In conclusion, it should be added that, in the course of another investigation in these laboratories, it has been found that the 6-nitro II (Ib) and 8-nitro II (Ic) derivatives of I also function as Lewis acids and that their salt formation is also accompanied by large bathochromic shifts.[9] Here, however, one cannot make an analogous comparison of the groups ArNH$^-$ and ArNHBR$_3^-$ since the ion ArNH$^-$ cannot of course exist in ethanol.

Experimental Section

^{11}B nmr spectra were measured with a Varian DP-60 spectrometer using procedures described[6] previously. Ultraviolet spectra were measured using a Beckman DK-2 spectrometer. The nmr spectra were measured on a Varian A-60 instrument.

10-Hydroxy-10,9-boroxaropheanthrene[5] (II).—The proton nmr spectrum of II in chloroform-*d* consists of multiplets at δ 8.2 and 7.4 (ratio of integrated intensities 1:3). There was no change in the multiplets position on using ethanol or 5 or 10% potassium hydroxide in ethanol as the solvent.

Registry No.—Ia, 17012-25-8; Ib, 15813-11-3; Ic, 15889-55-1; II, 14205-96-0; PhB(OH)$_2$, 98-80-6.

[9] M. J. S. Dewar, R. Jones, and R. Logan, Jr., *J. Org. Chem.*, **33**, 1359 (1968).

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cis- and *trans*-Bicyclo[6.1.0]nonan-2-one

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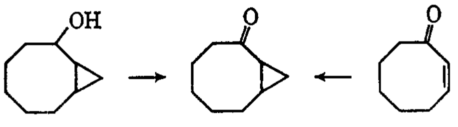
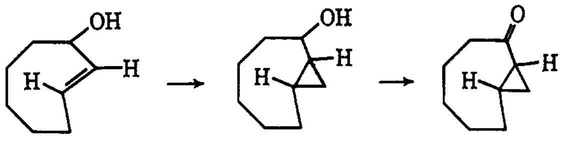
In connection with our continuing interest in cyclopropane chemistry, we have had occasion to synthesize both *cis*- and *trans*-bicyclo[6.1.0]nonan-2-one (I and II, respectively). We wish to report this synthesis and to describe the behavior of the strained *trans* isomer II.

Strained bicyclic compounds are ordinarily quite stable. However, in the case of II, a ready pathway is available for isomerization to the *cis* isomer I, *viz.*, enolization. We were interested in knowing how facile this epimerization process was. Furthermore, studies with molecular models indicated that there just might be little difference between the free energies of I and II. We therefore were interested in determining if substantial amounts of II existed when equilibrium was established between the two isomers.

The *cis* ketone I was synthesized by the Jones oxidation[1] of *cis*-bicyclo[6.1.0]nonan-2-ol[2] (III) and also by the Corey procedure[3] by allowing *cis*-cycloocten-3-one[4] (IV) to react with dimethyloxosulfonium methylide. The material obtained by either route was identical in all respects.


III I IV

The *trans* ketone II was synthesized by the Jones oxidation[1] of *trans*-bicyclo[6.1.0]nonan-2-ol (VI), which was prepared by the Simmons–Smith reaction[5] of *trans*-cycloocten-3-ol[6] (V).


V VI II

Samples of I and II were shown to be different by comparison of their nmr and infrared spectra and vpc retention times and by comparison of the melting points of their 2,4-dinitrophenylhydrazone derivatives. The structure of the *trans* ketone was conclusively established when it was found that the ketone could be isomerized to the *cis* ketone I by treatment with base (*vide infra*).

It was first established that the *cis* ketone I was inert to the usual acid or base treatments. When treated with sodium methoxide in methyl alcohol, potassium *t*-butoxide in *t*-butyl alcohol, or 2 *N* sulfuric acid in ether, I was recovered unchanged.

Next, the *trans* ketone II was subjected to a variety of basic and acidic reaction conditions. After being treated with 2 *N* sulfuric acid in ether for 15 hr at room temperature, or after being eluted through grade I neutral Woelm alumina, II was recovered unchanged. However, after being treated with 1.5 *M* sodium methoxide in methyl alcohol for 87 hr at room temperature, II was completely converted into the *cis* ketone I (>99%); the half-life for this conversion was found to be about 8 hr. When treated with 1.5 *M* sodium hydroxide in methyl alcohol, the rate of isomerization was about the same. The *trans* ketone II could also be isomerized with sodium carbonate in 50:50 water–methyl alcohol, but the reaction was slower; after 16 hr at room temperature, about 2% conversion into I had occurred, whereas after 15 hr at reflux (73°), complete conversion into I had occurred.

These isomerization studies thus establish that I and II are epimers and that the structure of II is that formulated above. These studies further prove that the *cis* ketone I is much more thermodynamically stable than the *trans* ketone II. Finally, it has been shown that II is stable under mild acidic treatment but is readily isomerized by base.

There is one reference in the literature to the *cis* ketone I. Gutsche[7] has claimed that I is one of the products obtained when N,N′-dicarbethoxy-N,N′-dinitroso-1,3-propane is treated with cyclohexanone in the presence of base. However, the infrared and nmr data of his ketone and the melting point (113–114°) and color (blood red) of its 2,4-dinitrophenylhydrazone derivative are clearly incompatible with those of the ketone and its 2,4-dinitrophenylhydrazone derivative studied by us. In view of the two unambiguous syntheses of I described in this communication, we feel that

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[1] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967).

[2] A. C. Cope, *et al.*, *ibid.*, **79**, 3900 (1957).

[3] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

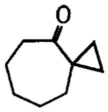
[4] A. C. Cope, M. R. Kinter, and R. T. Keller, *ibid.*, **76**, 2757 (1954).

[5] W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

[6] G. H. Whitham and M. Wright, *Chem. Commun.*, 294 (1967). We are indebted to Dr. Whitham for supplying us with the detailed procedure for synthesizing V.

[7] C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).

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



VII

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*-Cycloocten-3-one[4] (6.99 g) was converted by the Corey procedure[3] into 0.945 g (12%) of I, bp 99–100° (5 mm), $\nu_{\max}$ 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), $\nu_{\max}$ 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]

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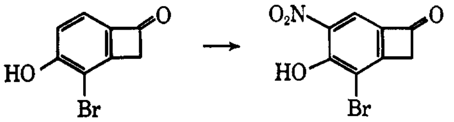
The electrophilic substitution of the now readily available benzocyclobutene has become well documented. The nitration of benzocyclobutene has been carried out by Horner[2] and by Lloyd and Ongley.[3]

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

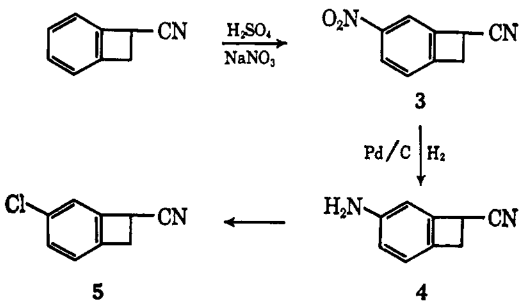


1 **2**

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

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[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).