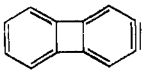
Communications

2,3-Dehydrobiphenylene

Summary: Thermal decomposition of 2-biphenylenediazonium 3-carboxylate affords 2,3-dehydrobiphenylene which forms 2-chlorobiphenylene with 1,2-dichloroethane, biphenylenebicyclo[2.2.2]octatriene with benzene, and 1,2,3,4-tetraphenylbenzo[*b*]biphenylene with tetraphenylcyclopentadienone.

Sir: As part of our program to synthesize the higher homologs of biphenylene which incorporate four-membered rings into an annellated system, we have been able to generate and trap the novel aryne, 2,3-dehydrobiphenylene (**1**). The precursor[1] of **1**, 2-biphenylenediazonium 3-carboxylate (**2**), was prepared starting with 2-acetamido-3-bromobiphenylene[2] which on treatment with cuprous cyanide in dimethylformamide gave 2-acetamido-3-cyanobiphenylene. Hydrolysis of the cyano group with hot concentrated hydrochloric acid afforded 2-acetamidobiphenylene-3-carboxylic acid which on treatment with sodium hydroxide in aqueous ethanol gave 2-aminobiphenylene-3-carboxylic acid (**3**). Diazotization of **3** with isoamyl nitrite in tetrahydrofuran containing a trace of trichloroacetic acid gave **2**. Thermal decomposition of **2** in the presence of tetraphenylcyclopentadienone yielded the adduct **4** isolated *via* chromatography (neutral alumina–pentane) in 10% yield: white needles; mp 316–317.5°; uv max (cyclohexane) 251 nm (ϵ 27,500), 274 (50,700), 282 (66,700), 296 (42,800), 309 (55,100), 341 (7250), 353 (5070), 373 (6520), 394 (6520); nmr ($CDCl_3$) δ 7.15 (s, 10, C-1 and C-4 phenyls), 6.80 (s) and 6.76 (s) (16, C-2 and C-3 phenyls + biphenylene); mass spectrum *m/e* 506 (parent).



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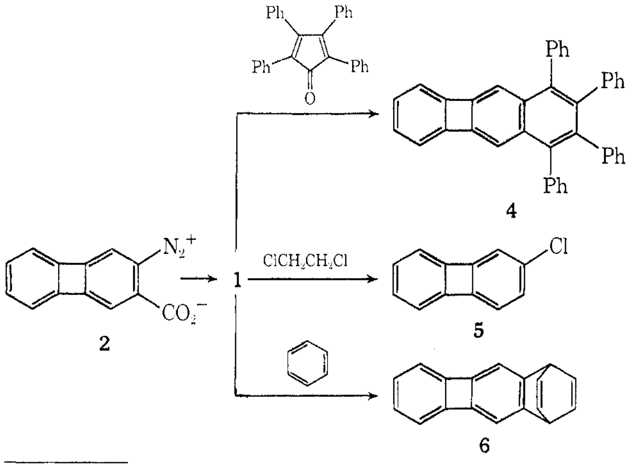

Attempts to isolate the dimer of **1** have thus far been unsuccessful. Thus, the thermal decomposition of **2** in refluxing 1,2-dichloroethane affords as the main product (9% yield) 2-chlorobiphenylene **5**.[3] In refluxing benzene **2** affords mostly polymeric material accompanied by a small amount (1%) of biphenylenebicyclo[2.2.2]-octatriene (**6**): a yellow solid; mp 156–158°; nmr ($CDCl_3$) δ 7.2–6.3 (m, 10, aromatic plus olefinic), 5.0–4.7 (m, 2, bridgehead); mass spectrum *m/e* 228 (parent) 202 ($P - C_2H_2$).

Attempts at crossing 2,3-dehydrobiphenylene with benzyne resulted primarily in the independent dimerization of benzyne to yield biphenylene.

It is evident from the trapping experiments that 2,3-dehydrobiphenylene generated from the diazonium carboxylate **2** is a true aryne, undergoing cycloaddition reactions typical of the highly reactive intermediates. However, under conditions generally favorable for aryne dimerization, **1** either does not undergo aryne coupling (*i.e.*, dimerization or crossing) or does so in such a myriad of concomitant reactions that the expected products are not isolable.

Regardless of this, 2,3-dehydrobiphenylene is in itself an interesting intermediate warranting further synthetic and theoretical investigation.[4]

Supplementary Material Available.—Details of the syntheses of the compounds reported here along with spectral information will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-1973-3812.

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(1) See paragraph at end of table regarding supplementary material.

(2) W. Baker, J. F. W. McOmie, D. R. Preston, and V. Rogers, *J. Chem. Soc.*, 414 (1960).

(3) W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 2666 (1958).

(4) This investigation was assisted financially by a grant from the National Science Foundation.

(5) Taken in part from the thesis of E. N. Losey, submitted in partial fulfillment of the requirement for the Ph.D. degree at Michigan State University, 1973.

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Three-Electron Oxidations. V. The Rapid Reaction of Chromic Acid with Two-Component Substrate System[1,2]

Summary: The chromic acid oxidation of binary systems containing isopropyl alcohol and bifunctional compounds such as dicarboxylic acids, hydroxy acids, and aldehydo or keto acids can be much faster than

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(1) Part IV: F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **95**, 5421 (1973).

(2) This investigation was supported by the National Science Foundation.