

Tm^{3+} were irradiated with (1) γ -rays, (2) the output of a low pressure mercury lamp, or (3) with a low pressure hydrogen discharge produced within the quartz reaction tube itself. The oxidized anionic species were swept out or trapped out of the reaction tube. Upon cooling the molten bromides, each of the three radiation treatments showed significant quantities of divalent thulium. A typical spectrum of Tm^{2+} in BaBr_2 taken at 77°K . is shown in Fig. 1.

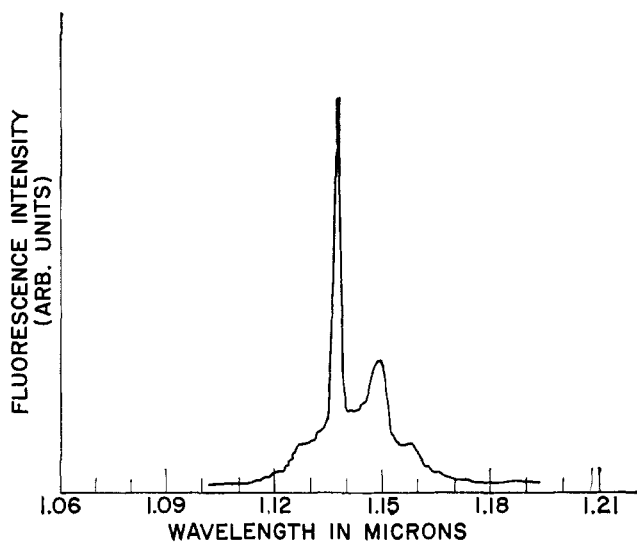


Fig. 1.—Fluorescence of γ -ray reduced (in the fused state) Tm^{2+} in BaBr_2 ($T = 77^\circ\text{K}$).

In the case of the γ -ray treatment, a dosage of less than 10^4 rads was used. Generally, dosages of up to 10^7 rads were found to be necessary for similar reduction in the solid.⁵ The light from the quartz mercury vapor lamp was focused on the surface of the melt from outside the furnace and the reaction tube. Illumination was carried out for about 1 hr. The low pressure hydrogen discharge was obtained by placing a Tesla coil on the reaction tube with about 0.1 mm. pressure of hydrogen flowing through the tube. The discharge was maintained for about 30 min.

The intensity of the Tm^{2+} fluorescence obtained from the low pressure hydrogen discharge material indicates a level of reduction much greater than that possible through reduction by solid-state irradiation. The extent of reduction in the solid-state irradiation is limited by the site-selection mechanism mentioned above.^{5,6} In the molten state, the ionization of the anions by radiation and their subsequent removal from the solution should permit the reduction of all the rare earth ions present. The BaBr_2 - Tm^{2+} crystals were fused and regrown several times with little or no loss of the divalent state. This is indicative of the stability of the reduced rare earth ions produced by radiation in the fused state to thermal reoxidation. No optical reoxidation experiments were done, but in the absence of known electron traps, such processes are not expected to occur.

Further work on other halide hosts containing various rare earth ions and on the mechanism of the reduction process is in progress and will be described more fully at a later date.

(6) P. M. Heyman and Z. Kiss, private communication.

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1,6-Oxido[10]annulene and 1-Benzoxepin¹

Sir:

We have found that base treatment of 2,3,6,7-tetrabromo-9,10-oxidodecahydronaphthalene (II) gives rise to 1,6-oxido[10]annulene (IV), as well as to 1-benzoxepin (VI).² This synthesis of IV resembles the recently described synthesis of the related 1,6-methano[10]annulene by Vogel and Roth.³

The tetrabromide II was prepared by addition of bromine to 9,10-oxido-1,4,5,8,9,10-hexahydronaphthalene (I)⁴ in chloroform solution, whereby one isomer (m.p. 160 – 162°) was isolated by crystallization in *ca.* 45% yield. Dehydrobromination of this substance with ethanolic potassium hydroxide at 50 – 55° , followed by chromatography on alumina, produced first the oxepin VI (*ca.* 20% yield) and then the annulene IV (*ca.* 50% yield).

1,6-Oxido[10]annulene (IV), $\text{C}_{10}\text{H}_8\text{O}$, formed light-yellow crystals, m.p. 53 – 54° , infrared band (KBr) at 6.51μ . The ultraviolet spectrum [$\lambda_{\text{max}}^{\text{EtOH}}$ 255 m μ , 299, and complex band at *ca.* 392 (ϵ 72,000, 6900, and 240)] resembled that of the corresponding 1,6-methano-compound,³ and pointed to the fully conjugated structure IV rather than to the alternative tricyclic formulation III. The n.m.r. spectrum⁵ showed an A_2B_2 pattern in the τ 2.23–2.81 region (centered at τ 2.52), similar to that of naphthalene (τ 2.05–2.71, centered at 2.38).

The annulene IV is a ten π -electron system, and therefore complies with Hückel's rule. Moreover the carbon skeleton is presumably not seriously distorted from a mean plane, and the substance should consequently be aromatic.⁶ That the compound in fact is aromatic is shown by the n.m.r. band positions at low field, demonstrating the existence of a ring current. The annulene is best represented by the expression V, indicating delocalization of the π -electron system.

1,6-Oxido[10]annulene can be made to undergo electrophilic substitution reactions. For instance, nitration with cupric nitrate and acetic anhydride for 5 min. at room temperature produced two isomeric mononitro compounds, $\text{C}_{10}\text{H}_7\text{NO}_3$, each in *ca.* 30% yield. The more strongly absorbed on alumina [m.p. 48 – 49° ; $\lambda_{\text{max}}^{\text{EtOH}}$ 242 m μ , 279, and 349 (ϵ 21,500, 26,500, and 7500)] proved to be the β -nitro isomer VII, since the lowest field bands in the n.m.r. spectrum⁵ consisted of a one-proton singlet (H^1) at τ 1.22 as well as a one-proton doublet (H^2) at τ 1.40 ($J = 10$ c.p.s.). The

(1) Part XXXIII in the series "Unsaturated Macroyclic Compounds." For part XXXII, see A. E. Beezer, C. T. Mortimer, H. D. Springall, F. Sondheimer, and R. Wolovsky, *J. Chem. Soc.*, in press.

(2) The isomeric 3-benzoxepin has been reported previously [K. Dimroth and G. Pohl, *Angew. Chem.*, **73**, 436 (1961); for derivatives of 3-benzoxepin, see K. Dimroth and H. Freyschlag, *Ber.*, **90**, 1623 (1957)].

(3) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964).

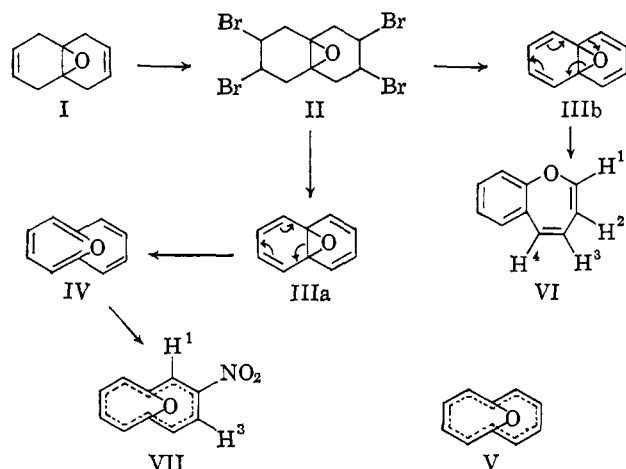
(4) This substance is readily available from naphthalene in high yield by a two-step sequence [W. Hückel and H. Schlee, *Ber.*, **88**, 346 (1955); C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960)].

(5) All n.m.r. spectra were determined in deuteriochloroform solution at 60 Mc./sec.

(6) See F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963).

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).

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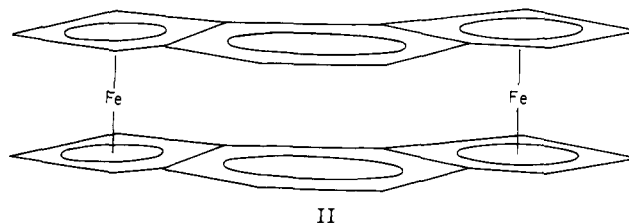
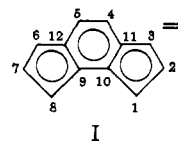
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The *as*-Indacenyl Dianion and Bis(*as*-indacenyliron)

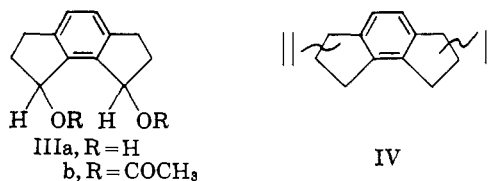
The *as*-indacenyl dianion (I),¹ is a simple polycyclic aromatic ligand that can form a bimetallic sandwich

(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*-indacenyl 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*-indacenide and bis(*as*-indacenyliron) (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*-indacenide (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 pentalenide: T. J. Katz and M. Rosenberger, *ibid.*, **84**, 865 (1962); T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).