Table I. Aliphatic Diazo Ketones Prepared by the Method [a] of eq 1

Registry no.	Diazo ketone	Yield, %	Purity, % N_2 evol (NMR)
10290-42-3	$C_6H_5CH_2CH_2C(=O)CHN_2$	96	82 (83)
31151-40-3	c-$C_6H_{11}C(=O)CHN_2$	96	85 (77)
58697-26-0	$CH_3(CH_2)_7C(=O)CHN_2$	96	87 (85)
14088-55-2	$(CH_3)_2CHC(=O)CHN_2$	86[b]	85 (76)
	$C_6H_5CH_2C(=O)CHN_2$		(<10%)

[a] Optimized only for the first entry. [b] Lower yield due to partial solubility of the product in water.

reaction, the mixture grew more viscous and then thinned out again. After warming to room temperature, the reaction mixture was diluted with water. The organic layer was separated and washed successively with 10% aqueous acetic acid, water, saturated sodium bicarbonate solution, water, and saturated sodium chloride solution. The resulting solution was dried over calcium sulfate[13] and concentrated under vacuum to a deep yellow oil: 12.8–13.9 g, 92–100% yield.

A weighed aliquot of the crude product was dissolved in ethanol and treated with concentrated hydrochloric acid;[2,3] the nitrogen evolved corresponded to 76–87% of that expected for pure diazo ketone. NMR analysis of the crude product revealed 1-diazo-4-phenyl-2-butanone (76–90%), 1-chloro-4-phenyl-2-butanone (4–5%), methyl 3-phenylpropanoate (2–3%), 3-phenylpropanoic anhydride, and benzylcyclobutanone (both isomers), all of which were isolated by chromatography on silica gel (15% ethyl acetate/petroleum ether) for identification purposes.

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Registry No.—Diazomethane, 334-88-3; 3-phenylpropanoyl chloride, 645-45-4; 1-chloro-4-phenyl-2-butanone, 20845-80-1; methyl 3-phenylpropanoate, 103-25-3; cyclohexylcarbonyl chloride, 2719-27-9; nonanoyl chloride, 764-85-2; 2-methylpropanoyl chloride, 79-30-1.

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(8) Distilled under nitrogen from sodium/benzophenone.
(9) Caution Explosive. Diazomethane was prepared according to the procedure of J. A. Moore and D. E. Reed, "Organic Syntheses", Collect. Vol. V, 1973, 351, and standardized by duplicate titrations according to the procedure of F. Arndt, "Organic Syntheses," Collect. Vol. II, 1943, p 165. Reagent grade ether (ethanol free) must be used to avoid contamination of the final product by ethyl ester. After distillation, the diazomethane solution still contains at least 1% water which can be removed by drying over potassium hydroxide pellets for 30 min at 0 °C. Omission of this drying step leads to a considerable amount of methyl ester in the final product. When properly dried, no cloudiness (ice crystals) developes in the ethereal diazomethane on cooling to −78 °C; further drying over sodium wire proved unnecessary.
(10) Prepared from hydrocinnamic acid and thionyl chloride in 95% yield after distillation.
(11) Even in the absence of diazomethane, a thick white precipitate forms instantly. Hydrolysis of the resulting mixture gives hydrocinnamic anhydride, the expected product from an acylammonium salt. [See J. V. Paukstelis and M.-g. Kim, *J. Org. Chem.*, **39**, 1503 (1974)]. The reactive species may actually be this acylammonium salt, although formation of the diazo ketone does not occur at −78 °C.
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(13) Magnesium sulfate should be avoided, as it slowly decomposes diazo ketones.

A Convenient Large-Scale Preparation of Benzobarrelene

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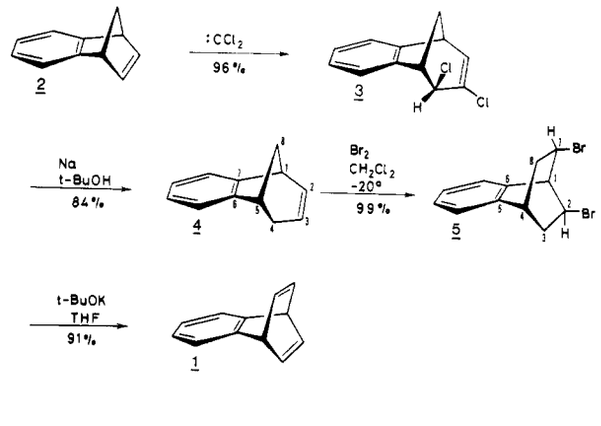
Benzobarrelene (**1**) is a molecule of considerable potential mechanistic interest, but studies of its chemistry have been few on account of its relative unavailability. Neither of the existing synthetic routes, the addition of benzyne to benzene,[1] nor the cycloaddition of maleic anhydride to β-naphthol,[2] is suitable for large-scale preparation. However, Heaney and co-workers have recently reported[3] a high-yield preparation which consists of the reductive dechlorination of tetrachlorobenzobarrelene, obtained from the cycloaddition of tetrachlorobenzyne to benzene. We now present here an alternative large-scale preparation of benzobarrelene which has considerable flexibility and should allow efficient isotopic labeling of the bicyclic skeleton, as well as preparation of aromatic substituted derivatives.

The addition of dichlorocarbene to the readily available benzonorbornadiene (**2**)[4] gives a rearranged adduct which on reductive dechlorination affords benzo[6,7]bicyclo[3.2.1]-octa-2,6-diene (**4**).[5] In the present work, the method of Parham and Schweizer[6] was used for generating dichlorocarbene. Dechlorination of the adduct was effected with sodium and *tert*-butyl alcohol (Scheme I) and **4** was obtained in an overall yield of 80% for the two steps.

Bromination of hydrocarbon **4** in dichloromethane at −20 °C proceeded with rearrangement to give di-*anti*-bromo adduct **5** in essentially quantitative yield. This key step serves both to bring about the requisite skeletal rearrangement and to provide the functionality which permits the easy introduction of two double bonds. The structure of adduct **5** was securely assigned from its ^1H and ^{13}C NMR spectra (see Experimental Section) which unambiguously provide evidence for the symmetry of the molecule. Analogous stereospecific bromination rearrangements have been observed for the homologues, benzonorbornadiene (**2**)[7] and benzo[7,8]bicyclo[4.2.1]nona-2,7-diene,[8] and present no particular mechanistic problems.

In the final step, the double dehydrobromination of **5** was achieved with surprising efficiency using the classical method of potassium *tert*-butoxide in tetrahydrofuran. Essentially pure benzobarrelene was isolated in yields greater than 90%, after sublimation. Benzobarrelene (**1**) may thus be prepared

Scheme I



from benzonorbornadiene (2) in four steps with an overall yield of ca. 70%.

The presently described synthesis offers several advantages over previous methods. Although relatively lengthy, it begins with a readily available starting material (2), and the subsequent steps are all efficient and readily amenable to large scale-up, since there are no troublesome purifications necessary. However, in addition to simply offering a means of preparing large quantities of the parent 1, this route offers several possibilities for isotopically labeling the bicyclic skeleton. For example, the use of ^{13}C- or ^{12}C-labeled chloroform in the phase-transfer method[9] for carbene generation would lead to 1 selectively labeled at C(2). Alternatively, several deuterated benzonorbornadienes are known,[10] which could serve as precursors to deuterated 1. Finally, this route allows straightforward synthesis of aromatic-substituted benzobarrelenes.[11]

Experimental Section

Addition of Dichlorocarbene to Benzonorbornadiene (2). A mixture of benzonorbornadiene (19.0 g, 0.133 mol), sodium methoxide (32.3 g, 0.597 mol), and dry hexane (150 mL) was cooled in an ice bath and vigorously stirred while ethyl trichloroacetate (100.4 g, 0.545 mol) was added dropwise during 3 h. The reaction temperature was maintained below 5 °C throughout the addition. After an additional 4 h at 0 °C, the mixture was allowed to warm gradually to ambient temperature and was stirred overnight, before being poured into ice water (500 mL). The organic layer was separated and the water layer was extracted with ether (3 × 100 mL). Combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated at reduced pressure to afford a brown oil. Distillation at reduced pressure, then under vacuum, yielded adduct 3 (29.02 g, 96.5%) as a viscous yellow oil (bp 98–105 °C at 0.7 mm), which crystallized on standing.

Recrystallization of a small sample from pentane afforded slightly yellow crystals: mp 75–75.5 °C (lit.[5b] 68–69 °C). The ^1H NMR spectrum was as reported.

Benzo[6,7]bicyclo[3.2.1]octa-2,6-diene (4). Metallic sodium (28.5 g, 1.24 mol) was cut into small pieces and combined with 300 mL of anhydrous ether. This was mechanically stirred at gentle reflux under a nitrogen atmosphere while a mixture of dichloride 3 (29.02 g, 0.129 mol), *tert*-butyl alcohol (74.0 g, 1.0 mol), and ether (50 mL) was added dropwise during 3 h. After stirring at reflux overnight, heating was discontinued and methanol (50 mL) and then water (100 mL) were added dropwise. The mixture was poured into water (200 mL), the organic layer was separated, and the water layer was extracted with ether (3× 100 mL). Combined organic layers were washed with water and brine, dried ($MgSO_4$), and concentrated. Distillation afforded alkene 4 (16.42 g, 83.5%) as a colorless oil: bp 45 °C (0.1 mm); ^1H NMR was as reported;[5b] ^{13}C NMR ($CDCl_3$) 151.8, 146.2, 134.2, 126.0, 125.9, 123.4, 123.3, 120.3, 41.2, 40.7, 40.3, 32.3 ppm.

***anti,anti*-2,7-Dibromobenzo[5,6]bicyclo[2.2.2]oct-5-ene (5).** A solution of alkene 4 (7.58 g, 48.6 mmol) in dichloromethane (20 mL) was stirred at −20 °C while a solution of bromine in dichloromethane (ca. 10% solution) was added dropwise until no further reaction was noted. Warming to ambient temperature and solvent removal at reduced pressure yielded dibromide 5 (15.22 g, 99.2%) as slightly orange crystals.

Recrystallization of a small sample from hexane afforded white crystals: mp 133.5–134.5 °C; IR (KBr) prominent maxima at 2900, 1470, 1322, 1267, 1235, 951, 835, 767 and 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20–2.60 (apparent d of d, 2 H_3, 2 H_8), 3.04 (quint J = 3.0 Hz, H_4), 3.69 (t, J = 2.4 Hz, H_1), 4.12 (t of d, J = 8.0, 2.4 Hz, H_2, H_7), 7.25 (s, four aromatics); ^{13}C NMR ($CDCl_3$) 140.8, 139.8, 128.1, 127.0, 124.7, 123.9, 48.2 (C(1)), 44.8 (C(2), C(7), 38.7 (C(3), C(8)), 35.6 (C(4)).

Anal. Calcd for $C_{12}H_{12}Br_2$: C, 45.61; H, 3.82; Br, 50.57. Found: C, 45.66; H, 3.98; Br, 50,47.

Benzobarrelene (1). The crude dibromide 5 from above (15.22 g, 0.048 mol) was dissolved in dry tetrahydrofuran (60 mL) and added dropwise during 30 min to a stirring ambient temperature solution of potassium *tert*-butoxide (27.2 g, 0.243 mol) in dry tetrahdyrofuran (200 mL), maintained under a nitrogen atmosphere. After 3 h more, the mixture was heated at gentle reflux for 1.5 h, then cooled, quenched by dropwise water addition (100 mL), and poured into cold water (600 mL). The mixture was extracted with pentane (4× 125 mL) and combined extracts were washed with water and brine, dried ($MgSO_4$), and concentrated at reduced pressure to afford 7.48 g of off-white crystals. Sublimation at 80 °C (0.7 mm) yielded benzobarrelene (6.77 g, 91.1%) as white needles: mp 63–65 °C. Recrystallization from pentane and resublimation gave material with mp 65–66 °C (lit.[1] 65.5–66 °C). The ^1H NMR spectrum was as reported.[1]

Registry No.—1, 7322-47-6; 2, 4453-90-1; 3, 54647-00-6; 4, 2409-43-1; 5, 63216-61-5; dichlorocarbene, 1605-72-7.

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(11) For example, nitration of dibromide 5 with Ac_2O/HNO_3 afforded a 94% yield of mixed β and β′-NO_2 derivatives. Treatment of this isomeric mixture with potassium *tert*-butoxide in THF gave β-nitrobenzobarrelene. Classical transformations of this nitro derivative and use of an appropriate base for dehydrohalogenation should allow preparation of a variety of aromatic substituted benzobarrelenes.

The First Observation of Splitting by a "Peripheral" Substituent in a Radical Cation Containing a Tetravalent Phosphorus Atom

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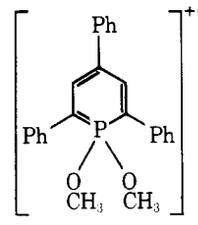
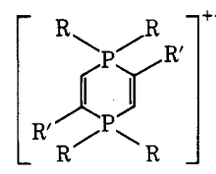
Recently, a number of stable radicals containing tetravalent phosphorus have been reported.[2-6] In all of these cases, coupling was not observed from groups attached to phosphorus which were not part of the delocalized π system containing the unpaired electron. This is best illustrated through examples. In I hyperfine splittings are observed from the phenyl substituents on the hetrocyclic ring and from the two protons on the ring, but no splittings are observed from the methoxy substituents.[4] Similarly, in the spectrum of II there are splittings from R′ and the ring protons, but no evidence is



I



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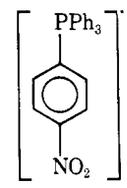
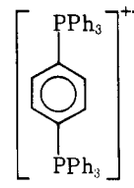


III



IV