from the Dowex 2 with 1.5 normal hydrochloric acid in the second column volume, along with the neutral amino acids. The amphoteric material thus obtained was chromatographed in two dimensions, using *sec*-butyl alcohol/formic acid/water (70/10/20) as the first dimension and phenol/water/ammonia (80/20/0.3) as the second. A radioautograph was made of the chromatogram to locate the radioactive material, and the material was "fingerprinted" as follows: The radioactive material occurring in the region which corresponded in location to selenomethionine,[7] and which contained approximately one μg. of selenium, was eluted from the first chromatogram and divided into two equal fractions. One fraction was treated with ninhydrin and gave no reaction. The second fraction was mixed with 150 μg. of carrier selenomethionine and chromatographed. A radioautograph was taken of this chromatogram, and the chromatogram was then sprayed with ninhydrin. The location, shape, size, and form of the spot on the radioautograph corresponded precisely with that spot produced by the ninhydrin test for carrier selenomethionine.

Thus, a chromatographic "fingerprint" identified the amphoteric radioactive material obtained after column fractionation and chromatography of the protein hydrolysate as selenomethionine. To further substantiate the identification, mild oxidation, followed by chromatography, of a mixture of the unknown radioactive material and carrier selenomethionine produced exact "fingerprints" which chromatographically corresponded to the seleno-analogs of a sulfoxide and a sulfone.

Our data indicate that selenocystine may also be produced by *E. coli* grown in the presence of selenite, and studies concerning the identification of this compound will be the subject of a forthcoming paper.

(7) The authors are indebted to Mr. D. B. Cowie, Department of Terrestrial Magnetism, Carnegie Institution of Washington, for a generous sample of selenomethionine, which was originally synthesized by Dr. Alex Shrift, of the University of Pennsylvania, and which was used in the experiments described in reference (2).

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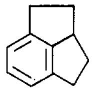
2,2a,3,3a,4,5-HEXAHYDRO-1H-CYCLOPENT[jkl]-AS-INDACENE

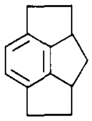
Sir:

Recently the synthesis of 2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (I) was reported.[1] Although previous statements had predicted a very high degree of strain for this system, possibly to the point of excluding its existence, this was found not to be the case. Very little evidence of strain was manifest, the only departure from normal being the extreme ease of hydrogenation.

Continuing the search for a compound in which the strain imparted by a fused ring system would be sufficient to bend the benzene ring and hence decrease significantly its resonance stabilization, we have prepared 2,2a,3,3a,4,5-hexahydro-1H-cyclopent[jkl]-as-indacene(II). Examination of its properties clearly demonstrates a departure from the usual aromaticity of benzenoid compounds and the appearance of olefinic-type characteristics.

The synthesis of III was achieved by starting with 1-oxo-2,2a,3,4-tetrahydro-1H-cyclopent[cd]-indene,[1] which was reduced with sodium borohydride to the alcohol. Hydrogen chloride gave the 1-chloro compound which was converted to the acetic acid with malonic ester, and thence to the propionic acid [m.p. 95.7–96.1°. *Anal.* Calcd. for $C_{14}H_{16}O_2$: C, 77.8; H, 7.5; equiv. wt., 216. Found: C, 77.7; H, 7.4; equiv. wt., 214] by Arndt–Eistert homologation. The propionic acid was cyclized quantitatively with hydrogen fluoride to the ketone (III), which was ring-opened to the carboxyacetic acid by oximination, rearrangement with benzenesulfonyl chloride, and hydrolysis. Pyrolysis of the dibasic acid lead salt gave the ketone IV [m.p. 89–91°. *Anal.* Calcd. for $C_{13}H_{12}O$: 84.8: H, 6.6; mol. wt., 184. Found: C, 85.0; H, 6.5; mol. wt. (Rast), 190]. Wolff re-


I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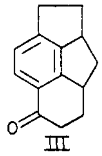
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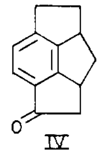
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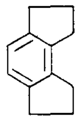
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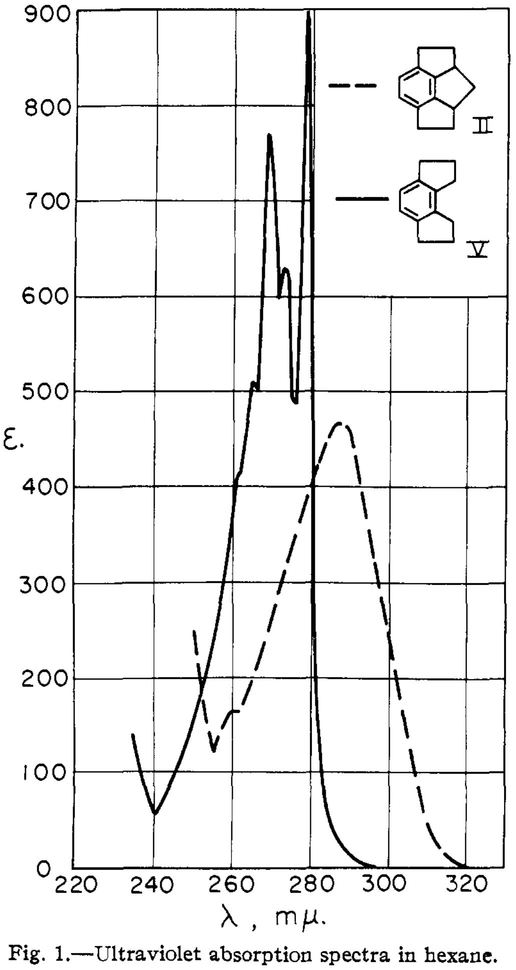

Fig. 1.—Ultraviolet absorption spectra in hexane.

(1) H. Rapoport and J. Z. Pasky, THIS JOURNAL, 78, 3788 (1956).

duction of IV-semicarbazone in ethanol led to some ethyl ether. However, using potassium *tert*-butylate in *tert*-butyl alcohol, pure hydrocarbon II was obtained [liq., *Anal.* Calcd. for $C_{13}H_{14}$: C, 91.7; H, 8.3. Found: C, 91.7; H, 8.5].

As a model, compound 1,2,3,6,7,8-hexahydro-*as*-indacene (V) was prepared from *o*-carboxymethylhydrocinnamic acid by successive ring-closure, hydrogenation, homologation to the propionic acid, ring-closure, and hydrogenation, using polyphosphoric acid for the cyclizations and palladium-on-carbon in the hydrogenations.

The chemical properties of II reflected a high degree of unsaturation. On standing, it absorbed oxygen and lost its ultraviolet absorption. Hydrogenation in methanol with palladized carbon proceeded very rapidly (20 min.) with the absorption of 300 mole % of hydrogen. At room temperature in chloroform, 300 mole % of perbenzoic acid was consumed and a diepoxyhydroxybenzoate was isolated. In comparative experiments, V was almost completely unreactive.

Comparison of the ultraviolet absorption of II with V, Fig. 1, shows a decreased extinction coefficient, a decided bathochromic shift (8 mμ), and the disappearance of fine structure. These effects must be attributed to ring-strain and departure from co-planarity.[2,3,4] Furthermore, the present case provides a clear-cut example of this effect since the absorbing systems of II and V are identically substituted. Thus we may conclude that sufficient strain has been produced in II to cause bending of the benzene ring and hence decreased resonance stabilization.

(2) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

(3) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955.

(4) E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).

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RECEIVED SEPTEMBER 27, 1957

PLATINUM HEXAFLUORIDE[1]

Sir:

Volatile hexafluorides have been reported for the adjacent group of elements W, Re, Os and Ir.[2,3] For platinum, the next and "noblest" member of this series, the highest fluoride that has been isolated is the tetrafluoride. In view of the improved techniques presently available for the preparation and handling of reactive fluorine compounds, an attempt was made to produce PtF_6. The reactor was constructed chiefly of Pyrex glass and contained the platinum in the form of a spiral filament Directly above and very close to the platinum filament was a surface cooled with liquid nitrogen. A reaction between the platinum and fluorine vapor at 300 mm. pressure was initiated by briefly passing a current through the platinum wire. The reaction continued exothermally as evidenced by the incandescence of the wire and stopped when either fluorine or platinum was consumed completely. The major product was a non-volatile yellowish brown solid (PtF_4) that uniformly coated the walls. In addition a volatile material collected on the liquid nitrogen cooled condenser. After purification this volatile fraction amounted to 1.4 g. compared to 10 g. of platinum wire reacted.

This volatile fraction has been identified as PtF_6 by vapor density determinations and chemical analysis. Approximate solid vapor pressures at 0° and 21° are 29 and 96 mm., respectively, in agreement with values extrapolated from the properties of the four adjacent hexafluorides.

Solid PtF_6, which melts at 56.7°, is dark red in color when viewed with a microscope although the massive material appears black. Its vapor is brownish red in color resembling bromine. Solid PtF_6 has been found to be isostructural with OsF_6 and IrF_6 by X-ray powder determinations.

Platinum hexafluoride is probably the least stable and most reactive of the known hexafluorides. When stored in Pyrex or quartz it decomposes slowly leaving a reddish brown residue. This may be due to photochemical decomposition or to a very slow reaction with glass. However, in nickel containers it may be stored for weeks at room temperature without any evidence of decomposition. A striking example of its reactivity occurred when 100 mg. of PtF_6 was stored in a container that previously had been used for storing NpF_6. After several days the PtF_6 was no longer present having been used up quantitatively in the formation of NpF_6 from some Np residue in the container. All subsequent studies with PtF_6 have therefore been made in new equipment in which more stable hexafluorides have not previously been handled.

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RECEIVED SEPTEMBER 23, 1957

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. H. Simons, ed., "Fluorine Chemistry," Vol. I, Chap. 2, Academic Press, Inc., New York, N. Y., 1950.

(3) John G. Malm and Bernard Weinstock, "Osmium Hexafluoride and Its Probable Identity with the Previously Reported Octafluoride," paper presented at the 131st meeting of the American Chemical Society in Miami, April, 1957.

THE NITROSATION AND NITRATION OF AMINES AND ALCOHOLS WITH NITROGEN TETROXIDE

Sir:

We wish to report several new reactions of nitrogen tetroxide. These reactions (Table I) represent simple methods for the syntheses of nitrosamines, nitroamines, nitrites, and nitrates; they also illustrate that nitrogen tetroxide can react cleanly either as a nitrosating agent (path a) or as a nitrating agent (path b).

In each run of Table I, a 1 *M* solution of N_2O_4[1] in methylene chloride (distilled from P_2O_5) at the given temperature was added slowly to an excess of the organic reactant in the appropriate solvent at the same temperature. Precautions were taken to exclude oxygen, water and carbon dioxide. The reaction mixture was allowed to warm to room

(1) A mixture of tank NO_2 (The Matheson Co.) and oxygen was passed over P_2O_5 and into a trap at −80°. The white crystals obtained were allowed to melt and the liquid N_2O_4 was removed as required with a calibrated pipet.