 8.2 Hz, J_{AB} = 12.5 Hz), H$_X$ ~ 4.69 (1 H, J_{AX} = 7.0 Hz, J_{BX} = 8.2 Hz), 7.0–7.4 (4 H, aromatic) CDCl$_3$)]. IIa and IIb are syn or anti isomers of the two possible cyclobutane adducts.[5]

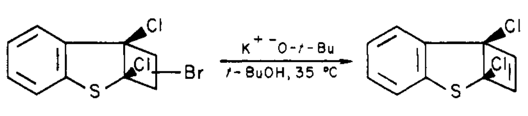


IIa



IIb

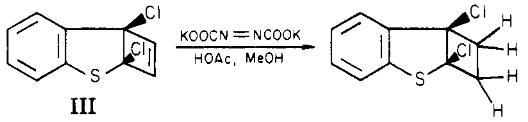
When treated with potassium *tert*-butoxide in *tert*-butyl alcohol at 35 °C, the mixture of isomers could be dehydrobrominated to III in 77% isolated yield.[6] A mixture



IIa,b III

of IIa,b (1.0 g, 3.25 mmol) was treated with an excess of *t*-BuO$^-$K$^+$ in *t*-BuOH at 35 °C added in portions until the starting material disappeared. Crude product (0.67 g) was flash chromatographed over silica gel to give III. The structure of III (mp 60–2 °C) was confirmed by its mass spectrum [*m*/*e* 228 (M$^+$, 35), − Cl (100), − 2 Cl (44)], its NMR spectrum [δ 6.06 (AB, 2 H, *J* = 2.4 Hz), 6.9–7.5 (m, 4 H, aromatic)], and its characteristic UV spectrum (λ_{max} 300 (1800), 293 (1870), 238 (8460)].

When treated with diimide, III[8] gave IV (79%). To III



III

IV

(1.63 g, 7.15 mmol) in 20 mL of MeOH were added potassium azodicarboxylate (13.87 g, 71.5 mmol) and 20 mL of glacial HOAC over a period of time so as to give a slow decomposition. For isolation of IV water was added *slowly* to destroy excess potassium azodicarboxylate, and the solution was extracted 3 times with ether followed by extraction 3 times with saturated NaHCO$_3$ solution or until basic and then extraction with water until neutral and dried over MgSO$_4$. Column chromatography over silica gel gave product crystals. IV (mp 28–29 °C) had the following spectral characteristics: mass spectrum, *m*/*e* 230 (M$^+$, 25), − CH$_2$=CH$_2$ (11), −CH$_2$Cl (100); NMR δ 2.81 (4 H, A$_2$B$_2$), 7.25–7.80 (m, 4 H); UV λ_{max} 299 (915), 243 (10 000).

---

[1] J. H. Dopper and D. C. Neckers, *J. Org. Chem.*, **36**, 3755 (1971).

[2] D. C. Neckers and A. H. A. Tinnemans, *Acc. Chem. Res.*, manuscript submitted for publication.

[3] (a) A. H. Schlesinger and D. T. Maury, *J. Am. Chem. Soc.*, **73**, 2614 (1951); (b) G. Komppa, *Chem. Abstr.*, **24**, 112 (1930).

[4] The triplet energy of most benzo[*b*]thiophene is between 67 and 70 kcal/mol. Both benzophenone and acetophenone are commonly used as sensitizers as are the polymeric sensitizers reported by this group previously (N. Asai, and D. C. Neckers, *J. Org. Chem.*, **45**, 2903 (1980); L. Thijs, S. N. gupta, and D. C. Neckers, *Macromolecules*, **13**, 1037–1041 (1980).

[5] X-ray crystal structure studies are in progress.

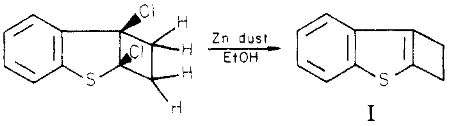
[6] I. Murata, T. Tatsuoka, and Y. Sugihora, *Tetrahedron Lett.*, 199 (1974).

[7] J. A. Berson, M. S. Poonian, and W. J. Libbey, *J. Am. Chem. Soc.*, **91**, 5567 (1969).

[8] Activated by procedure 1, L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, 1973, p 1276.

0022-3263/81/1946-3939$01.25/0

With activated zinc dust in ethanol, IV gave I (oil) in 57.5% yield: mass spectrum, *m/e* 160 (M^+, 100), HC≡CH (8), S (16); NMR δ 3.27 (4 H, A_2B_2), 7.0–7.9 (4 H, aromatic); UV λ_{max} 300 (2350), 291 (3020), 282 (3930), 269 (7640), 265 (7420), 238 (24500). To IV (40 mg, 0.174 mmol) in 2 mL of EtOH was added excess Zn dust[8] (200 mg) and the mixture was stirred overnight. After chromatography on silica gel (hexanes solvent), I was isolated as a pure clear oil.[9]



IV I

More experiments with related systems are in progress.

Acknowledgment. We gratefully acknowledge support of the National Institutes of Health (5-R01-NS-14883-02) and many discussions with Dr. M. Sindler-Kulyk.

Registry No. I, 78514-38-2; IIa, 78514-39-3; IIb, 78514-40-6; III, 78514-41-7; IV, 78514-42-8; 2,3-dichlorobenzo[*b*]thiophene, 5323-97-7; vinyl bromide, 593-60-2.

D. C. Neckers,* F. L. Wagenaar
Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

Received June 12, 1981

---

(9) All new compounds had satisfactory elemental analysis.