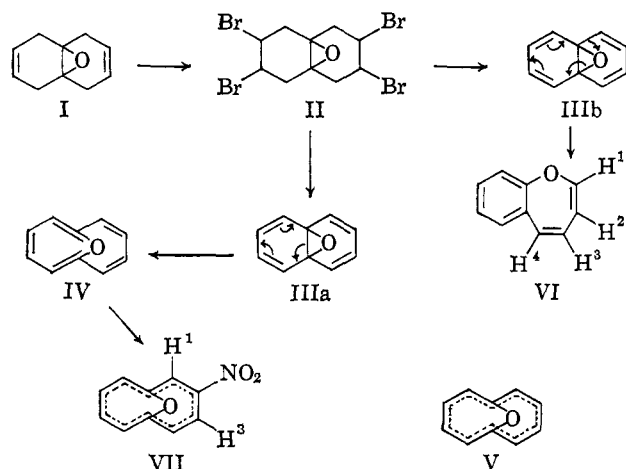


second nitro compound [m.p. 86.5–87.5°; $\lambda_{\text{max}}^{\text{EtOH}}$ 238 m μ , 283, and 364 (ϵ 24,300, 15,400, and 6700)] is most probably the α -nitro isomer, although this assignment cannot be made unequivocally on the basis of the n.m.r. spectrum.

1-Benzoxepin (VI), C₁₀H₈O, was obtained as a yellow-green liquid, b.p. 50° (bath temperature, 0.5 mm.); infrared bands (neat) at 6.08 μ and 6.26; $\lambda_{\text{max}}^{\text{EtOH}}$ 211 m μ , 231, and 288 (ϵ 14,700, 10,700, and 2900). The structure of VI follows from the n.m.r. spectrum⁵; this showed a complex four-proton band (benzenoid protons) at τ 2.50–3.20, a one-proton doublet (H¹) at



τ 3.37 ($J_{\text{H}^1-\text{H}^2} = 11$ c.p.s.), a one-proton doublet (H⁴) at τ 3.79 ($J_{\text{H}^4-\text{H}^3} = 5.5$ c.p.s.), a one-proton doublet (H²) at τ 4.03 ($J_{\text{H}^2-\text{H}^3} = 5.5$ c.p.s., $J_{\text{H}^2-\text{H}^1} = 11$ c.p.s.), and a one-proton double doublet (H³) at τ 4.60 (equivalent coupling, $J_{\text{H}^3-\text{H}^1}$ and $J_{\text{H}^3-\text{H}^2} = 5.5$ c.p.s.). Confirmation of this structure was obtained through catalytic hydrogenation in pentane over palladium-charcoal. This reaction smoothly yielded homochroman, identified by direct comparison with an authentic sample.⁷

The formation of IV and VI can easily be rationalized. Dehydrobromination of II presumably leads first to the tetraene oxide III, which by the path indicated in formula IIIa gives rise to the annulene IV, whereas the path indicated in formula IIIb gives rise to the oxepin VI. It could be shown that the two products IV and VI are formed by independent routes, since each was recovered unchanged on base treatment under the conditions used for its formation. Further reactions of IV and VI are under investigation, and will be reported subsequently.

(7) Prepared according to G. Baddeley, N. H. P. Smith, and M. A. Vickars, *J. Chem. Soc.*, 2455 (1956).

DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

FRANZ SONDHEIMER
ARNON SHANI

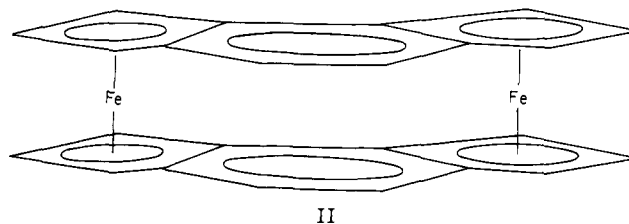
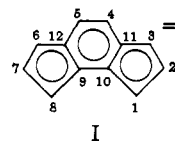
RECEIVED JUNE 16, 1964

The *as*-Indacenyli Dianion and Bis(*as*-indacenyliiron)

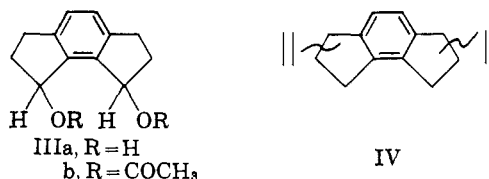
The *as*-indacenyli dianion (I),¹ is a simple polycyclic aromatic ligand that can form a bimetallic sandwich

(1) (a) Cf. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 300–301. (b) The *sym*-indacenyli dianion has been synthesized: K. Hafner, K. H. Hafner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H.

compound based on the ferrocene structure. The synthesis of dilithium *as*-indacenyli and bis(*as*-indacenyli-iron) (presumably II or the ring-inverted isomer of C_{2h} symmetry) is reported below.



Lithium aluminum hydride reduction of 1,8-dioxo-2,3,6,7-tetrahydro-*as*-indacene² yields a mixture of the diastereoisomeric alcohols IIIa, separable by crystallization into isomer A, m.p., 143.6–144.1°, and B,



m.p. 111.0–111.8°. *Anal.* Calcd. for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found for A: C, 75.91, 75.94; H, 7.64, 7.81. Diol B upon acetylation with acetic anhydride in pyridine yields a diacetate (IIIb), m.p. 148.6–150.0°. *Anal.* Calcd. for C₁₆H₁₈O₄: C, 70.05; H, 6.61. Found: C, 69.99; H, 6.38. Diol A similarly yields an epimeric diacetate (IIIb), m.p. 131.6–132.6°. The infrared, ultraviolet, and n.m.r. spectra of the alcohols and the diacetates are in accord with the assigned structures. A mixture of diacetates (IIIb), prepared from a mixture of diols, gives upon pyrolysis in a nitrogen stream at 630°, in 73% yield after recrystallization from *n*-pentane at –78°, dihydro-*as*-indacene (IV) as a liquid, partially crystalline at room temperature. *Anal.* Calcd. for C₁₂H₁₀: C, 93.46; H, 6.54. Found: C, 93.67; H, 6.71. The n.m.r. spectrum of this material suggests that it is a mixture of double bond isomers. Peaks are exhibited by the neat sample at τ 2.87 (doublet, 1.7 H), 2.92 (singlet, 0.3 H), 3.27 (multiplet, 2.0 H), 3.82 (multiplet, 1.9 H), 6.95 (multiplet, 2.9 H), and 7.22 (triplet, 1.2 H). Hydrogenation of IV in ethanol solution at room temperature with a 5% palladium on charcoal catalyst gives 1,2,3,6,7,8-hexahydro-*as*-indacene.²

Dilithium *as*-indacenyli (I) forms when dihydro-*as*-indacene in dimethoxyethane (DME) is treated with *n*-butyllithium in *n*-hexane.³ The salt is a white crystal-

Vöpel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 123 (1963); K. Hafner, *Angew. Chem.*, **75**, 1041 (1963).

(2) H. H. Wasserman and A. R. Doumaux, Jr., *J. Am. Chem. Soc.*, **84**, 4611 (1962). We are grateful to Professor Wasserman and Mr. Doumaux for providing us with experimental details of their work and with a sample of 1,2,3,6,7,8-hexahydro-*as*-indacene.

(3) The reaction is similar to the one used to synthesize dilithium pentalene: T. J. Katz and M. Rosenberger, *ibid.*, **84**, 865 (1962); T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

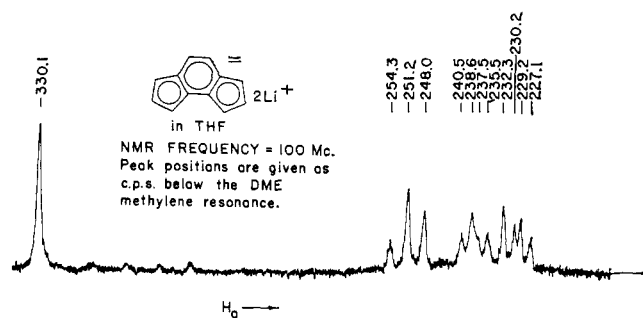


Fig. 1.—N.m.r. spectrum of dilithium *as*-indacene in THF.

line solid insoluble in DME, but soluble in tetrahydrofuran (THF). It reacts with deuterium oxide to give dideuterated dihydro-*as*-indacene. *Anal.* Calcd. atom % excess D for $C_{12}H_8D_2$: 20.00. Found: 19.85. That the deuterium atoms are in the allylic positions is shown by the decrease by a factor of two, relative to the other n.m.r. peaks, of the peaks at τ 6.95 and 7.22. The n.m.r. spectrum of dilithium *as*-indacene, determined in THF solution at an n.m.r. frequency of 100 Mc., is shown in Fig. 1.⁴ The spectrum, analyzed in Table I, consists of an ABX pattern⁵ and a singlet.

TABLE I

N.M.R. SPECTRUM OF DILITHIUM *as*-INDACENIDE IN THF

Proton	Observed chemical shift (in τ -units)	Relative intensity	Position assignment ^a	Charge density ^b
ϕ	3.155 ± 0.005	2.0	4, 5	-0.10
A	4.076 ± 0.006	6.4	1, 8	-0.24
B	4.158 ± 0.006		3, 6	-0.23
X	3.944 ± 0.003		2, 7	-0.18
(Av. 9,10,11,12				-0.13) ^c

$$J_{AX} = J_{BX} = \pm(3.12 \pm 0.13) \text{ c.p.s.}$$

$$|J_{AB}| = 2.06 \pm 0.17 \text{ c.p.s.}$$

^a The position assignments for the protons A and B may be reversed. The assignment of the X protons as the ones attached to carbon atoms 2 and 7 is based on the presumption that the lowest negative charge density in the five-membered ring resides on those carbons (*cf.* ref. 3 and 6). ^b The charge density associated with carbon atoms 4 and 5 is given as $\rho = -a/10.7$, where ρ is the charge density and a is the proton chemical shift relative to benzene, corrected for differential ring-current effects. For the carbons 1, 2, 3, 6, 7, and 8 the density is given as $-(0.2 + a/10.7)$, where a is the proton chemical shift relative to lithium cyclopentadienide in THF (τ 4.472),⁷ corrected for differential ring-current effects. ^c The average charge density of positions 9, 10, 11, and 12 is given as

$$-1/4 \left(2 + \sum_{i=1}^8 \rho_i \right)$$

The negative charge densities associated with each carbon atom of I were estimated (Table I) by a procedure similar, with one exception, to that used by Schaeffer and Schneider for other hydrocarbon anions.⁶ The chemical shifts of the protons 1, 2, 3, 6, 7, and 8, after correcting for the ring-current effects of the other rings, were compared, not with the chemical shift of benzene, but with the chemical shift of lithium cyclo-

(4) The n.m.r. spectrum was determined with the help of Mr. T. K. Wu.

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 132.

(6) T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

pentadienide in THF,⁷ and the difference was evaluated as proportional to the difference in charge density. The charge densities at carbon atoms 4 and 5 were evaluated by comparing the corrected chemical shift with that of benzene.

Dilithium *as*-indacene in THF reacts with a suspension of ferrous chloride to give in 10% yield, after chromatography on silica gel and crystallization from a mixture of ethanol and methylene chloride, bis(*as*-indacenylium). *Anal.* Calcd. for $C_{12}H_8Fe$: C, 69.28; H, 3.88; Fe, 26.84; mol. wt., 416. Found: C, 68.94; H, 3.96; Fe, 26.95; mol. wt., 434 (vapor pressure osmometry). The compound is a rust colored crystalline solid that does not melt, but darkens between 250 and 300°. The ultraviolet spectrum in methylene chloride⁸ has a maximum at 509 $m\mu$ ($\log \epsilon$ 2.51) and an inflection at 395 $m\mu$ ($\log \epsilon$ 2.92).

No polymeric material in which metal atoms and ligand molecules alternate has yet been identified.

Acknowledgment.—We are grateful to the National Science Foundation and the Alfred P. Sloan Foundation for their financial support.

(7) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960). *Cf.* ref. 6. The chemical shift of benzene was taken to be τ 2.734.

(8) The compound is only slightly soluble in methylene chloride and insoluble in saturated hydrocarbons or ethanol. Chlorinated hydrocarbon solvents, however, are known to produce marked changes in the ultraviolet spectrum of ferrocene [J. C. D. Brand and W. Sneeden, *Trans. Faraday Soc.*, **53**, 894 (1957)].

(9) National Science Foundation Predoctoral Fellow, 1960–1963, National Science Foundation Cooperative Fellow, 1963–1964.

DEPARTMENT OF CHEMISTRY

COLUMBIA UNIVERSITY

NEW YORK, NEW YORK 10027

THOMAS J. KATZ

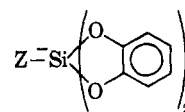
JEROME SCHULMAN⁹

RECEIVED JUNE 13, 1964

Pentacoordinate Silicon Derivatives. II.¹ Salts of Bis(*o*-arylenedioxy)organosiliconic Acids

Sir:

Finely divided silica was reported by Rosenheim² to react with catechol in the presence of various bases to yield crystalline salts containing the dibasic hexacoordinate silicate anion, $[\text{Si}(\text{C}_6\text{H}_4\text{O}_2)_3]^{-2}$. We have confirmed and extended this little known work to include examples containing carbon-silicon bonds. These organosilicon salts are believed to possess anions in which the silicon atom is *penta*-coordinate (I).



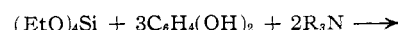
I, Z = alkyl or aryl

We have found these compounds to be prepared most conveniently from alkoxysilanes,³ *i.e.*

(1) Paper I: C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Am. Chem. Soc.*, **83**, 996 (1961).

(2) A. Rosenheim, B. Raibmann, and G. Schendel, *Z. Anorg. Allgem. Chem.*, **196**, 160 (1931).

(3) In like manner, the *tris*(*o*-arylenedioxy)siliconates described by Rosenheim are also easily prepared from ethyl silicate; *i.e.*



The use of alkoxysilanes rather than aqueous reactants conveniently avoids the uncertainty associated with the *hydrated* products encountered in earlier work: