

Supplementary Material Available: Full ^1H NMR data (Table and spectra) of the urobiliverdin isomers, as well as their melting points, mass spectral data of urobiliverdin I octamethyl ester, and r_T of the HPLC separation (7 pages). Ordering information is given on any current masthead page.

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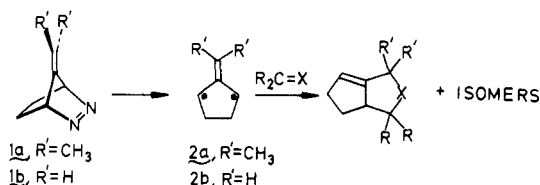
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Use of Heteroatom-Containing π Systems as Diylophiles in the Intermolecular 1,3-Diyl Trapping Reaction. Construction of Heterocycles

Summary: Reactions illustrating the intermolecular cycloaddition of heteroatom-containing π systems and alkenes to 2-alkylidenecyclopentane-1,3-diyls are described.

Sir: Unlike [4 + 2] cycloaddition reactions wherein a wide range of dienophiles have been used,¹ the diyl trapping reaction has been restricted to examples wherein the trapping agent (the diylophile) consists of a simple C-C π bond, most often substituted with an electron-withdrawing group.² We now report that *diylophiles* which incorporate heteroatoms (viz., C=O, C=N, and C=S) can also serve as trapping agents, thereby extending the scope of the diyl trapping reaction and also suggesting its use in the construction of heterocycles.³

Most of our attention has focused upon the use of the dimethyl diazene **1a** ($R' = \text{CH}_3$). It, when heated in refluxing THF, presumably serves as a precursor to diyl **2a**, which in turn is trapped with a variety of diylophiles $R_2\text{C}=\text{X}$ ($X = \text{O}, \text{N}, \text{S}$); thereby leading to the formation



of fused (i.e., those with a bicyclo[3.3.0]octene skeleton) and bridged (i.e., those with a 7-alkylidenebicyclo[2.2.1]heptane skeleton) cycloadducts **3-15**. To promote the encounter of diylophile and diyl and to minimize dimer-

(1) For a recent review concerning the use of heterodienophiles in Diels-Alder reactions, see: Weinreb, S. M.; Staib, R. R. *Tetrahedron Report No. 136*, 1982, 38, 3087. For an up-to-date review of the intramolecular Diels-Alder reaction, see: (a) Fallis, A. G. *Can. J. Chem.* 1984, 62, 183-234. (b) Ciganek, E. In "Organic Reactions"; Wiley: New York, 1984; Vol. 32, Chapter 1.

(2) For some recent examples of the intramolecular 1,3-diyl trapping reaction, refer to: (a) Little, R. D.; Stone, K. J. *J. Am. Chem. Soc.* 1983, 105, 6976. (b) Little, R. D.; Highby, R. G.; Moeller, K. D. *J. Org. Chem.* 1983, 48, 3139. (c) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* 1981, 37, 4371. (d) Stone, K. J.; Little, R. D. *J. Am. Chem. Soc.* 1985, 107, 2495-2505.

(3) Recently, Trost and Bonk reported an interesting [3 + 2]-type cycloaddition reaction between [2-(acetoxymethyl)-3-allyl]tri-*n*-butylstannane and both aldehydes and imines, leading to the production of heterocycles. See: Trost, B. M.; Bonk, P. J. *J. Am. Chem. Soc.* 1985, 107, 1778-1781.

Table I

entry	diylophile	diyl	cycloadducts (isolated yields)	dimer (%)
1	PhCHO	2a	 3a , 33% β -Ph 3b , 4% α -Ph	15
2	$\text{E}_2\text{C}=\text{O}$ $\text{E}=\text{CO}_2\text{Et}$	2a	 5 (27%) 6 (19%) 7 (17%)	14
3	$\text{E}_2\text{C}=\text{O}$	2b	 8 (75%) ^a	b
4	$\text{Ph}_2\text{C}=\text{S}$	2a	 9 (50%) 10 (22%) 11 (19%)	4
5	$\text{PhN}=\text{CHPh}$	2a	 12a , 3% α -Ph 12b , 37% β -Ph 13 (35%)	8
6	$(\text{CH}_2\text{O})_n$ ZnCl_2	2a	 14 (87%) ^a	b
7	$\text{EC}\equiv\text{CE}$ $\text{E}=\text{CO}_2\text{CH}_3$	2a	 15 (76%)	b

^aRegioisomer and dimer not detected. ^bDimer not detected.

ization, the diazene was added via syringe pump to a refluxing solution of the diylophile in THF.

Examination of Table I reveals several points worth noting. First, in all cases, fused cycloadducts are formed to a larger extent than are bridged. Second, in many instances dimerization occurred despite the use of syringe pump techniques. Third, of the diylophiles tested, thio-benzophenone proved to be the most reactive. To illustrate this point, a series of competition experiments were conducted, each involving equimolar amounts of a pair of diylophiles. From a run using benzaldehyde and thio-benzophenone, only thio-benzophenone-derived cycloadducts could be detected by capillary column GC analysis. Dimethyl fumarate proved to be a more successful competitor. Even so, approximately 4 to 5 times as much

thiobenzophenone-derived cycloadducts were obtained relative to the amount resulting from a trap with dimethyl fumarate.

Not surprisingly, a regiochemical mixture of fused cycloadducts was often obtained. Two interesting exceptions to this generalization are evident from entries 3 and 6. In the first, diethyl ketomalonate undergoes cycloaddition with the diprotio diyl **2b** leading to the isolation of **8** in 75% yield. In contrast, reaction of the same diylophile with the dimethyl diyl **2a** affords a mixture of regioisomers **5** and **6** in a ratio of 1.4:1. Interestingly, the former result is in accord with the principles of simple frontier molecular orbital theory.⁴ Presumably the obtention of a mixture of products in the reaction with **2a** simply reflects the dominance of steric over electronic effects. In the second instance, formaldehyde, generated thermally from paraformaldehyde (in THF), proved unreactive unless zinc chloride was added. In addition to assisting in the depolymerization of the paraformaldehyde, the zinc chloride must also exert an electronic effect, since we were able to detect and isolate only one cycloadduct, **14**. We are presently investigating the generality of Lewis acid promoted diyl trapping reactions and the results will be reported on another occasion.

Finally, the last entry in Table I, illustrating the use of dimethyl acetylenedicarboxylate, deserves a brief comment. In previous reports, it was noted that polymeric products were obtained when acetylenes were used and it was suggested that this side reaction might be caused by the reaction of the acetylene and the diazene prior to deazetation.⁵ Indeed, this is probably so. However, our results demonstrate that useful amounts (viz., 76%) of a fused cycloadduct can be obtained when the concentration of the diazene and diyl are maintained at a very low level through the use of syringe pump techniques.

In a typical experiment, 0.5 mmol of the diazene dissolved in 10 mL of dry, oxygen-free THF was added to a refluxing solution of the diylophile by using a syringe pump at a drop rate of 0.74 mL/h. An excess of the diylophile, also dissolved in THF, was used in each case.⁶ Once the addition was complete, reflux was continued for an additional hour at which time the solvent was removed and the products were isolated using HPLC.

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Registry No. **1a**, 31689-32-4; **1b**, 69442-65-5; **2a**, 32553-01-8; **2b**, 60743-11-5; **3a**, 96556-11-5; **3b**, 96614-13-0; **4a**, 96556-12-6; **4b**, 96614-14-1; **5**, 96556-13-7; **6**, 96556-14-8; **7**, 96556-15-9; **8**, 96556-16-0; **9**, 96556-17-1; **10**, 96556-18-2; **11**, 96556-19-3; **12a**,

96556-20-6; **12b**, 96614-15-2; **13**, 96556-21-7; **14**, 96556-22-8; **15**, 96556-23-9; PhCHO, 100-52-7; (CO₂Et)₂C=O, 609-09-6; Ph₂C=S, 1450-31-3; PhN=CHPh, 538-51-2; CH₂O, 50-00-0; ZnCl₂, 7646-85-7; CH₃CO₂C≡CCO₂CH₃, 762-42-5.

Supplementary Material Available: Listing of spectral data for each product (7 pages). Ordering information is given on any current masthead page.

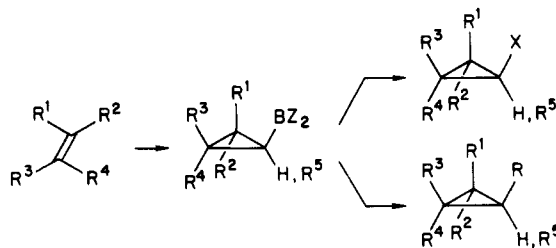
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Applications of Cyclopropylboranes in Organic Synthesis. 1. A Stereocontrolled Route to Substituted Cyclopropanol Derivatives

Summary: Secondary and tertiary cyclopropanols are produced stereoselectively via the sequential treatment of 1,1-dibromocyclopropanes with *n*-butyllithium, catecholborane (or a trialkylborane), and alkaline hydrogen peroxide.

Sir: Cyclopropane derivatives are valuable synthetic intermediates, with considerable utility in the preparation of a variety of cyclic and acyclic organic compounds. Thus, we have recently reported a general [4 + 1] annulation approach to substituted cyclopentenes based on the accelerated rearrangement of 2-vinylcyclopropanol salts.¹ In connection with this methodology, we have recently been concerned with the development of new synthetic routes to both vinylcyclopropane and cyclopropanol derivatives, particularly the more highly substituted systems which are not available by employing existing methodology. In this paper we describe a general synthesis of cyclopropylboranes and demonstrate their potential utility for the preparation of a variety of highly substituted and functionalized cyclopropane derivatives.



The application of cyclopropylboranes in organic synthesis has received little attention previously, and few examples of this potentially valuable class of cyclopropane derivatives appear in the literature.² The most popular

(4) Berson, J. A. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982; pp 151-194. Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976.

(5) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* 1980, 102, 276-287. The diyl generated thermally from 5-isopropylidenebicyclo[2.1.0]pentane adds smoothly to dimethyl acetylenedicarboxylate to give **15**. This result is reported in the Ph.D. Thesis of J. Mondo (1982) and A. Sabatelli (1984), Yale University. We are grateful to Professor Berson for informing us of this result and these references.

(6) The excesses ranged from 1.2- to 64-fold. Specifically, for benzaldehyde, 64.5 equiv at 9 M; for diethyl ketomalonate, 10 equiv at 4 M; for thiobenzophenone, 1.23 equiv at 0.18 M; for PhN=CHPh, 3.02 equiv at 4.6 M; and for dimethyl acetylenedicarboxylate, 20 equiv of 6.7 M. The concentrations listed above refer to that of the diylophile prior to the addition of the diazene.

(1) (a) Danheiser, R. L.; Martinez-Davila, C.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* 1981, 103, 2443. (b) Danheiser, R. L.; Martinez-Davila, C.; Morin, J. M. *J. Org. Chem.* 1980, 45, 1340.

(2) (a) Binger, P.; Köster, R. *Angew. Chem.* 1962, 74, 652. (b) Köster, R.; Arora, S.; Binger, P. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 205. (c) Cowley, A. H.; Furtch, T. A. *J. Am. Chem. Soc.* 1969, 91, 39. (d) Brown, H. C.; Rhodes, S. P. *J. Am. Chem. Soc.* 1969, 91, 4306. (e) Utimoto, K.; Tamura, M.; Tanouti, M.; Sisido, K. *Tetrahedron* 1972, 28, 5697. (f) Dunkelblum, E. *Isr. J. Chem.* 1973, 11, 557. (g) Haubold, W.; Stanzl, K. *Chem. Ber.* 1978, 111, 2108. (h) Odum, J. D.; Szafran, Z.; Johnston, S. A.; Li, Y. S.; Durig, J. R. *J. Am. Chem. Soc.* 1980, 102, 7173. (i) Mikhailov, B. M.; Bubnov, Yu. N. "Organoboron Compounds in Organic Synthesis"; Harwood: London, 1984; pp 402-406.