Cyclopropene: A New Simple Synthesis and Diels−Alder Reactions with Cyclopentadiene and 1,3-Diphenylisobenzofuran

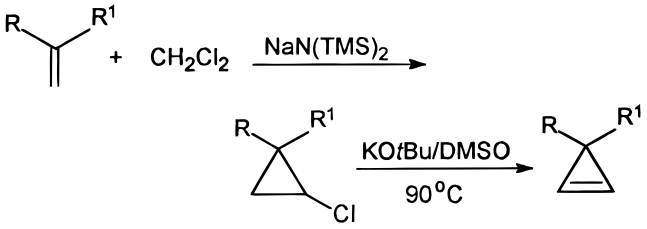
Paul Binger,*,† Petra Wedemann,† Richard Goddard,† and Udo H. Brinker*,‡

Max-Plank-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany, and State University of New York at Binghamton, Department of Chemistry, P.O. Box 6016, Binghamton, New York 13902-6016

Received April 22, 1996

Due to its short double bond of 1.296 Å[1] and its calculated strain energy of 54.5 kcal/mol,[2] cyclopropene (**1**) is a highly reactive molecule. While the increased angular strain of the molecular σ framework contributes to the destabilization of **1**, it is release of ring strain which drives its reactions. The synthesis of cyclopropene (**1**), a potentially explosive gas (bp −36 °C), was first reported in 1922 by Demjanov and Doyarenko.[3] Even at temperatures below −30 °C, **1** is said to oligomerize rapidly *via* ene reactions.

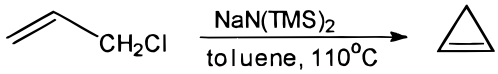
Cyclopropenes are important building blocks for organic synthesis and their preparation and reactions have been reviewed extensively.[4] Lower boiling 3,3-disubstituted cyclopropenes can simply be obtained in a two-step synthesis[5] with overall yields as high as 80%.



Higher boiling cyclopropenes could conveniently be prepared *via* dehydrohalogenation of the corresponding monobromocyclopropanes at *ca.* 40 °C.[6] In contrast, for the preparation of the parent compound—cyclopropene (**1**)—quite a variety of diverse synthetic methods has been employed. Schlatter[7a] and Demjanov and Doyarenko[7b] pyrolyzed cyclopropyltrimethylammonium hydroxide at 320 °C using platinized asbestos as the catalyst. About equal amounts of cyclopropene (**1**) and cyclopropyldimethylamine are formed contaminated with some dimethyl ether and ethylene. Treatment with dilute hydrochloric acid removed the amine from the gas stream and **1** was separated from the other products by gas chromatography. Alder−Rickert cleavage of the Diels−Alder adduct formed from cycloheptatriene and dimethyl acetylenedicarboxylate resulted only in the formation of a polymer and trace amounts of **1**.[8] A simple approach by Closs and Krantz[9] based on the synthesis of 1-methylcyclopropene[10] involved the addition of allyl chloride to a suspension of sodium amide at 80 °C. Under the conditions employed, **1** could readily escape the reaction mixture.[9] Though a number of variations were tried, the yield of **1** never exceeded 10%.

The common feature of all previous attempts at cyclopropene (**1**) is either very laborious methods or unacceptable yields, from a preparative point of view. Over the last 25 years we have developed in our laboratories simple syntheses for substituted cyclopropenes on a multigram scale.[4a,5a,11] At this time we would like to disclose our efforts toward an improved synthesis of parent compound **1**.

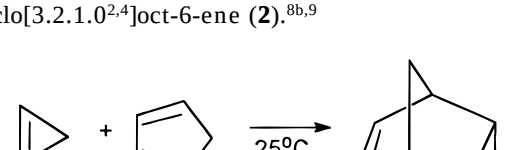
When allyl chloride was dropped into a solution of sodium bis(trimethylsilyl)amide[12] in boiling toluene, *ca.* 40% of cyclopropene could be isolated in a trap kept at −80 °C. Compared with the published procedure,[9] under



1

these conditions allyl chloride seems to react more rapidly, affording a quadrupled yield of **1**. Furthermore, as could be established by NMR spectroscopy at −80 °C, the cyclopropene (**1**) collected as a colorless liquid is nearly pure (>95%), containing only traces of allyl chloride. Compound **1**, prepared in this manner, was found to be stable in toluene solution at −78 °C for at least 1 week. Upon warming up, **1** begins to oligomerize at −30 °C (NMR control).

When **1** was reacted with cyclopentadiene, no reaction took place, as could be monitored by NMR spectroscopy at −80° nor at −30 °C. At room temperature, however, the Diels−Alder reaction afforded quantitatively *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**2**).[8b,9]



1 **2**

It is known that **1** and many substituted cyclopropenes[4] add to dienes with predominant *endo* selectivity in agreement with Alder's "*endo* rule".[13] According to

† Max-Plank-Institut für Kohlenforschung.
‡ State University of New York at Binghamton.

(1) Stigliani, W. M.; Laurie, V. W.; Li, J. C. *J. Chem. Phys.* **1975**, *62*, 1890. Kasai, P. H.; Myers, R. J.; Eggers, D. F. Jr.; Wiberg, K. B. *J. Chem. Phys.* **1959**, *30*, 512. Dunitz, J. D.; Feldman, H. G.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1708.
(2) von R.-Schleyer, P.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.
(3) Demjanov, N. Y.; Doyarenko, M. N. *Bull. Acad. Sci. USSR*, **1922**, *16*, 297.
(4) (a) Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77. (b) Review: Halton, B.; Banwell, M. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed., Wiley: New York, 1987; Chapter 21, 1223. (c) Deem, M. L. *Synthesis* **1972**, 675. (d) Wendisch, D. In Houben-Weyl, *Methoden der Organischen Chemie*, 1971; Thieme: Stuttgart, Vol. *4/3*, pp 679. (e) Closs, G. L. In *Advances in Alicyclic Chemistry*; Hart, H., Karabatsos, G., Eds.; 1966; Vol. 1, p 53. (f) Carter, F. L.; Frampton, V. L. *Chem. Rev.* **1964**, *64*, 497.
(5) (a) Binger, P. *Synthesis* **1974**, 190. (b) Dijachenko, A. I.; Agre, S. A.; Rudashevskaya, T. Y.; Shafran, R. M.; Nefedov, O. M. *Izv. Akad. Nauk. SSSR*, **1984**, 2820; Engl. Transl. **1984**, *33*, 2585.
(6) Binger, P., unpublished results.
(7) (a) Schlatter, M. J. *J. Am. Chem. Soc.* **1941**, *63*, 1733. (b) Demjanov, N. J.; Dojarenko, M. *Ber. Dtsch. Chem. Ges.* **1923**, 56, 2200.
(8) (a) Alder, K.; Jacobs, G. *Chem. Ber.* **1953**, *86*, 1528. (b) Wiberg, K. B.; Bartley, W. J. *J. Am. Chem. Soc.* **1960**, *82*, 6375.
(9) Closs, G. L.; Krantz, K. D. *J. Org. Chem.* **1966**, *31*, 638.
(10) Fisher, F.; Applequist, D. E. *J. Org. Chem.* **1965**, *30*, 2089.
(11) Köster, R.; Arora, S.; Binger, P. *Liebigs Ann.* **1973**, 1219.
(12) Sodium bis(trimethylsilyl)amide was prepared according to the following references: (a) Wannagat, U.; Niederprüm, H. *Chem. Ber.* **1961**, *94*, 1540. (b) Krüger, C.; Rochow, E. G.; Wannagat, U. *Chem. Ber.* **1963**, *96*, 2132.
(13) Alder, K.; Stein, G. *Angew. Chem.* **1937**, *50*, 510.

S0022-3263(96)00728-1 CCC: $12.00

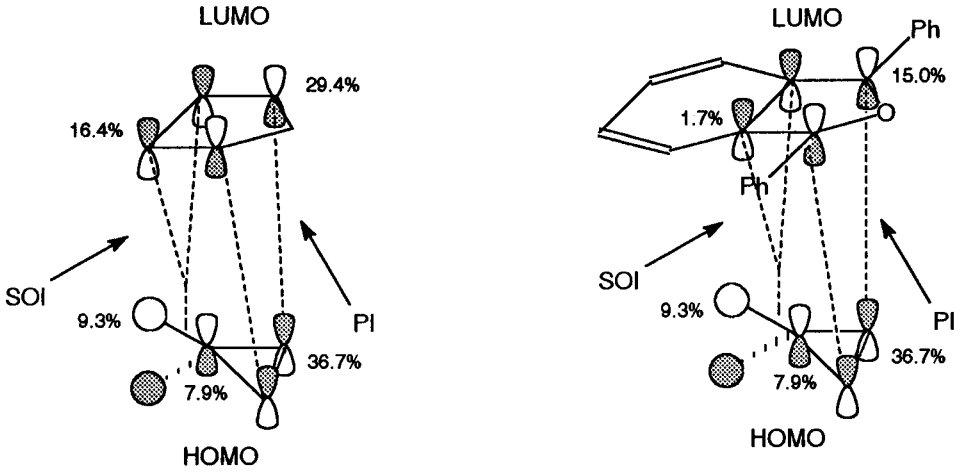
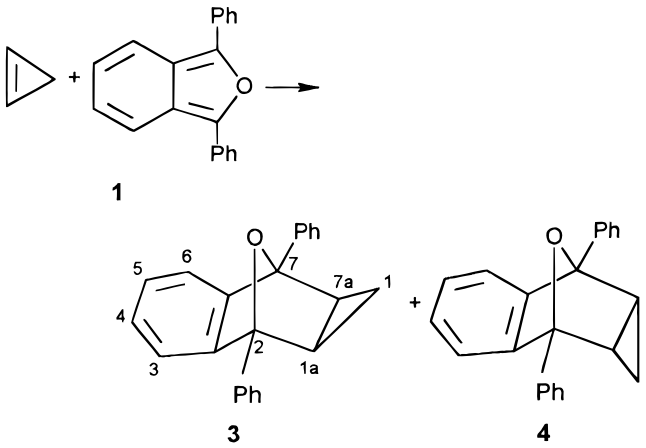


Figure 1. Compared with that for cyclopentadiene, the *endo*-activated complex for DPIBF with **1** does not profit from enhanced SOI due to severely reduced electron density (1.7% each) at C3a and C7a. (Percentages represent the squares of LCAO coefficients and reflect actual sizes of orbitals.)

Woodward and Hoffmann,[14] the preferred *endo* stereoselectivity is the result of favorable secondary orbital interactions (SOI) between the dienophile and the diene which do not lead to bonds in the adduct as opposed to primary interactions (PI) which do. Apeloig's *ab initio* calculations[15] have recently provided evidence for the dominant role of secondary orbital interactions in dictating the *endo*:*exo* ratio of the products resulting from **1** and dienes. As Wiberg[8b] had already reported some 35 years ago, the reaction of **1** with cyclopentadiene affords exclusively *endo*-adduct **2**. Though our AM1 calculations predict the *exo*-adduct of **1** and cyclopentadiene to be more stable than **2** by *ca*. 3 kcal/mol, Apeloig's calculations[15] reveal weaker steric repulsions in the *endo*-activated complex, thus favoring the formation of the higher energy *endo*-adduct **2** in agreement with experiment.



The reaction of **1** with 1,3-diphenylisobenzofuran[16] (DPIBF) had already been studied before.[17−19] Geibel and Heindl[17] prepared **1** by applying the method of Closs and Krantz.[9] According to these authors, when **1** was reacted with DPIBF in chloroform, 75% of **4** and 13% of **3** was obtained in adddition to a *trans*-diol. This diol results from a proton-catalyzed cleavage of the ether bridge with dilute sulfonic acid which was used for the washing of **1** during its preparation.[17] Battiste and Sprouse,[18] however, avoided the acid washing of **1** and isolated only one adduct in 63% yield. They could clearly show by an independent synthesis of **3** that the stereochemical assignments of Geibel and Heindl[17] were in error and should be reversed. The *endo* isomer **4**, however, could not be detected. Finally, Cava and Narasimhan[19] generated cyclopropene according to the method described earlier.[9] After a stream of **1** in nitrogen was passed through a trap cooled in dry ice and then led into a solution of DPIBF in benzene at 20 °C, again, only the *exo*-adduct **3** could be isolated.

By our method, when **1**, which had been kept at −80 °C, was added to a solution of DPIBF in toluene at −30 °C, after purification by flash chromatography followed by HPLC, 72% of the *exo*-adduct **3** and 24% of the *endo*-adduct **4** were isolated. The ^{1}H NMR spectrum (200 MHz) of **3** in C_6D_6 agreed with the one reported in the literature.[18] The mass spectrum of the minor compound **4** revealed a M^+ peak at *m*/*e* 310, like that of **3**. The proton NMR spectrum displayed three signals at higher field representing four aliphatic hydrogen atoms (a doublet of triplets at δ 0.07 and 1.14 for the geminal methylene protons and a doublet of doublets at δ 2.47 ppm for the cyclopropyl methylidyne bridge hydrogens). While the data pointed to the structure of **4**, in order to finally be absolutely certain about the stereochemical assignments of **3** and **4**, an X-ray structure determination[20] of **4** was undertaken which proved the minor component to be the *endo*-adduct **4**.

The discrepancies concerning the exclusive formation of *endo*-adduct **2** and the preponderant formation of *exo*-adduct **3** may point to possible differences in the potential energy surfaces for these Diels−Alder reactions. Orbital coefficients of the LUMO of DPIBF obtained from AM1 calculations (Figure 1) show that the coefficients at C3a and C7a necessary for SOI[15] with the π_{CH_2} part of the HOMO ($2B_1$) of **1** are severely diminished compared with

(14) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1971.
(15) Apeloig, Y.; Matzner, E. *J. Am. Chem. Soc.* **1995**, *117*, 5375.
(16) Wiersum, U. E. *Aldrichimica Acta* **1981**, *14*, 53.
(17) Geibel, K.; Heindl, J. *Tetrahedron Lett.* **1970**, 2133.
(18) Battiste, M. A.; Sprouse, C. T., Jr. *Tetrahedron Lett.* **1970**, 4661; *Tetrahedron Lett.* **1969**, 3165.
(19) Cava, M. P.; Narasimhan, K. *J. Org. Chem.* **1971**, *36*, 1419.
(20) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystalographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

the corresponding orbitals of cyclopentadiene. This undermines SOI arguments for a preferred *endo*-adduct **4** formation.

It is also interesting to compare our results with those obtained from the reaction of cyclopropenone and DPIBF by Breslow and co-workers.[21] Here, the [4 + 2] cycloaddition affords only the *exo*-adduct. Recently Berson *et al*.[22] confirmed these findings by providing a crystal structure of the *exo*-adduct. Furthermore, some evidence was provided that at −30 °C the missing *endo*-isomer converts to the *exo*-isomer through a ring-opening reaction. Here, the preferred formation of the *exo*-adduct seems to benefit from an attractive nucleophilic ether−carbonyl interaction.

Experimental Section

General Methods. Melting points are uncorrected. IR spectra were recorded as KBr pellets on a FT spectrophotometer. ^{1}H (and ^{13}C) NMR spectra were acquired on instruments at 300 (75), 200 (50) and 400 (100) MHz, respectively. For the ^{1}H NMR spectra, TMS served as an internal chemical shift reference. ^{13}C spectra were referenced to the center line of $CDCl_3$ at 77.0 ppm. Coupling constants are reported in hertz. Low resolution mass spectra were obtained on either a spectrometer or by GC−MS using a gas chromatograph and a mass selective detector. Analytical gas chromatography was performed using a 15 m SE 54/G 124 glass capillary column (FID, H_2). Flash chromatography was done on a 2.5 cm (i.d. = 4.5 cm) column using silica gel (230−400 mesh). Preparative HPLC was performed using either a 23.0 cm column (i.d. = 2.6 cm; stationary phase: LiChroprep Si 100-C_{18}/A, 25−40 mm) or a 12.5 cm column (i.d. = 2.0 cm; stationary phase: Nucleosil-7−100-C_{18}/A, 95−26 mm). Crystal structure analysis was done with an Enraf Nonius CAD-4 Diffractometer. Combustion analyses were performed by Dornis and Kolbe, Mülheim/Ruhr, Germany.

Cyclopropene (1). In a 250 mL three-necked flask, equipped with a 25 mL dropping funnel, water-cooled Dimroth condenser, stirrer, an argon gas bubbler, and an inlet tube connected to a cold trap, 31.1 g (0.17 mol) of sodium bis(trimethylsilyl)amide[12] were dissolved in 100 mL of toluene. To this solution, at vigorous reflux, was added 11.5 g (0.15 mol) of allyl chloride, dropped over 20 min. Cyclopropene (**1**) escaped from the flask and was condensed in the trap at −80 °C. After an additional 30 min at reflux, 3.4 mL (d = 0.7 g/mL) (yield 40%) of cyclopropene (**1**) was collected as a colorless liquid. The ^{1}H NMR spectrum recorded at −80 °C is identical with a published spectrum and showed nearly pure **1** (>95%) with only traces of allyl chloride.

Reaction of Cyclopropene (1) with Cyclopentadiene. In an NMR tube, 0.2 mL (0.16 g, 4 mmol) of cyclopropene (**1**) was added at −80 °C to 0.4 mL (0.32 g, 48 mmol) of cyclopentadiene in 1 mL of toluene-d_8. The NMR spectrum recorded at −80 °C showed that no reaction had taken place (even after 24 h). Also, after 2 h, at −30 °C there was no reaction. At room temperature, however, *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (**2**) was formed quantitatively. Besides **2**, the NMR showed the presence of excess of cyclopentadiene and its dimer.

Reaction of Cyclopropene (1) with 1,3-Diphenylisobenzofuran. A 0.9 g (3.3 mmol) portion of 1,3-diphenylisobenzofuran was dissolved at −30 °C in 40 mL of toluene. To the yellow solution was added 0.2 g (5 mmol) of cyclopropene which had been kept at −80 °C. After 1 h at this temperature, a light decolorization had taken place and after further standing overnight at 0 °C, a clear colorless solution resulted. The solvent was removed *in vacuo* at room temperature to afford 1.18 g of a colorless oil which consisted of **3** and **4** (ratio 72:24) and oligomers of **1**. Purification by flash chromatography using a 25 cm silica gel filled column, hexane:ether = 5:1 as eluant, and 1 bar of argon pressure, gave 0.98 g of a highly viscous liquid which consisted of 735 mg of **3** (72%) and 245 mg of **4** (24%). HPLC separation on the 23.0 and 12.5 cm columns, respectively (CH_3CN and CH_3CN:H_2O = 95:5, at 20 mL and 10 mL/min, respectively) afforded **3** and **4** in a purity of 96% and 92%, respectively.

***exo*-1a,2,7,7a-Tetrahydro-2,7-diphenyl-2,7-epoxy-1*H*-cyclopropa[*b*]naphthaline (3):** mp = 95 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.69 (dt, H1, *anti* to oxygen bridge, $J_{1,1'} = -5.3$, $J_{1,1a} = 6.7$), 1.46 (dd, H1a, H7a, $J_{1,1a} = 6.7$, $J_{1a,1'} = 3.6$), 1.70 (H1′; *syn* to oxygen bridge), (400 MHz, $CDCl_3$), 6.9−7.1 (AA′ BB′, 4H, H3−6) 7.25−7.7 (m, 10 H); ^{13}C (50 MHz) 15.7 (t, C1), 25.4 (d, C1a, 7a), 88.7 (s, C2, 7), 119.3 (d), 126.0 (d), 126.7 (d) 128.0 (d), 128.4 (d), 136.6 (s), 150.9 (s); IR (KBr) 3060, 3002, 1603, 1495, 1454, 1448, 1369, 1309, 1056, 755, 698, cm^{-1}; MS (*m*/*e*) 310 (M$^+$), 292, 205 (100%), 165, 127, 105, 77, 51. Anal. Calcd. for $C_{23}H_{18}O$: C, 89.00; H, 5.84. Found: C, 88.67; H, 5.83.

***endo*-1a,2,7,7a-Tetrahydro-2,7-diphenyl-2,7-epoxy-1*H*-cyclopropa[*b*]naphthaline (4):** mp = 142 °C; ^{1}H NMR (300 MHz) δ 0.07 (dt, H1, *syn* to benzene ring, $J_{1,1'} = -6.1$, $J_{1,1a}$= 3.3), 1.14 (dt, H1′, $J_{1',1a} = 7.0$), 2.47 (dd, H1a, H7a, $J_{1',1a} = 7.0$, $J_{1,1a} = 3.3$), 6.7−7.15 (AA′ BB′, 4H, H 3−6), 7.25−7.6 (m, 10 H); ^{13}C NMR (75 MHz) δ 24.5 (t, C1), 27.2 (d, C1a, 7), 90.7 (s, C2, 7), 118.6 (d), 126.7 (d), 127.7 (d), 128.3 (d), 138.5 (s), 145.8 (s); IR (KBr) 3070, 3048, 3027, 2999, 1602, 1494, 1458, 1448, 1368, 1320, 1076, 754, 695 cm^{-1}; MS (*m*/*e*) 310 (M$^+$), 282, 206 (100%) 178, 126, 104, 71. Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.84. Found: C, 88.73; H, 5.81.

Acknowledgments. U.H.B. thanks the State University of New York at Binghamton for a sabbatical leave and those at the Max-Planck-Institut für Kohlenforschung for their generous hospitality. We are grateful to Murray G. Rosenberg for performing AM1 calculations on **2**, its *exo*-adduct, **3**, and **4**.

Supporting Information Available: ORTEP plots of **4** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960728R

(21) (a) Breslow, R.; Oda, M. *J. Am. Chem. Soc.* **1972**, *94*, 4787. (b) Oda, M.; Breslow, R.; Pecoraro, J. *Tetrahedron Lett.* **1972**, 4419.

(22) Cordes, M. H. J.; de Gala, S.; Berson, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 11161.

(23) According to AM1 calculations, *exo*-adduct **3** is 3.1 kcal/mol more stable than *endo*-adduct **4**. Rosenberg, M. G.; Brinker, U. H., unpublished.