by water aspirator while stirring vigorously in a 40 °C water bath. The oily residue was dissolved in 30 mL of anhydrous diethyl ether and the solution was cooled in an ice bath. Then 1.85 mL of ethanolamine (31 mmol) was injected with rapid stirring. The precipitate was filtered on a fritted-glass funnel and washed with 5 mL of ether. The filtrate was washed with 60 mL of a saturated sodium chloride solution, dried ($MgSO_4$), and concentrated under vacuum to yield the crude product. The alcohol may be isolated by distillation at reduced pressure or by chromatography and is generally pure by NMR and GLC.

The capacity of B-alkyl-9-BBN compounds as chemoselective as well as enantioselective[12] reducing agents for aldehydes has been demonstrated.[13] The reagent is exceptionally mild since the reaction proceeds under essentially neutral conditions. The Meerwein–Pondorf–Verley type of mechanism proposed for this reduction[1] suggests that this reagent should possess unique properties. We are continuing to investigate both the mechanism and scope of these reactions.

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References and Notes

(1) M. M. Midland, A. Tramontano, and S. A. Zderic, *J. Organomet. Chem.*, **134**, C17 (1977).

(2) H. C. Brown, E. F. Knights, and C. G. Scouten, *J. Am. Chem. Soc.*, **96**, 7765 (1974). 9-BBN is commercially available from the Aldrich Chemical Co.

(3) The reaction may be performed at room temperature. As standard conditions we have used 2 h in refluxing THF.

(4) Reduction via olefin elimination in the cyclooctyl ring has not been observed.

(5) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975.

(6) H. C. Brown and G. W. Kabalka, *J. Am. Chem. Soc.*, **92**, 714 (1970).

(7) (a) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, p 215; (b) R. O. Hutchins and D. Kandasamy, *J. Am. Chem. Soc.*, **95**, 6131 (1973); (c) G. W. Gribble and D. C. Ferguson, *J. Chem. Soc., Chem. Commun.*, 535 (1975); (d) C. S. Sell, *Aust. J. Chem.*, **28**, 1383 (1975); (e) Y. Yamamoto, H. Toi, A. Sonoda, and S-I. Murahashi, *J. Am. Chem. Soc.*, **98**, 1965 (1976); (f) H. C. Brown, S. Krishnamurthy, and N. M. Yoon, *J. Org. Chem.*, **41**, 1778 (1976); (g) G. H. Posner, A. W. Runquist, and M. J. Chapdelaine, *J. Org. Chem.*, **42**, 1202 (1977); see Table III of this reference for a comparison of aldehyde reducing agents.

(8) Ketones may be reduced in a reasonable time if the concentration of the organoborane is increased.

(9) All ketones tested were reduced at least 100–200 times slower than the aldehydes. *B*-Siamyl-9-BBN is slightly more reactive toward acetophenone than toward cyclohexanone.

(10) When *p*-nitrobenzaldehyde was reduced, the reaction was conducted at room temperature for 3 h. After destroying excess organoborane with acetaldehyde, the solvent was removed under vacuum at room temperature. The residue was dissolved in 200 mL of ether and 1.85 mL of ethanolamine was added. The solution was filtered and the ether was concentrated under vacuum to about 3 mL (a drop or two of methanol will redissolve any precipitate). The product was eluted with ether from a silica gel column then concentrated by rotary evaporator and distilled by Kugelrohr at 0.01 mmHg, 110 °C. The alcohol was obtained as light yellow crystals in 76% yield, mp 67–69 °C.

(11) *p*-Dimethylaminobenzaldehyde was refluxed for 8 h. The solution was cooled to room temperature and treated with 2 mL of water, stirred for 15 min, then extracted with 2 × 30 mL of acidified water (concentrated HCl added dropwise until the solution had a pH of 1). The aqueous extracts were combined, made basic to pH paper (with 3 N sodium hydroxide solution), and extracted with 2 × 20 mL of ether (saturing the water with potassium carbonate after the first extraction). The combined extracts were dried over magnesium sulfate, filtered, and concentrated under vacuum to yield the product (pure by NMR).

(12) M. M. Midland, A. Tramontano, and S. A. Zderic, *J. Am. Chem. Soc.*, **99**, 5211 (1977).

(13) **Note Added in Proof.** It has been reported that 9-BBN-pyridine will selectively reduce aldehydes [H. C. Brown and S. U. Kulkarni, *J. Org. Chem.*, **42**, 4169 (1977)].

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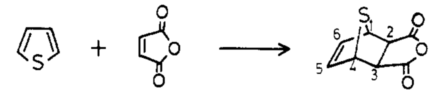
Diels–Alder Reaction of Thiophene with Maleic Anhydride at Very High Pressure[1,2]

Summary: The Diels–Alder reaction of thiophene with maleic anhydride proceeds under very high pressure conditions, affording the exo adduct.

Sir: There has been current interest in the Diels–Alder reaction of thiophenes. Because of the high aromaticity, it is a well-known fact that thiophene itself is inert to maleic anhydride.[3] The only recorded thiophene derivatives which are able to react with maleic anhydride in a Diels–Alder manner are thiophene 1,1-dioxide[4] and 2,5-dimethoxythiophene.[5] Recently it has been reported that some simple thiophene derivatives can combine with extremely reactive dienophiles such as dicyanoacetylene and dimethyl acetylenedicarboxylate.[6–10]

In this communication we wish to report the successful Diels–Alder reaction of thiophene with maleic anhydride at very high pressure (eq 1). In this way the 7-thiabicyclo[2.2.1]-hept-2-ene skeleton **3** is simply accessible.[11]



(1)

1 2 3

Thiophene failed to react with maleic anhydride in methylene chloride at 15 kbar and room temperature for 3 days. The reaction without solvent or with a Lewis acid catalyst (e.g., $MgCl_2$) was also fruitless.[12] These facts show a striking absence of diene character in thiophene, and contrast remarkably with the case of furan.[2] However, when we examined the reaction at higher temperatures at 15 kbar for 3 h in methylene chloride, we found that the reaction does occur (Table I). Inspection of the Table I reveals that the most favorable result is obtained at 100 °C. Thus, from the reaction mixture a highly crystalline compound **3**, mp 159.5–161.5 °C, of molecular formula $C_8H_6O_3S$ (MS, M^+ 182) was obtained in yields of 37–47% after recrystallization from ether or chloroform. On the stereochemistry of the adduct **3**, it is suggested that **3** has exo configuration from spectral data and chemical evidence as follows. In the ^1H NMR spectra, the C_2 and C_3 protons appear at δ 3.63 as a doublet signal ($J = 1$ Hz). When the dihedral angle between protons at C_1 and C_2 and also at C_3 and C_4 is taken into account, this fact indicates that **3** has exo configuration.[13] In agreement, the half methyl ester derived from **3** did not undergo iodolactonization (I_2–KI).[14]

Subsequently, the effect of solvent in the formation of the adduct **3** was investigated (Table II). The low yield in benzene is presumably due to the freezing of reaction medium at very high pressure.[15]

The following procedure for the Diels–Alder reaction of thiophene with maleic anhydride is representative.[16] A methylene chloride solution (1 mL) of thiophene (3 mmol) and

Table I. Temperature Dependence of the Yield[a] in the Adduct 3 between Thiophene and Maleic Anhydride

Room temp	No reaction	100 °C	37–47%
40 °C	No reaction	120 °C	18%
80 °C	8%	150 °C	Decomp

[a] The yield based on the isolated material.

Table II. Solvent Dependence of the Yield in the Adduct 3 between Thiophene and Maleic Anhydride (100 °C)

CH_2Cl_2	$CHCl_2CHCl_2$	C_6H_6	AcOEt
37–47%	47%	6–7%	15–19%

maleic anhydride (3 mmol) was injected into the Teflon reaction vessel of ~0.85 mL capacity. The reaction vessel was heated to 100 °C at 15 kbar for 3 h. After cooling of the reaction mixture to room temperature and pressure release, the solvent was evaporated and the product was recrystallized from ether or chloroform to give pure **3** in yields of 37–47%: mass spectrum (20 eV) *m/e* (rel intensity) 182 (36, M$^+$), 110 (27), 84 (44), 78 (100), 66 (25), 45 (12); IR (Nujol) 1850, 1795, 1085, 943, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 3.63 (d, $J = 1$ Hz), 4.59 (m), 6.61 (dd, $J = 2, 3$ Hz).

All attempted reactions between thiophene and other dienophiles such as dimethyl maleate, dimethyl fumarate, methyl acrylate, acrylonitrile, and acrolein under same conditions (100 °C, 15 kbar, 3 h, 3 M in methylene chloride) were fruitless, and no signs of adduct formation were observed.[17]

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References and Notes

(1) High Pressure Organic Chemistry. 2. For part 1, see H. Nishizawa, K. Hojo, K. Matsuoka, N. Yamasaki, H. Kotsuki, and M. Ochi, *Res. Lab. Hydrotherm. Chem. Rep.* (*Kochi Univ.*), **2,** 13 (1977).
(2) For a related work in this area, see W. G. Dauben and H. O. Krabbenhoft, *J. Am. Chem. Soc.,* **98,** 1992 (1976).
(3) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds", 3rd ed, Wiley, New York, N.Y., 1976, p 157.
(4) H. Wollweber, "Diels-Alder-Reaktion", Georg Thieme Verlag, Stuttgart, 1972, p 72.
(5) J. M. Baker, P. R. Huddleston, and S. W. Shutler, *J. Chem. Soc., Perkin Trans. 1,* 2483 (1975).
(6) R. Helder and H. Wynberg, *Tetrahedron Lett.,* 605 (1972).
(7) H. J. Kuhn and K. Gollnick, *Tetrahedron Lett.,* 1909 (1972).
(8) H. J. Kuhn and K. Gollnick, *Chem. Ber.,* **106,** 674 (1973).
(9) D. N. Reinhoudt, W. P. Trompenaars, and J. Geevers, *Tetrahedron Lett.,* 4777 (1976).
(10) K. Kobayashi and K. Mutai, *Chem. Lett.,* 1149 (1977).
(11) For another approach, see R. K. Murray, Jr., J. S. Polley, S. S. Abdel-Meguid, and V. W. Day, *J. Org. Chem.,* **42,** 2127 (1977).
(12) We thank Mr. K. Hojo for his experiment of this part.
(13) F. A. L. Anet, *Tetrahedron Lett.,* 1219 (1962).
(14) T. A. Eggelte, H. de Koning, and H. O. Huisman, *Tetrahedron,* **29,** 2491 (1973).
(15) A freezing point of benzene is ~100 °C at 4 kbar according to the Simon equation; cf. S. E. Babb, Jr., *Rev. Mod. Phys.,* **35,** 400 (1963).
(16) For a description of our high-pressure equipment, see ref 1.
(17) Under these conditions dimethyl maleate isomerized completely to dimethyl fumarate. In the case of acrylonitrile and acrolein, considerable polymerization was observed.

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