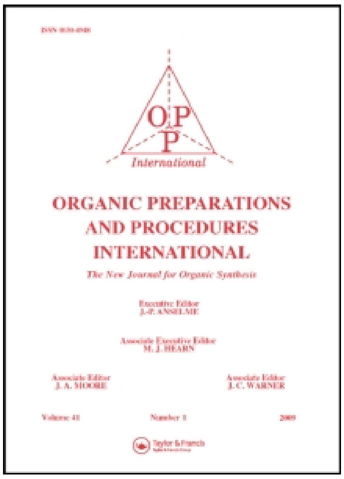


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A CONVENIENT SYNTHESIS OF DIBENZOBARRELENE

Peter W. Rabideau[a]
[a] Department of Chemistry Purdue School of Science at Indianapolis, Indiana University-Purdue University at Indianapolis, Indianapolis, Indiana

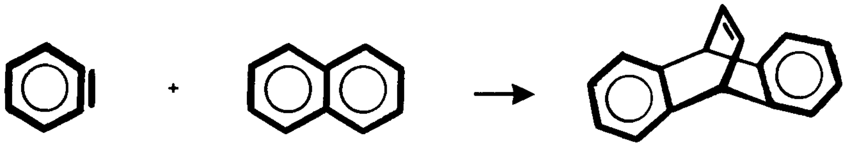
To cite this Article Rabideau, Peter W.(1986) 'A CONVENIENT SYNTHESIS OF DIBENZOBARRELENE', Organic Preparations and Procedures International, 18: 2, 113 — 116
To link to this Article: DOI: 10.1080/00304948609356831
URL: http://dx.doi.org/10.1080/00304948609356831

A CONVENIENT SYNTHESIS OF DIBENZOBARRELENE

Submitted by Peter W. Rabideau
(10/01/85)
Department of Chemistry
Purdue School of Science at Indianapolis
Indiana University-Purdue University at Indianapolis
Indianapolis, Indiana 46223

A number of methods for the synthesis of dibenzobarrelene (1, dibenzobicyclo[2.2.2]octatriene) have appeared recently.[1] Although the reaction of phenylvinyl sulfoxides and sulfones with anthracene provides higher yields than earlier routes,[2] modifications of this procedure have been pursued to avoid "tedious handling of massive quantities of toxic metallic mercury" necessary for larger scale reactions.[1d] In any event, these methods report the production of 198 mg,[1b] 225 mg[1c] and 510 mg[1d] of the desired product, and usually involve heating for an extended period, sometimes in a sealed tube. Herein we report a method by which up to 40 g of 1 can be produced from readily available starting materials in less than six hours. A convenient source of dibenzobarrelene is even more significant in terms of its easy conversion to other $C_{16}H_{12}$ hydrocarbons.[5]

The reaction of benzyne with naphthalene to produce 1 was first reported by Miller and Stiles[3] who used the zwitterion, benzenediazonium-2-carboxylate, to generate benzyne. The procedure herein is similar except the non-explosive (see Experimental Section) benzenediazonium-2-carboxylate hydrochloride salt is used according to procedures developed by Logullo and Friedman[4] for the preparation of triptycenes. This procedure[4c] offers


1

several advantages: a) the hydrochloride salt is not only non-explosive but appears to give better yields (20% vs 7%); b) excess naphthalene is easily removed by steam distillation and c) the dibenzobarrelene is conveniently isolated by co-distillation with ethylene glycol. For these reasons, it is not difficult to run this reaction on a molar scale in which case up to 40 g of 1 can be isolated.

EXPERIMENTAL SECTION

NOTE. The procedure herein involves the isolation of benzenediazonium-2-carboxylate hydrochloride according to the method of Stiles et al.,[3] with subsequent modification for the generation of benzyne by the method of Logullo and Friedman.[4] Although the former workers indicated both benzenediazonium-2-carboxylate and its HCl salt to be explosive, this issue was addressed in more detail by Logullo who found only the zwitterion to be explosive. Logullo reports that "the hydrochloride salt is not shock sensitive, but flashes on ignition, and that 30 g of this salt was ignited without explosion."[4a]

We have also found the hydrochloride salt to be non-explosive and have not encountered any difficulties. **Nonetheless the following precautions were always taken**. After the salt is added to the solvent/naphthalene mixture at ambient temperature, uniform stirring (but not heating) is achieved. Propylene oxide is then added and the mixture is slowly heated to reflux in order to avoid the possibility of "hot spots", and slow, uniform heating is begun only after all materials have been added and are being efficiently stirred. Furthermore, heating is continued until cessation of gas evolution resulting in a clear, brown solution (i. e., do not interrupt heating and filter suspended particles).

Dibenzobicyclo[2.2.2]octatriene (1).- Benzenediazonium-2-carboxylate hydrochloride was prepared by adding conc. HCl (100 ml) to a stirred solution of anthranilic acid (136 g, 1 mole) in absolute ethanol (1500 ml) contained in a 4 liter breaker. Isoamyl nitrite (250 ml) was then added to the cooled solution (~ 10°, ice bath), and stirring was continued for 30 minutes. Anhydrous ether (1200 ml) was then added to precipitate the salt which is collected, washed with ether and briefly dried on the filter. This salt was then added to 2.5 l. of 1,2-dichloroethane in a 5 l. round-bottomed flask containing the naphthalene (450 g, 3.5 eq). Stirring, but not heating, was begun and 125 ml propylene oxide was added. The reaction mixture was then heated slowly to reflux, during which time gas was evolved. The reaction was over when gas evolution stopped, and a clear, dark brown solution resulted. Most of the 1,2-dichloroethane was removed by rotary evaporation, and the solution was then washed with dilute sodium hydroxide and steam distilled to remove the excess naphthalene.[6] Water was decanted from the dark residue, and ethylene glycol (~ 1.5 l.) added. After being made just alkaline by the addition of potassium hydroxide pellets, the mixture was distilled and the ethylene glycol/dibenzobarrelene azeotrope was collected above 185° (principally at 196°). After distillation was complete (determined by adding a little water to a sample of distillate), the solution was diluted with water (~ 800 ml), and the milky suspension was allowed to stand several hours until crystallization was complete. The solid was collected, washed with water, and air dried to give 40 g dibenzobarrelene (20% yield), mp. 115-117°, lit.[1] 118.5-119°. Further purification, if necessary, was accomplished by recrystallization from ethanol. NMR (CCl_4): δ 7.08 (m, aryl + vinyl); 5.01 (m, bridgehead).

Acknowldgements.- We would like to acknowledge the U. S. Department of Energy, Office of Basic Energy Sciences, for support of this work. We also thank Dr. Lester Friedman for suggestions which led to the development of the benzyne procedure.

REFERENCES

1. a) L. A. Paquette, R. E. Moerck, B. Harirchian and P. D. Magnus, J. Am. Chem. Soc., 100, 1597 (1978). b) R. V. C. Carr, R. V. Williams and L. A. Paquette, J. Org. Chem., 48, 4976 (1983). c) G. L. Cantrell and R. Filler, ibid., 49, 3406 (1984). d) A. C. Brown and L. A. Carpino, ibid., 50, 1749 (1985).
2. S. J. Cristol and N. L. Hause, J. Am. Chem. Soc., 74, 2193 (1952); S. J. Cristol and R. K. Bly, ibid., 82, 6155 (1960).

3. R. G. Miller and M. Stiles, ibid., 85, (1978).

4. a) F. M. Logullo, Ph. D. Thesis, Case Institute of Technology, Cleveland, Ohio, 1965. b) See also L. Friedman and F. M. Logullo, J. Am. Chem. Soc., 85, 1549 (1960). c) See also P. W. Rabideau, Ph. D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1968.

5. P. W. Rabideau, J. B. Hamilton and L. Friedman, J. Am. Chem. Soc., 90, 4465 (1968).

6. This requires a reasonable amount of time depending on equipment. Usual techniques for the steam distillation of a solid must be employed. We have found steam distillation through a short air condenser into a 3-neck flask immersed in an ice bath and fitted with an upright condenser to be quite satisfactory.