

Tetrahedron Letters 39 (1998) 1695-1696

TETRAHEDRON LETTERS

Improved Synthesis of Benzocyclobutenone by Flash Vacuum Pyrolysis

Laurence Suzzarini, Jian Lin and Zhi Yuan Wang* Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

Received 10 November 1997; revised 4 December 1997; accepted 7 December 1997

Abstract: Flash vacuum pyrolysis of o-toluoyl chloride at 780 °C under 0.5 mmHg afforded benzocyclobutenone in higher yield (80%) than previously reported one (28%). © 1998 Elsevier Science Ltd. All rights reserved.

Benzocyclobutenone (bicyclo[4.2.0]octa-1,3,5-triene-7-one, 1) is known to react with dienophiles, carbonyls compounds and nucleophiles.¹ Reaction of 1 with C_{60} gave the Diels-Alder adduct where a carbonyl group is introduced directly onto the fullerene core.² Compound 1 is also a precursor to benzocyclobutenedione which has been used to produce a variety of cyclopentenones³⁴ and quinones.³ Benzocyclobutenedione monoketal has been used for the synthesis of quinone-type antibiotics,⁴ as well as complex organic molecules with potential antiviral activity.⁵ Benzocyclobutenone was first synthesized in 42% yield by oxidation of benzocyclobutenedi.⁶ The only large-scale (80 g) synthesis of 1, reported by Liebeskind et al. was done via cycloaddition of benzyne and vinylidene chloride.⁷ However, this synthetic route, like the others involving benzyne as an intermediate,⁸ requires the use of large quantities of solvent, and generates a large amount of solid wastes. On the other hand, flash vacuum pyrolysis (FVP) is a gas-phase reaction and is a more environment-friendly process as no solvent is needed and no or little solid wastes are produced. Several compounds were reported to yield benzocyclobutenone by FVP. 1,2-Indandione (2),⁹ homophthalic anhydride (3),¹⁰ bicyclo[2.2.1]hepta-2,5-diene-2,3-carboxylic anhydride (4)¹¹ and o-toluoyl chloride (5)¹² generate benzocyclobutenone, by loss of CO, CO₂, CO₂ and HCl, in 54%, 45%, 11%, and 28% yields, respectively (Scheme 1).

In connection with the studies on benzocyclobutenone and its applications in polymers, we needed to have compound 1 in large quantities. Our efforts were directed towards gas-phase pyrolysis, rather than the solution process. We chose to use o-toluoyl chloride as it is easily derived from inexpensive o-toluic acid (5). Whereas compounds 2, 3 and 4 have to be made by multistep synthesis, rendering them less readily available.



The reported pyrolysis was carried out at 630 °C and 14 mmHg, producing 1 in 28 % yield (run 1, Table 1).¹² The formation of 1 was accompanied by the evolution of hydrochloric acid. We studied the pyrolysis of o-toluoyl chloride under different conditions by varying the pyrolysis temperature and the system pressure (Table 1). We found that the pyrolysis of o-toluoyl chloride was very sensitive to slight changes in pressure and temperature in the system. These parameters can greatly affect the yield.

Run		2	3	4	5	6	7	8
Column Temperature (°C)	630	630	780	780	780	800	800	780
Pressure (mmHg)	14	5	5	5	1.75	1.75	1.5	0.5
yield (%)	28	53	59	60	35	32	75	80

Table 1. Parameters for the pyrolysis of o-toluoyl chloride.

The yield of 1 was significantly increased when decreasing the system pressure (run 2). The reactant 5 must stay in the hot reaction zone long enough for the reaction to occur, but not too long so as to prevent any further side reactions. Furthermore, the product 1 should be removed from the hot zone as quickly as possible in order to avoid thermal decomposition. Some of the thermal decomposition products from 1 were identified, e.g., benzocyclopropene (6),⁹ fluvenallene (7)^{9,10} and ethynylcyclopentadiene (8) (Scheme 2).⁹ An increase in the column temperature from 630 to 780 °C had little effect on the yield (runs 3 and 4). A decrease of the system pressure lowered the yield (run 5). Comparing runs 5 and 6, the yield dropped slightly (32%) at higher temperature (800 °C, run 6). However, a significant increase in yield (75%) was observed when the pressure was further decreased to 1.5 mmHg (run 7). After further fine tuning, an optimized condition (e.g., 780 °C, 0.5 mmHg) was established, which allowed a large-scale (>200 g) synthesis of 1 in high yield (e.g., 80%, run 8).



A typical pyrolysis is as follows: A horizontal type of FVP apparatus was used. A quartz tube (30 cm x Φ 2 cm) filled with quartz beads (1 cm x Φ 0.4 cm) was placed horizontally in a tube furnace. The reactant 5 was placed in a round-bottomed flask which was connected to the hot tune. The reactant was distilled under vacuum at 90-100 °C (oil bath temperature). The pyrolyzate was collected in a cold trap (-78 °C) attached at the end of the tube. Hydrochloric acid gas was trapped into a column packed with solid potassium hydroxide pellets. The collected pyrolyzate was then diluted with diethyl ether and was washed with aqueous potassium carbonate solution (5%) and water. The organic phase was dried over anhydrous MgSO₄, concentrated and vacuum distilled to give benzocyclobutenone: Bp_{nos} 35-37 °C (lit¹³: Bp_{0.1} 50 °C).

This work was supported by Environmental Science and Technology Alliance Canada and the Natural Sciences and Engineering Research Council of Canada.

References

- (a) Schiess, P.; Eberle, M.; Huys-Francotte, M.; Wirz, J. Tetrahedron Lett. 1984, 25, 2201; (b) Wang, Z.
 Y.; Suzzarini, L.; Gao, J. P. Tetrahedron Lett. 1997, 38, 5745.
- 2. Tomioka, H.; Yamamoto, K. J. Chem. Soc. Chem. Commun. 1995, 1961.
- (a) Liebeskind, L. S. Tetrahedron 1989, 45, 3053; (b) Jung, M. E.; Lowe, J. A. J. Org. Chem. 1977, 42, 2371; (c) Decker, O. H. W.; Moore, H. W. J. Org. Chem. 1987, 52, 1174
- 4. Jackson, D. K.; Narasimhan, L.; Swenton, J. S. J. Am. Chem. Soc. 1979, 101, 3989.
- 5. Mitchell, D.; Liebeskind, L. S. J. Am. Chem. Soc. 1990, 112, 291.
- 6. Cava, M. P.; Muth, K. J. Am. Chem. Soc. 1960, 82, 652.
- 7. South, M. S.; Liebeskind, L. S. J. Org. Chem. 1982, 47, 3815.
- (a) Stevens, R. V.; Bisacchi, G. S. J. Org. Chem. 1982, 47, 2393; (b) Hosoya, T.; Hasegawa, T.; Kuriyama, Y.; Matsumoto, T.; Suzuki, K. Synlett 1995, 177.
- 9. Hedaya, E.; Kent, M. E. J. Am. Chem. Soc. 1970, 92, 2149.
- 10. Spangler, R. J.; Kim, J. H. Tetrahedron Lett. 1972, 13, 1249.
- 11. Mamer, O. A.; Lossing, F. P.; Hedaya, E.; Kent, M. E. Can. J. Chem. 1970, 48, 3606.
- 12. Schiess, P.; Heitzmann, M. Angew. Chem. Int. Ed. Engl. 1977, 16, 469.
- 13. Dürr, H.; Nickels, H.; Pacala, L. A.; Jones, M., Jr. J. Org. Chem. 1980, 45, 973.