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Synthesis of Benzvalene[†]

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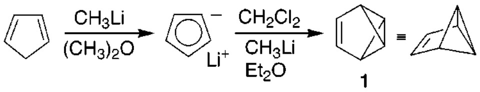
Benzvalene (**1**, tricyclo[3.1.$0.0^{2,6}$]hex-3-ene) was first prepared in 1966 by photoirradiating benzene,[1] but the amount that could be made in this way was tiny.[2] Since 1971, the combination of cyclopentadiene, methylene chloride, and methyllithium (eq 1) has made benzvalene available easily and in quantity[3] and has allowed it to be used as the starting material for the synthesis of a variety of its derivatives[4,5] and of the parents and derivatives of a number of other skeletons, including **2**−**12**.[4,6]



2

3

4

5

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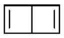
$(CH{=}CH)_n$

9

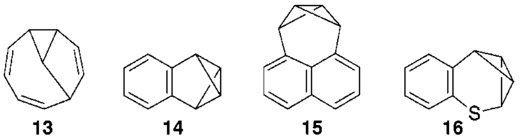
10

11



12

The mechanism of the transformation has been analyzed,[7] and the method used to prepare **1** has been applied to synthesize a number of ring systems, of which **13**−**16** are illustrative.[8,9]



13 **14** **15** **16**

The source of the benzvalene for all the studies described above was an unpublished procedure available until recently from Organic Syntheses, Inc.[10] Because it is no longer available,[11] we are publishing it here. The synthesis was developed after it had been discovered that the combination of lithium cyclononatetraenide, methylene chloride, and *n*-butyllithium gives isobullvalene (**13**),[12,8a,b] a structure related to [10]annulene as benzvalene is to benzene. It has been used by Professor Manfred Christl to prepare, during a period of a number of years, more than 5 kg of benzvalene.[4−6,13]

Discussion

The choice of solvent for the synthesis is important because carbenoid reactions of lithium halomethides occur best in those that solvate lithium cations poorly.[14] However, diethyl ether, the solvent commonly used for carbenoid reactions, gives only a low yield of benzvalene, probably because it dissolves only a small amount of lithium cyclopentadienide. Dimethyl ether, in contrast, gives a good yield, and although it also offers the advantage that distillation separates it easily from benzvalene,[15] the preparation of large samples of pure benzvalene by distillation has not been studied because of benzvalene's explosiveness.[3] Instead, the synthesis is performed in mixtures of dimethyl and diethyl ethers, so that when the product is distilled, the benzvalene is diluted by an inert solvent. Pure benzvalene, when subjected to shock, explodes. However, its solutions have never been reported to do so although they have been used for innumerable experiments during the past 28 years.

[†] Dedicated to Prof. Manfred Christl (University of Würzburg) with appreciation for the many structures he has synthesized from benzvalene.

(1) Wilzbach, K. E.; Ritscher, J. S.; Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 1031.

(2) Light also destroys it: Kaplan, L.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 3291.

(3) Katz, T. J.; Wang, E. J.; Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782.

(4) Review: Christl, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 529.

(5) (a) Schlüter, A.-D.; Belzner, J.; Heywang, U.; Szeimies, G. *Tetrahedron Lett.* **1983**, *24*, 891. (b) Christl, M.; Freund, S. *Chem. Ber.* **1985**, *118*, 979. (c) Christl, M.; Mattauch, B.; Irngartinger, H.; Goldmann, A. *Chem. Ber.* **1986**, *119*, 950. (d) Kunz, U.; Krimm, S.; Fischer, T.; Kottke, T.; Stalke, D.; Christl, M. *Eur. J. Org. Chem.* **1998**, *2171*, 1.

(6) In addition to those in Christl's review (ref 4), references include the following. For **3**: (a) Hashmi, A. S. K.; Szeimies, G. *Chem. Ber.* **1994,** *127*, 1075. (b) Graf, S.; Szeimies, G. *Tetrahedron* **1993**, *49*, 3101. (c) Freund, S.; Henneberger, H.; Christl, M. *Chem. Ber.* **1988**, *121*, 1665. (d) Reference 5c. (e) Christl, M.; Leininger, H.; Kemmer, P. *Chem. Ber.* **1984**, *117*, 2963. (f) Leininger, H.; Kemmer, P.; Beck, K.; Christl, M. *Chem. Ber.* **1982**, *115*, 3213. For **4**: (g) Christl, M.; Herzog, C.; Brückner, D.; Lang, R. *Chem. Ber.* **1986**, *119*, 141. For **5**: (h) Christl, M.; Herzog, C.; Kemmer, P. *Chem. Ber.* **1986**, *119*, 3045, and earlier work cited therein. For **6**: (i) Christl, M.; Türk, M.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1639. For **7**: (j) Christl, M.; Brunn, E.; Lanzendörfer, F. *J. Am. Chem. Soc.* **1984**, *106*, 373; ref 6e. For **8**: (k) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 3927. (l) Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 4413. (m) Leininger, H.; Lanzendörfer, F.; Christl, M. *Chem. Ber.* **1983**, *116*, 669. (n) Leininger, H.; Christl, M.; Wendisch, D. *Chem. Ber.* **1983**, *116*, 681. For **9**: ref 6l. For **10**: ref 6e. For **12**; (o) Christl, M.; Mattauch, B. *Chem. Ber.* **1985**, *118*, 4203.

(7) Review: Burger, U.; Thorel, P. J.; Mentha, Y. *Chimia* **1987**, *41*, 26.

(8) **13**: (a) Katz, T. J.; Cheung, J. J.; Acton, N. *J. Am. Chem. Soc.* **1970**, *92*, 6643. (b) Hojo, K.; Seidner, R. T.; Masamune, S. *J. Am. Chem. Soc.* **1970**, *92*, 6641. **14**: ref 3. **15**: (c) Murata, I.; Nakasuji, K. *Tetrahedron Lett.* **1973**, 47. (d) Pagni, R. M.; Watson, C. R. *Tetrahedron Lett.* **1973**, 59. **16**: Murata, I.; Tatsuoka, T.; Sugihara, Y. *Tetrahedron Lett.* **1974**, 199.

(9) A number of related examples are cited in ref 7. Others are in (a) Pagni, R. M.; Burnett, M.; Hazell, A. C. *J. Org. Chem.* **1978**, *43*, 2750. (b) Burger, U.; Thorell, P.-J.; Schaller, J.-P. *Tetrahedron Lett.* **1990**, *31*, 3155.

(10) Katz, T. J.; Roth, R. J.; Acton, N.; Carnahan, E. J. *Org. Synth.* **1973**, *53*, 157, unpublished procedure. There are 39 citations to this reference in the *Science Citation Index*. Organic Syntheses did not publish the procedure because its execution “demands too high a skill”, because “the yields obtained by the checker are too low”, because the “product is too dangerous”, and because “the reaction probably lacks generality”.

(11) Organic Syntheses, Inc., has discontinued distributing unpublished procedures.

(12) Katz, T. J.; Cheung, J. J. *J. Am. Chem. Soc.* **1969**, *91*, 7772.

(13) Prof. Manfred Christl, University of Würzburg, private communication.

(14) (a) Closs, G, L.; Closs, L. E. *J. Am. Chem. Soc.* **1960**, *82*, 5723. (b) Köbrich, G.; Merkele, H. H. *Chem. Ber.* **1966**, *99*, 1782. (c) Köbrich. G.; et al. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 41. (d) Burger, U.; Huisgen, R. *Tetrahedron Lett.* **1970**, 3049.

(15) Dimethyl ether boils at −25 °C.

10.1021/jo990883g CCC: $18.00

According to Christl's students[13] and Swager and Grubbs,[6l] the second batch of methyllithium in eq 1 can be replaced by the cheaper *n*-butyllithium in hexanes, and according to Christl's students, so can the first batch. In this latter case, because the reaction is more vigorous, the cyclopentadiene must be added more slowly.[13]

Experimental Section

A flame-dried 2 L round-bottomed flask was fitted with an airtight mechanical stirrer, dropping funnel, and low-temperature thermomether and was connected via a branched inlet to a source both of gases and (through a tube filled with Drierite) aspirator vacuum (the "gas inlet") and to a stopcock sealed with a serum-bottle cap. Methyllithium in diethyl ether (400 mL, 1.6 M, containing 0.4% lithium chloride) was introduced by syringe. The aspirator was then used to remove the ether. While the flask was cooled in a bath of dry ice and acetone, dimethyl ether (ca. 1 L) was distilled from $LiAlH_4$ into the flask through the gas inlet.[16] The temperature was raised to −35 °C, and cyclopentadiene (52 mL, 640 mmol) was added slowly by syringe (at ca. 1 mL/min). After the vigorous evolution of methane had subsided, methylene chloride (60 mL, 940 mmol) was added to the slurry (again at ca. 1 mL/min). Methyllithium in ether (440 mL, 1.6 M, containing 0.4% lithium chloride) was then added in drops from the dropping funnel. (The slurry was now yellow.) While the apparatus was flushed with nitrogen, the stopcock with the serum-bottle cap was replaced by a distillation head, condenser, and receiver, all of which had been washed with aqueous ammonia and dried. The dimethyl ether was distilled at atmospheric pressure and ambient temperature into a receiver that was cooled in dry ice−acetone.[17] When the pot temperature reached 20 °C, the receiver was replaced by a 500 mL flask, which was cooled in the dry ice−acetone mixture. The product, a solution of benzvalene in ether, was distilled at aspirator vacuum into this flask. The yield was ca. 400 mL of 0.7 M benzvalene in ether.[18] The benzvalene was contaminated with only 5−10% of benzene. In seven experiments, the yields of benzvalene ranged from 30 to 59% and averaged 45 ± 5%.

Caution: The distillation residue should be destroyed cautiously, for explosions have occurred when the residue was simply exposed to air or water. While the flask was being flushed with nitrogen, the distillation head was replaced by a stopcock sealed with a serum-bottle cap connected to a Teflon tube through which diethyl ether (100 mL) was syringed. The mixture was stirred, and wet ether (20 mL) was added in drops, followed by methanol (100 mL) and, very slowly, water (100 mL).[19]

Pure benzvalene can be isolated by GLPC, but it explodes when scratched. The GLPC was conducted as recommended by Wilzbach, Ritscher, and Kaplan,[1] using an unheated 5 ft × 1/4 in. aluminum column, packed with 5% isodecyl phthalate and 1.25% triethanolamine on 45/60 Chromosorb G, and a helium flow of 100 mL/min. The injector and detector were heated to 75 °C.

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[16] In Christl's lab, the dimethyl ether was distilled from the tank into the flask through two towers (each 6 cm in diameter, 40 cm high), the first filled with P_2O_5 on pumice, the second with KOH pellets.[13]

[17] Christl's students do not collect the Me_2O, but by sending its vapors through a rubber or plastic tube to a Bunsen burner in an adjacent fume hood, burn it.[13]

[18] Approximately 20 mg of nitrobenzene was weighed into a base-washed NMR tube. A 0.5 mL aliquot of the benzvalene solution was added, and the yield was analyzed by comparing the intensities of the olefinic and aromatic ^1H NMR absorptions.

[19] Brunn, E. Ph.D. Dissertation, University of Würzburg, 1983, destroyed the residue by adding to it 700 mL of petroleum ether (bp 50−70 °C) and then carefully in succession EtOAc, EtOH, and H_2O.