Unlike $Co_2(CO)_6(C_6H_5C_2C_6H_5)$,[8] which is prepared from $Co_2(CO)_8$, the formation of $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ from $Co_4(CO)_{12}$ does not involve a direct substitution of an acetylene for two bridging carbonyls, provided that Corradini's proposed structure[17] for $Co_4(CO)_{12}$ is correct. A two-dimensional X-ray study of $Co_4(CO)_{12}$ by Corradini[17] revealed the cobalts at the vertices of a tetrahedron, but a crystal disorder prevented a completely unambiguous determination of the molecular geometry of the carbonyl groups. Our structural results show that Corradini's model would necessitate molecular reorganization of carbonyl groups during the formation of $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ from $Co_4(CO)_{12}$, contrary to the predictions of Hübel and co-workers[5a] based on the experimental reaction conditions. Hübel and Krüerke[12] have suggested possible alternative structures for $Co_4(CO)_{12}$, and in this connection structural work on the iridium and rhodium carbonyls is in progress in this laboratory.

We are pleased to acknowledge the use of the computing facilities of NAL at the University of Wisconsin and the financial support of this research by the National Science Foundation (Grant No. 86-3474).

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RECEIVED APRIL 7, 1962

γ-PYRAN

Sir:

Although the chemistry of pyran has been the subject of research for over a century, the parent compounds, α- and γ-pyran, hitherto have remained unknown.[1] Numerous attempts at the synthesis of these compounds resulted either in ring opening or extensive decompositions.[1] We became interested in these heterocyclic compounds during the course of our synthetic studies on oxepin. We now wish to submit final evidence for the existence of unsubstituted γ-pyran (I).

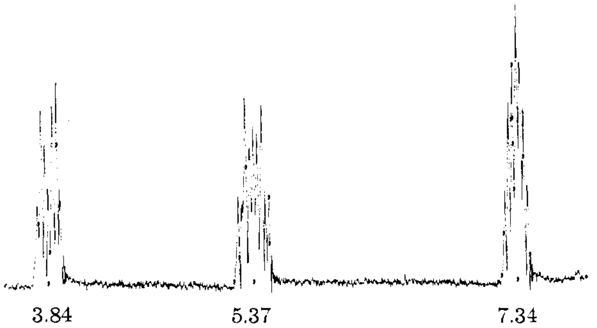
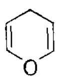
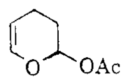


Fig. 1.—The n.m.r. spectrum of γ-pyran in carbon tetrachloride.



I



II

A column (2.5 × 35 cm.) was packed with glass beans (0.5 cm. in diameter) and heated to 350°. 2-Acetoxy-3,4-dihydro-2H-pyran (II)[2] (5 g.) was added dropwise onto the column over a period of 2.5 minutes and the product was trapped in a Dry-Ice cooled flask containing hydroquinone in ether. Nitrogen was used as a carrier gas. Identification of acrolein, vinyl acetate and acetic acid in the reaction mixture indicates that the acetate pyrolysis is competing with the reverse Diels–Alder reaction.[3] Due to the extreme instability of I (*vide infra*) the isolation of I was achieved only by gas chromatography[3] at 50° after treatment of an ethereal solution of the pyrolysis product with wet sodium bicarbonate at 0° for two hours.[4] The yield is 15 or 30% based on starting material consumed. I boils at 84° with slight decomposition.[5]

The chemical proof for the structure of I was obtained by i) the conversion of I to tetrahydropyran[3,6] by catalytic hydrogenation and ii) the preparation of glutaraldehyde bis-dinitrophenylhydrazone[7] from I (m.p. and m.m.p., 186–188°).

Spectral evidence for structure I is given below. The n.m.r. spectrum is very similar to that of 1,4-dihydropyridine[8] and shows one kind of aliphatic and two kinds of olefinic hydrogens, each having an equal intensity. Spin–spin coupling constants are: $J_{34} \simeq 3.0$ c.p.s., $J_{24} \simeq 1.5$ c.p.s.[9] This eliminates α-pyran as a possible structure. The infrared spectrum (chloroform) is simple: 3.28μ (m), 3.42 (m), 3.52 (m), 5.93 (s), 6.12 (s), 7.98 (s), 8.90 (m), 9.36 (s), 9.90 (m), 10.23 (m), 10.40 (m), 11.02 (s) and 11.38 (m). The two bands (5.93, 6.13) in the double bond region are believed to correspond in nature to a doublet observed for an acid anhydride.[10] Only a strong end absorption was observed in the ultraviolet spectrum (methanol).

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(1) For instance, see: A. Albert, "Heterocyclic Chemistry," Essential Books, Fair Lawn, N. J., 1959, p. 265; N. Campbell, "Chemistry of Carbon Compound," Vol. IVB, ed. by E. H. Rodd, Elsevier Publishing Co., Amsterdam, 1959, Chap. VIII; J. Fried, "Heterocyclic Compound," Vol. I, ed. by R. C. Elderfield, John Wiley & Sons, Inc., New York, N. Y., 1950, Chap. 7.

(2) C. W. Smith, D. G. Norton and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5270 (1951); R. H. Snyder, H. J. Shine, K. A. Leibbrand and P. O. Tawney, *ibid.*, **81**, 4299 (1959).

(3) Gas chromatography and infrared spectra were employed for identification of the liquid compounds described in this Communication. Gas chromatography was operated with a 9 mm. × 15-cm. column containing 10% Apiezon L on Anakrom ABS (80–90 mesh). Column conditions were: temperature, 50°; helium flow rate, 45 ml./min. Relative retention times are: acetic acid (1.000), acrolein (0.225), vinyl acetate (0.544), γ-pyran (1.820) and tetrahydropyran (2.499).

(4) This treatment removed most of the acrolein and vinyl acetate as well as acetic acid.

(5) Determined by the Emich method, A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., London, 1957, p. 86. A sample in a capillary was introduced in a preheated bath.

(6) D. W. Andrus and J. R. Johnson, "Organic Syntheses," Vol. 23, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 90.

(7) M.p. 186–187° was reported by R. H. Hall and B. K. Howe, *J. Chem. Soc.*, 2480 (1951), and 189–190° and 192° in ref. 3.

(8) M. Saunders and E. H. Gold, *J. Org. Chem.*, **27**, 1439 (1962).

(9) The n.m.r. spectrum was taken with a Varian Associates 60-Mc high resolution spectrometer.

(10) The nature of this splitting has not been thoroughly understood: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 127–128. Divinyl ether and its homologs show similar doublets, A. Kirrmann and P. Chancel, *Bull. Soc. Chim. France*, 1338 (1954).

γ-Pyran is extremely unstable at room temperature,[11] particularly when exposed to air, while a moderately slow decomposition takes place at −80° in an ethereal solution containing a small amount of hydroquinone. We are searching for an efficient inhibitor to preserve a sufficient quantity of I for the further investigation.[12]

[11] Within 10 minutes coloration of I is noticeable and it decomposes completely overnight. Accordingly, elementary analysis was not possible.

[12] We are indebted to Dr. B. L. Shapiro and Mr. J. J. Burke for the n.m.r. spectrometric measurement.

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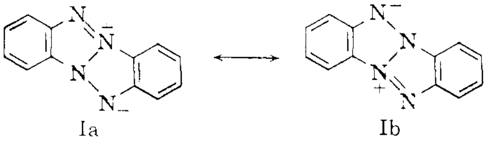
RECEIVED MAY 23, 1962

DIBENZO-1,3a,4,6a-TETRAAZAPENTALENE—A NEW HETEROAROMATIC SYSTEM

Sir:

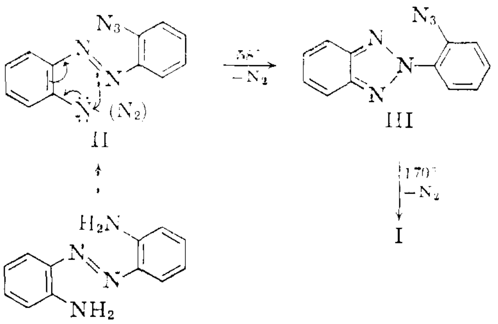
We wish to report the preparation of a stable, new heterocyclic system represented by dibenzo-1,3a,4,6a-tetraazapentalene (I).[1] This meso-ionic molecule can be represented as a hybrid of several dipolar resonance structures (two of which are Ia and Ib).



Ia Ib

The planar tetraazapentalene I can assume the electronic character of a pentalene dianion[2] molecule by virtue of a contribution to the π-electron system of six electrons by the four nitrogen atoms. This conjugation is reflected by the pronounced stability displayed by the molecule I. I is unaffected by heating in solvents above 300° and can be sublimed unchanged at atmospheric pressure. The solid dissolves in concentrated sulfuric acid and can be reprecipitated by diluting with water. An acetone solution of I is stable to potassium permanganate.

By contrast, dibenzopentalene is reported to exhibit distinct olefinic properties about the central pentalene nucleus.[3]



The dibenzo-1,3a,4,6a-tetraazapentalene was prepared in greater than 90% yield by thermal decomposition of *o,o'*-diazidoazobenzene (II).[4] Compound I also forms when a benzene solution of II is exposed to sunlight.

o,o'-Diaminoazobenzene[5] was tetrazotized, then treated with aqueous sodium azide to obtain *o,o'*-diazidoazobenzene (II), yield 93%, m.p. 116–117° (dec.).

Anal. Calcd. for $C_{12}H_8N_8$: C, 54.54; H, 3.05; N, 42.41. Found: C, 54.75; H, 3.31; N, 42.37.

When a solution of II in decalin was heated, decomposition proceeded in two stages with evolution of nitrogen. One mole of gas was released at the remarkably low temperature of 58° to yield 2-(*o*-azidophenyl)-2,1,3-benzotriazole (III), m.p. 78–79°, in good yield.

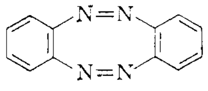
Anal. Calcd. for $C_{12}H_8N_6$: C, 61.01; H, 3.41; N, 35.58. Found: C, 61.04; H, 3.65; N, 35.94.

The structure of III was confirmed by independent synthesis. At 170°, another mole of nitrogen was evolved, and compound I was obtained as long, yellow needles, m.p. 237–238°.

Anal. Calcd. for $C_{12}H_8N_4$: C, 69.22; H, 3.87; N, 26.91; mol. wt., 208. Found: C, 69.06; H, 3.99; N, 26.96; mol. wt. (Rast), 221.

The infrared spectrum exhibited peaks at 6.2, 6.3 and 6.7 μ. The ultraviolet spectrum (in ethanol) showed three main areas of absorption, with peaks at 254.5 mμ (ϵ 65,000), 322.5 mμ (ϵ 4575) and 402μ (ϵ 40,000).[6] The dipole moment, measured in benzene, was approximately zero.

An alternative structure which could accommodate many of the physical properties of this molecule as well as its mode of formation is dibenzo-1,2,5,6-tetraazacycloöctatetraene (IV). Derivatives of the simple tetraazacycloöctatetraene ring system have been described[7] as high-melting, fluorescent solids of high thermal stability. However, the complexity of the proton n.m.r. spectrum of the present dibenzo compound compared to naphthalene (A_2B_2 system), would appear to favor the dibenzotetraazapentalene I.[8]



IV

Chemical evidence supporting this conclusion was obtained by the synthesis of an analogous molecule in which one of the benzene rings is replaced by a naphthalene nucleus with fusion at the α,β-positions.

Two *nonsuperimposable* isomers (Va and Vb) would be expected on thermal decomposition of 2-(*o*-azidophenyl)-2,1,3-α,β-naphthotriazole (VI) by formation of a bond between the azido nitrogen and

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[1] This compound may be named 5,11-dehydrobenzotriazolo[2,1-a-]benzotriazole. The trivial name dibenzo-1,3a,4,6a-tetraazapentalene is henceforth used in this article.

[2] T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).

[3] C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

[4] R. A. Carboni, U. S. Patent 2,904,544 (1959).

[5] R. Willstätter and A. Pfannenstiel, *Ber.*, 2349 (1905).

[6] Only the most intense bands are given for the two longer wavelength regions, each of which displays prominent fine structure.

[7] R. Metze, *Angew. Chem.*, **68**, 581 (1956); R. Pfleger and H. G. Hahn, *Ber.*, **90**, 2411 (1957).

[8] The authors express their thanks to Professor J. D. Roberts for this interpretation.