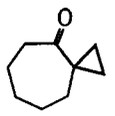
Gutsche has isolated a different compound. We further suggest that Gutsche's compound is actually spiro[2.5]nonan-4-one (VII). Published data on an au-



VII

thentic sample of VII and its 2,4-dinitrophenylhydrazone derivative[8] are completely in agreement with the data reported by Gutsche for his ketone.

Experimental Section

Melting points are uncorrected. Infrared spectra were obtained on a Beckman IR-10 infrared spectrophotometer. Vapor phase chromatographic work was performed with an F & M Model 700 gas chromatograph using 15% Apiezon L on Chromosorb W.

cis-**Bicyclo[6.1.0]nonan-2-one** (I).—*cis*-Bicyclo[6.1.0]nonan-2-ol[2] (3.00 g) was converted by the Jones oxidation[1] into 1.92 g (65%) of I, bp 72–74° (2.5 mm). *cis*-Cyclooctene-3-one[4] (6.99 g) was converted by the Corey procedure[8] into 0.945 g (12%) of I, bp 99–100° (5 mm), ν_{max} 1695 cm^{-1} (C=O).

A 2,4-dinitrophenylhydrazone derivative was prepared,[9] yellow-orange prisms (eluted through grade I neutral Woelm alumina with benzene and recrystallized from 95% ethyl alcohol), mp 159–160.5°.

Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.70; N, 17.60. Found: C, 56.77; H, 5.91; N, 17.73.

trans-**Bicyclo[6.1.0]nonan-2-one** (II).—A sample of *trans*-cycloocten-3-ol[6] (V) (8.87 g) was converted by the Simmons-Smith reaction[5] into 7.83 g (80%) of VI, a viscous clear oil, bp 63–65° (0.3 mm). A sample of VI (4.00 g) was converted by the Jones oxidation[1] to 2.74 g (70%) of II, bp 75–76° (2.5 mm), ν_{max} 1702 cm^{-1} (C=O).

A 2,4-dinitrophenylhydrazone derivative was prepared,[9] fine yellow needles (eluted through grade I neutral Woelm alumina with benzene and recrystallized from 95% ethyl alcohol), mp 177–179.5°. A mixture melting point with the 2,4-dinitrophenylhydrazone derivative of I was depressed, mp 141–149°.

Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.60; H, 5.70; N, 17.60. Found: C, 56.46; H, 5.88; N, 17.77.

Registry No.—I, 16793-31-0; I (2,4-dinitrophenylhydrazone), 16793-32-1; II, 16793-33-2; II (2,4-dinitrophenylhydrazone), 16793-34-3.

Acknowledgment.—This work was supported by a postdoctoral fellowship to J. L. M. from the National Institutes of Health, Public Health Service (GM-31, 823-01 and GM-31, 823-02).

(8) P. Leriverend and J. M. Conia, *Bull. Soc. Chim. Fr.*, 121 (1966).

(9) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 219.

Benzocyclobutenes. I. Nitration of 1-Cyanobenzocyclobutene[1]

IRWIN L. KLUNDT AND WALLACE K. HOYA

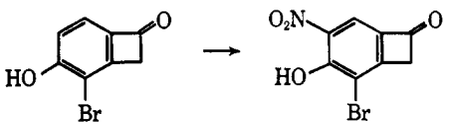
Research Laboratories, Aldrich Chemical Co., Milwaukee, Wisconsin 53210

Received December 13, 1967

The electrophilic substitution of the now readily available benzocyclobutene has become well documented. The nitration of benzocyclobutene has been carried out by Horner[2] and by Lloyd and Ongley.[3]

Lloyd and Ongley have shown that, in benzocyclobutene, electrophilic substitution takes place preferentially at the 4 or 5 position. These positions are equivalent in benzocyclobutene but are nonequivalent in 1-substituted benzocyclobutenes.

There is only one report of an electrophilic reaction of a benzocyclobutene containing a functional group in the four-membered ring.[4] Birch nitrated 3-bromo-4-hydroxybenzocyclobuten-1-one (**1**) with nitric acid in aqueous acetic acid and obtained **2** in 46% yield. In



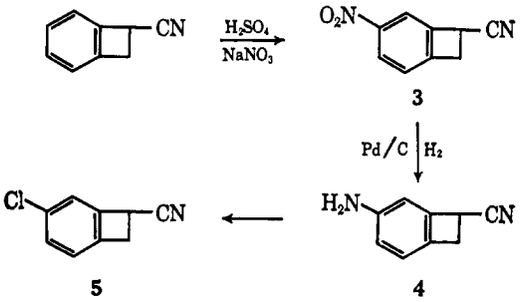
1 **2**

this molecule there is only one pertinent position for electrophilic substitution, *i.e.*, the 5 position.

We have now successfully nitrated 1-cyanobenzocyclobutene with sodium nitrate in concentrated sulfuric acid.[5] The product which is easily isolated by crystallization from ethanol is 1-cyano-5-nitrobenzocyclobutene (**3**).

The infrared spectrum of the crude product possessed bands corresponding to nitrile, nitro, and amide functional groups with the amide band being a minor peak. Tlc showed **3** to be the major component and also the presence of three minor components which ran faster than **3**. Crystallization of a portion of the crude nitration mixture followed by column chromatography of the mother liquors gave **3** in a total yield of 73%. 1-Cyano-5-nitrobenzocyclobutene (**3**) was the only nitronitrile that was isolated from the reaction. The minor components of the reaction mixture (9%) were shown *via* their infrared spectra to contain nitro and amide functional groups. These could be ring-opened products as well as the product resulting from the hydrolysis of **3**. Lloyd and Ongley[3] have shown that nitration of benzocyclobutene produces a mixture of ring-opened products in 31% yield.

SCHEME I



Catalytic reduction of **3** over 5% palladium on carbon (Scheme I) gave 5-amino-1-cyanobenzocyclobutene (**4**). Treatment of **4** with nitrous acid and

(1) The numbering of positions is according to M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **79**, 1701 (1957).

(2) (a) L. Horner, H.-G. Schmelzer, and B. Thompson, *Chem. Ber.*, **93**, 1774 (1960); (b) L. Horner, K. Muth, and H.-G. Schmelzer, *ibid.*, **92**, 2953 (1959).

(3) J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, **20**, 2185 (1964).

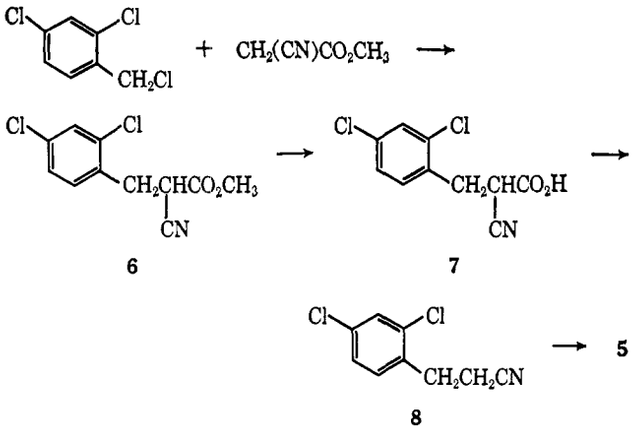
(4) A. J. Birch, J. M. Brown, and F. Stansfield, *J. Chem. Soc.*, 5343 (1964).

(5) H. H. Hodgson and H. G. Beard, *ibid.*, 147 (1926).

cuprous chloride gave 5-chloro-1-cyanobenzocyclobutene (**5**).

An alternate synthesis of **5** using the procedure of Bunnett[6] was carried out as shown in Scheme II.

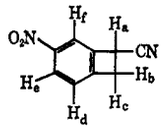
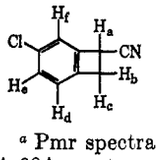
SCHEME II



The pmr spectra of **3** and **5** (Table I) agree with the assigned structure and reasonably well with those of similar compounds.[7] The samples of **5** prepared by both routes gave superimposable pmr and infrared spectra and showed no depression on mixture melting point.

TABLE I[a]

PMR SPECTRA OF BENZOCYCLOBUTENES

Compound	H_a	H_b, H_c	H_d	H_e	H_f
	4.36 (t) $J \approx 4.5$ Hz	3.72 (m)	7.33 (d)	8.25 (d) $J_{de} = 8$ Hz	8.08 (s)
	4.25 (t) $J \approx 4$ Hz	3.60 (m)	7.11 (d)	7.38 (d) $J_{de} = 9$ Hz	7.30 (s)

[a] Pmr spectra are determined in $CDCl_3$ solution on a Varian A-60A spectrometer and the absorption peaks are given in parts per million downfield from tetramethylsilane (TMS) used as an internal standard. Abbreviations used here include s = singlet; d = doublet; t = triplet; m = multiplet.

Experimental Section[8]

5-Nitro-1-cyanobenzocyclobutene (3).—In a 250-ml three-necked flask were placed 90 ml of concentrated sulfuric acid and 9.4 g (0.11 mol) of sodium nitrate. The mixture was cooled to −5° and 13 g (0.10 mol) of 1-cyanobenzocyclobutene[6] added dropwise at such a rate as to keep the temperature below 2°. The reaction mixture was then stirred at 0–5° for 30 min, poured onto 700 g of ice, and extracted with four 200-ml portions of methylene chloride. The methylene chloride solution was washed with four 100-ml portions of 10% sodium bicarbonate and once with 200 ml of water and dried over anhydrous magnesium sulfate. Removal of the solvent gave 17 g of residue which was recrystallized from 125 ml of absolute ethanol to give 8.6 g (49% yield) of product, mp 107–110°. Several recrystallizations from ethanol gave an analytical sample, mp 111.5–113°.

Anal. Calcd for $C_9H_6N_2O_2$: C, 62.06; H, 3.48; N, 16.08. Found: C, 62.16; H, 3.58; N, 16.17.

Chromatographic Examination of the Nitration Mixture.—A nitration on the same scale as that described above was repeated. Removal of the solvent gave 16.3 g of a light yellow solid. Tlc on silica gel with isopropyl ether as the solvent revealed one major spot, **3**, and three minor spots moving faster than **3** and one spot at the origin. A portion (5 g) of the crude product was recrystallized twice from ethanol to give 2.8 g of **3**, mp 111–112.5°. The mother liquors were concentrated and chromatographed over 200 g of neutral alumina (Ventron Corp., activity 1); 100-ml fractions were collected. Nothing was obtained from the column after elution with 500 ml of petroleum ether, 1500 ml of 5% benzene, and 1200 ml of 10% benzene. Elution with 1000 ml of 20% benzene gave 0.16 g of a mixture of products. The infrared spectrum showed the presence of amide and nitro functional groups and the absence of a nitrile group. Elution with 1500 ml of 30% benzene produced an additional 0.34 g of a mixture identical with the previous fraction. Elution with 1600 ml of 40% benzene gave 1.07 g of **3**. A dark band remained at the top of the column.

5-Amino-1-cyanobenzocyclobutene Hydrochloride (4).—A mixture of 1.75 g (0.01 mol) of 5-nitro-1-cyanobenzocyclobutene, 0.6 ml glacial acetic acid, 0.4 g of 5% palladium on carbon, and 100 ml of ethanol was hydrogenated at atmospheric pressure and ambient temperature. The catalyst was removed by filtration and the mixture was evaporated to dryness. The residue was treated with sodium hydroxide solution. The aqueous solution was extracted with three 25-ml portions of ether. The extracts were dried over potassium carbonate, filtered, and acidified with ether saturated with dry hydrogen chloride. The solid that formed was isolated by filtration and triturated in 50 ml of hot acetonitrile to give 1.3 g (72.3%) of a white solid, mp >300°.

Anal. Calcd for $C_9H_9ClN_2$: C, 59.83; H, 5.02; Cl, 19.63; N, 15.51. Found: C, 59.55; H, 5.20; Cl, 19.68; N, 15.16.

5-Chloro-1-cyanobenzocyclobutene (5) (*via* the Sandmeyer Reaction).—A mixture of 4.4 g (25.3 mmol) of 5-nitro-1-cyanobenzocyclobutene, 1 ml of glacial acetic acid, 1 g of 5% palladium on carbon, and 250 ml of ethanol was hydrogenated at 1 atm of pressure and room temperature. The catalyst was removed by filtration and the solution was evaporated to dryness. The residue was treated with 29 ml of 2 *N* hydrochloric acid and cooled to 0°. To the above suspension was added 1.94 g (28.2 mmol) of sodium nitrite and the reaction mixture was stirred for 5 min and then transferred under nitrogen to a solution of 3.35 g (33.8 mmol) of commercial cuprous chloride in 6 ml of concentrated hydrochloric acid cooled to 0°. After the evolution of nitrogen ceased (about 3 min), the reaction was heated to about 50° on a steam bath and then cooled. The green aqueous layer was decanted from an insoluble semisolid. The insoluble solid was triturated with three 100-ml portions of hot chloroform and filtered. The aqueous solution was extracted once with chloroform. The chloroform extracts were combined, washed with three 100-ml portions of 10% sodium bicarbonate, and dried over magnesium sulfate. The residue obtained after removal of the solvent was purified *via* "Kugelrohr" distillation to give 1.3 g (31%) of product: bp 40–80° (0.02 mm); mp 54–57.5°. This was recrystallized from pentane to give 1.2 g, mp 57–58.5°. Mixture melting point with an authentic sample of 5-chloro-1-cyanobenzocyclobutene was undepressed, mmp 57.5–58.5°.

Anal. Calcd for C_9H_6ClN: C, 66.07; H, 3.70; Cl, 21.68; N, 8.56. Found: C, 66.27; H, 3.64; Cl, 21.3; N, 8.43.

Methyl α-Cyano-2,4-dichlorohydrocinnamate (6).—A solution of 54 g (1 mol) of commercial sodium methoxide in 650 ml of absolute methanol was cooled to 15° and 296 g (4 mol) of methylcyanoacetate was added over a 15-min period with stirring. To the above solution was added 196 g (1 mol) of α-2,4-trichlorotoluene over a 1-hr period. The mixture was slowly heated to reflux and held there for 10 hr. The salt was filtered off and washed with methanol. The filtrate was concentrated to dryness, diluted with 600 ml of ether, washed with three 250-ml portions of water, dried over magnesium sulfate, and then fractionally distilled to give 134 g (52%) of a liquid which solidified on standing: bp 145–148° (0.4 mm); mp 53–58°.

Anal. Calcd for $C_{11}H_9Cl_2NO_2$: C, 51.19; H, 3.52; N, 5.43. Found: C, 51.43; H, 3.71; N, 5.48.

α-Cyano-2,4-dichlorohydrocinnamic Acid (7).—To a stirred solution of 61.4 g (1.54 mol) of sodium hydroxide in 555 ml of water at 25° was added 132 g (0.51 mol) of methyl α-cyano-2,4-dichlorohydrocinnamate as a melt. The reaction was stirred at 25° for 1 hr and then acidified at 25° (cooling required) with 450 ml of 4 *N* hydrochloric acid. The resulting mixture was stirred

(6) J. F. Bunnett and J. A. Skorcz, *J. Org. Chem.*, **27**, 3836 (1962).

(7) H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafos, *ibid.*, **31**, 2244 (1966), and references therein.

(8) Melting points are taken on a Thomas–Hoover Unimelt and are uncorrected. Boiling points are uncorrected.

for 0.5 hr and then filtered. The solid was washed with water until the washings were neutral and dried in a vacuum oven at 50° to give 120 g (97.5% yield) of a white solid, mp 145–147°.

Anal. Calcd for $C_{10}H_7Cl_2NO$: C, 49.20; H, 2.89; Cl, 29.04; N, 5.74. Found: C, 49.21; H, 2.82; Cl, 29.03; N, 5.38.

2,4-Dichlorohydrocinnamonitrile (8).—A solution of 560 g (2.29 mol) of α-cyano-2,4-dichlorohydrocinnamic acid in 950 ml of dimethylacetamide was heated at 150° for 1.5 hr. The reaction mixture was cooled and poured into 1 l. of water with stirring. The dark organic layer was separated from the water and the water was extracted with three 500-ml portions of ether. The ether extracts were combined with the original organic layer and then washed with 300 ml of water, 300 ml of 5% hydrochloric acid, and again with 300 ml of water. The ether solution was dried over magnesium sulfate and evaporated to dryness, and was fractionally distilled to give 360 g (79%) of a colorless liquid, bp 121° (0.3 mm).

Anal. Calcd for $C_9H_7Cl_2N$: C, 54.00; H, 3.50; N, 7.00. Found: C, 53.90; H, 3.61; N, 6.83.

5-Chloro-1-cyanobenzocyclobutene (5).[9]—To a well-stirred suspension of 27.7 g (0.71 mol) of commercial sodium amide and 400 ml of liquid ammonia under nitrogen was added 36 g (0.18 mol) of 2,4-dichlorohydrocinnamonitrile over a 10-min period. The mixture was stirred at reflux for 3 hr, neutralized with 62.5 g (0.78 mol) of solid ammonium nitrate, and allowed to stand overnight. The residue was diluted with 350 ml of water and the organic material was extracted with four 150-ml portions of chloroform. The combined extracts were washed with three 150-ml portions of 5% hydrochloric acid and two 100-ml portions of water and dried over magnesium sulfate. The residue (19.2 g after removal of the solvent) was fractionally distilled to give 11.3 g (38.5% yield) of **5**: bp 76–78° (0.08 mm), mp 50–52.5°. An analytical sample was prepared by crystallization from pentane, mp 56.5–57.5°.

Anal. Calcd for C_9H_6ClN: C, 66.07; H, 3.70; N, 8.56. Found: C, 66.32; H, 3.77; N, 8.55.

Registry No.—1-Cyanobenzocyclobutene, 6809-91-2; **3**, 16994-04-0; **4** HCl, 16994-05-1; **5**, 16994-06-2; **6**, 16994-07-3; **7**, 16994-08-4; **8**, 16994-09-5.

(9) Caution: the addition of 2,4-dichlorohydrocinnamonitrile is exothermic.

Deoxygenation of Organic Nitrites[1]

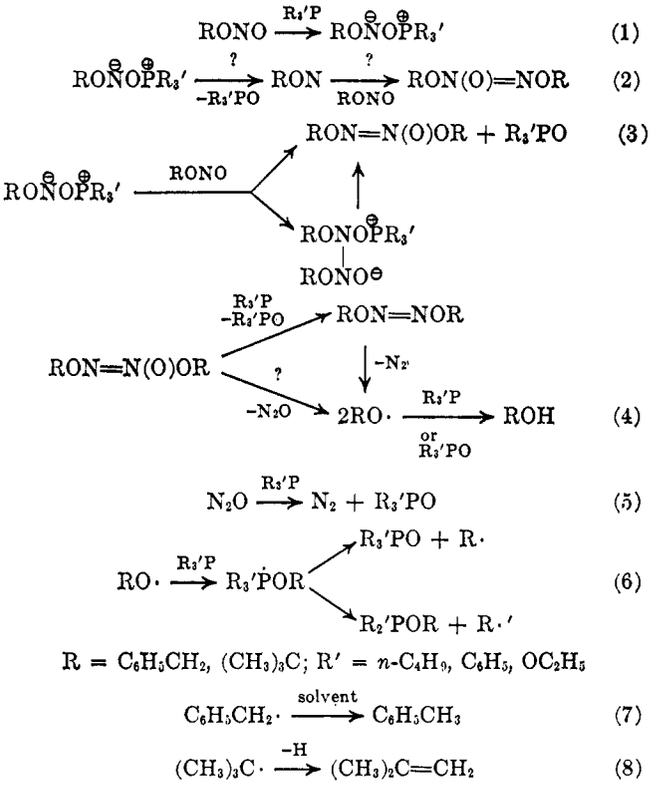
J. H. BOYER[2] AND J. D. WOODYARD

Chemistry Department, Chicago Circle Campus, University of Illinois, Chicago, Illinois 60680

Received February 19, 1968

In an attempt to produce examples of the unknown alkoxy nitrenes, the deoxygenation of nitrite esters by tervalent phosphorus reagents was investigated.[3] Benzyl and *t*-butyl nitrite have been transformed into the corresponding alcohol by both tri-*n*-butyl- and triphenylphosphine and triethyl phosphite as a phosphine oxide or triethyl phosphate is formed.[4] The intermediacy of an alkoxy nitrene is not required; however, a hyponitrite ester, which may be recognized as the formal dimer of an alkoxy nitrene, is a probable intermediate.[5]

An initial nucleophilic attack by tervalent phosphorus upon the terminal nitrite oxygen is proposed (eq 1).[6] Since attempts to trap the monomeric nitrene, which might have been produced by dissociation of the zwitterionic adduct (eq 2), through addition to an olefinic bond or by insertion with a C—H bond were unsuccessful, it is tentatively assumed that an alkoxynitrene is not generated. This evidence does not rigorously exclude capture of the nitrene on formation of a nitrite ester molecule in a reaction leading directly to a hyponitrite N-oxide (eq 2). It is assumed, however, that the initial adduct combines with another nitrite ester molecule to bring about the formation of the azoxy compound in a reaction requiring either concerted or stepwise elimination of a phosphine oxide (eq 3). Conceivably, alkoxy radicals could be produced directly by the fragmentation of the proposed, but unknown, hyponitrite N-oxide ester. In an alternate sequence a hyponitrite may result from deoxygenation of its N-oxide and subsequently undergo loss of nitrogen with the generation of alkoxy radicals (eq 4 and 5).[7] Abstraction of hydrogen from the organophosphorus solvent then accounts for the formation



(1) Financial support was received from NASA Grant No. NGR 14-012-004.

(2) Address inquiries to this author.

(3) Arylnitrenes have been assumed intermediates in the deoxygenation of aromatic C-nitroso compounds by tervalent phosphorus reagents [G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, **31**, 3882 (1966); R. J. Sundberg, *J. Amer. Chem. Soc.*, **88**, 3781 (1966); J. I. G. Cadogan and M. J. Todd, *Chem. Commun.*, 178 (1967)]. Triphenylphosphine was found to be inert to nitrosamines [L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956)].

(4) Isolation of ethyl nitrite from the reaction between *o*-dinitrobenzene and triethylphosphite [J. I. G. Cadogan, D. J. Sears, and D. M. Smith, *Chem. Commun.*, 491 (1966)] apparently requires the escape of the gaseous ester on formation.

(5) P. J. Bunyan and J. I. G. Cadogan [*J. Chem. Soc.*, 42 (1963)] reported the formation of azoxybenzene during the deoxygenation of nitrosobenzene by triphenylphosphine. Further deoxygenation by the same reagent gives azobenzene [L. Horner and H. Hoffmann, *Angew. Chem.* **68**, 473 (1956)].

(6) Deoxygenation of aromatic nitroso compounds has been accounted for by both nucleophilic [J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and J. G. Searle, *J. Chem. Soc.*, 4831 (1965)] and electrophilic [L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956)] attack by tervalent phosphorus on nitroso oxygen.

(7) Tervalent phosphorus is known to deoxygenate nitrous oxide (eq 5): R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 191 and 192.