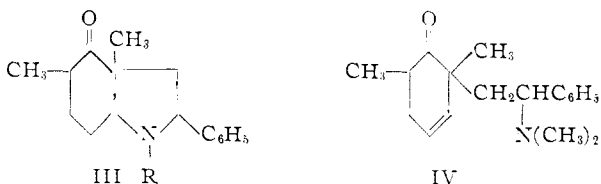
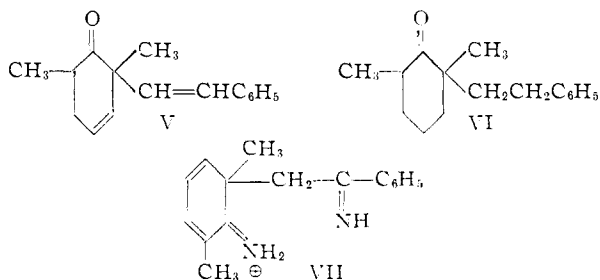


6.12 μ and 6.24 μ in acid solution. The ultraviolet absorption spectrum in ethanol showed a major band at 242 $m\mu$ (ϵ , 21,500) which split into two bands in acid solution (λ_1 242 $m\mu$; ϵ_1 10,500; λ_2 273 $m\mu$; ϵ_2 , 16,500). Both the infrared and the ultraviolet spectra are characteristic of the conjugated carbonyl and conjugated imine chromophores.¹

Hydrogenation of II over Adams catalyst in acetic acid afforded stereoisomeric forms of III (R = H), m.p. 56.5–58° and 92.5–93.5° (Calcd. for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.01 and 78.94, resp.; H, 8.80 and 8.86, resp.; N, 5.67 and 5.60, resp.). Oximes, m.p. 162–164° and 177–179°, resp. (Calcd. for $C_{16}H_{22}N_2O$: C, 74.38; H, 8.58; N, 10.84. Found: C, 74.44 and 74.32, resp.; H, 8.40 and 8.39, resp.; N, 10.74 and 10.83, resp.)



Formaldehyde and formic acid converted either stereoisomeric form of III (R = H) to the same III (R = CH_3) which infrared data indicated to be a mixture of two stereoisomers of which only one was obtained in crystalline form, m.p. 42–44° (Calcd. for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.12; H, 9.16; N, 5.48). Oxime, m.p. 138–140° (Calcd. for $C_{17}H_{24}N_2O$: C, 74.96; H, 8.88; N, 10.29. Found: C, 75.26; H, 8.89; N, 10.18). The methiodide of III (R = CH_3) (Calcd. for $C_{18}H_{26}NOI$: C, 54.14; H, 6.56; N, 3.51. Found: C, 54.27; H, 6.65; N, 3.61) was converted to the methohydroxide by passage of its water solution through a column of the hydroxide form of Amberlite IRA-400. Heating the methohydroxide at 120° (1 μ) afforded IV (methiodide, m.p. 158–213° (dec.), Calcd. for $C_{18}H_{28}NOI$: C, 55.21; H, 6.83; N, 3.39. Found: C, 55.33; H, 7.18; N, 3.26). Action of 30% hydrogen peroxide on IV gave the amine oxide (picrate, m.p. 133–134.5°, Calcd. for $C_{24}H_{28}N_4O_9$: C, 55.81; H, 5.46; N, 10.85. Found: C, 56.13; H, 5.56; N, 10.95) which decomposed² at 100° (15–20 mm.) to V, not obtained analytically pure, (Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 83.60; H, 7.71). Hydrogenation of V in absolute methanol over Adams catalyst yielded VI.



(1) B. Witkop, *Experientia*, **10**, 420 (1954).

(2) A. C. Cope, T. T. Foster and P. H. Towle, *THIS JOURNAL*, **71**, 3929 (1949).

The formation of both I and II can be rationalized in terms of a single intermediate VII, an analog of the kind of intermediate shown to take part in the *para* Claisen rearrangement³ and also an analog of intermediates postulated in the Fischer reactions of acetophenone 2,6-dihalogenphenylhydrazones.⁴ A more complete account of the degradation of II to VI, with the properties of this new group of hydroindole derivatives, and a mechanism to account for the formation of I and II through VII will be forthcoming.

(3) H. Conroy and R. A. Firestone, *ibid.*, **78**, 2290 (1956); D. Y. Curtin and H. W. Johnson, *ibid.*, **78**, 2611 (1956).

(4) R. B. Carlin and G. W. Larson, *ibid.*, **79**, 934 (1957).

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RECEIVED JUNE 10, 1957

BENZOCYCLOBUTADIENOQUINONE

Sir:

Although no stable cyclobutadiene has yet been found, the monophenyl derivative of cyclobutadienoquinone has been prepared and appears to have considerable stability despite the great ring strain which it possesses.¹ It has been suggested¹ that the quinones of other unstable cyclic polyolefin systems might have a corresponding stability. We now wish to report some confirmation of this principle in the synthesis of a stable quinone of the unstable benzocyclobutadiene.²

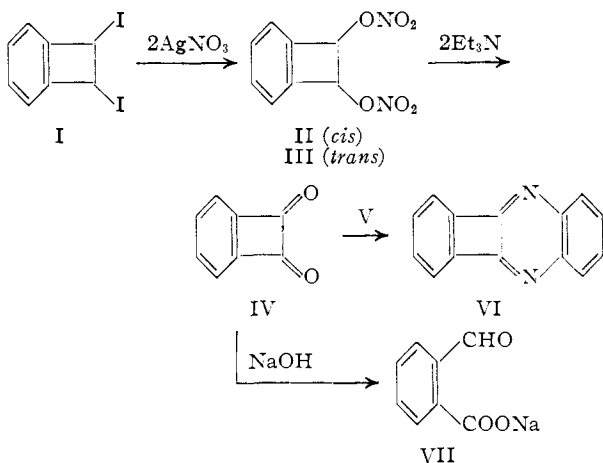
A solution of 1,2-diiodobenzocyclobutene^{2a} (I) and two equivalents of silver nitrate in acetonitrile gave, after stirring eight days at room temperature, a mixture of the isomeric *cis*-benzocyclobutene-1,2-diol dinitrate (II) and *trans*-benzocyclobutene-1,2-diol dinitrate (III), separable by crystallization from methanol. Isomer A:³ m.p. 110°. *Anal.* Calcd. for $C_8H_8N_2O_6$: C, 42.48; H, 2.67; N, 12.39. Found: C, 42.50; H, 2.59; N, 12.42. Isomer B:³ m.p. 55.5–56.5°. *Anal.* Found: C, 42.24; H, 2.88; N, 12.29. Either isomer, when refluxed one hour with 1:1 methylene chloride-triethylamine gave, in 75% yield, the pale yellow 1,2-diketobenzocyclobutene, or benzocyclobutadienoquinone (IV), m.p. 132.5°. *Anal.* Calcd. for $C_8H_4O_2$: C, 72.73; H, 3.05. Found: C, 72.77; H, 3.08; λ_{max}^{EtOH} 271 $m\mu$ ($\log E = 3.45$), 277 $m\mu$ ($\log E = 3.83$). In the infrared (CS_2 solution), the strained carbonyls absorbed as a doublet at 5.51 and 5.61 μ .

The quinone IV was quite stable thermally and sublimed unchanged at 100° (0.2 mm. pressure). It reacted rapidly with *o*-phenylenediamine (V) to give the first known heterocyclic biphenylene analog, 1,4-diaza-benzo[b]biphenylene (VI), m.p. 238–239°. *Anal.* Calcd. for $C_{14}H_8N_2$: C, 82.33; H, 3.95; N, 13.72. Found: C, 82.21; H, 3.84; N, 13.83.

(1) E. J. Smutney and J. D. Roberts, *THIS JOURNAL*, **77**, 3420 (1955).

(2) (a) M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957); (b) M. P. Cava and J. F. Stucker, *ibid.*, **79**, 1706 (1957).

(3) The configurations of isomers A and B remain unassigned as yet.



The quinone IV was oxidized rapidly and quantitatively by peracetic acid to phthalic acid.

A dilute solution of IV in 5% aqueous methanolic sodium hydroxide was decolorized completely after five hours at 25°, the sodium salt of phthalaldehydic acid (VII) being produced in 94% yield.

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RECEIVED MAY 25, 1957

THE FORMATION OF A CYCLIC DIANHYDRODIADENYLIC ACID (I) BY THE ALKALINE DEGRADATION OF ADENOSINE-5'-TRIPHOSPHORIC ACID (II)¹

Sir:

It has been shown that barium hydroxide hydrolysis of (II) yields adenosine-5'-phosphoric acid (III) and inorganic pyrophosphate.² Hock and Huber³ recently demonstrated that at least one other product is formed in this reaction.

Experiments in this laboratory show that the degradation of (II) by barium hydroxide is complex and that a number of previously unreported products are formed. One of these (I) exhibits sufficiently unexpected properties to merit description, particularly since it appears to be identical with a recently isolated, naturally-occurring compound.⁴ In the preparation of (I), 250 mg. of (II)⁵ and 3 ml. of 0.4 *N* barium hydroxide were heated for 30 min. at 100° and then the barium ion was precipitated. The solution was chromatographed on paper using 70% 2-propanol-ammonia as the developing solvent.⁶ The fastest-moving substance is adenosine and this is closely followed by (I) (yield *ca.* 5–10%⁷).

(1) This research was supported in part by the U. S. Atomic Energy Commission.

(2) K. Lohmann, *Biochem. Z.*, **233**, 460 (1931); S. E. Kerr, *J. Biol. Chem.*, **139**, 131 (1941).

(3) A. Hock and G. Huber, *Biochem. Z.*, **328**, 44 (1956).

(4) E. W. Sutherland and T. W. Rall, *THIS JOURNAL*, **79**, 3608 (1957).

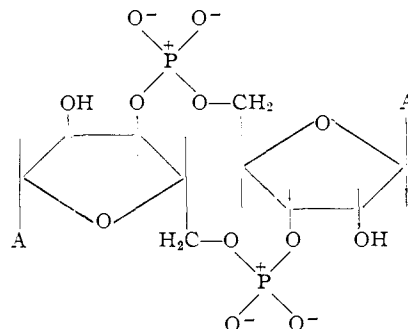
(5) We wish to thank Pabst Laboratories for the gift of a generous sample of (II).

(6) R. Markham and J. D. Smith, *Biochem. J.*, **52**, 552 (1952).

(7) Low yields of (I) also are obtained by the action of barium hydroxide on adenosine-5'-pyrophosphoric acid or by trifluoroacetic anhydride on (III).

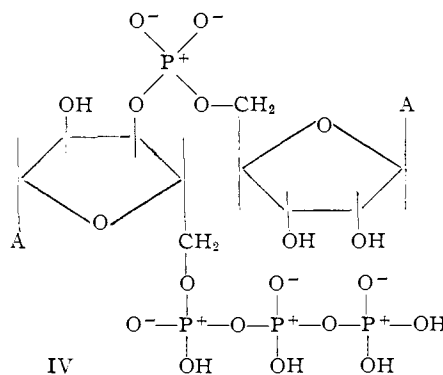
The new compound (I) has the following properties: (1) the molar ratio of adenine:phosphorus is unity; (2) adenosine is slowly formed from it by the action of *Crotalus adamanteus* venom; (3) it is not attacked by prostate phosphomonoesterase; (4) it is not oxidized by periodate; (5) it is deaminated by nitrite to the inosine analog, which also has been prepared from inosine-5'-triphosphoric acid; (6) its electrophoretic mobility on paper⁸ relative to (III) is 1.2 at *pH* 3.5 (formate), 0.57 at *pH* 7.2 (phosphate) and 0.49 at *pH* 9.2 (borate); and (7) it is eluted from a Dowex-2 formate column by ammonium formate (*pH* 5.0) after all four known adenine-containing monoribonucleotides and just prior to adenosine-5'-pyrophosphoric acid.

A structural formula for (I) which is in accord with the above data is (A = adenine-9 residue)



There is no evidence at present to indicate that the phosphate ester bonds involve only the 3', in addition to the 5', carbon atoms. A study of models indicates, however, that this is the most likely phosphate diester structure and explains the surprising stability of (I) toward alkali. The positions of the phosphorus atoms in (I) are such that the formation of a 2',3' cyclic phosphate ester is hindered. The compound also is exceptionally stable toward acid hydrolysis.

The formation of (I) may take place by one of two paths. Two molecules of (II) suitably oriented may react simultaneously at two sites to give (I) directly, or (IV)



and inorganic pyrophosphate may form followed by intramolecular cyclization to give (I). Alternatively, (IV) could yield equivalent amounts of adenosine and 3'(or 2')-phosphoadenosine-5'-phosphoric acids. The latter, which we have tenta-

(8) R. Markham in K. Paech and M. V. Tracey, "Modern Methods of Plant Analysis," Springer-Verlag, Berlin, 1955, Vol. IV, p. 278.